The reactions of some activated aromatic halides with Piperidine, and n-butylamine in dipolar aprotic and dipolar protic solvents.

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This is to certify that the whole of the work described in this thesis was done by Mrs. A.M. Adenle under our supervision from December 1968 to December 1971.

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Finally the author wishes to dedicate the work to the memory of her daughter.

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Abstract

The reactions of 2-chloro-5-nitro pyridine with piperidine have been studied in acetone and in methanol. In acetone, the rate constants are measured as a function of the amine concentration. In methanol, the Arrhenius parameters are obtained.

In methanol, except for a very slight (almost negligible) downward trend of rate constants at very high concentration which is explained in terms of charge - transfer complexes, there is no base catalysis and the observed rate constants are the rates of formation of the intermediate complex.

The rates of reaction of 1-X-2, 4-dinitrobenzene (X=F, Cl) with piperidine and n-butylamine in methanol, acetone, and chloroform (stabilised and destabilised) have been measured as a function of the amine concentration.

In acetone, the reactions of both substrates with piperidine show true base catalysis with $k_3/k_2 > 50$ in both cases.

In chloroform with n-butylamine, there is very little rate increase with increasing amine concentration. For both substrates, $k_3/k_2 \simeq 3$. This is explained in terms of hydrogen-bonding in the intermediate state.

In methanol, the reaction of the chloro substrate with piperidine gives a small linear increase of rate constants with increasing amine concentration; while for the fluoro substrate, the graph of rate constants

against amine concentration gives a doubly sloped curve. This is due to some special unknown medium effects.

In acetone, the reactions with n-butylamine give rather peculiar results. The chloro substrate appears to be more sensitive to catalysis by amine than the fluoro substrate - a situation hitherto unknown.

In general, for the reactions in methanol and chloroform, there is not much base influence; while those in acetone are dependent on the base strength.

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CHAPTER

INTRODUCTION

Aromatic Nucleophilic Substitution has been known since the second half of the nineteenth century; but systematic and intensive research in the field dates back to the work of Brady and Cropper[1] in 1950. The comprehensive literature on aromatic nucleophilic substitutions includes the reviews and studies of Bunnett and Zahler[2], Miller[3,4] Berliner and Monack[5] and Ross[6].

Initially, aromatic nucleophilic substitution reactions were classified as SN1 and SN2[7] by analogy with nucleophilic substitution in the aliphatic series.

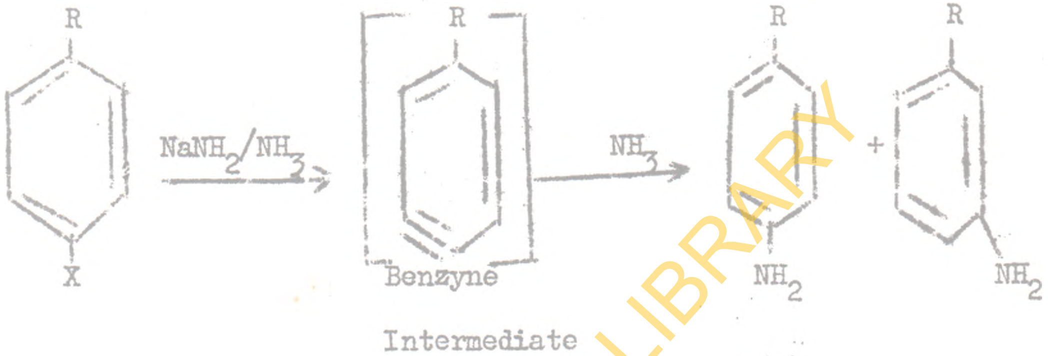
The SN1 mechanism is the one proposed for the uncatalysed decomposition of diazonium salts[8,9] in aqueous solutions.

$$ArN_2^+ \longrightarrow Ar^+ + N_2 \quad \ldots\ldots\ldots \quad (1.1)$$

The reaction is first order in aqueous solution[10,11,12] and its rate is unaffected by the concentration or even the identity of the anions of the salts even when these anions enter into the formation of the products[7,13].

In the bimolecular reactions, two types were recognised:

a) those that proceed with rearrangement for example the reactions involving the 'benzyne' intermediates[14]. These reactions proceed via the elimination - addition mechanism and only take place either in the presence of very strong bases e.g. $NaNH_2/NH_3$ or under very drastic conditions. One such reaction can be represented by the scheme below:



I(2)

b) those that take place without rearrangement. These constitute the vast majority of aromatic nucleophilic substitution reactions.

In the 1950's and early '60's there was a lot of controversy as to the mechanism of this type of reaction. Initially, it was thought that bond - breaking and bond - making processes were synchronous by analogy with the straight - forward SN_2 mechanism. Quantum - mechanical considerations show that this type of mechanism is impossible.

The transition states for this mechanism would be either a or b

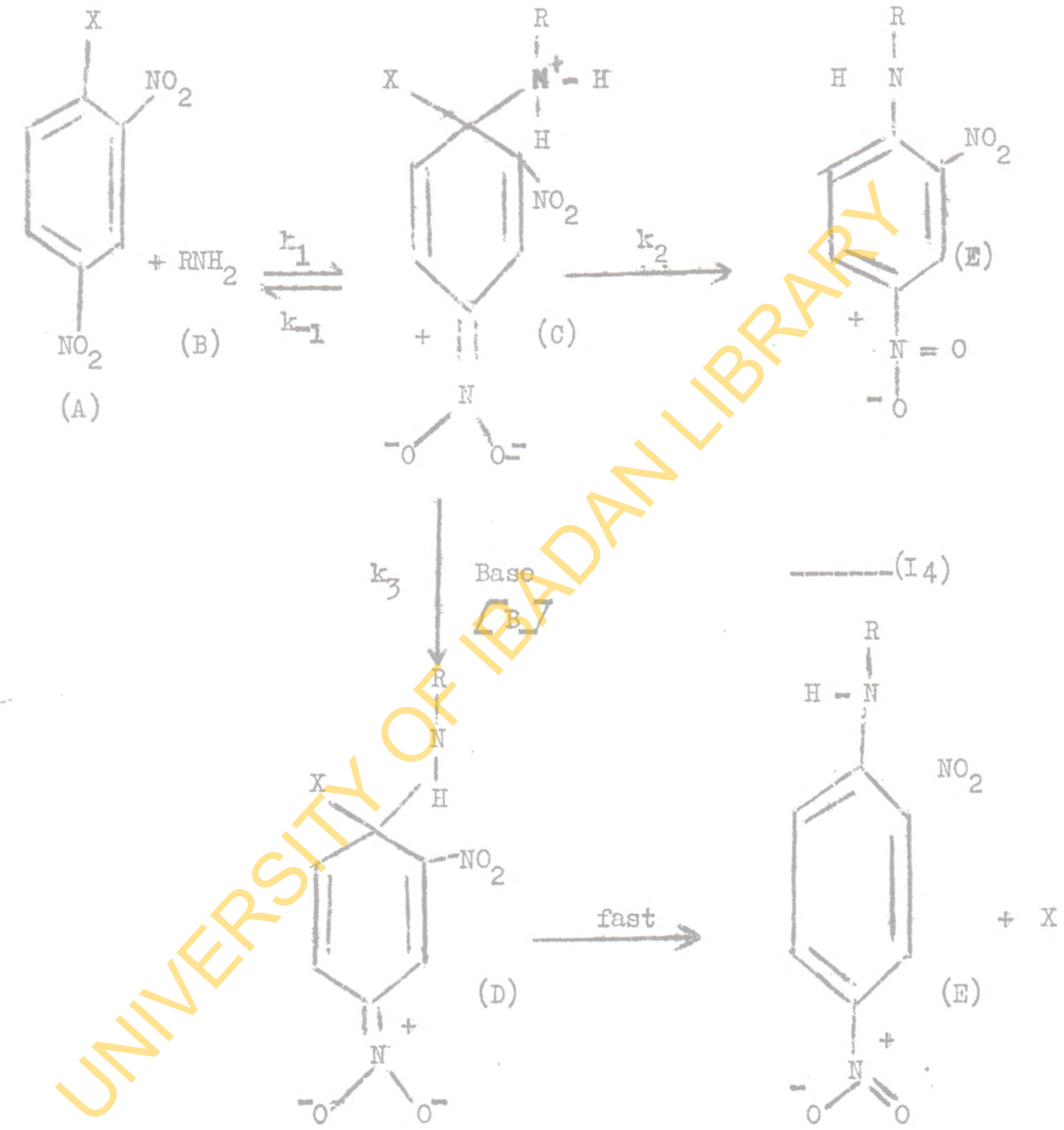
(a) (b)

.... (I3)

In (a), X - Y is perpendicular to the plane of the benzene ring and as such is impossible because the p-orbitals which are supposed to hold X and Y are those used for the π bonds and an acceptance of it will lead to a violation of the Pauli Principle.

Also in (b), X - Y is planar with the benzene ring and is impossible because Y and the benzene ring cannot occupy the same space.[15] Bunnett and Zahler have strongly advocated the intermediate complex mechanism. This mechanism requires that in the formation of the transition state of the reaction, the benzenoid resonance of the ring is lost and is replaced by a pentadienate ion resonance. The reagent forms a complex, the intermediate complex, with the substrate during the process. This intermediate complex then decomposes into products at a definite rate.

The intermediate complex formulation with an amine as nucleophile and an activated halide as the substrate is given below:



———————(I4)

At any given base concentration $[B]$, the rate of formation of (E) is given by $V = ko [A] [B]$ ——————— (I5)

where ko is the observed specific rate constant for the formation of E. Applying the steady state approximation to the above reaction scheme: $$V = k_1 [A] [B] \left[\frac{k_2 + k_3 [B]}{k_{-1} + k_2 + k_3 [B]} \right] \text{---} \quad (I6)$$

A comparison of equations (I(5) and (I(6) will give

$$ko = k_1 \left[\frac{k_2 + k_3 [B]}{k_{-1} + k_2 + k_3 [B]} \right] \text{---} \quad (I7)$$

Three different forms of the equation (I7) arise depending on the relative magnitudes of k_1, k-1, and k_2.

1. When $k_2 + k_3 [B] >> k\text{-}1$ then equation (I7) become $ko = k_1$. Under this condition, the reaction is insensitive to base catalysis regardless of the concentration or catalytic power of the base.

2. When $k\text{-}1 >> k_2 + k_3 [B]$ then equation (I7) becomes $ko = k_1 \left[\frac{k_2 + k_3 [B]}{k_{-1}} \right]$ and the rate is linearly dependent on the concentration of the base $[B]$ as is the the case in the potassium acetate - catalysed reaction of 1- fluoro -2, 4 - dinitrobenze with N - methylamine in ethanol.[16]

3. When k_{-1} and $k_2 + k_3 [B]$ are comparable in magnitude, the rate is curvilinearly dependent on the concentration of the base.

All the recorded evidence is in favour of the intermediate complex mechanism. These have been summarised in various reviews and articles.[17-22]

The relative orders in which halogens are displaced in aromatic nucleophilic substitution reactions have been advanced generally as arguments in favour of the intermediate complex mechanism.

Generally, in protic solvents the order $F \gg Cl > Br > I$ has been observed[23] suggesting that the formation rather than the decomposition of the complex is rate determining supporting the intermediate complex mechanism.

The reverse order $F < Cl \lesssim Br \lesssim I$ is less frequently encountered. In fact, it has only been observed in few cases 24, 51 though there are several examples of this order in non - protic solvents such as benzene. In all cases where this sequence has been observed the reactions of the fluoro - substrate are base catalysed.

The effect of the solvent in aromatic nucleophilic substitution reactions has been measured by many workers and in this department by Okafor[26] and Ette[27]. In these studies, base catalysis has been observed in some solvents such as water - dioxane mixture and benzene. Except for the work of Suhr[28], where base catalysis has been observed in methanol, most workers have observed no base catalysis in methanol and in most of the dipolar aprotic solvents.

The aim of the present work is to investigate the kinetic form of the reactions between activated fluoro - and chloro - benzene and pyridine with amines in various solvents. The results will be used to elucidate the changes which occur in the mechanism of aromatic nucleophilic substitution reactions as the solvent is varied.

CHAPTER 2

SOLVENT EFFECTS

Liquid solutions offer both practical and theoretical advantages for the study of chemical reactions. It is easy to obtain macroscopically homogeneous solutions of many reactants, to vary the nature of the liquid, to add other reagents, to control physical conditions with great uniformity. Most of the physical organic chemical theories are based on the study of reactions carried out in liquid solution. The formulation of many reaction mechanisms can be aided by data on the effect of solvents on the rates and products of the reactions.

There are many parameters which can be utilised to predict solvent effects on reaction rates and mechanisms.

EFFECT OF DIELECTRIC CONSTANT (D) OF THE SOLVENT ON REACTION RATE:

Forces between reactants are altered and their rates of reactions modified depending upon the medium in which the reaction is taking place. The greatest physical effect which a solvent exerts upon the reactants immersed in it is the modification of the electrostatic forces among the reactant particles through the Dielectric Constant influence of the medium. These electrostatic forces affect markedly the ability of reactant particles to contact each other.

The dielectric constant does not provide a direct measure of the interactions on the molecular scale as is to be expected due to the complexity of the interactions.

Many theoretical treatments of electrostatic interactions are available all based on the dielectric constant of the solvent.[30]

Considering dipole - dipole reactions, a theory for the influence of the dielectric constant of the medium on the free energy of a polar molecule has been given by Kirkwood.[31] By considering electrostatic forces only (neglecting van der waals' forces) the change in free energy when a molecule with dipole moment μ and radius r passes from a medium of dielectric constant of unity 1 into a medium of dielectric constnt D is given by

$$\Delta G = - \frac{\mu^2}{r^3} \cdot \frac{D - 1}{2D + 1} \quad \ldots\ldots\ldots 11\ (1)$$

Applying this to the transition - state theory for the reaction,

$$A + B \rightleftharpoons M^{\#}$$

where A, B, and $M^{\#}$ are polar species and taking note that

$$k = \left(\frac{RT}{Nh}\right) e^{-\frac{\Delta G^{\#}}{RT}}$$

where k = rate constant in solution, the equation

$$\mathrm{In}\ k = \mathrm{In}\ ko - \frac{N}{RT} \frac{(D - 1)}{(2D + 1)} \left[\frac{\mu^2{}_A}{r^3{}_A} + \frac{\mu^2{}_B}{r^3{}_B} - \frac{\mu^2{}_{M^{\#}}}{r^3{}_{M^{\#}}} \right] 11(2)$$

where ko is the constant in a medium of dielectric constant unity and where the non - electrostatic forces are the same for the activated complex as for the reactants. This equation 11(2), predicts that if the activated complex is more polar than the reactants, as is the case where the products are ions, then the rate of the reaction increases with the dielectric constant of the medium. For reactions in solvent mixtures, a straight line is often obtained by plotting $\ln k$ versus $(D - 1/2D + 1)$[32].

This equation is not always obeyed and is not valid in general if reaction rates in different types of solvents of different dielectric constants are compared. This and other instances 33, 34, 35, indicate the limited application of the dielectric constant as a measure of the solvating power of the solvent. For this reason, the use of the linear free energy relationship may be of tremenduous help.

HUGHES - INGOLD QUALITATIVE SOLVENT THEORY:

The qualitative solvent theory of Hughes, Ingold and their collaborators relates the relative solvation energies of the transition and initial states to the mechanism and charge - type of the reaction. It proposes that strongly solvating (ionising) solvents facilitate an increase in the magnitude of the charges, inhibit a decrease and retard the distribution of a given charge in going from the ground state to the transition state. Also that a reaction in which the formation of the transition state involves an increase or decrease in the magnitude of the charges will be subject to stronger solvent influences than one wherein a given charge is distributed in the transition state.

For nucleophilic substitution reactions, it states that there are four possible charge types. In the reaction: $Y + RX \longrightarrow YR + X$

a) Initially Y negative x neutral

b) Initially Y neutral X neutral

c) Initially Y negative X positive

d) Initially Y neutral X positive

There are two types of mechanistic paths by which these reactions can occur: S_N2 and S_N1. For each mechanism and each charge type the change in charge distribution on going from the initial to the transition state has to be considered. When this is done, the general conclusions of the theory are summarised below:

Predicted Solvent Effects on Nucleophilic Substitutions

Charge Type	Charge Distribution		Change in Distribution (a)	Predicted effect of increased solvent polarity on rate
	Initial State	Transition State		
		Bimolecular Mechanism S_N2		
a)	Y^-+RX	$Y^{\delta-}$—R—$X^{\delta-}$	Dispersed	Small decrease
b)	$Y+RX$	$Y^{\delta+}$—R—$X^{\delta-}$	Increased	Large Increase
c)	Y^-+RX^+	$Y^{\delta-}$—R—$X^{\delta+}$	Reduced	Large decrease
d)	$Y+RX^+$	$Y^{\delta+}$—R—$X^{\delta+}$	Dispersed	Small decrease
		Unimolecular Mechanism S_N1		
a) and b)	RX	$R^{\delta+}$—$X^{\delta-}$	Increased	Large increase
c) and d)	RX^+	$R^{\delta+}$—$X^{\delta+}$	Dispersed	Small decrease

(a) on proceeding from the initial state to the transition state.

The theory assumes that energy changes will be more important than entropy changes, although in many systems, the two effects would be in opposition, and the theory therefore considered only solvation energies. This theory has been found to work well for many reations of alkyl halides and 'onium salts. However, it ignores specific interactions such as hydrogen-bonding and also entropy effects.[36]

SPECIFIC INTERACTIONS BETWEEN SOLVENT AND REACTANTS:

All the relationships between the rate of reaction and the polarity of the solvent hitherto discussed take into account only some interactions and ignored all specific effects such as hydrogen - bonding and polarisability and as such give only a rough picture of the effect of a solvent on a given reaction.

The solvent effects on the rate of the Menschutkin reaction illustrates the importance of these interactions.

$$R_3N: + R^1X \longrightarrow R_3N^{\delta+} — R — X^{\delta-} \quad R_3N^+R^1 + X^- \text{ ——— } (113)$$

The Hughes - Ingold theory predicts that the rate should be greatest in more polar solvents. For hydrolytic solvents the activation energy decreases with increasing dielectric constant, while the entropy of activation is little affected.[37] The reaction is, as predicted, faster in ethanol than in benzene. However, if comparison is made between different types of solvents, the theory is less satisfactory.

The Hughes - Ingold theory is based on electrostatic effects and does not take into account specific solvent - solute interactions such as hydrogen - bonding. These special interactions between solvent and reactants are of fundamental importance in bimolecular substitutions and hence limits the applicability of the theory.

A theory of solvent effects on the rates of reaction based on specific solvent effects is due to Miller & Parker.

PROTIC AND APROTIC SOLVENTS:

Solvents are classified as protic or dipolar aprotic depending on whether they possess labile hydrogen atoms or not. Hydrogen - donors e.g. methanol are classified as protic solvents and they have high dielectric constants. D methanol = 32.6. Solvents with D$>$15 which though containing hydrogen atoms but which cannot be donated to form hydrogen - bonding with an appropriate species are known as dipolar aprotic solvents e.g. dimethyl formamide D = 38 acetone D = 21.5

Solvents like benzene which are non - polar may be classified as non - polar aprotic solvents.

Parker[39] has demonstrated that most anions in dipolar aprotic solvents are much less solvated than in protic solvents, but large polarisable charged transition states in dipolar aprotic solvents are more solvated than in protic solvents. The result is that bimolecular reactions of anions which pass through a large polarisable state containing that anion are much faster in dipolar aprotic solvents than in protic solvents.[39, 40] Reactions of small anions are most accelerated, but reactions of large polarisable anions are least accelerated, in the change from protic to dipolar aprotic solvents.[39]

In protic solvents anions are solvated by ion-dipole interactions on which is superimposed a strong hydrogen - bonding which is greatest for small anions.[39] Thus solvation by protic solvents decreases strongly in the series OH^-, $F^- \gg Cl^- > Br^- > N_3^- > I^-$ In dipolar aprotic solvents, anions are solvated by ion - dipole interactions on which is superimposed an interaction due to the mutual polarisability of the anion and the solvent molecule which is greatest for large ions. There is no significant contribution to solvation by hydrogen - bonding in dipolar aprotic solvents. Solvations of anions by dipolar aprotic solvents thus decreases slightly in the reverse order to that given for protic solvents.

QUANTITATIVE DETERMINATION OF SOLVENT EFFECTS (LINEAR FREE ENERGY RELATIONSHIPS):

The formulation of many reaction mechanisms can be aided by data on the effects of solvents on the rates and products of the reaction.

In order to make use of data on solvent effects for reaching conclusions about mechanisms, an unambiguous way of defining what effect is expected for a given solvent is required. As of present, all parameters used to describe solvents result from experimental measurements. In order to utilise these parameters properly, the molecular basis of the process which provided the data for defining the parameter must be understood.[41] In order to have a definite basis for comparison of solvent effects, linear free energy relationships are employed. These relationships do not provide a theory of kinetic solvent effects; but they attempt to correlate solvent properties in terms of parameters which are independent of the reacting substrate. Grunwald and Winstein [42a,b] suggested the two parameter linear free energy equation

$$\log \frac{k}{k_o} = mY \quad \text{---------}(II(4))$$

where k is the rate constant for the solvolysis of a compound in any solvent; k_o is the rate constant for the solvolysis of the same compound in a standard solvent (80% ethanol); Y is a measure of the ionizing power of the solvent and m gives the sensitivity of the substrates to changes in the medium.

The application of the equation requires that Y values be determined with respect to a standared compound and this has been chosen as tert-butyl chloride (m = 1.00) These standard solvent and substrate were chosen because of the numerous instances of reactions involving both of them.

This equation is found to be satisfactory for correlating solvolysis rate for many simple S_N1 reactions in which the carbonium ion is rapidly converted into the products. The agreement for S_N2 solvolysis is less general.

Later on, other more complicated equations have been devised to correlate rates of solvolysis reactions.[43] Swain's original view was that all polar displacement reactions involve concerted action of a nucleophilic reagent (N) attacking the substrate (S) as an electrophilic reagent (E) pulls off the displaced group

$$N + S + E \rightleftharpoons [\text{Transition State}] \longrightarrow \text{products.}$$

This view led to the expectation that displacement rates could be correlate by the four parameter equation thus:

$$\log \frac{k}{k_o} = Sn + S^1e \text{ -------- II 5}$$

where k is the rate of reaction of the substrate being considered, k_o is the rate of the reaction of the same substrate with water in which both N and E are water for which both n and e are defined as zero.

n is a nucleophilic constant characteristic of N and e is an electrophilic constant charateristic of E.

S and S^1 represent the respective senstivity of the substrate (S) to the nucleophile (N) and to the electrophilic reagent (E).

Fierens and his co-workers [44] examined a number of features of the Grunwald - Winstein [42a,b] equation. While finding the correlations useful as a diagnosis of mechanism in the solvolytic reactions studied, they consider the Y values to be so dependent upon the choice of standard substrate as to have limited application.

CHAPTER 3

Literature Survey of Solvent Effects in Aromatic Nucleophilic Substitution

Many reactions of amines with nitro-activated halobenzenes have been described as base catalysed i.e. the second-order rate constants increased with increasing amine concentration or on addition of other bases while other systems do not show catalysis.

Applying the steady-state approximation to the catalysed mechanism the observed rate constants ko is given by:

$$ko = \frac{k_1(k_2 + k_3[B])}{k_{-1} + k_2 + k_3[B]}$$

The three cases which can arise depending on the relative magnitude of k_{-1} and $k_2 + k_3[B]$ have already been discussed in Chapter I.

Also three striking characteristics have been observed from the various studies of these reactions in many solvents namely:

Many reactions are accelerated mildly by bases;

some are strongly accelerated and a few have been known to be slightly retarded.

In the class of reactions where $k_{-1} \gg k_2 + k_3[B]$, there is a linear relationship between the base concentration and the rate.

Experimentally, the many known reactions belonging to this class obey the mathematical expression:

$$ko = k' + k''[B]$$

where ko is the observed second-order rate coefficient, k' and k'' are second- and third-order coefficients respectively. k''/k' is a measure of the relative magnitude of the accelerated and unaccelerated parts of the reaction.

Bunnett and his co-workers[17] have pointed out that two types of this apparent catalysis can be distinguished based on the value of k"/k'.

Strongly accelerated reactions are those for which $k''/k' > 50$. Mildly accelerated reactions are those with k"/k' significantly lower than 50 and more commonly 5 or lower.

Several factors such as polarity of solvents or medium effects, the nature of the leaving group and other factors such as basicity of the nucleophile are known to affect the base catalysis.

For the strongly accelerated reactions there is at least a qualitative relationship between the base strength of the catalyst and its catalytic effect For instance, in the reactions[17] of 1-fluoro-2, 4-dinitro benzene with N-methylaniline and various catalysts; when OH^- is the catalyst, $k''/k_, = 350$, when CH_3COO^- is the catalyst, $k''/k' = 150$. With N-methylaniline as nucleophile there was little acceleration. Thus the order of catalytic effect is $OH^- > CH_3COO^- > RNH_2$.

For the mildly accelerated reactions, the chemical character is not yet clear. For instance, in many of the reactions of 2,4-dinitrohalobenzenes with various amines, there is little or no relationship between the base strength of the catalyst and its ability to increase the reaction rate. Amines, hydroxide ions and acetate ions appear to be equally effective as catalysts.

Bunnett[17, 45] suggests that for mildly catalysed reactions, the formation of the intermediate is rate-determining, and that the slight augmentation of rate with increasing concentration of various solutes is due to some unspecifi effects.

From the results discussed below, it would appear that kinetic behaviour observed experimentally depends principally on the nature of the group displaced i.e. whether it is a 'good' or a 'poor' leaving group; but for border-line cases, e.g. fluorine, the solvent and/or nucleophile used can have a large effect. A change of solvent can result in either a change in the kinetic form of the reaction, or, if the kinetic form of the reaction remains the same, the rate of reaction changes.

A survey of the reactions producing the various types of kinetic effects discussed above is now given.

Reactions in which the rate constant decreases with increasing base concentration have been recorded by many workers[45,46,47,48]. The reactions of 1-fluoro-2,4-dinitrobenzene with aniline in methanol[45] show a decrease in rate coefficient ko of about 30% as the aniline concentration is increased from 5×10^{-4}M to 1×10^{-2}M. This observation by Bunnett and Garst is in general agreement with the results of Ross and Kuntz[48] in the reactions of 1-chloro-2, 4-dinitrobenzene with aniline in ethanol and in 50% ethanol - 50% ethyl acetate. Results of other workers including that by Bamkole and Hirst[46] on the reactions of 2-chloro-5-nitropyridine and 2-fluoro-5-nitropyridine with aniline in methanol at high temperatures (F at + 104.3°C, Cl at +102.9°C) also show this decrease in rate with increase in amine concentration. Bernasconi[47] also noticed this decrease in the reaction of piperidine with the ethers of 2-4-dinitrophenol in 10% dioxane - 90% water.

Ross and Kuntz[48] explained their observation in terms of charge-transfer complexes. This explanation is also assumed valid for all the other instances where this phenomenon is observed.

There are very many cases of mildly accelerated reactions reported by various workers[17, 45]. These include the reactions of 1-chloro-2,4-dinitrobenzene with several amines in chloroform[17] and/or ethanol for which k''/k' varies from 0.24 to 4.6 and those of p-nitrofluorobenzene with piperidine in several polar solvents[28] for which $k''/k' \leq 3.2$. The reactions of 1-chloro-2,4-dinitrobenzene with amines in benzene[40a, b, 50] are at most mildly augmented by excess amines. The effects of neutral and basic salts on the rates of the reactions of 1-chloro-2,4-dinitrobenzene with aniline in methanol is mild,[17] $k''/k' \simeq 2$. When the solvent is t-butanol, the rate was found to increase steadily with increasing aniline concentration but k''/k' is still about 2.6.

In the reactions[45] of N-methylaniline with 1-X_ 2,4-dinitrobenzene (X = F, Cl, Br) in various hydroxylic solvents, it was found that when X=Cl, and Br, there were mild accelerations with $k''/k' \leq 5$. Suhr[51] reported work on the reactions of p-nitrofluorobenzene with piperidine in alcoholic solvents for which $k''/k' < 5$.

Now, by Bunnett's classification, only systems for which $k''/k' > 50$ are regarded as cases of true base catalysis.

Therefore in the reactions reported by Suhr[51], Bunnett[17], and other workers for which $k''/k' < 5$, from our proposed mechanism in Chapter I, the formation of the intermediate is rate limiting: there is no base catalysis.

These reactions belong to the class of reactions with

$k_2 + k_3[B] \gg k_{-1}$ - a situation which is mostly encountered for 'good' leaving groups.

Bunnett and Bernasconi[46a, 47] investigated the reactions of Piperidine with the ethers of 2,4-dinitro phenol in 10% dioxane - 90% water leading to 2,4-dinitrophenyl piperidine. They showed that the occurrence of base catalysis depends on the group displaced. Reactions with good leaving groups such as Cl, Br, I, were little or not sensitive to catalysis by bases whereas base catalysis was found to be strong for poor leaving groups such as the ethers.

However, Ross[22] has studied the rates of reactions of 1-chloro-2,4-dinitrobenzene with n-butylamine in chloroform as functions of amine concentrations and added salts, viz, benzyl triethylammonium nitrate. He observed mild general base catalysis in these reactions and on this basis, proposed that base catalysis in the reactions involving a good leaving group is due to hydrogen bonding between the amine and the suitable acceptor for hydrogen bonding in this case, another molecule of nucleophile, in the transition state for the intermediate complex formation.

Few instances of base catalysis involving the Cl group have been reported. One unequivocal instance is reported by Bernasconi and Zollinger[52] in the reaction of 1-chloro-2,4-dinitrobenzene with p-anisidine in benzene.

Other strongly accelerated reactions include the reactions[17] of 1-fluoro-2,4-dinitrobenzene with N-methyl aniline in ethanol in the presence of potassium acetate for which $k''/k' = 150$. The reaction is strongly catalysed by oxyanion bases, $k''/k' = 350$ for the hydroxide catalysed system with 60% water - 40% dioxane as solvent. The corresponding chloro compound shows no such base catalysis.

Reactions[28, 53] of p-nitrofluoro benzene and 1-fluoro-2,4-dinitrobenzene with piperidine in benzene are so strongly dependent on amine concentration that they are second-order in amine except at very low amine concentration[28].

Pietra and Vitali[54] also showed that there is base catalysis in the reaction of 1-fluoro-2,4-dinitrobenzene with piperidine in benzene in the presence of such addenda as α-pyridone and N-methyl α-pyridone.

Reactions of 4-fluoro-nitrobenzene with piperidine in benzene[55] show linear increase of rate constants with increasing amine concentration. Bernasconi and others[56] investigated the reactions of 1-fluoro-2,4-dinitrobenzene with benzylamine and N-methylbenzylamine in benzene with and without the addition of pyridine and 1,4-diaza-bicyclo (2.2.2) - octane (DABCO) as catalysts. Both reactions are catalysed by the reacting amine, pyridine and by DABCO. The dependence of the reaction rate on base concentrations is linear for N-methylbenzylamine and curvilinear for benzylamine. The sensitivity of both reactions to base catalysis is much greater than that of the reaction of piperidine with 1-fluoro-2,4-dinitrobenzene but is found to be considerably smaller than in the reaction of p-anisidine with the same substrate[52]; thus suggesting a correlation between the basicity of the reacting amine and the sensitivity of the reaction to base catalysis.

The reaction[52] of 1-fluoro-2,4-dinitrobenzene with morpholine in benzene have been studied with and without pyridine, and DABCO as catalysts. The reaction is catalysed by all three nucleophiles although the reaction is more sensitive to pyridine and DABCO catalysis than the same substrate with the sterically identical but more basic piperidine. These observations confirm a previously found trend of greater sensitivity to base catalysis with decreasing base strength of the reacting amine.

The rates of reactions of 1-fluoro- and 1-chloro-2,4-dinitrobenzene with piperidine as influenced by the addition of dimethylsulfoxide and aqueous dioxane have been measured[57] in benzene solution. For the fluoro substrate, the reaction is about as strongly catalysed by dimethylsulfoxide as by DABCO but much more strongly than by pyridine. A change in the dependence on piperidine concentration upon the addition of dimethylsulfoxide is an indication that a medium effect is operating. Another evidence is furnished by the reaction of the chloro substrate. This substrate, whose reaction is known to be insensitive to base catalysis, is nevertheless accelerated by dimethylsulfoxide. The dimethyl sulfoxide does not simply accelerate the rate of reaction via base catalysis but also via a medium effect notably its high polarity. It is less basic than pyridine in benzene therefore it cannot act as a base catalyst as proposed by Suhr[28].

For the strongly accelerated reactions mentioned above, the situation is that $k_{-1} \gg k_2 + k_3 \ [B]$ and the overall equation:

$$ko = \frac{k_1 k_2 + k_1 k_3 [B]}{k_{-1} + k_2 + k_3 [B]}$$

reduces to:

$$ko = \frac{k_1 k_2 + k_3 [B]}{k_{-1}}$$

There is a linear relationship between the rate constants and the amine concentrations.

Some reactions have been found to undergo base catalysis in such a way that ko increases less than linearly with increasing catalyst concentration. Among such are the reactions[58] of secondary amines and p-nitrophenyl phosphates and ethers of 2,4-dinitrophenol with piperidine in hydroxylic solvents which show strong dependence of rates on amine concentration. In these reactions, a limiting rate is obtained at high concentration of the catalyst. The plot of the rate constant versus amine concentration is curvilinear. This is interpreted as involving a change in the rate-determining step which in turn requires that there be an intermediate in the reaction pathway. Such observations constitute the most convincing evidence for the prediction that when k_{-1} and ($k_2 + k_3[B]$) are of comparable order, of magnitude, then a non-linear relationship exists between the base concentration and the rate of reaction. And it is generally agreed[22] that the observed rate accelerations are due to catalysis of intermediate decomposition to products.

Curvilinear relationship between amine concentration and the rate constant arises when

$$k_{-1} \simeq k_2 + k_3 [B]$$

At sufficiently high amine concentration, the condition

$$k_3 [B] \gg k_2 \text{ holds.}$$

If the original equation

$$ko = \frac{k_1 K_2 + k_1 k_3 [B]}{k_{-1} + k_2 + k_3 [B]}$$

is inverted to

$$\frac{1}{ko} = \frac{1}{k_1} \left(\frac{k_{-1} + k_2 + k_3 [B]}{k_2 + k_3 [B]} \right)$$

and the assumption $k_3 [B] \gg k_2$ holds, then the equation above becomes

$$\frac{1}{ko} = \frac{1}{k_1} + \frac{k_{-1}}{k_1 k_3 [B]}$$

A plot of $\frac{1}{ko}$ versus $\frac{1}{[B]}$ will be linear except at low amine concentration when this assumption may not hold. Such plots would then be linear initially, and later deviate towards the B axis. From such plots, slope will be

$$\frac{k_{-1}}{k_1 k_3} \quad \text{and intercept} \quad \frac{1}{k_1}$$

From the equations above, the values of

k_1, k_{-1}/k_3, k_{-1}/k_2 and k_3/k_2 can be obtained. The ratio k_3/k_2 indicates the extent of acceleration by bases. Such predictions are now fully satisfied and observed by many workers among them Bunnett et al.[15-17]

In general, the order of halogen mobility in protic solvents is $F \gg Cl \simeq Br > I$. For example, in methanol, a protic solvent, the departure of the smaller more strongly bound halide ion is favoured over the departure of the larger and more loosely bound halide ions. This suggests that the step at which the C - halide bond is broken is not rate limiting.

In non-protic solvents such as benzene the reverse order i.e. $F < Cl \simeq I$ is observed. When the reverse order is observed, the leaving group tends to depart slowly, $(k_2 + k_3[B])$ being small, while the solvent e.g. benzene - a non-polar aprotic solvent with a dielectric constant of 2.28 causes K_{-1} to be large. Thus in non-polar aprotic solvents, strong accelerations have been found for the reactions of piperidine with 2,4-dinitroanisole and 2,4-dinitrophenyl ether[53] which possess poor leaving groups.

The change from a non-polar aprotic solvent such as benzene to a protic and dipolar aprotic ones has a profound effect on the reactions of 4-fluoro and 4-chloro nitrobenzenes[51] in various solvents such as methanol, dimethylsulfoxide and dimethylformamide.

In methanol, and in dimethyl sulfoxide, the reactivity sequence $ArF > ArCl$ is observed[28, 51]. From Parker's work[39a], it has been established that the increase in rate in changing from protic to dipolar aprotic solvent is general for anion-dipolar molecular reactions proceeding via a large negatively charged transition state. Parker attributed this behaviour to the fact that solvation energy of simple ions are lower in dipolar aprotic solvents than in water.

However, when reaction is between neutral molecules such as nitro-activated halides and amines, this is not always true as there are instances when reactivity is higher in protic solvents over dipolar aprotic solvents.

More support for this view is supplied by Habbersfield's work[29]. On carrying out the Menschutkin reactions of pyridine with six benzyl halides, he found a decrease in enthalpy of activation in changing from protic to dipolar aprotic solvents. This lower activation energy in dipolar aprotic solvent notably dimethylformamide is caused entirely by greater solvation of the transition complex in this solvent.

The reactions of p-nitrofluorobenzene with piperidine[28] proceed faster in the dipolar aprotic dimethylsulfoxide and dimethylformamide than in the protic solvents and solvents with similar dielectric constants - acetonitrile and nitromethane. Suhr attributed this behaviour to base catalysis but Bunnett disagreed with this view[17, 45]. Bernasconi[57] has, in his work, demonstrated that dimethylsulfoxide is not capable of accelerating reaction rates by base catalysis. Both Bunnett and Bernasconi conclude therefore that these solvents accelerate reaction velocity through their high polarity.

Rates of reaction of many primary[62a] and secondary[62b] amines with p-nitrofluorobenzene have been measured in dimethylsulfoxide. Addition of varying quantities of dimethylsulfoxide to benzene was found to cause great increases in the rates of reaction. Addition of dipolar aprotic solvent notably dioxane also caused increase in rates though of a smaller order than by dimethylsulfoxide. The explanation given by Miller[61] is in general agreement with previous views that the presence of dimethylsulfoxide in the solvents causes a relative enhancement of the solvation of the transition state.

Also, in the work of Ross[22] on the catalysis of the intermediate complex formation in Nucleophilic Aromatic substitution, he found that in the mildly catalysed reactions of halonitrobenzene . with amines, solvent effects are very large in general paralleling the polarity as indicated by their dielectric constant. For example, the reaction of p-nitrofluorobenzene and piperidine at 50°C is four times faster in dimethylsulfoxide (= 48.5) than in dibutylether (= 3.06)

There are few cases of exception to the rule of greater rate enhancement in dipolar aprotic solvents than in protic solvents. For example in the work of Bamkole and Hirst[59] on the reactions of 1-fluoro- and 1-chloro- 2,4-dinitro benzene with aniline, and piperidine and 2-chloro- and 2-fluoro-5-nitropyridine in acetone and methanol; also the work of Chapman and Parker[60] on these substrates with ethanol as solvent. In all cases, it was found that the rates of reaction are greater in the hydroxylic solvents by factors ranging from 3 to 30. For instance, in the reaction between 2-fluoro-5-nitropyridine and aniline at high temperatures $\simeq 103^{\circ}$C, the rate of reaction in methanol at 104.3°C is 3.14×10^{-2} l.mol.^{-1} sec.^{-1} and in acetone, the corresponding rate is 2.38×10^{-5} l.mol^{-1} sec^{-1}. Also in the reactions of 1-chloro-2,4-dinitrobenzene with piperidine, the rate constant at 50°C is 6.54×10^{-5} l mol^{-1} sec^{-1} in acetone and 5.53×10^{-3} $\text{lmol}^{-1}\text{sec}^{-1}$ in methanol.

In these instances, reactions are faster in protic solvents than in dipolar aprotic ones.

Despite these exceptions, in general, in reactions between uncharged molecules, e.g. activated halides with amines, the trend of rate enhancement in dipolar aprotic solvents over protic solvents is established.

CHAPTER 4

EXPERIMENTAL SECTION

a) Preparation and Purification of Materials

i) 1 - fluoro -2, 4- dinitrobenzene:

This yellow liquid was purified by crystallisation at low temperature (-10°C).

Since the compound is stored in sealed tubes, one of the tubes was chilled, cut open, and the yellow liquid quickly filtered into 100-ml. of sodium dried ether in a 250 ml. round bottomed flask. The flask was scratched with a glass rod to facilitate crystallisation, stoppered and finally stored in a deep freeze (about -10°C) for 24 hours. Fine yellow crystals separated, were quickly filtered off by suction to avoid moisture gathering on it, stored in a quick fit specimen bottle and dried in a vacuum desiccator over phosophorus pentoxide for 2 hours. The substance was stored as a liquid in the vacuum desiccator.

melting point = 27°C

Literature[60] m.pt. = 26.5 - 27°C

ii) 1 - chloro -2, 4- dinitrobenzene:

Commercial 1-chloro 2, 4-dinitrobenzene (60 gms) was dissolved in hot methanol and decolourising charcoal. The mixture was heated to boiling and while still hot, filtered by suction into a preheated receiver. The pale yellow liquid was kept in a quick fit conical flask. On cooling, pale yellow crystals separated, which were filtered off by suction, stored in a quick fit specimen bottle, and dried by suction over $CaCl_2$ grains. The substance was then stored in the vacuum dessicator.

Melting point = 49-50°C
Literature[44b] m.pt. = 50-51°C

iii) 2-chloro -5 - nitropyridine:

Commercial 2-chloro- 5 nitropyridine (20 gm.) was dissolved in 30 ml. of Analar methanol. A small sample was left undissolved. Decolorising charcoal was added and the mixture boiled for about 2 minutes. The hot mixture was filtered and the filterate stored in a quick fit conical flask. On cooling, flakes of a pale yellow substance separated, were filtered by suction and then vacuum dried over $CaCl_2$. The substance was then stored in a quick fit specimen bottle.

Melting point = 110 - 110.5°C
Literature[44c] m.pt. = 109 - 110°C

iv) Piperidine:

Analar Piperidine (100 ml.) was refluxed with sodium metal for six hours and then distilled in an all quick fit distilling assembly. The distillate was protected from atmospheric moisture by a $CaCl_2$ guard tube.

The middle portion of the distillate, distilling at 105°C was collected in a 100 ml. quick fit round bottomed flask and kept for kinetic runs. The procedure was repeated after three weeks of storage to maintain a high degree of purity.

v) N-Butylamine:

Analar N-butylamine (100 ml.) was distilled in an all quick fit distilling assembly over zinc dust and potassium hydroxide pellets. The distillate was protected from moisture by a $CaCl_2$ guard tube. The middle portion distilling at 77°C was collected for kinetic runs. The procedure was repeated after three weeks to maintain high degree of purity.

vi) Acetone:

Analar acetone (1.5 litre) was refluxed with $KMnO_4$ until the violet colour of the permanganate persisted. The acetone was then distilled off. Magnesium perchlorate (anhydrone) was added to saturation point and then the acetone was distilled in an all quick fit assemblage. The middle portion distilling at 56°C was collected and used for kinetic runs.

vii) Methanol:

The method of Luud and Bjerrum[44d] was used. Into a 3- litre quick fit round bottomed flask was put dry magnessium turnings (10 gm.) resublimed iodine (0.5 gm.) and Analar methanol (300 ml.). The methanol was converted to the methoxide and the reacting mixture had to be cooled. More analar methanol (2 litres) was added to the flask and the contents refluxed for 30 minutes using a double surface condenser. Methanol was distilled and the middle portion which distilled at 64°C was collected into a dry quick fit flask. (2 litres)

viii) Absolute Chloroform:

Chloroform is stabilised with 2% ethanol. To destabilise it, analar chloroform (2 litres) was shaken up with 50% sulphuric acid (400 ml.). This shaking was repeated three times after which there was no more reaction in the flask. The chloroform was then washed several times with distilled water; the washings being tested with blue litmus paper. When the washing was neutral to litmus, calcium chloride (100 grams) was added and shaken up. The cloudy chloroform became clearer. The calcium chloride was filtered off. A further 100 gm of calcium chloride was shaken up with the chloroform and left over night. The calcium chloride was filtered off and the already dry chloroform was distilled gently in an all quick fit assemblage. The middle portion distilling at 61°C was collected for kinetic runs.

The following tests were conducted to show that there was no more OH radical present in the chloroform:

a) The N.M.R. spectrum was obtained and this showed no OH peak.

b) The Vapour Phase Chromatograph showed only one peak.

c) The I.R. spectrum showed no OH peak.

These three tests showed the solvent to be free from any mixtures hence to be 100% pure.

ix) Preparation of Piperidine Hydrochloride:

HCl gas formed by dropping concentrated H_2SO_4 onto concentrated HCl and dried by being passed through two jars containing concentrated H_2SO_4, was bubbled into a solution of piperidine in dry acetone. The white precipitate which formed was filtered off and washed with dry acetone. This product, being hygroscopic was quickly collected and stored in a well stoppered reagent bottle for use.

x) 2, 4 -dinitrophenylpiperidine:

50 ml. each of standard solutions of 1-chloro-2, 4-dinitrobenzene (2N) and Piperidine (2N) in sodium dried ether, were mixed in a 100 ml quick fit conical flask and left in a thermostat at 30°C overnight. The contents were then poured into 100 mls of distilled water, the orange precipitate filtered off, recrystallised from methanol and dried in a vacuum dessicator.

Melting poing = 93°C

Literature m.pt.[44e] = 92 - 94°C

xi) Preparation of 2, 4 dinitrophenyl -N-butylamine:

1 gram of 2,4-dinitrochlorobenzene was weighed into a beaker and very cautiously enough n-butylamine to dissolve it was added.

The contents on cooling were stirred with dry acetone and the precipitate of n-butylamine hydrochloride was filtered off. The filtrate was evaporated down to an oil which solidified on stirring with dilute HCl. The precipitate was filtered off and recrystallised from boiling methanol and decolorising charcoal. The product, bright yellow crystals, was stored for runs.

Melting Point = 81 - 82°C

Lit.[17] mpt. = 81°C

xii) Preparation of 2-piperidino -5 -nitropyridine:

2- chloro - 5-nitropyridine (1.0 gm) and piperidine (1.5 gm.) were heated on the water bath for 30 minutes. The product was then dissolved in the minimum amount of 80% ethanol, heated with decolorising charcoal, filtered and then allowed to cool.

Yellow crystals separated.

Melting point = 82°C

Literature[44f] melting point = 84°C

xiii) Preparation of Quenching Mixture:

A mixture of known proportion of concentrated H_2SO_4 in dry methanol was employed in quenching the reactions in this work. The acidity of the medium was dependent on the particular reaction.

For 2-chloro -5-nitrophyridine the concentration of the H_2SO_4 was 0.01N. For all the other reactions the concentration was 0.05N.

The quenching mixture acted by fixing the amine as amine hydrogen sulphate and rendering it ineffective as a nucleophile.

(b) DESCRIPTION OF SPECIAL APPARATUS

i) Thermostats:

Two types of thermostats were used for the temperature range of $-30^{\circ}C$ to $+50^{\circ}C$ at which the kinetic studies reported here were carried out.

For work carried out from $+20^{\circ}C$ to $+50^{\circ}C$ a well lagged glass bath containing water was used. Heating was done by an electric coil and a mechanical stirrer kept the temperature uniform. The electric coil heated the fluid to a fraction of a degree lower than that required before control was effected by an intermittent heater, a Sunvic relay and a regulator.

For work carried out below room temperature, a 'black box' thermostat containing methanol was used. There was a cooling system which continually withdrew heat until a fraction of a degree below that required. Control was then effected by a Sunvic relay and a regulator.

In each case, the required temperatures were maintained to within $\pm 0.05^{\circ}C$ and readings were taken with standard thermometer with an accuracy of $\pm 0.01^{\circ}C$.

ii) The Dreischenkelrohr called D.R. tube:

For fast runs, this apparatus was used. It consisted of a glass tube with three separate compartments.

Two tubes, about 1.5 cm. in diameter and 5 cm. long were joined to a stem which was about 3 cm. in diameter at a common juncture so that they were inclined at about 60° to each other but about 120° to the stem. About 4 cm. to this juncture along the main stem, another tube about 5 cm. long and of the same diameter as the stem was joined. This third tube pointed in an opposite direction to the other smaller tubes and was inclined to the stem at about 60°. The ends of the three tubes were then rounded up and the stem provided with a B24 socket and stopper.

The apparatus thus had three legs on which it could stand solidly.

Different solutions could be pipetted into each compartment without them mixing until so desired. By tilting the stem side ways, the solutions in the lower arms can be mixed when also desired.

The third larger compartment which is normally used to hold the quenching solution was not used in this reaction.

iii) Gilford (2400) Recording Spectrophotometer:

For runs, for which the D.R. tube technique was too slow, the Gilford instrument was used. The reaction took place in the cell compartment whose temperature had been regulated via the thermostat. The instrument simply recorded the optical density against time.

iv) Gibson Spectrophotometer:

For runs for which even the Gilford Instrument proved too slow, the Gibson Durrurd's Stopped - Flow Spectrophotometer was used. The dead time of the instrument was 2 m. sec.

(c) INVESTIGATION OF KINETICS

Because the products of all the reactions in this work were brightly coloured progress of reaction was followed spectrophotometrically in each case.

A. Reaction of 1 - fluoro -2, 4 -dinitrobenzene with Piperidine in dry Methanol:

The optical absorptions of samples of the reaction mixture were measured on a Unicam spectrophotometer S.P. 500.

Choice of Wavelength:

The wavelength at which the progress of the reaction was followed was one at which only the product absorbed and maximally too, to the exclusion of the reagents. Standard solutions of Piperidine (0.0002M), 1- fluoro -2, 4-dinitrobenzene (0.0001M) and the product: 2,4 dinitrophenylpiperidine (0.0001M) were prepared in acetone and Quenching Mixture 0.05M H_2SO_4 in Methanol. These solutions were used to scan the spectrum from 200 m/u to 450 m/u. The product absorbed maximally at 380 m/u while the reagents did not absorb.

Calibration Curve or Beer's Law test for 2-4 dinitrophenyl-Piperidine at 380 m/u:

From the 10^{-4} M standard solution used for scanning, dilute solutions were prepared by making up 10 ml., 20 ml., 30 ml. up to 90 ml. to 100 ml. with Quenching mixture. The final concentrations are shown on the table.

Solutions and how they are prepared.	Concentration of diluted solutions.	Mean optical density at 380 m/u
10 ml. of 10^{-4}M diluted to 100 ml.	1×10^{-5}M	0.163
20 ml. of 10^{-4}M " "	2×10^{-5}M	0.315
30 ml. of 10^{-4}M " "	3×10^{-5}M	0.456
40 ml. of 10^{-4}M " "	4×10^{-5}M	0.608
50 ml. of 10^{-4}M " "	5×10^{-5}M	0.755
60 ml. of 10^{-4}M " "	6×10^{-5}M	0.901
70 ml. of 10^{-4}M " "	7×10^{-5}M	1.054
80 ml. of 10^{-4}M " "	8×10^{-5}M	1.210
90 ml. of 10^{-4}M " "	9×10^{-5}M	1.360
10^{-4}M	10^{-4}M	1.500

A plot of optical density against concentrations in moles per litre was made. The slope of this linear graph = 6.70×10^{-3} moles per litre per unit optical density and this was used to convert optical density measurements in the runs to moles per litre of product present.

Procedure for a run:

Exact quantities of piperidine and fluoro compound to make 0.025M and 0.0025M respectively were weighed out. These were made into solutions with dry methanol (about 90 ml.) in 100 ml.

standard flasks. These flasks were labelled with their respective contents and immersed in the thermostat. After about 20 minutes, by which time, the solutions must have attained thermostat temperature, more dry methanol was added to make up to the marks. 5 ml. of each reactant was carefully pipetted by means of a rubber pipette filter and deposited rather carefully into the small tubes of the D.R. tube taking care they did not mix. The D.R. tube was then stoppered. About 20 ml. of Q.M. was put in a 50 ml beaker. The D.R. tube was submerged in the thermostat such that the reactants in the small tubes were fully immersed. After some time, the D.R. tube was tilted to bring the contents into contact while at the same time, a stop clock was started. At the desired time, the 20 ml Q,N, in the beaker was used to stop the reaction. All the contents of the D.R. tube was then transferred to a 50 ml. dry standard flask. The D.R. tube was then rinsed twice or more with small quantities of Q.M. and the washings added to the standard flask care being taken not to overshoot the mark. The solution was then made up to the mark with more Q.M. 10 ml of this was further diluted to 50 ml. in another 50 ml. standard flask with Q.M. The optical density of this last solution was then taken. One such reaction in the D.R. tube was left overnight and the optical density after appropriate dilution was found to agree with the theoretical infinity obtained from the calibration curve.

This procedure was used for all the runs for this reaction.

<u>Calculation of Rate Constants from Experimental data</u>:

The reaction can be represented by the equation:

$$ArF + R_2NH = ArNR_2 + HF$$

$${+}$$

$$R_2NH + HF = R.NH_2F^-$$

where ArF = 1- fluoro -2, 4-dinitrobenzene

R_2NH = Piperidine

$ArNR_2$ = 2, 4-dinitrophenylpiperidine.

Let the initial concentrations of R_2NH and ArF be a and b respectively. Then after time t let x moles of products be formed then the rate equation is $\frac{dx}{dt} = k\,(a - 2x)\,(b - x)$ ...A(i),

This is assuming that the piperidinium fluoride so formed above is not as good as a nucleophile as piperidine itself. But if it is assumed that HF is such a weak acid that it does not lead to the production of piperidinium fluoride under the run conditions or that even if this is formed, it is as good a nucleophile as the piperidine itself, then the rate equation will be:

$$\frac{dx}{dt} = k\,(a - x)\,(b - x) \quad \ldots\ldots \quad A(ii)$$

In either case, if the concentration of the nucleophile a is very much greater than that of the substrate b we can assume that

$$a - 2x \simeq a - x \simeq a$$

So the equations (i) and (ii) become $\frac{dx}{dt} = k''\,a(b - x)$ .... A(iii)

For truly first order reactions, the nucleophile is in such an excess that the rate equation:

$$\frac{dx}{dt} = k\,a(b - x) \quad \text{(where the notations above still apply)}$$

can be rewritten as

$$\frac{dx}{dt} = k^1(b - x) \;\ldots\ldots\; (iv) \text{ where } ka = k^1$$

first order rate constant.

Comparison of this with that equation (iii) obtained from 2nd order kinetics gives

$$\frac{dx}{dt} = k^1(b - x) \quad \ldots\ldots A(iv)$$

$$\frac{dx}{dt} = k''a(b - x) \;\ldots\ldots a(v)$$

$$\frac{k^1}{k''a} = 1$$

$$k'' = \frac{k^1}{a}$$

Thus the second order rate constant can be obtained by dividing the first order rate constant by the amine concentration.

For first order kinetics,

$$\frac{dx}{dt} = ka\ (b - x) \quad \text{or}$$

$$\frac{dx}{dt} = k^1\ (b - x)$$

on integration we have

$$k^1 = \frac{1}{t} \ln \left(\frac{b}{(b - x)}\right)$$

A graph obtained by plotting $\log_{10}$ of optical density at infinity less that at the time t versus time t will give a straight line whose slope will be $\frac{k^1}{2.303}$ from here, k^1 can be obtained and hence k".

This was the method used to calculate second order rate constants for this reaction.

B. The reaction of 1-chloro-2, 4-dinitrobenzene with Piperidine in dry Methanol.

The progress was followed spectrophotometrically at wavelength 380 $m\mu$ just as in the case of the fluoro compound.

Procedure for a run:

For amine concentrations of 0.0355M to 0.300M, the method whereby aliquots are withdrawn from a reacting mixture and quenched was used.

Enough quantities of both reagents were made up to standard solutions at thermostat temperatures as described before. Into a third 100 ml. standard flask also immersed in the thermostat, 50 ml. of the substrate solution and 50 ml. of the solution containing the nucleophile were pipetted and at the same time a stop clock was started. After all the nucleophile had been added, the reaction mixture was shaken quickly. At intervals, 5 ml aliquots were pipetted into a 50 ml. standard flask containing about 30 ml. of Q.M. More Q.M. was added to make it up to the mark. 5 ml. of this was further diluted to 50 ml. and the O.D. of the last solution was taken.

For nucleophile concentrations of 0.600M and 1.20M, the D.R. tubes were used.

Calculation of Rate Constants from Experimental Data:

The reaction can be represented by the equations:

$$ArCl + R_2NH \qquad Ar\text{-}N\text{-}R \ + HCl$$

$$HCl + R_2NH \qquad H_2-\overset{+}{N}-R_2Cl^-$$

where ArCl $=$ 1 - chloro-2, 4- dinitrobenzene

R_2NH $=$ Piperidine and

$ArN-R_2$ $=$ 2, 4-dinitrophenylpiperidine.

Unlike HF, HCl is a stronger acid and is highly ionised in solution and as such it combines with a second amine molecule to form piperidinium hydrochloride. Two molecules of Piperidine are therefore used up. Using the same notations as before, the rate equation is

$$\frac{dx}{dt} = k(a - 2x)(a - x) \text{ ....B(i)}$$

From this differential equation, it can be derived that

$$k = \frac{2.303}{t(a-2b)} \log \frac{b(0.5a - x)}{0.5a(b - x)} \text{ .... B (ii)}$$

Experimental quantities obtained from the runs can be introduced into the equation.

OD_o is the Optical Density at time zero.

OD_t is the optical Density at time

OD_∞ is the optical density at infinity,

Then b is proportional to $OD_\infty - OD_o$

and x is proportional to $OD_t - OD_o$

and a is proportional to X $-$ 20.Do

where X is calculated on the assumption that were all the piperidine converted to products this would be the optical density after appropriate dilution. f is the dilution factor which is the number of times the run mixture is diluted before the optical density is taken. F is the conversion factor which is the value of the slope of the calibration curve. We will then have:

$$k_2 = \frac{1}{F}\,\frac{1}{f}\,\frac{2.303}{X-2\,OD_{\infty}}\cdot\frac{1}{t}\log_{10}\frac{OD_{\infty}-OD_{c}}{0.5X-OD_{o}}\cdot\frac{0.5X-OD_{t}}{OD_{\infty}-OD_{t}} \quad \ldots B(iii)$$

In equation B(iii), X has to be greater than 2 OD_o or the initial concentration of piperidine has to be greater than twice the initial concentration of the chloro compound. This assumption held in all runs for this reaction.

C. Reaction of 2-chloro-5-nitropyridine with Piperidine in dry Methanol.

Preparation of Quenching Mixture:

It was discovered that the more acidic the medium used the less absorption the product in this reaction gave. This is probably due to the possible protonation of the Nitrogen atom in the pyridine ring. In order to get as high an absorption as possible, 0.01N H_2HO_4 was prepared in Analar methanol; this was used as quenching mixture.

Choice of Wavelength:

The same concentrations of the nucleophile, substrate and product as were taken previously were used. The product absorbed maximally at wavelength 370 m/u.

Test for Beer's Law:

Solutions of strengths ranging from 10^{-5}M to 10^{-4}M were also used.

Solutions and how they are prepared	Concentration of diluted solution	Mean optical density OD. at 370 m/u
10 ml. of 10^{-4} diluted to 100 ml.	1×10^{-5}M	0.171
20 ml. of 10^{-4} " " "	2×10^{-5}M	0.328
30 ml. of 10^{-4} " " "	3×10^{-5}M	0.499
40 ml. of 10^{-4} " " "	4×10^{-5}M	0.680
50 ml. of 10^{-4} " " "	5×10^{-5}M	0.890
60 ml. of 10^{-4} " " "	6×10^{-5}M	1.055
70 ml. of 10^{-4} " " "	7×10^{-5}M	1.255
80 ml. of 10^{-4} " " "	8×10^{-5}M	1.450
90 ml. of 10^{-4} " " "	9×10^{-5}M	1.650
10^{-4}	10^{-4}M	1.950

Slope of plot of optical density against concentration = 1.750×10^{-4}. The section of OD = 0.171 to OD. =1.055 was used.

Procedure for a run: Standard solutions of the reagents were prepared at thermostat temperatures as described earlier on with solvent also at thermostat temperature. In this way, there was no necessity for the calculation of coefficient of cubical expansion. 50 ml. of each of the reagents was mixed in a standard flask and 5 ml. aliquots withdrawn at suitable time intervals into 20 ml. of Q.M. in a 50 ml standard flask. More Q.M. was added to make up to the mark. 5 ml. of this was further diluted to

50 ml. in another standard flask and the OD of this latter solution was taken.

Calculation of Rate Constants:

This followed the same procedure as that of 1-fluoro- 2,4-dinitrobenzene. The slope of graph obtained by plotting the $\log_{10}$ of $(OD_{\infty} - OD_t)$ versus time in seconds will give the value of $\frac{k^1}{2.303}$ where

OD_{∞} = optical density at infinity obtained by leaving the reacting mixture for more than 48 hours.

OD_t = optical density at any time t and k^1 = first order rate constant.

$k_2 = \frac{k^1}{[R_2NH]}$ where R_2NH is the amine.

For the reaction of 2-chloro-5-nitropyridine with Piperidine in dry acetone, exactly the same procedure as that above was followed.

D. The reaction of 1 - fluoro-2, 4 -dinitrobenzene and Piperidine in dry acetone.

Choice of Wavelength:

The same wavelength 380 mμ was used here as for the same reaction carried out in methanol since the products of both reactions are the same.

Procedure for a run:

Gilford (2400) Recording Spectrophotometer, was used.

It contains a cell - compartment whose temperature can be regulated by a flow of water to that desired. This regulation was achieved by means of a water thermostat whose temperature was slightly higher than that required in the cell. The cell temperature gave the desired reading.

1.00×10^{-2}M of the fluoro compound was prepared in a 50 ml standard flask. This was diluted a further 1,000 times to give 1.00×10^{-5}M; 2.5 ml. of this was carefully pipetted into a silica cell and placed in the cell compartment. Now, 0.2M of Piperidine was prepared and this was further diluted 10 times to give 0.02M.

With an Agla Micrometer All - Glass Syringe used with Shardlow micrometer screw gauge 0.01 ml of this base was added to the fluoro compound in the cell and the instrument started.

The concentration of the base was then $\frac{0.01 \times 0.02}{2.51}$ M = 7.97×10^{-5}M. Higher concentrations were obtained by dropping 0.01 ml of stronger solutions onto the substrate.

The instrument gave a plot of optical density versus time in chosen units. From this graph, OD_{∞} and OD_t were obtained. And a plot of log $(O.D_{\infty} - O.D_t)$ versus time in seconds gave a graph whose slope $= \frac{k^1}{2.303}$

k^1 being first order rate constant.

k^2, second order rate constant was then obtained from this.

E. Reaction of 1 - chloro-2, 4 - dinitrobenzene with Piperidine in dry acetone:

Wavelength of 380 m/u was also used. The calibration curve used for the same reaction in dry methanol was also used.

Procedure for a run:

Enough reagents to give twice the desired concentrations in the run were weighed out. The solutions were prepared in the thermostat as earlier described. 50 ml. of each of the reagents were then mixed and at suitable time intervals 5 ml. aliquots were withdrawn and diluted 100 fold with quenching mixture before the optical densities were taken.

Calculation of rate constants:

The equation B(iii) was used here also

$$k = \frac{1}{F} \cdot \frac{1}{f} \cdot \frac{2.303}{X-2\,O.D_{\infty}} \frac{1}{t} \log_{10} \frac{OD_{\infty} - OD_{e}}{0.5X - OD_{o}} \cdot \frac{0.5X - OD_{t}}{OD_{\infty} - OD_{t}}$$

where the symbols retain their significance.

F. Reaction of 1 - fluoro - 2,4 - dinitrobenzene with n-Butylamine in acetone:

This followed precisely the same pattern as the reaction of the fluoro compound with piperidine. The only difference is that here, since the products differed, the wavelength used also differed.

The method used for scanning and calibration were precisely the same. The optimum wavelength was found to be 350 m/u.

Procedure for runs:

Enough reagents to give twice required run concentrations were weighed and prepared in the solvent. With 1 ml bulb pipettes, 1 ml. of each reagent was mixed in the cell and the optical density was recorded. Care was taken to maintain the cell at the required temperature.

Calculation of Rate Constants:

Plots of log $(OD_{\infty} - OD_t)$ versus time in seconds for each concentration were obtained. From the slopes of these graphs, first order rate constants were obtained. From these, second order rate constants were calculated.

G. Reaction of 1 - chloro 2,4 - dinitrobenzene with n-Butylamine in acetone:

The wavelength used was also 350 m/u and the calibration curve gave a slope of 5.548×10^{-3} moles per litre per unit optical density.

Procedure for a run:

The method of mixing 50 ml. of standard solutions of the reagents and quenching 5 ml. aliquots at predetermined time intervals was used.

Calculation of Rate Constant:

2nd order rate constants were calculated using equation B(iii).

$$k2 = \frac{1}{F} \cdot \frac{1}{f} \cdot \frac{2.303}{X-2.OD_{\infty}} \cdot \frac{1}{t} \log_{10} \frac{OD_{\infty} - OD_o}{0.5X - OD_o} \cdot \frac{0.5X - OD_t}{OD_{\infty} - OD_t}$$

H. Reaction of 1 - chloro-2.4 -dinitrobenzene with n - Butylamine in Chloroform:

The wavelength used was 350 m/u and the slope of calitration curve has 1, 5.548 x 10^{-3} moles per litre per unit optical density as above. The procedure for runs was the same as that above.

Calculation of Rate Constants:

The run concentration of the chloro compound in each case was 2.5 x 10^{-2}M. The equation B(iii) is only applicable in cases when the concentration of the amine concentration was less or the same as the substrate concentration, then a modification of B(iii) was employed.

$$k2 = \frac{1}{F} \cdot \frac{1}{f} \cdot \frac{2.303}{X-2\,OD_{\infty}} \cdot \frac{1}{t} \log \frac{OD_{\infty} - OD_{o}}{0.5X - OD_{o}} \cdot \frac{0.5X - OD_{t}}{OD_{\infty} - OD_{t}} \quad \ldots\ldots \text{B(iii)}$$

where the symbols still retain their usual significance.

This modification would be

$$k2 = \frac{1}{F} \cdot \frac{1}{D} \cdot \frac{2.303}{2(Y-OD_{\infty})} \cdot \frac{1}{t} \cdot \log \frac{OD_{\infty} - OD_{e}}{Y - OD_{o}} \cdot \frac{Y - OD_{t}}{OD_{\infty} - OD_{t}} \quad \ldots \text{H(i)}$$

where OD_o in this case is the optical density corresponding to half of the initial concentration of n-Butylamine going to products and Y is the calculated optical density corresponding to conversion of all the chloro compound into products.

I. Reaction of 1 - fluoro-2.4 -dinitrobenzene with N-Butylamine in Chloroform.

Wavelength used = 350 m/u

Calibration curve used was the same as that for H. Slope

$= 5.548 \times 10^{-3}$ moles per litre per unit optical density.

Amine Concentration 0.025M and 0.10M:

These reactions were carried out in the cell compartment of the Gilford (2400) recording spectrophotometer.

Amine concentrations 0.20M up to 1.00M

The Gibson Durrurd's stopped - flow spectrophotometer was used. The dead time of the instrument was 2 m.sec.

Optical Densities:

The optical densities of each reaction at infinity were calculated from the calibration curve. The experimental infinity optical densities in the runs were also obtained. Theoretical optical density at infinity is denoted OD_{∞} calc. Experimental optical density at infinity is denoted OD_{∞} experiment. In cases where OD_{∞} calculation were used, both values were written. In cases where no OD_o experimental was obtained but inferred, then OD_{∞} calculated only were written.

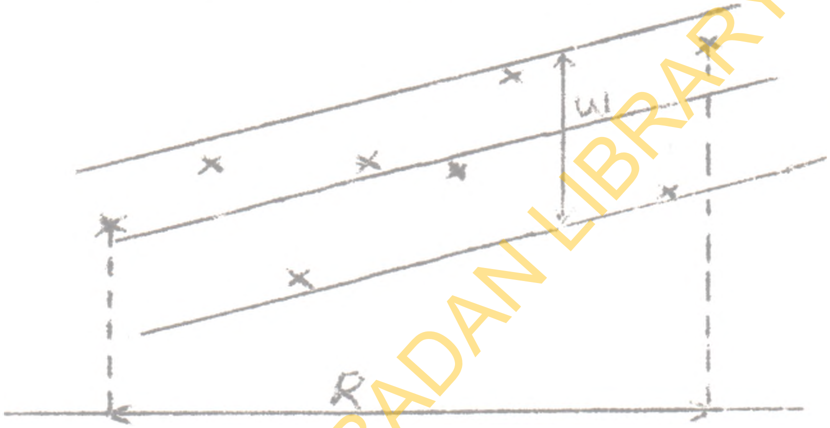
Calculation of limits of accuracy:

1. For those rate constants calculated using the equation B(iii) or its modification H(i) the limit of error was simply the maximum deviation of any of the separate rate constants from the average obtained.
2. For the graphical determinations, the error of the slope may be calculated from the scatter of the points by the formula $S_g = \frac{4w}{nR} \quad (3 \leq n \leq 12)$

where n = number of points

w = range of vertical scatter

R = total range of the x coordinate between the first and last points of the graph.



k_1 = 2.303 x slope

error in k_1 is then the relative error calculated from above.

$$k_2 = \frac{k_1}{[B]} \quad \ldots\ldots\ldots(i)$$

where $[B]$ is concentration of amine in run; error in k_2 is then the fractional or relative error calculated using the equation (i).

Calculation of Arrhenius parameters is made from the Arrhenius equation $k = Be^{-E/RT}$. The activation energy E for a reaction can be calculated from the rate constants for the reaction at two different temperatures. Thus, if k_1 and k_2 are the two rate constants at kelvin temperatures T_1 and T_2 respectively, then

$$\log \frac{k_2}{k_1} = \frac{E}{2.303R} \left(\frac{T_2 - T_1}{T_1 \; T_2}\right)$$

where R is the molar gas constant = 1.987 cal, gram mol^{-1}.

The pre-exponential factor B can be calculated at any temperature T where E is known from the equation

$$\log k = \log B - \frac{E}{2.303 \; RT}$$

(d) KINETIC RESULTS.

EXPERIMENT 1

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with Piperidine in the presence of piperidine hydrochloride in dry methanol at 29.6 ± 0.05°C.

Wavelength = 380 m/u

Initial Concentrations: Piperidine = 1.25×10^{-2}M

Fluoro = 1.25×10^{-3}M

Pip. Hcl. = 1.00×10^{-1}M

OD_{∞} calc. = 0.754 f = 25.

OD_{∞} expt. = 0.755

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 380 m/u per 10 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$OD_{\infty} - OD_t$	$2 + \log (OD_{\infty} - OD_t)$
30	0.623	1.7945
90	0.476	1.6776
180	0.417	1.6201
240	0.389	1.5899
360	0.262	1.4183
480	0.223	1.3483
600	0.165	1.2175
750	0.129	1.1106
900	0.093	0.9685

Slope of $2 + \log (OD_{\infty} - OD_t)$ versus time in secs

$K1 = 2.11 \times 10^{-3} = 9.17 \pm 0.5 \times 10^{-4}$

$k_2 = 1.69 \pm 0.09 \times 10^{-1}$ litre mole^{-1} sec^{-1}

Duplicate $k_2 = 1.65 \pm 0.09 \times 10^{-1}$ litre mole $^{-1}$ sec^{-1}

Mean $k_2 = 1.67 \times 10^{-1}$ litre mole $^{-1}$ sec^{-1}

EXPERIMENT 2

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with Piperidine in the presence of piperidine Hydrochloride in dry methanol at - 29.6 ± 0.05°C.

Wavelength = 380 m/u

Initial Concentrations: Piperidine = 2.50×10^{-2}M

Fluoro = 1.25×10^{-3}M

Pip. HCl = 1.00×10^{-1}M

OD_{∞} calc. = 0.754

OD_{∞} expt. 0.755

f = 25.

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 380 m/u per 10 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$OD_{\infty} - OD_t$	$2 + \log OD_{\infty} - OD_t$
15	0.594	1.7738
30	0.540	1.7324
45	0.440	1.6474
90	0.372	1.5705
180	0.238	1.3766
300	0.140	1.1644
450	0.090	0.9542
600	0.030	0.4771

Slope of $2 + \log (OD_{\infty} - OD_t)$ versus time in secs = $2.15 \pm 0.06 \times 10^{-3}$

$k_1 = 4.96 \times 10^{-3}$

$k_2 = 1.99 \pm 0.02 \times 10^{-1}$ litre mole^{-1} sec^{-1}

Duplicate $k_2 = 1.99 \pm 0.01 \times 10^{-1}$ " " "

Mean $k_2 = 1.99 \times 10^{-1}$ " " "

EXPERIMENT 3

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with Piperidine in the presence of piperidine Hydrochloride in dry methanol at - 29.6 ± 0.05°C.

Wavelength = 380 m/u

Initial Concentrations: Piperidine = 3.75×10^{-2}M

Fluoro = 1.25×10^{-3}M

Pip. HCl = 1.00×10^{-1}M.

OD_{∞} calc. = 0.754

OD_{∞} expt. = 0.755

f = 25

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 380 m/u per 10 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$OD_{\infty} - OD_t$	$2 + \log (OD_{\infty} - OD_t)$
10	0.583	1.7657
30	0.507	1.7050
45	0.402	1.6042
60	0.350	1.5441
90	0.275	1.4393
150	0.194	1.2878
300	0.099	0.9956
450	0.060	0.7782

Slope of $2 + \log (OD_{\infty} - OD_t)$ versus time in secs = $3.63 \pm 0.41 \times 10^{-3}$

$k_1 = 8.35 \times 10^{-3}$

$k_2 = 2.22 \pm 0.09 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 2.22 \pm 0.08 \times 10^{-1}$ " " "

EXPERIMENT 4

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with Piperidine in the presence of piperidine Hydrochloride in dry methanol at - 29.6 ± 0.05°C.

Wavelength = 380 m/u.

Initial Concentrations: Piperidine = 4.40×10^{-2}M

Fluoro = 1.25×10^{-3}M

Pip. HCl = 1.00×10^{-1}M

OD_{∞} calc. = 0.755

OD_{∞} expt. = 0.748

f = 25

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 380 m/u per 10 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$OD_{\infty} - OD_t$	$2 + \log (OD_{\infty} - OD_t)$
5	0.648	1.8116
15	0.580	1.7634
30	0.458	1.6609
45	0.384	1.5843
60	0.330	1.5185
90	0.239	1.3784
180	0.130	1.1139

Slope of $2 + \log (OD_{\infty} - OD_t)$ versus time in secs = $5.651 \pm 0.05 \times 10^{-}$

$k_1 = 1.30 \times 10^{-2}$

$k_2 = 2.96 \pm 0.01 \times 10^{-1}$ litre $\text{mole}^{-1}\text{sec}^{-1}$

Duplicate $k_2 = 3.20 \pm 0.03 \times 10^{-1}$ " " "

Mean $k_2 = 3.08 \times 10^{-1}$ " " "

EXPERIMENT 5

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with Piperidine in the presence of Piperidine Hydrochloride in dry methanol at - 29.6 ± 0.05°C.

Wavelength = 380 m/u.

Initial Concentrations: Piperidine = 4.75×10^{-2}M

Fluoro = 1.25×10^{-3}M

Pip. HCl = 1.00×10^{-1}M

OD_{∞} calc. = 0.754

OD_{∞} expt. = 0.755

f = 25

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 380 m/u per 10 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$OD_{\infty} - OD_t$	$1 + \log (OD_{\infty} - OD_t)$
5	0.625	0.7959
10	0.529	0.7235
20	0.448	0.6513
30	0.394	0.5955
45	0.267	0.4265
60	0.248	0.3945
90	0.198	0.2967
180	0.142	0.1510

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs = $9.29 \pm 1.4 \times 10^{-3}$

$k_1 = 2.13 \times 10^{-3}$

$k_2 = 4.46 \pm 0.01 \times 10^{-1}$ litre $\text{mole}^{-1}\text{sec}^{-1}$

Duplicate $k_2 = 4.38 \pm 0.01 \times 10^{-1}$ " " "

Mean $k_2 = 4.42 \times 10^{-1}$ " " "

EXPERIMENT 6

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with Piperidine in the presence of Piperidine Hydrochloride in dry methanol at - 29.6 ± 0.05°C.

Wavelength = 380 m/u.

Initial Concentrations: Piperidine = 5.00×10^{-2}M

Fluoro = 1.25×10^{-3}M

Pip. HCl = 1.00×10^{-1}M

OD_{∞} calc. = 0.755

OD_{∞} expt. = 0.748

f = 25

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 380 m/u per 10 mls of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$OD_{\infty} - OD_t$	$1 + \log (OD_{\infty} - OD_t)$
5	0.591	0.7716
10	0.497	0.6964
15	0.432	0.6355
20	0.347	0.5410
25	0.324	0.5100
30	0.282	0.4500
40	0.258	0.4112
60	0.201	0.3010
90	0.111	0.0410

Slope of $1 + \log (OD_{\infty} - OD_t$ versus time in secs = 1.441 ± 0.113 x 1

$k_1 = 3.33 \times 10^{-2}$

$k_2 = 6.60 \pm 0.01 \times 10^{-1}$ litre $mole^{-1} sec^{-1}$

Duplicate $k_2 = 6.40 \pm 0.00 \times 10^{-1}$ " " "

Mean $k_2 = 6.50 \times 10^{-1}$ " " "

EXPERIMENT 7

Reactions of 1 - fluoro - 2, 4 - dinitrobenzene with Piperidine in dry methanol at - 29.6 ± 0.05°C.

Wavelength = 380 m/u.

Initial Concentrations: Piperidine = 1.25×10^{-2}M

Fluoro = 1.25×10^{-3}M

OD_{∞} calc. = 0.755

OD_{∞} expt. = 0.749

f = 25

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 380 m/u per 10 mls of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$OD_{\infty} - OD_t$	$2 + \log (OD_{\infty} - OD_t)$
30	0.619	1.7917
90	0.469	1.6712
180	0.415	1.6180
240	0.381	1.5809
360	0.256	1.4082
480	0.217	1.3365
600	0.158	1.1987
900	0.085	0.9294

Slope of $2 + \log (OD_{\infty} - OD_t)$ versus time in secs = 1.02 ± 0.04 x 10

$k_1 = 2.34 \times 10^{-3}$

$k_2 = 1.80 \pm 0.01 \times 10^{-1}$ litre $mole^{-1} sec^{-1}$

Duplicate $k_2 = 1.72 \pm 0.01 \times 10^{-1}$ " " "

Mean $k_2 = 1.76 \times 10^{-1}$ " " "

EXPERIMENT 8

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with Piperidine in dry methanol at - 29.6 ± 0.05°C.

Wavelength = 380 m μ.

Initial Concentrations: Piperidine = 2.50×10^{-2} M

Fluoro = 1.25×10^{-3} M

OD_{∞} calc. = 0.755

OD_{∞} expt. = 0.760

f = 25

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 380 m μ per 10 mls of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$OD_{\infty} - OD_t$	$2 + \log (OD_{\infty} - OD_t)$
15	0.633	1.8014
30	0.603	1.7803
60	0.500	1.6990
90	0.447	1.6503
120	0.375	1.5740
180	0.279	1.4456
240	0.235	1.3711
300	0.155	1.1903
420	0.095	0. 977

Slope of $2 + \log (OD_{\infty} - OD_t)$ versus time in secs = $2.05 \pm 0.07 \times 10$

$k_1 = 472 \times 10^{-3}$

$k_2 = 1.88 \pm 0.00 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 1.96 \pm 0.01 \times 10^{-1}$ " " "

Mean $k_2 = 1.92 \times 10^{-1}$ " " "

EXPERIMENT 9

Reaction of 1 - fluoro - 2,4 - dinitrobenzene with Piperidine in dry methanol at - 29.6 ± 0.05°C.

Wavelength = 380 m/u.

Initial Concentrations: Piperidine = 3.75×10^{-2}M

Fluoro = 1.25×10^{-3}M

OD_{∞} calc. = 0.755

OD_{∞} expt. = 0.760

f = 25

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 380 m/u per 10 mls of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$OD_{\infty} - OD_t$	$2 + \log (OD_{\infty} - OD_t)$
10	0.532	1.7259
20	0.498	1.6972
30	0.474	1.6758
40	0.395	1.5968
60	0.340	1.5315
90	0.269	1.4298
120	0.195	1.2906
150	0.165	1.2175
240	0.090	0.9542

Slope of $2 + \log (OD_{\infty} - OD_t)$ versus time in secs = 3.683 ± 0.16 x 10

$k_1 = 8.47 \times 10^{-3}$

$k_2 = 2.26 \pm 0.03 \times 10^{-1}$ litre $\text{mole}^{-1}\text{sec}^{-1}$

Duplicate $k_2 = 2.35 \pm 0.02 \times 10^{-1}$ " " "

Mean $k_2 = 2.30$ x 10 " " "

EXPERIMENT 10

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with Piperidine in dry methanol at - 29.6 ± 0.05°C.

Wavelength = 380 m/u.

Initial Concentrations: Piperidine = 4.40×10^{-2}M

Fluoro = 1.25×10^{-3}M

OD_{∞} calc. = 0.755

OD_{∞} expt. = 0.750

f = 25

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 380 m/u per 10 mls of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$OD_{\infty} - OD_t$	$1 + \log (OD_{\infty} - OD_t)$
5	0.652	0.8142
10	0.628	0.7980
15	0.580	0.7634
20	0.542	0.7340
30	0.462	0.6646
45	0.379	0.5789
60	0.312	0.4942
90	0.245	0.3892
120	0.177	0.2355
180	0.120	0.0792

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs = 6.113 ± 0.10x10^{-3}

$k_1 = 12.80 \times 10^{-3}$

$k_2 = 3.19 \pm 0.00 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 3.07 \pm 0.01 \times 10^{-1}$ " " "

Mean $k_2 = 3.13 \times 10^{-1}$ " " "

EXPERIMENT 11

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with Piperidine in dry methanol at - 29.6 ± 0.05°C.

Wavelength = 380 mμ.

Initial Concentrations: Piperidine = 4.75×10^{-2}M

Fluoro = 1.25×10^{-3}M

OD_{∞} calc. = 0.754

OD_{∞} expt. = 0.749

f = 25

$(OD_{\infty} - OD_t)$. is expressed as optical density units at 380 mμ per 10 mls of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$OD_{\infty} - OD_t$	$1 + \log (OD_{\infty} - OD_t)$
5	0.622	0.7938
10	0.529	0.7235
15	0.490	0.6902
20	0.448	0.6513
30	0.389	0.5899
45	0.267	0.4265
60	0.245	0.3892
90	0.190	0.2788
180	0.135	0.1303

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs = $8.75 \pm 0.50 \times 10^{-3}$

$k_1 = 2.02 \times 10^{-2}$

$k_2 = 4.24 \pm 0.00 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 4.09 \pm 0.01 \times 10^{-1}$ " " "

Mean $k_2 = 4.17 \times 10^{-1}$ " " "

EXPERIMENT 12

Reaction of 1 - fluoro-2,4 - dinitrobenzene with Piperidine in dry methanol at -29.6 ± 0.05.

Wavelength = 380 mμ

Initial Concentrations: Piperidine = 5.00×10^{-2}M

OD_∞ calc. = 0.754 Fluoro = 1.25×10^{-3}M

OD_∞ expt. = 0.750

f = 25

$(OD_\infty - OD_t)$ is expressed as optical density units at 380 mμ per 10 mls of reaction mixture after appropriate dilution. Rate constants are calculated on OD_∞ experiment.

Time (secs)	$OD_\infty - OD_t$	$1 + \log(OD_\infty - OD_t)$
5	0.592	0.7723
10	0.490	0.6902
15	0.430	0.6335
20	0.345	0.5378
25	0.325	0.5119
30	0.286	0.4564
40	0.260	0.4150
60	0.200	0.3010
90	0.109	0.0374

slope of $1 + \log(O.D_\infty - O.D_t)$ versus time in secs

$= 1.45 \pm 0.16 \times 10^{-2}$

$k_1 = 2.90 \times 10^{-2}$

$k_2 = 6.68 \pm 0.01 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 6.58 \pm 0.01 \times 10^{-1}$ " " "

Mean $k_2 = 6.63 \times 10^{-1}$ " " "

EXPERIMENT 13

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with Piperidine in the presence of Piperidine Hydrochloride in dry methanol at + 30.2 ± 0.05°C.

Wavelength = 380 m/u

Initial Concentrations: Piperidine = 0.0355M

Chloro = 5×10^{-3}M

OD_{∞} calc. = 0.754 Pip. HCl = 1×10^{-1}M

OD_{∞} expt. = 0.761 F = 6.70×10^{-3}

f = 100 X = 5.362

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 380 m/u per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k2 \times 10^{-2}$ litre $mole^{-1}$ sec^{-1}
0	2.570	0.650	-
300	2.477	0.556	1.56
600	2.396	0.476	1.58
900	2.322	0.419	(1.48)
1,500	2.222	0.302	1.62
2,100	2.142	0.217	1.71
3,000	2.077	0.156	1.59
3,900	2.016	0.097	1.67
5,100	1.978	0.058	1.64

Average $k_2 = 1.63 \pm 0.08 \times 10^{-2}$ litre $mole^{-1}$ sec^{-1}

Duplicate $k_2 = 1.70 \pm 0.05 \times 10^{-2}$ " " "

Mean $k_2 = 1.67 \times 10^{-2}$ litre $mole^{-1}$ sec^{-1}

EXPERIMENT 14

Reaction of 1 - chloro -2, 4 - dinitrobenzene with Piperidine in the presence of Peridine Hydrochloride in dry methanol at + 30.2 + 0.05°C.

Wavelength = 380 m/u

Initial Concentrations: Piperidine = 0.075M

Chloro = 5×10^{-3}M

Pip. Hcl = 1.00×10^{-1}M

OD_{∞} calc. = 0.754

OD_{∞} expt. = 0.750 F = 6.67×10^{-3}

f = 100 X = 11.31

$(OD_{\infty} - OD_t)$ and $(0.5X - OD_t)$ are expressed as optical density units at 380 m/u per 5 mls of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-2}$ litre $mole^{-1} sec^{-1}$
0	5.573	0.668	-
190	5.431	0.526	1.73
360	5.337	0.433	1.66
490	5.274	0.370	1.68
780	5.174	0.269	1.65
1,095	5.093	0.188	1.66
1,380	5.040	0.135	1.67
1,980	4.974	0.068	1.69

Average k_2 = 1.68 ± 0.05 x 10^{-2} litre $mole^{-1} sec^{-1}$

Duplicate k_2 = 1.66 ± 0.03 x 10^{-2} " " "

Mean k_2 = 1.67 x 10^{-2} " " "

EXPERIMENT 15

Reaction of 1 - chloro - 2,4- dinitrobenzene with Piperidine in the presence of Piperidine Hydrochloride in dry methanol at + 30.2 ± 0.05°C.

Wavelength = 380 m/u

Initial concentrations - Piperidine = 0.150M

Chloro = 5×10^{-3}M

OD_{∞} calc. = 0.754 Pip. HCl = 0.1 M

OD_{∞} expt. = 0.750 $F = 6.67 \times 10^{-3}$

f = 100 X = 22.61

$(OD_{\infty} - OD_t)$ and $(0.5X - OD_t)$ are expressed as optical density units at 380 m/u per 5 mls of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-2}$ litre $mole^{-1} sec^{-1}$
0	11.12	0.566	-
90	11.01	0.455	(2.02)
180	10.91	0.356	1.77
300	10.81	0.267	1.72
360	10.79	0.241	1.63
480	10.71	0.161	1.77
660	10.67	0.122	1.62
960	10.61	0.056	1.69
1,380	10.58	0.026	1.57

Average k_2 = $1.68 \pm 0.09 \times 10^{-2}$ litre $mole^{-1} sec^{-1}$

Duplicate = $1.77 \pm 0.07 \times 10^{-2}$ " " "

Mean = 1.72 $\times 10^{-2}$ " " "

EXPERIMENT 16

Reaction of 1 - chloro - 2,4 - dinitrobenzene with Piperidine in the presence of Piperidine Hydrochloride in dry methanol at + 30.2 ± 0.05°C

Wavelength = 380 m/u

Initial Concentrations - Piperidine = 0.300M

Chloro = 5×10^{-3}M

Pip. HCl = 1.00M

OD_{∞} calc. = 0.754

OD_{∞} expt. = 0.765 F = 6.67×10^{-3}

X = 45.23 f = 100

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed is optical density units at 380 m/u per 5 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-2}$ litres mole^{-1}sec^{-1}
0	22.47	0.612	-
30	22.37	0.523	1.76
60	22.30	0.453	1.69
90	22.23	0.385	1.74
120	22.18	0.334	1.70
150	22.13	0.287	1.71
180	22.09	0.247	1.66
240	22.03	0.185	1.69
330	21.95	0.113	1.74
450	21.90	0.059	1.77

Average k_2 = $1.72 \pm 0.05 \times 10^{-2}$ litres mole^{-1}sec^{-1}

Duplicate k_2 = $1.72 \pm 0.03 \times 10^{-2}$ " " "

Mean k_2 = 1.72×10^{-2} " " "

EXPERIMENTAL 17

Reaction of 1 - chloro - 2,4 - dinitrobenzene with Piperidine in the presence of piperidine Hydrochloride in dry methanol at + 30.2 ± 0.05°C

Wavelength = 380 m/u

Initial Concentrations - Piperidine = 0.600M

Chloro = 5×10^{-3}M

Pip. HCl = 0.1M

OD_{∞} calc. = 0.754

OD_{∞} expt. = 0.753 F = 6.67×10^{-3}

f = 100 X = 90.46

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 380 m/u per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-2}$ litre mole^{-1}sec^{-1}
0	45.09	0.618	-
10	45.04	0.572	2.11
15	45.00	0.532	2.10
25	44.89	0.441	1.98
55	44.78	0.322	1.96
85	44.68	0.212	2.08
145	44.58	0.099	2.09

Average k_2 = $2.04 \pm 0.08 \times 10^{-2}$ litre mole^{-1}sec^{-1}

Duplicate k_2 = $2.05 \pm 0.07 \times 10^{-2}$ " " "

Mean k_2 = 2.05 $\times 10^{-2}$ " " "

EXPERIMENT 18

Reaction of 1 - chloro - 2,4 - dinitrobenzene with Piperidine in the presence of Piperidine Hydrochloride in dry methanol at + 30.2 ± 0.03°C

Wavelength = 380 mμ

Initial Concentrations - Piperidine = 1.20M

Chloro = 5×10^{-3}M

Pip. HCl = 0.1M

OD_{∞} calc. = 0.754

OD_{∞} expt. = 0.750 F = 6.67×10^{-3}

f = 100 X = 180.9

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 380 mμ per 5 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t)$	$k_2 \times 10^{-2}$ litre mole^{-1} sec^{-1}
0	90.08	0.382	-
5	90.01	0.335	2.200
10	90.00	0.300	2.02
15	89.99	0.265	2.04
20	89.91	0.230	2.13
25	89.89	0.210	2.00
35	89.86	0.170	(1.94)
45	89.80	0.115	2.24
55	89.78	0.090	2.15

Average k_2 = $2.16 \times 10^{-2} \pm 0.16$ litre mole^{-1}sec^{-1}

Duplicate k_2 = $2.18 \pm 0.10 \times 10^{-2}$ " " "

Mean k_2 = 2.17 $\times 10^{-2}$ " " "

EXPERIMENT 19

Reactions of 1 - chloro - 2, 4 - dinitrobenzene with Piperidine in dry methanol at 30.2 ± 0.05°C

Wavelength = 380 mμ

Initial Concentrations - Piperidine = 0.0355M

Chloro = 5×10^{-3}M

OD_{∞} calc. = 0.754

OD_{∞} expt. = 0.747 F = 6.70×10^{-3}

f = 100 X = 5.362

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 380 mμ per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on 0.D00 experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-2}$ litre mole^{-1} sec^{-1}
0	2.577	0.643	-
300	2.480	0.547	1.61
600	2.396	0.462	1.68
900	2.338	0.404	1.59
1,500	2.231	0.297	1.64
2,400	2.122	0.189	1.67
3,300	2.060	0.126	1.66
5,100	1.993	0.058	1.64

Average k_2 = $1.64 \pm 0.05 \times 10^{-2}$ litre mole^{-1} sec^{-1}

Duplicate k_2 = $1.62 \pm 0.03 \times 10^{-2}$ " " "

Mean k_2 = 1.63 $\times 10^{-2}$ " " "

EXPERIMENT 20

Reaction of 1 - chloro - 2,4 - dinitrobenzene with Piperidine in dry methanol at 30.2 ± 0.05°C

Wavelength = 380 m/u

Initial Concentrations - Piperidine = 0.075M

Chloro = 5×10^{-3}M

OD_{∞} calc. = 0.754

OD_{∞} expt. = 0.750 $F = 6.67 \times 10^{-3}$

f = 100 $X = 11.31$

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 380 m/u per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞}, experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-2}$ litre mole^{-1}sec^{-1}
0	5.557	0.652	-
180	5.134	0.530	1.58
480	5.279	0.375	1.61
660	5.171	0.266	1.63
1,080	5.078	0.183	1.68
1,395	5.034	0.129	1.68
1,980	4.967	0.062	1.70
2,880	4.944	0.040	1.65

Average $k_2 = 1.65 \pm 0.07 \times 10^{-2}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 1.64 \pm 0.08 \times 10^{-2}$ " " "

Mean $k_2 = 1.65 \times 10^{-2}$ " " "

EXPERIMENT 21

Reaction of 1 - chloro - 2,4 - dinitrobenzene with Piperidine in dry methanol at + 30.2 ± 0.05°C

Wavelength 380 mμ

Initial Concentrations - Piperidine = 0.150M

Chloro = 5×10^{-3}M

OD_∞ calc. = 0.754

OD_∞ expt. = 0.748 F = 6.67×10^{-3}

f = 100 X = 22.61

$(0.5X - OD_t)$ and $(OD_\infty - OD_t)$ are expressed as optical density units at 380 mμ per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_∞ experiment.

Time (secs)	$0.5X - OD_t$	$OD_\infty - OD_t$	$k_2 \times 10^{-2}$ litre mole^{-1}sec^{-1}
0	11.12	0.564	-
90	11.01	0.457	1.62
210	10.90	0.343	1.66
360	10.74	0.240	1.64
660	10.68	0.120	1.68
960	10.61	0.058	1.67
1,380	10.57	0.028	1.63

Average $k_2 = 1.65 \pm 0.03 \times 10^{-2}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 1.68 \pm 0.04 \times 10^{-2}$ " " "

Mean $k_2 = 1.66 \times 10^{-2}$ " " "

EXPERIMENT 22

Reaction of 1 - chloro - 2, 5 - dinitrobenzene with Piperidine in dry methanol at + 30.2 ± 0.05°C

Wavelength = 380 m/u

Initial Concentrations - Piperidine = 0.300M

Chloro = 5×10^{-3}M

OD_{∞} calc. = 0.754

OD_{∞} expt. = 0.748 F = 6.67×10^{-3}

f = 100 X = 45.23

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 380 m/u per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} calculation.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-2}$ litre mole^{-1}sec^{-1}
0	22.48	0.623	-
30	22.41	0.545	1.76
60	22.36	0.494	1.74
90	22.26	0.399	1.76
150	22.16	0.304	1.78
210	22.07	0.212	1.69
270	22.02	0.157	1.75
330	21.96	0.103	1.72
390	21.93	0.076	(1.52)
450	21.91	0.052	1.78

Average k_2 = $1.75 \pm 0.06 \times 10^{-2}$ litre mole^{-1}sec^{-1}

Duplicate k_2 = $1.73 \pm 0.05 \times 10^{-2}$ " " "

Mean k_2 = 1.74 $\times 10^{-2}$ " " "

EXPERIMENT 23

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with Piperidine in dry methanol at + 30.2 ± 0.05°C

Wavelength = 380 m/u

Initial Concentrations - Piperidine = 0.600M
Chloro = 5×10^{-3}M

OD_∞ calc. = 0.754
OD_∞ expt. = 0.748 F = 6.67×10^{-3}
f = 100 X = 90.46

$(0.5X - OD_t)$ and $(OD_\infty - OD_t)$ are expressed as optical density units at 380 m/u per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_∞ experiment.

Time (secs)	$0.5X - OD_t$	$OD_\infty - OD_t$	$k_2 \times 10^{-2}$ litre mole^{-1}sec^{-1}
0	45.04	0.557	-
5	45.00	0.521	1.92
10	44.95	0.484	1.98
20	44.91	0.443	1.95
50	44.80	0.326	1.95
80	44.71	0.231	1.96
110	44.62	0.139	1.94
170	44.54	0.670	1.94

Average $k_2 = 1.95 \pm 0.03 \times 10^{-2}$ litre mole^{-1}sec^{-1}
Duplicate $k_2 = 1.96 \pm 0.05 \times 10^{-2}$ " " "
Mean $k_2 = 1.96 \times 10^{-2}$ " " "

EXPERIMENT 24

Reaction of 1 - chloro -2, 4 - dinitrobenzene with Piperidine in dry methanol at + 30.2 ± 0.05°C

Wavelength = 380 m/u

Initial Concentrations - Piperidine = 1.20M

Chloro = 5 x 10^{-3}M

OD_{∞} calc. = 0.755

OD_{∞} expt. = 0.751 F = 6.67 x 10^{-3}

f = 100 X = 180.92

($0.5X - OD_t$) and $OD_{\infty} - OD_t$ are expressed as optical density units at 380 m/u per 5 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-2}$ litre mole^{-1} sec^{-1}
0	90.09	0.388	-
5	90.00	0.332	2.20
10	89.98	0.329	2.22
15	89.89	0.262	2.28
20	89.82	0.230	2.25
30	89.79	0.211	2.26
40	89.77	0.172	(2.42)
50	89.74	0.116	2.27
60	89.71	0.083	2.29

Average k_2 = 2.25 ± 0.05 x 10^{-2} litre mole^{-1} sec^{-1}

Duplicate k_2 = 2.23 ± 0.01 x 10^{-2} " " "

Mean k_2 = 2.24 x 10^{-2} " " "

EXPERIMENT 25

Reaction of 2 - chloro - 5 - nitropyridine with Piperidine in dry methanol at 20.80 ± 0.05°C

Wavelength = 370 m/u

Initial Concentrations - Piperidine = 1.00×10^{-2}M

Chloro = 5.00×10^{-3}M

OD_{∞} calc. = 1.089

f = 400

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 370 m/u per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} calculation.

Time (mins)	$OD_{\infty} - OD_t$	$1 + \log OD_{\infty} - OD_t$
45	1.042	1.018
90	1.023	1.010
120	0.955	0.981
180	0.912	0.960
300	0.812	0.908
390	0.743	0.871
480	0.681	0.833
600	0.571	0.756
720	0.551	0.741

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs = $6.943 \pm 0.44 \times 10^{-6}$

$k_2 = 1.60 \times 10^{-5}$

$k_2 = 1.60 \pm 0.00 \times 10^{-3}$ litre $mole^{-1} sec^{-1}$

Duplicate $k_2 = 1.64 \pm 0.00 \times 10^{-3}$ " " "

Mean $k_2 = 1.62 \pm 0.00 \times 10^{-3}$ " " "

EXPERIMENT 26

Reaction of 2 - chloro - 5 - nitropyridine with Piperidine in dry methanol at 30.50 ± 0.05°C

Wavelength = 370 m/u

Initial Concentrations - Piperidine = 1.00×10^{-2}M

Chloro = 5.00×10^{-3}M

OD_∞ calc. = 1.089

f = 40

$(OD_\infty - OD_t)$ is expressed as optical density units at 370 m/u per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_∞ calculation.

Time (mins)	$OD_\infty - OD_t$	$1 + \log OD_\infty - OD_t$
15	1.047	1.020
30	1.009	1.004
45	0.968	0.986
60	0.938	0.972
90	0.886	0.947
175	0.744	0.872
235	0.692	0.840
310	0.579	0.763
370	0.531	0.725
480	0.431	0.634

Slope of $1 + \log (OD_\infty - OD_t)$ versus time in secs = $1.390 \pm 0.05 \times 10^{-5}$

$k_1 = 3.20 \times 10^{-3}$

$k_2 = 3.20 \pm 0.00 \times 10^{-3}$ litre $\text{mole}^{-1}\text{sec}^{-1}$

Duplicate $k_2 = 3.36 \pm 0.01 \times 10^{-3}$ " " "

Mean $k_2 = 3.28 \times 10^{-3}$ " " "

EXPERIMENT 27

Reaction of 2 - chloro - 5 - nitropyridine with Piperidine in dry methanol at 40.22 ± 0.05°C

Wavelength = 370 m/u

Initial Concentrations - Piperidine = 1.00×10^{-2}M

Chloro = 5.00×10^{-3}M

OD_{∞} calc. = 1.089

f = 40

$OD_{\infty} - OD_t$ is expressed as optical density units at 370 m/u per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} calculation.

Time (mins)	$OD_{\infty} - OD_t$	$1 + \log OD_{\infty} - OD_t$
5	1.059	1.025
10	1.033	1.014
20	0.993	0.997
35	0.932	0.969
66	0.824	0.916
100	0.733	0.865
160	0.580	0.761
204	0.550	0.740
270	0.466	0.668
330	0.408	0.611

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus tine in secs = $2.710 \pm 0.06 \times 10^{-5}$

$k_1 = 6.24 \times 10^{-5}$

$k_2 = 6.24 \pm 0.00 \times 10^{-3}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 6.39 \pm 0.00 \times 10^{-3}$ " " "

Mean $k_2 = 6.32 \pm 0.00 \times 10^{-3}$ " " "

EXPERIMENT 28

Reaction of 2 - chloro - 5 nitropyridine with Piperidine in dry methanol at 50.55 ± 0.05°C

Wavelength = 370 m/u

Initial Concentrations - Piperidine = 1.00×10^{-2}M

Chloro = 5.00×10^{-3}M

OD_{∞} calc. = 1.089

f = 40

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 380 m/u per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} calculation.

Time (mins)	$OD_{\infty} - OD_t$	$1 + \log OD_{\infty} - OD_t$
5	1.044	1.019
10	0.995	0.998
15	0.953	0.979
20	0.912	0.960
30	0.843	0.926
45	0.747	0.873
60	0.681	0.833
90	0.563	0.751
120	0.481	0.682

Slope of 1 + log $(OD_{\infty} - OD_t)$ versus time in secs = $5.426 \pm 0.36 \times 10^{-5}$

$k_1 = 12.5 \times 10^{-3}$

$k_2 = 12.5 \pm 0.0 \times 10^{-3}$ litre $\text{mole}^{-1}\text{sec}^{-1}$

Duplicate $k_2 = 12.1 \pm 0.0 \times 10^{-3}$ " " "

Mean $k_2 = 12.3 \times 10^{-3}$ " " "

EXPERIMENT 29

Reaction of 1 - fluoro - 2,4 - dinitrobenzene with Piperidine in dry acetone at + 30.0 ± 0.05°C

Wavelength = 380 m/u

Initial Concentrations - Piperidine = 7.97×10^{-5}M

Fluoro = 1.00×10^{-5}M

OD_{∞} = 0.880

$(OD_{\infty} - OD_t)$ is expressed as optical density units per 2.51 ml of the reaction mixture.

Time (secs)	$OD_{\infty} - OD_t$	$2 + \log(OD_{\infty} - OD_t)$
96	0.730	1.8633
168	0.636	1.7993
264	0.530	1.7243
408	0.410	1.6128
504	0.330	1.5185
600	0.280	1.4472
768	0.210	1.3222
954	0.150	1.1761
1,390	0.080	0.9031

Slope of $2 + \log(OD_{\infty} - OD_t)$ versus time in secs = $7.69 \pm 0.15 \times 10^{-4}$

$k_1 = 1.77 \times 10^{-3}$

$k_2 = 22.0 \pm 0.8$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 22.0 \pm 0.8$ " " "

Mean $k_2 = 22.0 +$ " " "

EXPERIMENT 30

Reaction of 1 - fluoro - 2,4 - dinitrobenzene with Piperidine in dry acetone at + 30.0 ± 0.05°C

Wavelength = 380 m/u

Initial Concentrations - Piperidine $= 1.594 \times 10^{-4}$M

Fluoro $= 1.00 \times 10^{-5}$M

$OD_{\infty} = 0.890$

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 380 m/u per 2.51 ml of reaction mixture.

Time (secs)	$OD_{\infty} - OD_t$	$1 + \log OD_{\infty} - OD_t$
25	0.74	1.8693
50	0.67	1.8265
60	0.63	1.7993
70	0.59	1.7709
120	0.51	1.7076
170	0.41	1.6128
240	0.31	1.4914
340	0.22	1.3424
480	0.13	1.1139
625	0.08	0.7782

Graph of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs $= 1.77 \times 10^{-3} \pm 0.05$

$k_1 = 4.08 \times 10^{-3}$

$k_2 = 24.30 \pm 1.2$ litre $\text{mole}^{-1} \text{sec}^{-1}$

Duplicate $k_2 = 24.00 \pm 1.2$ " " "

Mean $k_2 = 24.2 \pm 1.2$ " " "

EXPERIMENT 31

Reaction of 1 - fluoro - 2,4 - dinitrobenzene with Piperidine in dry acetone at + 30.0 ± 0.05°C

Wavelength = 380 m/u

Initial Concentrations - Piperidine = 2.446×10^{-4}M

Fluoro = 1.00×10^{-5}M

OD_{∞} = 0.900

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 380 m/u per 2.51 ml of reaction mixture.

Time (secs)	$OD_{\infty} - OD_t$	$\log OD_{\infty} - OD_t$
15	79	1.8976
30	71	1.8513
55	61	1.7853
70	55	1.7404
100	46	1.6628
130	39	1.5911
180	30	1.4771
245	22	1.3424
295	18	1.2553
345	15	1.1761

Slope of 1 + log $(OD_{\infty} - OD_t)$ versus time in secs = 2.80×10^{-3} ± 0.07

$k_1' = 6.45 \times 10^{-3}$

k_2 = 27.00 ± 1.3 litre mole^{-1}sec^{-1}

Duplicate k_2' = 27.0 ± 0.9 " " "

Mean k_2 = 27.0 " " "

EXPERIMENT 32

Reaction of 1 - fluoro - 2,4 - dinitrobenzene with Piperidine in dry acetone at 30.0 ± 0.05°C

Wavelength = 380 m/u

Initial Concentrations - Piperidine $= 3.181 \times 10^{-4}$M

Fluoro $= 1.00 \times 10^{-5}$M

$OD_{\infty} = 0.840$

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 380 m/u per 2.51 ml of reaction mixture.

Time (secs)	$OD_{\infty} - OD_t$	$1 + \log OD_{\infty} - OD_t$
20	0.610	1.7853
40	0.510	1.7076
55	0.420	1.6232
75	0.350	1.5441
95	0.280	1.4472
125	0.210	1.3222
175	0.140	1.1461
270	0.070	0.8451

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs $= 4.21 \pm 0.11 \times 10^{-3}$

$k_1 = 9.70 \times 10^{-3}$

$k_2 = 30.1 \pm 0.08$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 29.9 \pm 0.04$ " " "

Mean $k_2 = 30.0$ " " "

EXPERIMENT 33

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with Piperidine in dry acetone at 30.0 ± 0.05°C.

Wavelength = 380 m/u.

Initial Concentrations: Piperidine $= 3.984 \times 10^{-4}$M

Fluoro $= 1.00 \times 10^{-5}$M

$OD_{\infty} = 0.87$

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 380 m/u per 2.51 ml of reaction mixture

Time (secs)	$OD_{\infty} - OD_t$	$\log (OD_{\infty} - OD_t)$
5	0.63	1.7993
20	0.54	1.7324
30	0.47	1.6721
40	0.40	1.6021
65	0.30	1.4771
95	0.21	1.3222
125	0.15	1.1761
160	0.10	1.0000

Slope of $\log (OD_{\infty} - OD_t)$ versus time in secs $= 5.373 \pm 0.12 \times 10^{-2}$

$k_1 = 1.24 \times 10^{-1}$

$k_2 = 31.0 \pm 0.5$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 31.0 \pm 0.5$ litre " "

Mean $k_2 = 31.0$ " " "

EXPERIMENT 34

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with Piperidine in dry acetone at + 30.0 ± 0.05°C.

Wavelength = 380 m/u.

Initial Concentrations: Piperidine = 4.781×10^{-4}M

Fluoro = 1.00×10^{-5}M

$OD_{\infty} = 0.87$

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 380 m/u per 2.51 ml of reaction mixture.

Time (secs)	$OD_{\infty} - OD_t$	$1 + \log (OD_{\infty} - OD_t)$
10	0.58	1.7634
20	0.51	1.7076
30	0.44	1.6435
40	0.37	1.5682
60	0.28	1.4472
80	0.21	1.3222
100	0.15	1.1761
125	0.11	1.0414
160	0.07	0.8451

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs = $6.613 \pm 0.31 \times 10^{-3}$

$k_1 = 1.54 \times 10^{-2}$

$k_2 = 32.2 \pm 0.2$ litre $mole^{-1} sec^{-1}$

Duplicate $k_2 = 32.0 \pm 0.5$ " " "

Mean $k_2 = 32.1$ " " "

EXPERIMENT 35

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with Piperidine in dry acetone at 30.0 ± 0.05°C.

Wavelength = 380 m/u.

Initial Concentrations: Piperidine = 5.577×10^{-4}M

Fluoro = 1.00×10^{-5}M

$OD_{\infty} = 0.88$

$OD_{\infty} - OD_{t}$ is expressed as optical density units at 380 m/u per 2.51 ml of reaction mixture.

Time (secs)	$OD_{\infty} - OD_{t}$	$1 + \log (OD_{\infty} - OD_{t})$
15	0.46	1.6628
25	0.39	1.5911
35	0.32	1.5051
50	0.26	1.4150
60	0.21	1.3222
85	0.14	1.1461
105	0.10	1.000
150	0.05	0.6990

Slope of $1 + \log (OD_{\infty} - OD_{t})$ versus time in secs = $8.00 \pm 0.18 \times 10^{-3}$

$k_{1} = 1.84 \times 10^{-2}$

$k_{2} = 33.1 \pm 0.80$ litre $\text{mole}^{-1}\text{sec}^{-1}$

Duplicate $k_{2} = 33.0 \pm 0.12$ " " "

Mean $k_{2} = 33.0$ litre $\text{mole}^{-1}\text{sec}^{-1}$

EXPERIMENT 36

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with Piperidine in dry acetone at 30.0 ± 0.05°C.

Wavelength = 380 m/u.

Initial Concentrations: Piperidine = 6.374×10^{-4}M

Fluoro = 1.00×10^{-5}M

OD_{∞} = 0.87

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 380 m/u per 2.51 ml of reaction mixture.

Time (secs)	$OD_{\infty} - OD_t$	$1 + \log (OD_{\infty} - OD_t)$
10	0.45	1.6532
20	0.37	1.5682
35	0.27	1.4314
45	0.22	1.3442
55	0.18	1.2553
70	0.12	1.0792
95	0.07	0.8451
135	0.03	0.4771

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs = $9.806 \pm 0.12 \times 10^{-3}$

$k_1 = 2.26 \times 10^{-2}$

$k_2 = 35.2 \pm 0.1$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 35.2 \pm 0.1$ " " "

Mean $k_2 = 35.2$ " " "

EXPERIMENT 37

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with Piperidine in dry acetone at 30.0 ± 0.05°C.

Wavelength = 380 mμ.

Initial Concentrations: Piperidine = 7.171×10^{-4}M

Fluoro = 1.00×10^{-5}M

OD_{∞} = 0.88

$(OD_{\infty} - OD_{t})$ is expressed as optical density units at 380 mμ per 2.51 ml of reaction mixture.

Time (secs)	$OD_{\infty} - OD_{t}$	$1 + \log(OD_{\infty} - OD_{t})$
10	0.44	1.6435
20	0.37	1.5682
25	0.30	1.4771
40	0.22	1.3424
50	0.16	1.2041
65	0.11	1.0414
90	0.06	0.7782

Slope of $1 + \log(OD_{\infty} - OD_{t})$ versus time in secs = $1.135 \pm 0.21 \times 10^{-2}$

$k_1 = 2.56 \times 10^{-2}$

$k_2 = 36.1 \pm 0.2$ litre $\text{mole}^{-1}\text{sec}^{-1}$

Duplicate $k_2 = 36.1 \pm 0.2$ " " "

Mean $k_2 = 36.1$ " " "

EXPERIMENT 38

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with Piperidine in dry acetone at 30.0 ± 0.05°C.

Wavelength = 380 m/u.

Initial Concentrations: Piperidine = 7.968×10^{-4} M

Fluoro = 1.00×10^{-5} M

$OD_{\infty} = 0.815$

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 380 m/u per 2.51 ml of reaction mixture

Time (secs)	$OD_{\infty} - OD_t$	$1 + \log (OD_{\infty} - OD_t)$
10	0.365	1.5623
15	0.305	1.4843
25	0.235	1.3711
35	0.165	1.2175
50	0.115	1.0607
65	0.075	0.8751
110	0.025	0.3979

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs = $1.356 \pm 0.15 \times 10^{-2}$

$k_1 = 3.11 \times 10^{-2}$

$k_2 = 39.0 \pm 0.3$ litre $mole^{-1} sec^{-1}$

Duplicate $k_2 = 39.2 \pm 0.1$ " " "

Mean $k_2 = 39.1$ " " "

EXPERIMENT 39

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with Piperidine in dry acetone at 30.0 ± 0.05°C.

Wavelength = 380 m/u.

Initial Concentrations: Piperidine $= 1.00 \times 10^{-3}$M

Fluoro $= 1.00 \times 10^{-5}$M

$OD_{\infty} = 0.76$

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 380 m/u per 2.51 ml of reaction mixture.

Time (secs)	$OD_{\infty} - OD_t$	$1 + \log (OD_{\infty} - OD_t)$
5	0.470	1.6721
10	0.430	1.6335
13	0.380	1.5798
15	0.340	1.5314
20	0.310	1.4914
25	0.250	1.3979
35	0.180	1.2553
45	0.120	1.0792
60	0.080	0.9031
65	0.06	0.7782
90	0.03	0.4771

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs $= 1.782 \pm 0.23 \times 10^{-2}$

$k_1 = 4.10 \times 10^{-2}$

$k_2 = 41.0 \pm 0.4$ litre $mole^{-1} sec^{-1}$

Duplicate $k_2 = 41.0 \pm 0.1$ " " "

Mean $k_2 = 41.0$ " " "

EXPERIMENT 40

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with Piperidine in dry acetone at 30.0 ± 0.05°C.

Wavelength = 380 m/u.

Initial Concentrations: Piperidine = 1.25×10^{-3}M

Fluoro = 1.00×10^{-5}M

$OD_{\infty} = 0.78$

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 380 m/u per 2.51 ml of reaction mixture.

Time (secs)	$OD_{\infty} - OD_t$	$1 + \log (OD_{\infty} - OD_t)$.
5	0.33	1.5185
15	0.25	1.3979
20	0.16	1.2041
25	0.12	1.0792
30	0.09	0.9542
60	0.03	0.4771

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs = $2.27 \pm 0.21 \times 10^{-2}$

$k_1 = 5.22 \times 10^{-2}$

$k_2 = 41.7 \pm 0.2$ litre $mole^{-1} sec^{-1}$

Duplicate $k_2 = 42.1 \pm 0.1$ " " "

Mean $k_2 = 42.0$ " " "

EXPERIMENT 41

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with Piperidine in dry acetone at 30.0 ± 0.05°C.

Wavelength = 380 m/u.

Initial Concentrations: Piperidine = 2.00×10^{-3} M

Fluoro = 1.00×10^{-5} M

$OD_{\infty} = 0.85$

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 380 m/u per 2.51 ml. of reaction mixture.

Time (secs)	$OD_{\infty} - OD_t$	$1 + \log (OD_{\infty} - OD_t)$
6	0.27	1.4314
9	0.20	1.3010
12	0.15	1.1761
18	0.09	0.9542
30	0.04	0.6021

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs = $4.00 \pm 0.27 \times 10^{-2}$

$k_1 = 9.21 \times 10^{-2}$

$k_2 = 46.2 \pm 0.4$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 46.8 \pm 0.3$ " " "

Mean $k_2 = 46.5$ " " "

EXPERIMENT 42

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with Piperidine in dry acetone at + 30 ± 0.05°C.

Wavelength = 380 mμ.

Initial Concentrations: Piperidine = 0.0105 M

Chloro = 5×10^{-3}M

OD_{∞} calc. = 0.733

OD_{∞} expt. = 0.733 F = 6.878×10^{-3}

f = 100 X = 1.552

$(OD_{\infty} - OD_t)$ and $(0.5x - OD_t)$ are expressed as optical density units at 380 mμ per 5 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5x - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-1}$ mole^{-1}sec^{-1}
0	0.4990	0.456	-
120	0.3650	0.322	(5.010)
240	0.3050	0.262	4.37
360	0.2590	0.216	4.33
480	0.2370	0.194	(3.91)
720	0.2240	0.181	(3.68)
960	0.1670	0.124	4.22
1,200	0.1240	0.081	4.29
1,440	0.1150	0.072	4.48
1,740	0.1050	0.062	4.48
1,980	0.093	0.050	4.56
2,280	0.089	0.046	4.36

Average k_2 = $4.40 \pm 0.16 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate k_2 = $4.31 \pm 0.09 \times 10^{-1}$ " " "

Mean k_2 = 4.36 $\times 10^{-1}$ litre mole^{-1}sec^{-1}

EXPERIMENT 43

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with Piperidine in dry acetone at + 30 ± 0.05°C.

Wavelength = 380 mμ.

Initial Concentrations: Piperidine = 0.015M

Chloro = 5×10^{-3}M

OD_{∞} calc. = 0.733

OD_{∞} expt. = 0.735 F = 6.878×10^{-3}

f = 100 X = 2.240

$(0.5\,x - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 380 mμ per ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-1}$ litre mole^{-1}sec^{-1}
0	0.981	0.596	-
30	0.884	0.499	4.65
60	0.809	0.423	4.79
90	0.746	0.361	4.82
150	0.666	0.281	4.63
210	0.607	0.222	4.60
330	0.522	0.137	4.84
450	0.485	0.100	4.67
570	0.460	0.075	4.40

Average $k_2 = 4.61 \pm 0.22 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 4.87 \pm 0.21 \times 10^{-1}$ " " "

Mean $k_2 = 4.76 \times 10^{-1}$ " " "

EXPERIMENT 44

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with Piperidine in dry acetone at +30 ± 0.05°C.

Wavelength = 380 m/u.

Initial Concentrations: Piperidine = 0.020M

Chloro = 5×10^{-3}M

OD_{∞} calc. = 0.733

OD_{∞} expt. = 0.742 F = 6.878×10^{-3}

f = 100 X = 3.056

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 380 m/u per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-1}$ litre mole^{-1}sec^{-1}
0	1.389	0.634	-
15	1.317	0.541	5.18
45	1.194	0.408	(5.54)
75	1.106	0.320	5.39
105	1.053	0.267	5.02
135	0.996	0.210	5.19
165	0.956	0.170	5.21
225	0.902	0.116	5.16
285	0.864	0.070	5.23

Average k_2 = $5.24 \pm 0.12 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate k_2 = $5.19 \pm 0.08 \times 10^{-1}$ " " "

Mean k_2 = 5.22 $\times 10^{-1}$ litre mole^{-1}sec^{-1}

EXPERIMENT 45

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with Piperidine in dry acetone at +30 ± 0.05°C.

Wavelength = 380 m/u.

Initial Concentrations: Piperidine = 0.026M

Chloro = 5×10^{-3}M

OD_∞ calc. = 0.733

OD_∞ expt. = 0.730 F = 6.878×10^{-3}

f = 100 X = 3.939

$(0.5X - OD_t)$ and $(OD_\infty - OD_t)$ are expressed as optical density units at 380 m/u per 5 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_∞ experiment.

Time (secs)	$0.5X - OD_t$	$OD_\infty - OD_t$	$k_2 = 10^{-1}$ litre $mole^{-1} sec^{-1}$
0	1.861	0.622	-
10	1.756	0.516	(7.49)
20	1.714	0.474	5.54
30	1.658	0.415	5.62
50	1.563	0.526	5.57
70	1.495	0.255	5.51
100	1.420	0.181	5.52
130	1.389	0.148	5.46
170	1.352	0.112	5.48

Average k_2 = $5.57 \pm 0.11 \times 10^{-1}$ litre $mole^{-1} sec^{-1}$

Duplicate k_2 = $5.41 \pm 0.10 \times 10^{-1}$ litre $mole^{-1} sec^{-1}$

Mean k_2 = 5.49 $\times 10^{-1}$ litre $mole^{-1} sec^{-1}$

EXPERIMENT 46

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with Piperidine in dry acetone at +30 ± 0.05°C.

Wavelength = 380 mμ.

Initial Concentrations: Piperidine = 0.030M

Chloro = 5×10^{-3}M

OD_{∞} calc. = 0.733

OD_{∞} expt. = 0.735 F = 6.878×10^{-3}

f = 100 X = 4.450

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 380 mμ per 5 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-1}$ litre mole^{-1}sec^{-1}
0	2.121	0.631	-
10	2.029	0.539	5.66
20	1.961	0.471	5.64
30	1.891	0.401	5.67
40	1.835	0.344	5.62
50	1.784	0.299	5.67
65	1.739	0.249	5.70
80	1.695	0.207	5.62
95	1.653	0.163	5.58

Average k_2 = $5.64 \pm 0.06 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate k_2 = $5.72 \pm 0.08 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Mean k_2 = 5.68 $\times 10^{-1}$ litre mole^{-1}sec^{-1}

EXPERIMENT 47

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with Piperidine in dry acetone at +30 ± 0.05°C.

Wavelength = 380 m/u.

Initial Concentrations: Piperidine = 0.035M

Chloro = 5×10^{-3}M

OC_{∞} calc. = 0.733

OD_{∞} expt. = 0.735 F = 6.878×10^{-3}

f = 100 X = 5.212

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 380 m/u per 5 ml. of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-1}$ litre mole^{-1}sec^{-1}
0	2.556	0.685	-
5	2.473	0.602	(7.68)
15	2.377	0.508	5.87
25	2.272	0.401	5.85
35	2.222	0.351	5.84
45	2.183	0.312	5.80
55	2.111	0.241	5.81
65	2.080	0.209	5.79
75	2.048	0.178	5.86

Average $k_2 = 5.83 \pm 0.06 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 5.87 \pm 0.01 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Mean $k_2 = 5.85$ $\times 10^{-1}$ litre mole^{-1}sec^{-1}

EXPERIMENT 48

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with N - Butylamine in dry acetone at 24.82 ± 0.01°C.

Wavelength = 350 m/u.

Initial Concentrations: n - Butylamine = 5×10^{-4}M

Fluoro = 5×10^{-5}M

$OD_{\infty} = 0.895$

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 350 m/u of reaction mixture.

Time (mins)	$OD_{\infty} - OD_t$	$1 + \log (OD_{\infty} - OD_t)$
20	0.796	0.901
60	0.758	0.880
120	0.729	0.863
180	0.682	0.837
240	0.644	0.809
300	0.610	0.786
360	0.580	0.764
420	0.542	0.734
480	0.513	0.710

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs = $6.75 \pm 0.29 \times 10^{-6}$

$k_1 = 1.55 \times 10^{-5}$

$k_2 = 3.11 \pm 0.00 \times 10^{-2}$ litre $\text{mole}^{-1}\text{sec}^{-1}$

Duplicate $k_2 = 3.21 \pm 0.00 \times 10^{-2}$ litre $\text{mole}^{-1}\text{sec}^{-1}$

Mean $k_2 = 3.17 \times 10^{-2}$ litre $\text{mole}^{-1}\text{sec}^{-1}$

EXPERIMENT 49

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in dry acetone at +24.82 ± 0.01°C.

Wavelength = 350 m/u.

Initial Concentrations: n - Butylamine = 10^{-3}M

Fluoro = 5×10^{-5}M

OD_{∞} = 0.895

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 350 m/u of reaction mixture.

Time (mins)	$OD_{\infty} - OD_t$	$1 \log (OD_{\infty} - OD_t)$
15	0.667	0.824
30	0.643	0.808
60	0.603	0.780
90	0.570	0.756
120	0.537	0.730
180	0.450	0.654
240	0.417	0.620
300	0.366	0.564

Slope of 1 + log $(OD_{\infty} - OD_t)$ versus time in secs = $1.52 \pm 0.11 \times 10^{-5}$

$k_1 = 3.50 \times 10^{-5}$

$k_2 = 3.50 \pm 0.00 \times 10^{-2}$ litre $\text{mole}^{-1} \text{sec}^{-1}$

Duplicate $k_2 = 3.58 \pm 0.00 \times 10^{-2}$ litre $\text{mole}^{-1} \text{sec}^{-1}$

Mean $k_2 = 3.54 \times 10^{-2}$ litre $\text{mole}^{-1} \text{sec}^{-1}$

EXPERIMENT 50

Reaction of 1 - fluoro - 2,4 - dinitrobenzene with n - Butylamine in dry acetone at + 24.8 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 2.5×10^{-3}M

Fluoro = 5×10^{-5}M

OD_{∞} = 0.895

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 350 m/u of reaction mixture.

Time (mins)	$OD_{\infty} - OD_t$	$2 + \log (OD_{\infty} - OD_t)$
10	0.570	1.756
20	0.520	1.716
40	0.458	1.661
60	0.421	1.624
90	0.356	1.550
120	0.300	1.477
180	0.219	1.341
240	0.150	1.176
300	0.110	1.041
360	0.084	0.905

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs = $4.08 \pm 0.02 \times 10^{-5}$

$k_1 = 9.40 \times 10^{-5}$

$k_2 = 3.76 \pm 0.00 \times 10^{-2}$ litre $mole^{-1} sec^{-1}$

Duplicate $k_2 = 3.89 + 0.00 \times 10^{-2}$ " " "

Mean $k_2 = 3.82 \times 10^{-2}$ " " "

EXPERIMENT 51

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in dry acetone at 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 5×10^{-3}M

Fluro = 5×10^{-5}M

OD_∞ = 0.895

$(OD_\infty - OD_t)$ is expressed as optical density units at 350 m/u of reaction mixture.

Time (mins)	$OD_\infty - OD_t$	$2 + \log(OD_\infty - OD_t)$
5	0.747	1.8733
10	0.672	1.8274
15	0.590	1.771
30	0.507	1.705
45	0.415	1.618
60	0.330	1.519
75	0.290	1.462
90	0.235	1.371
120	0.160	1.204
150	0.110	1.041
180	0.090	0.954

Slope of $2 + \log(OD_\infty - OD_t)$ versus time in secs = $9.29 \pm 0.5 \times 10^{-5}$

$k_1 = 2.14 \times 10^{-4}$

$k_2 = 4.28 \pm 0.00 \times 10^{-2}$ litre $\text{mole}^{-1}\text{sec}^{-1}$

Duplicate $k_2 = 4.16 \pm 0.00 \times 10^{-2}$ " " "

Mean $k_2 = 4.22 \times 10^{-2}$ " " "

EXPERIMENT 52

Reaction of 1 - fluoro - 2,4 - dinitrobenzene with n - Butylamine in dry acetone at 24.82 ± 0.01°C

Wavelength = 350 mμ

Initial Concentrations - n - Butylamine = 10^{-2}M

Fluoro = 5×10^{-5}M

$OD_{\infty} = 0.895$

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 350 mμ of reaction mixture.

Time (mins)	$OD_{\infty} - OD_t$	$2 + \log (OD_{\infty} - OD_t)$
5	0.565	1.752
10	0.490	1.690
15	0.422	1.625
20	0.360	1.556
25	0.320	1.505
30	0.260	1.415
40	0.200	1.301
50	0.150	1.176
60	0.115	1.061
75	0.085	0.924

Slope of $2 + \log (OD_{\infty} - OD_t)$ versus time in secs = $2.13 \pm 0.08 \times 10^{-4}$

$k_1 = 4.91 \times 10^{-4}$

$k_2 = 4.91 \pm 0.00 \times 10^{-2}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 4.80 \pm 0.00 \times 10^{-2}$ " " "

Mean $k_2 = 4.86 \times 10^{-2}$ " " "

EXPERIMENT 53

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in dry acetone at 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 5×10^{-2}M

Fluoro = 5×10^{-5}M

OD_{∞} - 0.895

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 350 m/u of reaction mixture.

Time (secs)	$OD_{\infty} - OD_t$	$1 + \log (OD_{\infty} - OD_t)$
0	0.754	0.877
60	0.654	0.816
120	0.565	0.752
180	0.482	0.686
240	0.408	0.613
300	0.348	0.550
360	0.301	0.480
420	0.208	0.332
540	0.182	0.260
600	0.150	0.190
660	0.128	0.114

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs = $1.17 \pm 0.01 \times 10^{-3}$

$k_1 = 2.69 \times 10^{-3}$

$k_2 = 5.37 \pm 0.00 \times 10^{-2}$ litre $\text{mole}^{-1}\text{sec}^{-1}$

Duplicate $k_2 = 5.67 \pm 0.00 \times 10^{-2}$ " " "

Mean $k_2 = 5.52 \times 10^{-2}$ " " "

EXPERIMENT 54

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in dry acetone at 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine $= 10^{-1}$M

Fluoro $= 5 \times 10^{-5}$M

$OD_{\infty} = 0.895$

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 350 m/u of reaction mixture.

Time (secs)	$OD_{\infty} - OD_t$	$1 + \log (OD_{\infty} - OD_t)$
0	0.750	0.875
30	0.595	0.775
60	0.470	0.672
90	0.370	0.574
120	0.300	0.477
150	0.244	0.387
180	0.200	0.301
210	0.170	0.230
240	0.142	0.152
270	0.123	0.086
300	0.108	0.033

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs $= 3.16 \pm 0.09 \times 10^{-3}$

$k_1 = 7.28 \times 10^{-3}$

$k_2 = 7.28 \pm 0.00 \times 10^{-2}$ litre $mole^{-1} sec^{-1}$

Duplicate $k_2 = 7.12 \pm 0.00 \times 10^{-2}$ " " "

Mean $k_2 = 7.20 \times 10^{-2}$ " " "

EXPERIMENT 55

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in dry acetone at 24.82 ± 0.01°C

Wavelength = 350 mμ

Initial Concentrations - n - Butylamine = 2×10^{-1}M

Fluoro = 5.0×10^{-5}M

OD_{∞} = 0.895

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 350 mμ of reaction mixture.

Time (secs)	$OD_{\infty} - OD_t$	$1 + \log (OD_{\infty} - OD_t)$
0	0.570	0.756
3	0.550	0.740
6	0.505	0.703
9	0.458	0.661
12	0.410	0.613
18	0.340	0.532
24	0.275	0.439
30	0.224	0.350
42	0.148	0.170
54	0.100	0.000

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs = $1.47 \pm 0.04 \times 10^{-2}$

$k_1 = 3.39 \times 10^{-2}$

$k_2 = 1.69 \pm 0.00 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 1.56 \pm 0.00 \times 10^{-1}$ " " "

Mean $k_2 = 1.63 \times 10^{-1}$ " " "

EXPERIMENT 56

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in dry acetone at 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 3×10^{-1}M

Fluoro = 5×10^{-5}M

OD_{∞} - 0.895

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 350 m/u of reaction mixture.

Time (secs)	$OD_{\infty} - OD_t$	$2 + \log (OD_{\infty} - OD_t)$
3	0.350	1.544
6	0.290	1.462
9	0.235	1.371
12	0.195	1.290
15	0.160	1.204
18	0.130	1.114
21	0.115	1.061
24	0.095	0.978
27	0.085	0.903
30	0.065	0.813
33	0.056	0.748

Slope of $2 + \log (OD_{\infty} - OD_t)$ versus time in secs = $2.91 \pm 0.08 \times 10^{-2}$

$k_1 = 6.72 \times 10^{-2}$

$k_2 = 2.24 \pm 0.02 \times 10^{-1}$ litre $mole^{-1} sec^{-1}$

Duplicate $k_2 = 2.19 \pm 0.01 \times 10^{-1}$ " " "

Mean $k_2 = 2.21 \times 10^{-1}$ " " "

EXPERIMENT 57

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in dry acetone at 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine $= 4 \times 10^{-1}$M

Fluoro $= 5 \times 10^{-5}$M

$OD_{\infty} = 0.895$

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 350 m/u of reaction mixture.

Time (secs)	$OD_{\infty} - OD_t$	$2 + \log OD_{\infty} - OD_t$
3	0.220	1.342
6	0.180	1.255
9	0.130	1.114
12	0.100	1.100
15	0.070	0.845
18	0.054	0.732
21	0.040	0.602
24	0.028	0.447
27	0.020	0.301
30	0.015	0.176

Slope of $2 + \log (OD_{\infty} - OD_t)$, versus time in secs $= 4.52 \pm 0.15 \times 10^{-2}$

$k_1 = 1.04 \times 10^{-2}$

$k_2 = 2.60 \pm 0.00 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 2.66 \pm 0.00 \times 10^{-1}$ " " "

Mean $k_2 = 2.63 \times 10^{-1}$ " " "

EXPERIMENT 58

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with n - Butylamine in dry acetone at + 30°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine $= 10^{-2}$M

Chloro $= 2 \times 10^{-2}$M

OD_{∞} calc. = 3.636 F $= 5.548 \times 10^{-3}$

f = 25 X = 14.54

$(OD_{\infty} - OD_t)$ and $(0.5X - OD_t)$ are expressed as optical density units at 350 m/u per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} calculation.

Time (mins)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-5}$ litre mole^{-1} sec^{-1}
0	14.50	3.546	-
90	14.43	3.523	2.77
180	14.41	3.499	2.77
300	14.36	3.466	2.86
420	14.35	3.447	2.62
540	14.32	3.420	2.63
660	14.30	3.396	2.62
1,440	14.12	3.218	2.80
1,920	14.03	3.124	2.71

Average $k_2 = 2.72 \pm 0.10 \times 10^{-5}$ litre mole^{-1} sec^{-1}

Duplicate $k_2 = 2.73 \pm 0.08 \times 10^{-5}$ " " "

Mean $k_2 = 2.73$ $\times 10^{-5}$ " " "

EXPERIMENT 59

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with n - Butylamine in dry acetone at + 30°C

Wavelength = 380 m/u

Initial Concentrations - n - Butylamine = 5×10^{-1}M

Chloro = 2×10^{-2}M

OD_{∞} calc. = 5.636 F = 5.548×10^{-3}

f = 100 X = 9.09

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 m/u per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} calculation.

Time (mins)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-5}$ litre mole^{-1}sec^{-1}
0	4.425	3.516	-
30	4.402	3.493	7.16
90	4.355	3.446	6.76
150	4.308	3.399	7.16
210	4.267	3.357	7.16
270	4.227	3.319	7.03
390	4.145	3.236	6.98
510	4.077	3.167	6.81
630	4.014	3.105	6.65
750	3.946	3.035	6.68

Average $k_2 = 6.93 \pm 0.28 \times 10^{-5}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 6.97 \pm 0.10 \times 10^{-5}$ " " "

Mean $k_2 = 6.95 \times 10^{-5}$ " " "

EXPERIMENT 60

Reaction of 1 - chloro - 2,4 - cinitrobenzene with n - Butylamine in dry acetone at + 30°C

Wavelength = 380 mμ

Initial Concentrations - n - Butylamine = 1.0×10^{-1}M

Chloro = 2×10^{-2}M

OD_{∞} calc. = 3.636   F = 5.548×10^{-3}

f = 100   X = 18.180

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 mμ per 5 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} calculation.

Time (mins)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-4}$ litre mole^{-1}sec^{-1}
0	8.995	3.541	-
10	8.971	3.516	1.22
15	8.954	3.501	1.24
30	8.915	3.461	1.28
55	8.820	3.367	1.28
85	8.772	3.317	1.27
145	8.572	3.127	(1.44)
205	8.494	3.040	1.24
295	8.335	2.881	1.26
415	8.116	2.655	1.22
595	7.819	2.356	1.24

Average k_2 = $1.25 \pm 0.03 \times 10^{-4}$ litre mole^{-1}sec^{-1}

Duplicate k_2 = $1.24 \pm 0.05 \times 10^{-4}$ " " "

Mean k_2 = 1.25 $\times 10^{-4}$ " " "

EXPERIMENT 61

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with n - Butylamine in dry acetone at + 30°C

Wavelength = 380 m/u

Initial Concentrations - n - Butylamine = 1.5×10^{-2}M

Chloro = 2×10^{-2}M

OD_{∞} calc. = 3.636 F = 6.667×10^{-3}

f = 100 X = 22.5

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 m/u per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} calculation.

Time (mins)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-4}$ litre mole^{-1} sec^{-1}
0	11.175	2.925	-
5	11.148	2.898	(1.33)
15	11.103	2.853	1.70
25	11.068	2.818	1.71
35	11.033	2.783	1.62
45	10.994	2.744	1.67
55	10.956	2.706	1.69
65	10.914	2.664	1.69
75	10.869	2.619	1.61
85	10.822	2.572	1.76
95	10.784	2.534	1.74
105	10.743	2.493	1.75
115	10.707	2.457	1.76

Average $k_2 = 1.67 \pm 0.09 \times 10^{-4}$ litre mole^{-1} sec^{-1}

Duplicate $k_2 = 1.68 \pm 0.06 \times 10^{-4}$ " " "

Mean $k_2 = 1.68 \times 10^{-4}$ " " "

EXPERIMENT 62

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with n - Butylamine in dry acetone at + 30°C

Wavelength = 380 mμ

Initial Concentrations - n - Butylamine = 2.00×10^{-1}M

Chloro = 2×10^{-2}M

OD_∞ calc. = 3.636 F = 6.667×10^{-3}

f = 100 X = 30

$(0.5X - OD_t)$ and $(OD_\infty - OD_t)$ are expressed as optical density units at 350 mμ per 5 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_∞ calculation.

Time (mins)	$0.5X - OD_t$	$OD_\infty - OD_t$	$k_2 \times 10^{-4}$ litre mole^{-1} sec^{-1}
0	14.903	2.903	-
5	14.851	2.851	(3.07)
15	14.781	2.781	(2.42)
25	14.720	2.720	(2.20)
35	14.667	2.667	2.00
45	14.599	2.599	2.09
55	14.510	2.540	2.07
65	14.479	2.479	2.07
75	14.420	2.420	2.07
85	14.360	2.360	2.08
95	14.312	2.312	2.05
105	14.256	2.256	2.06
115	14.194	2.194	2.09

Average k_2 = $2.07 \pm 0.02 \times 10^{-4}$ litre mole^{-1} sec^{-1}

Duplicate k_2 = $2.09 \pm 0.01 \times 10^{-4}$ " " "

Mean k_2 = 2.08 $\times 10^{-4}$ " " "

EXPERIMENT 63

Reaction of 1 - chloro - 2,4 - dinitrobenzene with n - Butylamine in dry acetone at + 30°C

Wavelength = 380 m/u

Initial Concentrations - n - Butylamine = 2.50×10^{-1}M

Chloro = 2×10^{-2}M

OD_{∞} calc. = 3.636 F = 6.667×10^{-3}

f = 100 X = 37.5

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 m/u per 5 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} calculation.

Time (mins)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-4}$ litre mole^{-1}sec^{-1}
0	18.577	2.827	-
2	18.530	2.800	(3.11)
4	18.525	2.775	(3.11)
6	18.505	2.775	2.72
8	18.483	2.733	2.71
10	18.465	2.715	2.65
12	18.444	2.694	2.63
14	18.426	2.676	2.64
16	18.409	2.659	2.70
18	18.388	2.638	2.60
20	18.375	2.625	2.59
22	18.350	2.600	2.58
24	18.335	2.585	2.71

Average $k_2 = 2.65 \pm 0.07 \times 10^{-4}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 2.67 \pm 0.06 \times 10^{-4}$ " " "

Mean $k_2 = 2.66 \times 10^{-4}$ " " "

EXPERIMENT 64

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with n - Butylamine in dry acetone at + 30°C

Wavelength = 380 m/u

Initial Concentrations - n - Butylamine = 3.00×10^{-1}M

Chloro = 2×10^{-2}M

OD_∞ calc. = 3.636 F = 6.667×10^{-3}

f = 100 X = 45.00

$(0.5X - OD_t)$ and $(OD_\infty - OD_t)$ are expressed as optical density units at 350 m/u per 5 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_∞ calculation.

Time (mins)	$0.5X - OD_t$	$OD_\infty - OD_t$	$k_2 \times 10^{-4}$ litre $mole^{-1} sec^{-1}$
0	22.342	2.842	-
2	22.314	2.814	(2.81)
4	22.276	2.776	3.32
6	22.250	2.750	(3.10)
8	22.215	2.715	3.23
10	22.184	2.684	3.21
12	22.154	2.654	3.21
14	22.118	2.618	3.31
16	22.090	2.590	3.26
18	22.057	2.557	3.32
20	22.025	2.525	3.34

Average $k_2 = 3.26 \pm 0.08 \times 10^{-4}$ litre $mole^{-1} sec^{-1}$

Duplicate $k_2 = 3.21 \pm 0.06 \times 10^{-4}$ " " "

Mean $k_2 = 3.24 \times 10^{-4}$ " " "

EXPERIMENT 65

Reaction of 1 - chloro - 2,4 - dinitrobenzene with n - Butylamine in dry acetone at + 30°C

Wavelength = 380 m/u

Initial Concentrations - n - Butylamine = 3.50×10^{-1}M

Chloro = 2×10^{-2}M

OD_{∞} calc. = 3.636 F = 6.667×10^{-3}

f = 100 X = 52.5

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 m/u per 5 ml. of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} calculation.

Time (mins)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-4}$ litre mole^{-1}sec^{-1}
0	26.158	2.908	-
2	26.114	2.864	3.65
4	26.072	2.822	3.66
6	26.028	2.778	3.65
8	25.983	2.733	3.72
10	25.942	2.692	3.70
12	25.896	2.646	3.72
14	25.855	2.605	3.75
16	25.811	2.561	3.78
18	25.769	2.519	(4.03)
20	25.726	2.476	3.75

Average k_2 = $3.72 \pm 0.07 \times 10^{-4}$ litre mole^{-1}sec^{-1}

Duplicate k_2 = $3.76 \pm 0.02 \times 10^{-4}$ " " "

Mean k_2 = 3.74×10^{-4} " " "

EXPERIMENT 66

Reaction of 2 - chloro - 5 - nitropyridine with Piperidine in dry acetone at 11.2 ± 0.05°C

Wavelength = 370 m/u

Initial Concentrations = Piperidine = 5.00×10^{-2}M

Chloro = 5×10^{-3}M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.895

f = 100

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 370 m/u per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$OD_{\infty} - OD_t$	$1 + \log (OD_{\infty} - OD_t)$
120	0.735	0.8663
180	0.704	0.8476
240	0.678	0.8312
420	0.594	0.7738
720	0.500	0.6990
960	0.434	0.6375
1,320	0.349	0.5428
1,800	0.283	0.4518
2,400	0.189	0.2765

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs = $2.71 \pm 0.01 \times 10^{-4}$

$k_1 = 6.25 \times 10^{-4}$

$k_2 = 1.25 \pm 0.00 \times 10^{-2}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 1.30 \pm 0.00 \times 10^{-2}$ " " "

Mean $k_2 = 1.28 \times 10^{-2}$ " " "

EXPERIMENT 67

Reaction of 2 - chloro - 5 - nitropyridine with Piperidine in dry acetone at 11.2 ± 0.05°C

Wavelength = 370 mμ

Initial Concentrations - Piperidine = 1.0×10^{-1}M

Chloro = 5.0×10^{-3}M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.895

f = 100

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 370 mμ per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$OD_{\infty} - OD_t$	$1 + \log (OD_{\infty} - OD_t)$
60	0.705	0.8482
120	0.644	0.8089
180	0.602	0.7796
240	0.548	0.7388
360	0.473	0.6749
480	0.405	0.6075
600	0.353	0.5478
780	0.274	0.4378
960	0.217	0.3365
1,200	0.168	0.2253
1,500	0.135	0.1303

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time secs = $5.54 \pm 0.10 \times 10^{-5}$

$k_1 = 1.27 \times 10^{-4}$

$k_2 = 1.27 \pm 0.00 \times 10^{-2}$ litre $\text{mole}^{-1}\text{sec}^{-1}$

Duplicate $k_2 = 1.30 \pm 0.00 \times 10^{-2}$ " " "

Mean $k_2 = 1.29 \times 10^{-2}$ " " "

EXPERIMENT 68

Reaction of 2 - chloro - 5 - nitropyridine with Piperidine in dry acetone at 11.2 ± 0.05°C

Wavelength = 370 m/u

Initial Concentrations - Piperidine = 2.00×10^{-1}M

Chloro = 5×10^{-3}M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.890

f = 100

$(OD_{\infty} - OD_t)$ is expressed as optical density units at 370 m/u per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$OD_{\infty} - OD_t$	$2 + \log (OD_{\infty} - OD_t)$
75	0.661	1.8202
150	0.542	1.7340
270	0.398	1.5999
420	0.277	1.4425
600	0.179	1.2529
840	0.098	0.9912
1,140	0.064	0.8062
1,500	0.035	0.5441

Slope of $2 + \log (OD_{\infty} - OD_t)$ versus time in secs = $1.08 + 0.01 \times 10^{-3}$

$k_1 = 2.49 \times 10^{-3}$

$k_2 = 1.25 \pm 0.00 \times 10^{-2}$ litre $mole^{-1} sec^{-1}$

Duplicate $k_2 = 1.22 \pm 0.00 \times 10^{-2}$ " " "

Mean $k_2 = 1.24 \times 10^{-2}$ " " "

EXPERIMENT 69

Reactions of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in Stabilised Chloroform at 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 0.001M

Fluoro = 2.5×10^{-4}M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.881 F = 5.548×10^{-3}

f = 5 X = 3.636

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 m/u per 10 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-1}$ litre mole^{-1}sec^{-1}
0	1.714	0.777	-
340	1.647	0.711	2.64
800	1.573	0.636	2.73
1,250	1.501	0.564	2.65
1,820	1.431	0.494	2.63
2,410	1.371	0.434	2.69
3,060	1.313	0.376	2.63
3,800	1.260	0.323	2.58
4,490	1.217	0.280	2.60
5,315	1.175	0.238	2.61

Average k_2 = $2.64 \pm 0.09 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate k_2 = $2.63 \pm 0.04 \times 10^{-1}$ " " "

Mean k_2 = 2.64 $\times 10^{-1}$

EXPERIMENT 70

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in stabilised chloroform at 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 0.004M

Fluoro = 2.5×10^{-4}M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.896 $F = 5.548 \times 10^{-3}$

f = 5 X = 14.54

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$. are expressed as optical density units at 350 m/u per 10 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-1}$ litre mole^{-1}sec^{-1}
0	7.184	0.810	-
120	7.081	0.708	2.63
275	6.982	0.608	2.68
465	6.871	0.496	2.72
700	6.772	0.398	2.65
940	6.679	0.305	2.70
1,230	6.612	0.237	2.66
1,740	6.528	0.154	2.61
2,340	6.463	0.089	2.60

Average $k_2 = 2.68 \pm 0.08 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 2.67 \pm 0.04 \times 10^{-1}$ " " "

Mean $k_2 = 2.68 \times 10^{-1}$ " " "

EXPERIMENT 71

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in stabilised chloroform at 24.82 ± 0.01°C.

Wavelength = 350 mμ.

Initial Concentrations: n - Butylamine = 0.01M

Fluoro = 2.5×10^{-4}M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.872 F = 5.548×10^{-3}

f = 5 X = 36.36

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 mμ per 10 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-1}$ litre mole^{-1}sec^{-1}
0	18.017	0.709	-
80	17.88	0.575	2.65
170	17.76	0.456	2.64
280	17.64	0.340	2.68
370	17.57	0.268	2.66
460	17.52	0.215	2.68
590	17.47	0.162	2.60
710	17.42	0.114	2.69
880	17.38	0.076	2.62

Average k_2 = $2.65 \pm 0.05 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate k_2 = $2.65 \pm 0.01 \times 10^{-1}$ " " "

Mean k_2 = 2.65 $\times 10^{-1}$ litre mole^{-1}sec^{-1}

EXPERIMENT 72

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in stabilised chloroform at 24.82 ± 0.01°C.

Wavelength = 350 m/u.

Initial Concentrations: n - Butylamine = 0.0125M

Fluoro = 2.5×10^{-4}M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.890 $F = 5.548 \times 10^{-3}$

f = 5 X = 45.44

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 m/u per 10 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-1}$ litre mole^{-1}sec^{-1}
0	22.512	0.682	-
50	22.40	0.572	2.84
115	22.28	0.454	2.87
170	22.21	0.382	2.76
240	22.14	0.312	2.77
300	22.08	0.257	2.70
360	22.04	0.208	2.70
420	21.99	0.167	2.72
500	21.96	0.131	2.73

Average $k_2 = 2.77 \pm 0.07 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 2.79 \pm 0.05 \times 10^{-1}$ " " "

Mean $k_2 = 2.78 \times 10^{-1}$ litre mole^{-1}sec^{-1}

EXPERIMENT 73

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in stabilised chloroform at 24.82 ± 0.01°C.

Wavelength = 350 mμ.

Initial Concentrations: n - Butylamine = 0.0

Fluoro = 2.5×10^{-1}M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.888 F = 5.548×10^{-3}

X = 90.88

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 mμ. per 2 ml of reaction mixture. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-1}$ litre mole^{-1}sec^{-1}
0	45.200	0.648	-
30	45.07	0.524	2.85
60	45.01	0.463	2.81
90	44.89	0.340	2.89
120	44.82	0.274	2.89
150	44.77	0.223	2.88
180	44.73	0.183	2.84
210	44.70	0.148	2.85
240	44.67	0.120	2.85

Average k_2 = $2.86 \pm 0.05 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate k_2 = $2.96 \pm 0.10 \times 10^{-1}$ " " "

Mean k_2 = 2.91 $\times 10^{-1}$ litre mole^{-1}sec^{-1}

EXPERIMENT 74

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in stabilised chloroform at 24.82 ± 0.0. °C.

Wavelength = 350 m/u.

Initial Concentrations: n - Butylamine = 0.1M

Fluoro = 2.5×10^{-4}M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.877 $F = 5.548 \times 10^{-3}$

$X = 363.6$

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 m/u per 2 ml reaction mixture. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-1}$ litre mole^{-1}sec^{-1}
0	181.420	0.497	-
6	181.3	0.402	3.17
12	181.2	0.331	3.20
18	181.2	0.280	3.07
24	181.1	0.232	3.09
30	181.1	0.191	3.12
45	181.0	0.116	3.19
60	181.0	0.079	3.05
84	181.9	0.038	3.06

Average $k_2 = 3.12 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 3.00 \times 10^{-1}$ " " "

Mean $k_2 = 3.06 \times 10^{-1}$ litre mole^{-1}sec^{-1}

CALCULATED FROM 1st ORDER FORMULA

EXPERIMENT 74

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in stabilised chloroform at 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 0.1M

Fluoro = 2.5×10^{-4}M

OD_{∞} calc. ≡ 0.895

OD_{∞} expt. = 0.877

$(OD_{\infty} - OD_{t})$ is expressed as optical density units at 350 m/u per 5 ml of reaction mixture. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$OD_{\infty} - OD_{t}$	$2 +$ long $(OD_{\infty} - OD_{t})$
0	0.497	1.6964
6	0.402	1.6042
12	0.331	1.5198
18	0.280	1.447
24	0.232	1.366
30	0.191	1.281
45	0.116	1.065
60	0.079	0.898
84	0.038	0.580

Slope of $2 + \log (OD_{\infty} - OD_{t})$ versus time in secs = $1.31 \pm 0.02 \times 10^{-2}$

$k_2 = 3.02 \pm 0.01 \times 10^{-1}$ litre $\text{mole}^{-1}\text{sec}^{-1}$

Duplicate $k_2 = 3.04 \pm 0.00 \times 10^{-1}$ " " "

Mean $k_2 = 3.03 \times 10^{-1}$ " " "

EXPERIMENT 75

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in stabilised chloroform at 24.82 ± 0.01°C.

Wavelength = 350 mμ.

Initial Concentrations: n - Butylamine = 0.2M

Fluoro = 2.5×10^{-4}M

Time (secs)	$OD_{\infty} - OD_t$	$1 + \log (OD_{\infty} - OD_t)$
1	1.636	1.214
2	1.515	1.180
3	1.400	1.146
4	1.299	1.114
5	1.203	1.080
6	1.113	1.047
7	1.040	1.017
8	0.933	0.970
9	0.879	0.944
10	0.805	0.906
11	0.741	0.870
12	0.680	0.833
13	0.643	0.808
14	0.599	0.777
15	0.556	0.745
16	0.505	0.703
18	0.445	0.648

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs = $3.33 \pm 0.07 \times 10^{-2}$

$k_1 = 7.67 \times 10^{-2}$

$k_2 = 3.84 \pm 0.$[illegible] $\times 10^{-1}$ litre $mole^{-1} sec^{-1}$

Duplicate $k_2 = 3.89 \pm 0.$[illegible] $\times 10^{-1}$ litre $mole^{-1} sec^{-1}$

Mean $k_2 = 3.86 \times 10^{-1}$ litre $mole^{-1} sec^{-1}$

EXPERIMENT 76

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in stabilised chloroform at 24.82 ± 0.01°C.

Wavelength = 350 m/u.

Initial Concentrations: n - Butylamine = 0.5M

Fluoro = 2.5×10^{-4}M

Time (secs)	$OD_{\infty} - OD_t$	$1 + \log (OD_{\infty} - OD_t)$
0.2	1.661	1.221
0.4	1.568	1.195
0.6	1.468	1.167
0.8	1.378	1.139
1.0	1.240	1.093
1.2	1.204	1.081
1.4	1.146	1.059
1.6	1.079	1.033
1.8	1.018	1.008
2.0	0.973	0.988

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs = $1.28 \pm 0.02 \times 10^{-1}$

$k_1 = 2.94 \times 10^{-1}$

$k_2 = 5.89 \pm 0.01 \times 10^{-1}$ litre $\text{mole}^{-1}\text{sec}^{-1}$

Duplicate $k_2 = 5.87 \pm 0.01 \times 10^{-1}$ " " "

Mean $k_2 = 5.88 \times 10^{-1}$ litre $\text{mole}^{-1}\text{sec}^{-1}$

EXPERIMENT 77

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in stabilised chloroform at 24.82 ± 0.01°C.

Wavelength = 350 mμ.

Initial Concentrations: n - Butylamine = 0.8M

Fluoro = 2.5×10^{-4}M

Time (secs)	$OD_{\infty} - OD_t$	$1 + \log (OD_{\infty} - OD_t)$
0.2	1.568	1.195
0.4	1.415	1.151
0.6	1.270	1.104
0.8	1.140	1.057
1.0	1.000	1.000
1.2	0.903	0.956
1.4	0.773	0.891
1.6	0.663	0.822
1.8	0.602	0.780
2.0	0.531	0.724

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs = $2.72 \pm 0.08 \times 10^{-1}$

$k_1 = 6.25 \times 10^{-1}$

$k_2 = 7.81 \pm 0.06 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 8.06 \pm 0.05 \times 10^{-1}$ " " "

Mean $k_2 = 7.94 \times 10^{-1}$ litre mole^{-1}sec^{-1}

EXPERIMENT 78

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in stabilised chloroform at 24.82 ± 0.01°C.

Wavelength = 350 mμ.

Initial Concentrations: n - Butylamine = 1.0M

Fluoro = 2.5×10^{-4}M

Time (secs)	$OD_{\infty} - OD_t$	$1 + \log (OD_{\infty} - OD_t)$
0.1	1.577	1.198
0.2	1.418	1.152
0.3	1.279	1.107
0.4	1.146	1.059
0.5	0.991	0.996
0.6	0.892	0.950
0.7	0.749	0.875
0.8	0.531	0.725

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs = $5.04 \pm 0.2 \times 10^{-1}$

$k_1 = 11.6$

$k_2 = 11.6 \pm 0.2 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 11.0 \pm 0.1 \times 10^{-1}$ " " "

Mean $k_2 = 11.3 \times 10^{-1}$ litre mole^{-1}sec^{-1}

EXPERIMENT 79

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in destabilised chloroform at 24.82 ± 0.01°C.

Wavelength 350 m/u.

Initial Concentrations: n - Butylamine = 0.001M

Fluoro = 2.5×10^{-4}M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.883 F = 5.548×10^{-3}

f 5 X = 3.636

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 m/u per 10 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-1}$ litre $mole^{-1}sec^{-1}$
0	1.776	0.841	-
390	1.699	0.764	(1.42)
1,080	1.588	0.652	2.57
1,760	1.491	0.557	2.262
2,540	1.413	0.478	2.58
3,460	1.340	0.408	2.49
4,640	1.261	0.326	2.53
6,440	1.175	0.240	2.53
8,020	1.116	0.181	2.60

Average k_2 = $2.56 \pm 0.07 \times 10^{-1}$ litre $mole^{-1}$ sec^{-1}

Duplicate k_2 = $2.53 \pm 0.06 \times 10^{-1}$ " " "

Mean k_2 = 2.54 $\times 10^{-1}$ litre $mole^{-1}sec^{-1}$

EXPERIMENT 80

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in destabilised chloroform at 24.82 ± 0.01°C.

Wavelength = 350 mμ.

Initial Concentrations: n - Butylamine = 0.004M

Fluoro = 2.5×10^{-4}M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.872 F = 5.548×10^{-3}

f = 5 X = 14.54

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 mμ per 10 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-1}$ litre mole^{-1}sec^{-1}
0	7.122	0.724	-
135	7.020	0.622	2.89
335	6.901	0.503	2.89
555	6.794	0.396	2.85
855	6.686	0.288	2.85
1,155	6.615	0.212	2.84
1,505	6.555	0.158	2.73
1,920	6.495	0.098	2.82
2,415	6.466	0.068	(2.67)

Average k_2 = $2.85 \pm 0.13 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate k_2 = $2.79 \pm 0.09 \times 10^{-1}$ " " "

Mean k_2 = $2.82 \pm$ $\times 10^{-1}$ litre mole^{-1}sec^{-1}

EXPERIMENT 81

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in destabilised chloroform at 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 0.01M

Fluoro = 2.5×10^{-4}M

OD_∞ calc. = 0.895

OD_∞ expt. = 0.887 F = 5.548×10^{-3}

f = 5 X = 36.36

$(0.5X - OD_t)$ and $(OD_\infty - OD_t)$ are expressed as optical density units at 350 m/u per 10 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_∞ calculation.

Time (secs)	$0.5X - OD_t$	$OD_\infty - OD_t$	$k_2' \times 10^{-1}$ litre $mole^{-1} sec^{-1}$
0	18.017	0.724	-
90	17.84	0.556	2.98
180	17.72	0.432	2.84
290	17.62	0.328	2.82
400	17.52	0.226	2.95
530	17.46	0.171	2.87
670	17.41	0.121	2.77
820	17.37	0.084	2.72
1,040	17.34	0.046	2.76

Average $k_2 = 2.84 \pm 0.14 \times 10^{-1}$ litre $mole^{-1} sec^{-1}$

Duplicate $k_2 = 2.85 \pm 0.10 \times 10^{-1}$ " " "

Mean $k_2 = 2.84$ $\times 10^{-7}$ " " "

EXPERIMENT 82

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in destabilised chloroform at 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 0.0125 M

Fluoro = 2.5×10^{-4}M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.890 F = 5.548×10^{-3}

f = 5 X = 45.44

$(0.5X - OD_t)$ and $OD_{\infty} - OD_t)$ are expressed as optical density units at 350 m/u per 10 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-1}$ litre mole^{-1}sec^{-1}
0	22.47	0.643	-
55	22.36	0.530	2.80
125	22.25	0.427	2.67
185	22.15	0.332	2.91
255	22.08	0.259	2.91
325	22.03	0.203	2.91
395	22.00	0.171	2.75
460	21.98	0.149	2.67

Average $k_2 = 2.81 \pm 0.14 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 2.81 \pm 0.08 \times 10^{-1}$ " " "

Mean $k_2 = 2.81$ $\times 10^{-1}$ " " "

EXPERIMENT 83

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in destabilised chloroform at 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations : n - Butylamine = 0.025M

Fluoro = 2.5×10^{-4}M

OD_∞ calc. = 0.895

OD_∞ expt. = 0.870 $F = 5.548 \times 10^{-3}$

$X = 90.880$

$(0.5X - OD_t)$ and $(OD_\infty - OD_t)$ are expressed as optical density units at 350 m/u per 2 ml of reaction mixture. Rate constants are calculated on OD_o experiment.

Time (secs)	$0.5X - OD_t$	$OD_\infty - OD_t$	$k_2 \times 10^{-1}$ litre mole^{-1}sec^{-1}
0	45.21	0.640	-
30	45.08	0.516	2.89
60	44.98	0.415	2.91
90	44.89	0.332	2.93
120	44.83	0.266	2.96
150	44.78	0.215	2.92
180	44.73	0.175	2.94
240	44.68	0.112	2.94
33	44.62	0.056	2.99

Average $k_2 = 2.94 \pm 0.05 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 2.90 \pm 0.06 \times 10^{-1}$ " " "

Mean $k_2 = 2.92 \times 10^{-1}$ " " "

EXPERIMENT 84

Reaction of 1 - fluoro - 2,4 - dinitrobenzene with n - Butylamine in destabilised chloroform at 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 0.1M

Fluoro = 2.5×10^{-4}M

OD_{∞} calc. = 0.895 $F = 5.548 \times 10^{-3}$

OD_{∞} expt. = 0.884 $X = 363.6$

($0.5X - OD_t$) and ($OD_{\infty} - OD_t$) are expressed as optical density units at 350 m/u per 2 ml of reaction mixture. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-1}$ litre mole^{-1}sec^{-1}
0	181.42	0.499	-
6	181.4	0.408	3.30
12	181.3	0.337	3.28
18	181.1	0.277	3.28
24	181.1	0.230	3.24
30	181.1	0.189	3.25
42	181.0	0.132	3.20
54	181.0	0.090	3.29
84	180.9	0.056	3.15

Average $k_2 = 3.25 \pm 0.15 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 3.23 \pm 0.09 \times 10^{-1}$ " " "

Mean $k_2 = 3.24$ $\times 10^{-1}$ " " "

EXPERIMENT 85

Reaction of 1 - fluoro - 2, 4 - dinitrobenzene with n - Butylamine in destabilised chloroform at 24.82 ± 0.01°C

Wavelength = 350 mμ

Initial Concentrations - n - Butylamine = 0.2M

Fluoro = 2.5×10^{-4}M

Time (secs)	$OD_{\infty} - OD_t$	$1 + \log (OD_{\infty} - OD_t)$
1	1.790	1.253
2	1.653	1.218
3	1.522	1.182
4	1.398	1.127
5	1.287	1.110
6	1.196	1.078
7	1.079	1.033
8	1.029	1.012
9	0.919	0.963
10	0.887	0.948

Slope of $1 + \log (OD_{\infty} - OD_t)$ versus time in secs = $3.50 \pm 0.12 \times 10^{-2}$

$k_2 = 4.03 \pm 0.00 \times 10^{-1}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 4.02 \pm 0.00 \times 10^{-1}$ " " "

Mean $k_2 = 4.03 \times 10^{-1}$ " " "

EXPERIMENT 86

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with n - Butylamine in stabilised chloroform at 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial concentrations - n - Butylamine = 0.001M

Chloro = 5×10^{-2}M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.909 F = 5.548×10^{-3}

f = 10 X = 90.90

$(X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 m/u per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (mins)	$X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-4}$ litre mole^{-1}sec^{-1}
0	90.83	0.842	-
60	90.76	0.787	1.75
120	90.74	0.732	1.80
210	90.63	0.667	1.72
360	90.53	0.552	1.83
490	90.46	0.485	1.72
600	90.40	0.419	1.82
720	90.35	0.370	1.78
1,370	90.18	0.206	(1.61)
1,820	90.04	0.150	(1.49)

Average k_2 = $1.78 \pm 0.06 \times 10^{-4}$ litre mole^{-1}sec^{-1}

Duplicate k_2 = $1.82 \pm 0.02 \times 10^{-4}$ " " "

Mean k_2 = 1.80×10^{-4} " " "

EXPERIMENT 87

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with n - Butylamine in stabilised chloroform at + 24.82 ± 0.01°C

Wavelength = 350 mμ

Initial Concentrations - n - Butylamine = 0.005 M

Chloro = 5×10^{-2} M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.909 F = 5.548×10^{-3}

f = 50 X = 18.180

$(X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 mμ per 5 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} experiment.

Time (mins)	$X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-4}$ litre mole^{-1}sec^{-1}
0	18.10	0.834	-
60	18.05	0.780	1.88
120	17.99	0.729	1.88
210	17.93	0.659	1.89
360	17.82	0.560	1.87
480	17.75	0.488	1.89
600	17.70	0.430	1.87
750	17.64	0.375	1.81
1,410	17.47	0.205	(1.70)
1,710	17.42	0.165	(1.63)

Average $k_2 = 1.87 \pm 0.06 \times 10^{-4}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 1.86 \pm 0.03 \times 10^{-4}$ " " "

Mean $k_2 = 1.87 \times 10^{-4}$ " " "

EXPERIMENT 88

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with n - Butylamine in stabilised chloroform at + 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 0.01M

Chloro = 5×10^{-2} M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.905 F = 5.548×10^{-3}

f = 100 X = 9.09

$(X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 m/u per 5 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-4}$ litre mole^{-1}sec^{-1}
0	8.914	0.734	-
1,800	8.892	0.713	1.89
3,600	8.865	0.687	1.88
6,600	8.826	0.648	1.93
10,200	8.782	0.603	1.98
13,800	8.746	0.568	1.91
21,700	8.658	0.489	1.97
32,520	8.602	0.423	1.95
87,000	8.259	0.158	1.87

Average k_2 = 1.92 ± 0.06 x 10^{-4} litre mole^{-1}sec^{-1}

Duplicate k_2 = 1.93 ± 0.06 x 10^{-4} " " "

Mean k_2 = 1.93 x 10^{-4} " " "

EXPERIMENT 89

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with n - Butylamine in stabilised chloroform at + 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 0.025M

Chloro = 5×10^{-2} M

OD_∞ calc. = 0.895

OD_∞ expt. = 0.909 F = 5.548×10^{-3}

f = 250 X = 3.636

$(X - OD_t)$ and $OD_\infty - OD_t)$ are expressed as optical density units at 350 m/u per 5 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_∞ experiment.

Time (secs)	$X - OD_t$	$OD_\infty - OD_t$	$k_2 \times 10^{-4}$ litre mole^{-1}sec^{-1}
0	3.492	0.767	-
3,600	3.438	0.713	2.13
7,200	3.390	0.665	2.10
10,800	3.352	0.627	1.98
19,800	3.248	0.524	2.08
25,200	3.200	0.474	2.08
31,800	3.152	0.428	2.03
37,800	3.098	0.377	2.08
79,800	2.912	0.193	2.00

Average $k_2 = 2.06 \pm 0.08 \times 10^{-4}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 2.04 \pm 0.02 \times 10^{-4}$ " " "

Mean $k_2 = 2.05 \times 10^{-4}$ " " "

EXPERIMENT 90

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with n - Butylamine in stabilised chloroform at + 24.82 ± 0.01 °C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 0.05 M

Chloro = 5×10^{-2} M

OD_{∞} calc. = 0.448

OD_{∞} expt. = 0.454 F = 5.548×10^{-3}

f = 1000 X = 0.909

$(X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 m/u per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-4}$ litre mole^{-1} sec^{-1}
0	0.874	0.420	-
3,600	0.846	0.392	2.03
7,200	0.820	0.366	2.05
16,080	0.764	0.3095	2.12
26,880	0.712	0.2575	2.11
38,400	0.658	0.2035	2.20
82,800	0.583	0.1285	2.09

Average k_2 = $2.10 \pm 0.10 \times 10^{-4}$ litre mole^{-1} sec^{-1}

Duplicate k_2 = $2.18 \pm 0.01 \times 10^{-4}$ " " "

Mean k_2 = 2.14 $\times 10^{-4}$ " " "

EXPERIMENT 91

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with n - Butylamine in stabilised chloroform at + 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 0.2M

Chloro = 5×10^{-2}M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.885 F = 5.548×10^{-3}

f = 1000 X = 3.636

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 m/u per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-4}$ litre mole^{-1} sec^{-1}
0	1.761	0.801	-
1,220	1.706	0.747	2.99
2,410	1.662	0.702	2.92
3,620	1.621	0.661	2.87
5,460	1.563	0.603	2.86
7,840	1.495	0.535	2.90
9,790	1.447	0.487	2.92
15,990	1.336	0.378	2.81
19,270	1.282	0.327	2.86
22,210	1.249	0.287	2.91

Average k_2 = $2.89 \pm 0.10 \times 10^{-4}$ litre mole^{-1}sec^{-1}

Duplicate k_2 = $2.92 \pm 0.06 \times 10^{-4}$ " " "

Mean k_2 = 2.90 $\times 10^{-4}$ " " "

EXPERIMENT 92

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with n - Butylamine in stabilised chloroform at + 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 0.5M

Chloro = 5×10^{-2}M

OD_∞ calc. = 0.895

OD_∞ expt. = 0.875 F = 5.548×10^{-3}

f = 1000 X = 9.090

$(0.5X - OD_t)$ and $(OD_\infty - OD_t)$ are expressed as optical density units at 350 m/u per 5 ml. of reaction mixture after appropriate dilution. Rate constants are calculated on OD_∞ experiment.

Time (secs)	$0.5X - OD_t$	$OD_\infty - OD_t$	$k_2 \times 10^{-4}$ litre mole^{-1}sec^{-1}
0	4.478	0.783	-
380	4.416	0.721	4.44
895	4.337	0.642	4.58
1,670	4.246	0.551	4.39
2,690	4.149	0.454	4.29
3,820	4.057	0.362	4.33
5,310	3.960	0.265	4.45
6,770	3.909	0.214	4.22
7,980	3.859	0.164	4.36

Average k_2 = $4.37 \pm 0.15 \times 10^{-4}$ litre mole^{-1}sec^{-1}

Duplicate k_2 = $4.46 \pm 0.02 \times 10^{-4}$ " " "

Mean k_2 = 4.42 $\times 10^{-4}$ " " "

EXPERIMENT 93

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with n - Butylamine in stabilised chloroform at + 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 0.8M

Chloro = 5×10^{-2}M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.868 F = 5.548×10^{-3}

f = 1000 X = 14.540

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$, are expressed as optical density units at 350 m/u per 5 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-4}$ litre mole^{-1}sec^{-1}
0	7.196	0.779	-
200	7.125	0.708	6.08
450	7.052	0.635	5.89
800	6.956	0.539	5.97
1,150	6.876	0.458	6.02
1,570	6.795	0.378	6.04
2,030	6.722	0.310	6.00
2,570	6.659	0.242	6.05
3,170	6.637	0.190	5.95
3,840	6.554	0.140	6.04

Average k_2 = 5.99 ± 0.09 x 10^{-4} litre mole^{-1}sec^{-1}

Duplicate k_2 = 6.04 ± 0.07 x 10^{-4} " " "

Mean k_2 = 6.02 x 10^{-4} " " "

EXPERIMENT 94

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with n - Butylamine in destabilised chloroform at + 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 0.001M

Chloro = 5×10^{-2} M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.909 F = 5.548×10^{-3}

f = 10 X = 90.90

$(X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 m/u per 5 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} experiment.

Time (mins)	$X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-4}$ litre mole^{-1}sec^{-1}
0	90.83	0.842	-
60	90.80	0.789	1.81
120	90.72	0.739	1.82
210	90.69	0.670	1.81
360	90.55	0.569	1.81
480	90.48	0.501	1.81
600	90.42	0.435	1.84
1,250	90.20	0.216	1.82
1,670	90.14	0.159	(1.67)

Average k'_2 = 1.81 ± 0.03 x 10^{-4} litre mole^{-1}sec^{-1}

Duplicate k_2 = 1.82 ± 0.01 x 10^{-4} " " "

Mean k_2 = 1.82 x 10^{-4} " " "

EXPERIMENT 95

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with n - Butylamine in destabilised chloroform at + 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 0.005 M

Chloro = 5×10^{-2} M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.909 F = 5.548×10^{-3}

f = 50 X = 18.18

$(X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 m/u per 5 ml. of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} experiment.

Time (mins)	$X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-4}$ litre mole^{-1}sec^{-1}
0	18.08	0.811	1.86
60	18.03	0.759	1.86
120	17.99	0.709	1.90
240	17.88	0.617	1.92
390	17.80	0.539	1.92
450	17.75	0.487	1.92
550	17.70	0.437	1.91
725	17.64	0.369	1.85
1,380	17.46	0.191	1.80
1,805	17.41	0.147	(1.63)

Average k_2 = $1.89 \pm 0.09 \times 10^{-4}$ litre mole^{-1}sec^{-1}

Duplicate k_2 = $1.89 \pm 0.05 \times 10^{-4}$ " " "

Mean k_2 = 1.89×10^{-4} " " "

EXPERIMENT 96

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with n - Butylamine in destabilised chloroform at + 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 0.01M

Chloro = 5×10^{-2}M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.903 F = 5.548×10^{-3}

f = 100 X = 9.09

$(X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 m/u per 5 ml. of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-4}$ litre mole^{-1}sec^{-1}
0	8.916	0.741	-
900	8.900	0.730	1.86
1,800	8.888	0.715	1.92
4,740	8.849	0.679	1.89
8,100	8.810	0.639	1.88
11,700	8.764	0.594	1.95
22,500	8.660	0.488	1.93
33,300	8.468	0.397	1.89
85,080	8.354	0.182	(1.75)

Average k_2 = $1.90 \pm 0.05 \times 10^{-4}$ litre mole^{-1}sec^{-1}

Duplicate k_2 = $1.95 \pm 0.08 \times 10^{-4}$ " " "

Mean k_2 = 1.93×10^{-4} " " "

EXPERIMENT 97

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with n - Butylamine in destabilised chloroform at + 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 0.025M

Chloro = 5×10^{-2}M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.909 F = 5.548×10^{-3}

f = 250 X = 3.636

$(X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 m/u per 5 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-4}$ litre mole^{-1}sec^{-1}
0	3.491	0.766	-
3,600	3.441	0.715	2.02
7,200	3.389	0.664	2.10
10,800	3.352	0.627	2.12
19,800	3.252	0.527	2.16
25,200	3.200	0.475	2.08
31,800	3.151	0.426	2.08
37,800	3.100	0.375	2.10
79,800	2.920	0.195	2.12

Average $k_2 = 2.09 \pm 0.07 \times 10^{-4}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 2.12 \pm 0.05 \times 10^{-4}$ " " "

Mean $k_2 = 2.11 \times 10^{-4}$ " " "

EXPERIMENT 98

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with n - Butylamine in destabilised chloroform at 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 0.05M

Chloro = 5×10^{-2}M

OD_{∞} calc. = 0.448

OD_{∞} expt. = 0.437 F = 5.548×10^{-3}

f = 1000 X = 0.909

$(X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 m/u per 5 ml of reaction mixture after appropriate dilution.

Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-4}$ litre mole^{-1}sec^{-1}
0	0.886	0.410	-
2,760	0.863	0.387	2.18
8,100	0.818	0.358	(2.40)
15,840	0.763	0.287	2.30
23,580	0.721	0.245	2.30
36,720	0.675	0.199	2.35
80,280	0.585	0.109	2.16
111,780	0.546	0.071	2.17

Average $k_2 = 2.24 \pm 0.11 \times 10^{-4}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 2.28 \pm 0.09 \times 10^{-4}$ " " "

Mean $k_2 = 2.26 \times 10^{-4}$ " " "

EXPERIMENT 99

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with n - Butylamine in destabilised chloroform at 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 0.2M

Chloro = 5×10^{-2}M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.870 F = 5.548×10^{-3}

f = 1000 X = 3.636

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 m/u per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-4}$ litre $mole^{-1} sec^{-1}$
0	1.770	0.820	-
680	1.743	0.793	(2.50)
1,620	1.699	0.749	2.92
3,100	1.639	0.689	3.00
4,900	1.574	0.624	3.04
6,720	1.509	0.559	3.18
8,500	1.468	0.517	3.08
15,480	1.315	0.365	3.17
21,060	1.248	0.307	2.89

Average $k_2 = 3.04 \pm 0.13 \times 10^{-4}$ litre $mole^{-1} sec^{-1}$

Duplicate $k_2 = 3.05 \pm 0.10 \times 10^{-4}$ " " "

Mean $k_2 = 3.05 \times 10^{-4}$ " " "

EXPERIMENT 100

Reaction of 1 - chloro - 2, 4 dinitrobenzene with n - Butylamine in destabilised chloroform at + 24.82 ± 0.01°C

Wavelength = 350 $m\mu$

Initial Concentrations - n - Butylamine = 0.5M

Chloro = 5×10^{-2}M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.875 F = 5.548×10^{-3}

f = 1000 X = 9.090

$(0.5X - OD_t)$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 $m\mu$ per 5 ml of reaction mixture after appropriate dilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-4}$ litre mole^{-1}sec^{-1}
0	4.462	0.777	-
420	4.387	0.707	4.53
960	4.312	0.632	4.44
1,620	4.236	0.547	4.54
2,520	4.133	0.453	4.53
3,720	4.042	0.356	4.51
5,240	3.952	0.272	4.35
7,020	3.872	0.192	4.42
9,120	3.787	0.135	4.39

Average $k_2 = 4.46 \pm 0.11 \times 10^{-4}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 4.56 \pm 0.15 \times 10^{-4}$ " " "

Mean $k_2 = 4.51$ $\times 10^{-4}$ " " "

EXPERIMENT 101

Reaction of 1 - chloro - 2, 4 - dinitrobenzene with n - Butylamine in destabilised chloroform at 24.82 ± 0.01°C

Wavelength = 350 m/u

Initial Concentrations - n - Butylamine = 0.8 M

Chloro = 5×10^{-2}M

OD_{∞} calc. = 0.895

OD_{∞} expt. = 0.865 F = 5.548×10^{-3}

f = 1000 X = 14.544

$(0.5X - OD_t$ and $(OD_{\infty} - OD_t)$ are expressed as optical density units at 350 m/u per 5 ml of reaction mixture after appropriate cilution. Rate constants are calculated on OD_{∞} experiment.

Time (secs)	$0.5X - OD_t$	$OD_{\infty} - OD_t$	$k_2 \times 10^{-4}$ litre mole^{-1}sec^{-1}
0	7.180	0.763	-
220	7.104	0.687	6.07
520	7.001	0.593	6.21
940	6.905	0.490	6.09
1,420	6.806	0.390	6.16
2,020	6.714	0.298	6.13
2,760	6.634	0.217	6.05
3,640	6.561	0.144	6.14
4,540	6.518	0.100	6.04

Average $k_2 = 6.11 \pm 0.07 \times 10^{-4}$ litre mole^{-1}sec^{-1}

Duplicate $k_2 = 6.10 \pm 0.05 \times 10^{-4}$ " " "

Mean $k_2 = 6.11 \times 10^{-4}$ " " "

SUMMARY OF RATE CONSTANTS

TABLE I

The reaction of 1-fluoro-2,4-dinitrobenzene with Piperidine in the presence of Piperidine Hydrochloride in dry methanol at - 29.6 °C

Substrate concentration is 1.25 x 10^{-3}M

10^{-2} [Piperidine] mole litre	[Piperidine HCl] mole litre^{-1}	10 k_2 l mol^{-1} sec^{-1}
1.25	0.10	1.67
2.50	0.10	1.99
3.75	0.10	2.22
4.40	0.10	3.09
4.75	0.10	4.42
5.00	0.10	6.56

Table 1a

The reaction of 1-fluoro-2,4-dinitrobenzene with Piperidine in dry methanol at - 29.6°C.

Substrate concentration is 1.25 x 10^{-3}M

10^{2} Piperidine mole litre	10 k_2 litre mol^{-1} sec^{-1}
1.25	1.76
2.50	1.92
3.75	2.30
4.40	3.13
4.75	4.17
5.00	6.63

TABLE 2

The reaction of 1-chloro-2,4-dinitrobenzene with Piperidine in the presence of Piperidine hydrochloride in dry methanol at

+ 30.20 + _0.05°C

Substrate concentration is 5.00 x 10^{-3} M

/Piperidine/ mole litre $_{-1}$	/Piperidine HCl/ mole litre $^{-1}$	10^{-2} k_2 litre mole^{-1} sec^{-1}
0.0355	0.10	1.66
0.075	0.10	1.67
0.150	0.10	1.72
0.300	0.10	1.72
0.600	0.10	2.07
1.200	0.10	2.17

TABLE 2a

The reaction of 1-chloro-2,4-dinitrobenzene with Piperidine in dry menthanol at 30.20 ± 0.05°C

Substrate concentration is 5.00 x 10^{-3}M

/Piperidine/	10^{2} k_2 litre mole^{-1} sec^{-1}
0.0355	1.63
0.075	1.65
0.150	1.66
0.300	1.74
0.600	1.96
1.200	2.24

TABLE 3

The reaction of 1-fluoro-2,4-dinitrobenzene with Piperidine in dry acetone at +30.0°C

Substrate concentration is 1.00 x 10^{-5}M

10^5 [Piperidine] mole $litre^{-1}$	k_2 litre $mole^{-1}$ sec^{-1}
7.97	22.0
15.94	24.2
24.46	27.0
31.81	30.0
39.84	31.0
47.81	32.1
55.77	33.0
63.74	35.2
71.71	36.1
79.68	39.1
100.00	41.0
125.00	42.0
200.00	46.5

TABLE 4

The reaction of 1-chloro-2,4-dinitrobenzene with Piperidine in dry acetone at + 30.0°C

Substrate concentration is 5.00 x 10^{-3}M

10^2 [Piperidine] mole $litre^{-1}$	10 k_2 litre $mole^{-1}$ sec^{-1}
1.05	4.36

1.53	4.76
2.05	5.22
2.65	5.49
3.05	5.68
3.55	5.85

TABLE 5

The reaction of 1-fluoro-2,4-dinitrobenzene with n-Butylamine in dry acetone at 24-82 ± 0.05°C

Substrate concentration is 5.0 x 10^{-5}M

10^{2} [n-Butylamine] mole litre^{-1}	10^{2} k_2 litre mole^{-1} sec^{-1}
0.05	3.17
0.10	3.54
0.25	3.82
0.50	4.22
1.00	4.86
5.00	5.57
10.00	7.20
20.00	16.4
30.00	22.1
40.00	26.3

TABLE 6

The reaction of 1-chloro-2,4-dinitrobenzene with n-Butylamine in dry acetone at + 30.0 ± 0.05°C

Substrate concentration is 2.00 x 10^{-2}M

10 /n-Butylamine/ mole litre^{-1}	10^4 k_2 litre mole-1 sec^{-1}
0.10	0.27
0.50	0.69
1.00	1.24
1.50	1.68
2.00	2.08
2.50	2.66
3.00	3.24
3.50	3.74

TABLE 7

The reaction of 1-fluoro-2,4-dinitrobenzene with n-Butylamine in stabilised chloroform at 24.82 ± 0.05°C

Substrate concentration is 2.5 x 10^{-4}M

/n-Butylamine/ mole litre^{-1}	10 k_2 litre mole^{-1} sec^{-1}
0.001	2.64
0.004	2.68
0.01	2.65
0.0125	2.78
0.025	2.91
0.100	3.06

0.200	3.86
0.500	5.88
0.800	7.94
1.00	11.33

TABLE 7a

The reaction of 1-fluoro-2,4-dinitrobenzene with n-Butylamine in destabilised chloroform at 24-82 ± 0.05°C

Substrate concentration is 2.5 x 10^{-4}M

[n-Butylamine] more $litre^{-1}$	10 k_2 litre $mole^{-1}$ sec^{-1}
0.001	2.55
0.004	2.81
0.010	2.84
0.0125	2.81
0.025	2.92
0.100	3.24
0.200	4.03

TABLE 8

The reaction of 1-chloro-2,4-dinitrobenzene with n-Butylamine in stabilised chloroform at + 24-82 ± 0.05°C

Substrate concentration is 5 x 10^{-2}M

[n-Butylamine] more litre^{-1}	10^4 k_2 litre mole^{-1} sec^{-1}
0.001	1.80
0.005	1.87
0.010	1.93
0.025	2.05
0.050	2.14
0.200	2.90
0.500	4.42
0.800	6.02

TABLE 8a

The reaction of 1-chloro-2,4-dinitrobenzene with n-Butylamine in destabilised chloroform at + 24.82 ± 0.05 °C

Substrate concentration is 5. x 10^{-2}M

[n-Butylamine] mole litre^{-1}	10^4 k_2 litre mole^{-1} sec^{-1}
0.001	1.82
0.005	1.89
0.010	1.93
0.025	2.11
0.050	2.26
0.200	3.05
0.500	4.51
0.800	6.11

TABLE 9

The reaction of 2-chloro-5-nitropyridine with Piperidine in try acetone at + 11.2°C

Substrate concentration is 5.00×10^{-3} M

10^2 [Piperidine] mole litre^{-1}	10^2 k_2 litre mole^{-1} sec^{-1}
5.00	1.28
10.00	1.28
20.00	1.23

TABLE 10

The reaction of 2-chloro-5-nitropyridine with Piperidine in dry methanol

Temperature °C	10^3 k_2 litre mole^{-1} sec^{-1}	$\log_{10} A$
20.80	1.62	6.72
30.50	3.28	6.75
40.22	6.32	6.73
50.55	12.28	6.74

Temperature Range	Activation Energy E (Kcal)
50.55 - 40.22	12.8
40.22 - 30.50	12.8
30.50 - 20.80	12.9

Mean $\log_{10} A$ = 6.74

Mean E = 12.8 kcal .

CHAPTER 5

DISCUSSION OF RESULTS

In the work reported in this thesis, the kinetics of the following reactions were studied:

1. 2-Chloro-5-nitropyridine with piperidine in acetone.
2. 2-Chloro-5-nitropyridine with piperidine in methanol.
3. 1-fluoro-2, 4-dinitrobenzene with piperidine in acetone.
4. 1-chloro-2, 4-dinitrobenzene with piperidine in acetone.
5. 1-fluoro-2, 4-dinitrobenzene with piperidine in methanol.
6. 1-chloro-2, 4-dinitrobenzene with piperidine in methanol.
7. 1-fluoro-2, 4-dinitrobenzene with n-butylamine in acetone.
8. 1-chloro-2, 4-dinitrobenzene with n-butylamine in acetone.

9&10. 1-fluoro-2, 4-dinitrobenzene with n-butylamine in stabilised and in destabilised chloroform.

11&12. 1-chloro-2, 4 - dinitrobenzene with n-butylamine in stabilised and in destabilised chloroform.

Each reaction can be represented by the following equations:

$$ArX + R_2NH \longrightarrow ArNR_2 + HX$$

$$HX + R_2NH \longrightarrow R_2N^+H_2X^-$$

The reactions were studied spectroscopically by following the absorbance of the orange-yellow products of reaction $ArNR_2$, at a wavelength region where it is the only species which absorbed.

The experiments were carried out partly under second-order run conditions and under pseudo-first order run conditions. The second order rate coefficients obtained by employing conditions leading directly to second order kinetics and those giving pseudo-first order kinetics were the same within experimental error limits.

The rate constants obtained for all these reactions increased with increasing amine concentration howbeit small except for the reactions of 2-chloro-5-nitropyridine with piperidine in acetone at 11.2 °C in which a small decrease in rate was obtained with increasing amine concentration.

Since a reasonable degree of peculiarity attaches to the reactions of individual substrates, the reactions are discussed separately for the different substrates.

The reactions of 2-halo-5-nitro-pyridine with aniline and piperidine in acetone and in methanol:

Bamkole and Hirst have reported [59] that the reactions of 1-X-2, 4-dinitrobenzenes (X, Cl, F) and 2-fluoro-5-nitropyridine with aniline and piperidine in methanol are not base catalysed; but that when the solvent is acetone[46], the reactions show varying degrees of catalysis depending on the substrate, and the nucleophile.

For instance, in the reactions of the 5-nitropyridine series, with aniline in acetone, their results show that the plots of the second order rate constants against aniline concentrations are slightly curvilinear.

When the nucleophile is changed to piperidine, a stronger base, the curvature of the plot increased for the reaction of 2-fluoro-5-nitropyridin and Bamkole and Hirst, from a plot of $^1/kobs$ versus $^1/(B)$ found that $^{k3}/k2$ = 612.

From the results of the studies reported here, the data now available for the reaction of 2-chloro-5-nitro pyridine with piperidine in acetone show that the rate constant do not increase with increasing piperidine concentration. Rather, there was an insignificant decrease in rate constant values with increasing amine concentrations as shown in table 6a.

Table 6a

Reactions of 2-chloro-5-nitropyridine with piperidine in acetone at 11.2 °C Initial substrate concentration $\simeq$ 5.00 x 10^{-3}M

10^2 (Piperidine)	5.00	10.00	20.00
10^2 k l mol^{-1} sec^{-1}	1.28	1.28	1.23

Similar rate decreases with increasing amine concentrations have already been recorded by Bernasconi[47], Bamkole and Hirst [59], Bunnett and Garst [17] and Ross and Kuntz [48] in similar reactions. Ross and Kuntz explained this observation in terms of charge-transfer complexes. In terms of the general intermediate complex mechanism, these reactions belong to the class when

$$k_2 + k_3 (B) \gg k - 1$$

and the general equation simplifies to

$$k_o = k_1$$

Data now available from the present work taken along with those in literature make certain interesting comparisons possible for these reactions in methanol and in acetone. However, since the reactions in acetone show varying degrees of base catalysis, such comparisons are only valid provided corresponding steps are compared. This means comparing the rates of reaction in methanol with k_1, the rate constants for the formation of the intermediate complex for the reactions in acetone.

Such comparisons include the following:

1. The relative reactivities of the fluoro and chloro compounds in methanol and in acetone.
2. Comparison of the nucleophilicity of piperidine with that of aniline in methanol for both the fluoro and the chloro substrates.
3. Comparison of the nucleophilicity of piperidine with that of aniline in acetone for both the fluoro and the chloro substrates.
4. Comparison of aniline in methanol with aniline in acetone for both the fluoro and the chloro substrates.
5. Comparison of piperidine in methanol with piperidine in acetone for both the fluoro and the chloro substrates.
6. Comparison of partial rate coefficients for the reactions in acetone i.e. k_1, $^{k-1}/k2$, $^{k3}/k2$ etc.

Since the reactions in methanol are not base catalysed, the activation energies as well as the pre-exponential factors (log B) can be obtained and these are assembled in table 6b below along with rate constants at 25°C and 50°C extrapolated from the Arrhenius equations:

Table 6b

The Arrhenius parameters and rate constants of reactions of 25°C and

and 50°C for the reactions of 2-X-5-nitro pyridine (X=F,Cl) with piperidine and aniline in methanol.

Substrate	Nucleophile	E (kcal)	log B	k_1 25°C	k_1 50°C
X = Cl	Aniline	13.1	3.78	1.50×10^{-6}	8.26×10^{-6}
* X = Cl	Piperidine	12.8	6.74	2.27×10^{-3}	1.20×10^{-2}
X = F	Aniline	10.5	2.96	1.83×10^{-5}	7.18×10^{-5}
63 X = F	Piperidine	10.6	7.46	4.89×10^{-1}	1.95

* result from author's work

Others from literature reference 59, 63b

From the table 6b above, it is seen that for a given substrate, in methanol, the activation energies appear to be the same whether the nucleophile is aniline or piperidine while log B fators are much higher (3-4.5 units) for piperidine.

Below are assembled Arrhenius parameters for the reactions of 1-X-2, 4-dinitrobenzene (X = F, Cl, Br) with aniline [60] in 99.8% ethanol and for the reactions of 1-X-2, 4-dinitrobenzene with piperidine [44e, 63b] (X = F, Cl, Br) in methanol. The comparison of reactions in ethanol and methanol is legitimate as . Bamkole and Hirst have already shown [59] that this change of solvent has little or no effect on the activation parameters.

Table 6c

Arrhenius parameters for the reactions of 1-X-2, 4-dinitrobenzene (X = F, Cl, Br) with aniline and Piperidine in 99.8 % ethanol and methanol respectively and rate constants at 50°C

Substrate	Nucleophile	Solvent	E (k cal)	log B	k 50°C
X = F	Aniline	Ethanol	6.4	2.55	1.68×10^{-2}
X = F	Piperidine	Methanol	8.4	6.76	11.94
X = Cl	Aniline	Ethanol	11.2	4.0	2.69×10^{-4}
X = Cl	Piperidine	Methanol	11.6	6.7	5.2×10^{-2}
X = Br	Aniline	Ethanol	11.2	4.2.	4.05×10^{-4}
X = Br	Piperidine	Methanol	11.8	8.5	3.36

From this table as for table 6B, it is seen that for the protic solvents ethanol and methanol, the activation energies are almost the same value for both piperidine and aniline with chloro and bromo substrates; whereas with the fluoro substrate, the activation energy is even less with aniline in ethanol than with piperidine in methanol. The log B units are again about 3-4.5 units higher for piperidine than for aniline.

Since piperidine is a stronger base than aniline (pka for piperidine is 11.13; pka for aniline is 4.6) one would have expected this factor to operate in favour of piperidine to produce a lower activation energy; but this is not the case. Evidently this is an anomaly, the cause of which is not yet presently understood.

In table 6d below are assembled the Arrhenius parameters for the reactions of 4-nitrofluorobenzene with aniline and piperidine in the nonhydroxylic solvent dimethylsulfoxide [51].

Table 6d

Arrhenius parameters for the reactions of 4-nitro fluorobenzene with Aniline and piperidine in dimethylsulfoxide.

Reagent	E (k cal)	log B
Aniline	12.7	2.20
Piperidine	9.5	4.88

In this case, unlike the others in tables 6b and 6c above, the activation energies show the expected trend, that is the activation energy for piperidine is less than that of aniline. The anomaly mentioned above does not appear to hold here. Thus, correlating the facts from the tables 6b, 6c and 6d, this observed anomaly appears to apply only when a hydroxylic solvent such as methanol or ethanol is used.

For a discussion of the mobility of the fluorine atom relative to the chlorine atom in methanol and in acetone, other useful data are assembled below:

Table 6e

A comparison of k_1 (the rate of formation of the intermediate) for both the fluoro and the chloro compounds in methanol and in acetone.

Solvent		Methanol		Acetone	
Substrate	Reagent	$k_1(103.6^{\circ}C)$	$k_1(11.2^{\circ}C)$	$k_1(103.6^{\circ}C)$	$k_1(11.2^{\circ}C)$
2-F-5-N.P.	Aniline	7.21×10^{-4}	8.02×10^{-6}	2.38×10^{-5}	-
2-Cl-5-NP	Aniline	1.47×10^{-4}	5.01×10^{-7}	1.55×10^{-5}	
		$\frac{k_1F}{k_1Cl} = 4.91$	$\frac{k_1F}{k_1Cl} = 16$	$\frac{k_1F}{k_1Cl} = 1.51$	-
2-F-5-NP	Piperidine	20.37	2.01×10^{-1}	-	8.93×10^{-1}
* 2-Cl-5-NP	Piperidine	2.07×10^{-1}	7.78×10^{-4}	-	1.28×10^{-2}
		$\frac{k_1F}{k_1Cl} = 98.6$	$\frac{k_1F}{k_1Cl} = 258.3$		$\frac{k_1F}{k_1Cl} = 69.7$

* results from authors work

Others are from reference 59.

Two facts emerge from this table namely:

(a) the relative rates of formation of the intermediate $\frac{k_1F}{k_1Cl}$ decrease as the solvent is changed from methanol to acetone and

(b) Ignoring the fact that different temperatures are involved for reactions in acetone, the ratios $\frac{k_1F}{k_1Cl}$ are considerably higher for piperidine in the two types of solvent than for aniline. This is in agreement with the general conclusion that the greater the basicity of the nucleophile, the greater is the activation by fluorine relative to chlorine in bimolecular nuclephilic substitution reactions.

From the values in table 6e, it can also be seen that in each solvent, $k_1F > k_1Cl$. This faster rate of reaction for the step 1 of the intermediate complex mechanism for the fluoro substrate than for the chloro substrate is likely to be due to the fact that the C-X bond is polarised (X = F, Cl). The degree of plarisation is greater for the fluoro substrate than for the chloro sunstrate due to the greater electionegativity of the former halogen atom. The polarisation can be shown as $C^{\delta+} \longrightarrow X^{\delta-}$

where $\delta+$, $\delta-$ are small residual positive and negative charges induced by the polarisation.

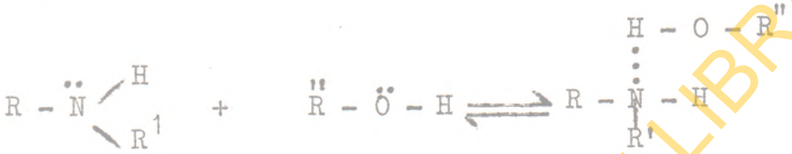
The attack by a nucleophile $R\ddot{N}H_2$ is thus more enchanced for the fluoro substrate than for the chloro.

Because the formation of the transition state involves charge separation, it is better favoured in methanol than in acetone because of the higher dielectric constant of the former.

It might also be noted from the table that k_1 (Piperidine) > k_1 (Aniline) for both substrates and in both solvents; this is solely due to the greater basicity of piperidine which leads to a stronger interaction between the reactive partially positive carbon (1) atom (see above) of the substrate and the basic nitrogen atom of the nucleophile.

The widely different nucleophilicities of aniline and piperidine precluded the measurement of rate constants of these reactions at the same temperature. A much lower temperature was used for piperidine than for aniline. Nevertheless, one contrast looks obvious from table 6e. While methanol appears to be a faster solvent than acetone for reactions involving aniline the reverse is the case for reactions where piperidine is used as the nucleophile. The Hughes-Ingold Theory of Solvent Action predicts that methanol would be the faster solvent. The reversed trend noted with piperidine as nucleophile suggests that a specific solvent effect is operating additionally and in opposition to the Hughes-Ingold effect. It is proposed here that this additional specific solvent effect is a ground state effect as explained below:

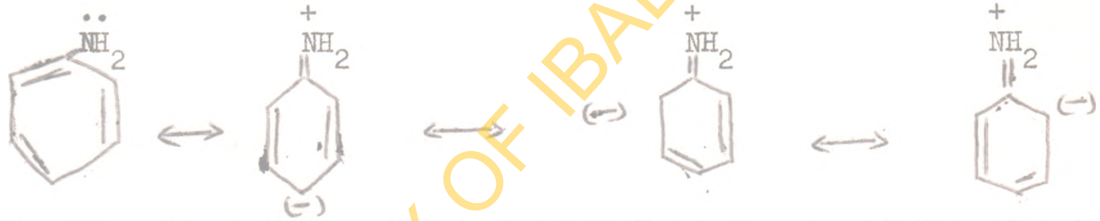
Two types of hydrogen-bonds are possible when a primary or secondary amine is in contact with a solvent which has an electron-donor atom. The first type involves the lone pair of electrons on the nitrogen atom thus



While the second type involves the electrons on the donor atom of the solvent:

It is obvious that while both types of hydrogen-bonds are possible with a protic alcholic solvent, only the latter is possible with a dipolar aprotic solvent such as acetone. It can also be seen that while the formation of H-bonds of the first type can markedly reduce the nucleophilicity of the amine, the H-bonds of the second type cannot, barring the circumstance that its formation might hinder sterically the access of the donor site of the nucleophile to the electrophilic site of the substrate. It is in these facts that the explanation of the anomalous 'fastness' of acetone relative to methanol in the reactions under consideration lies.- H-bond of the first type reduces the reactivity of piperidine in methanol apparently to such an extent that the reduction outweighs the Hughes-Ingold accelerating effect expected for methanol. Hence acetone is a faster solvent than methanol in the reaction of piperidine with 2-halo-5-nitropyridines.

When we consider aniline, H-bond of the first type will be expected to reduce the reactivity of aniline also but here, its effect will be very small, if not negligible, because of the fact that the nitrogen lone pair electrons involved is part of an aromatic, resonating system and in therefore not really available as a lone pair for H-bonding. Hence the situations



in methanol and acetone with respect to H-bonding are similar, leaving only the Hughes-Ingold effect operating in favour of methanol. As previously pointed out, there is little reason to expect that H-bonding of the second type will have much effect.

A comparison of the partial rate constants in acetone can now be carried out.

From the proposed mechanism, when

$$k_{-1} \gg k_2 + k_3 (B)$$

the original equation

$$k_o = \frac{k_1 k_2 + k_1 k_3 (B)}{k_{-1} + k_2 + k_3 (B)} \quad \text{———} \quad (61)$$

reduces to

$$k_o = \frac{k_1\ k_2}{k_1} + \frac{k_1\ k_3}{k_{-1}}\ (B) \quad \text{——} (6II)$$

i.e. it is of the general form

$$k_o = k^{1} + k^{11}\ (B) \quad \text{——} (6III)$$

and a plot of k_o versus amine concentration will be linear and k^{1} will be the intercept i.e. the rate constant for the uncatalysed reaction[61] k^{11}/k^{1} is a measure of the relative magnitude of the accelerated and unaccelerated parts of the reaction.

Now, if there is a factor such as the basicity of the amine which can increase k_3 relative to k_{-1}, the relationship between rate constants and amine concentration deviates from linearity because the relationship

$k_{-1} \gg k_2 + k_3\ (B)$

no longer holds. The more basic the amine, the more curvilinear is the plot and the relationship

$$k_{-1} \gg k_2 + k_3\ (B)$$

converts to

$$k_{-1} \bumpeq k_2 + k_3\ (B)$$

This explains the curvilinear plots obtained for piperidine in reference 59. Whenever the relationship

$$k_{-1} \bumpeq k_2 + k_3\ (B)$$

holds, the general equation (6I) ceases to lend itself to further simplification and a non-linear response of rate constants to base concentration is obtained. The majority of the reactions studied in acetone conformed to this behaviour and the typical plots are illustrated in reference 59.

If equation (6I) is inverted, equation (6IV) is obtained

$$\frac{1}{k_o} = \frac{1}{k_1} + \frac{k_{-1}}{k_1(k_2+k_3\,(B))} \quad \text{—— (IV)}$$

If it is further assumed that

$$k_3 \; (B) \gg k_2$$

as is the case with good bases, then the equation (6IV) reduces to (6V)

$$\frac{1}{k_o} = \frac{1}{k_1} + \frac{k_{-1}}{k_1\, k_3\, (B)} \quad \text{—— (6V)}$$

and except at low amine concentrations when the equation (6V) ceases to apply, a plot of $\frac{1}{k_o}$ versus $\frac{1}{(B)}$ should respond linearly but deviating towards the $\frac{1}{(B)}$ axis at low amine concentration; the slope is $\frac{k_{-1}}{k_1\, k_3}$ and the intercept is $\frac{1}{k_1}$.

From the data at low amine concentrations and equation 6IV, $\frac{k_2}{k_{-1}}$ and $\frac{k_3}{k_2}$ can be determined.

From such a rate dissection, the figures given in the table below were obtained.

Table 6f

Partial rate constants for the reactions of 2-X-5-nitropyridine (X=Cl,F) with piperidine and aniline in acetone.

Substrate	Nucleophile	Temp °C	k_1	k_{-1}/k_3	k_{-1}/k_2	k_3/k_2
2-F-5-nitropyridine	Aniline	103.6	2.38×10^{-5}	1.60	31.3	19.5
2-Cl-5- "	Aniline	103.6	1.55×10^{-5}	3.17×10^{-1}	1.53	4.95
2-F-5- "	Piperidine	11.2	8.93×10^{-1}	1.17×10^{-3}	7.19×10^{-1}	612
2-Cl-5- "	Piperidine	11.2	1.28×10^{-2}	-	-	-

The first and second reactions in the table above can be compared. The greater $\frac{k_{-1}}{k_2}$ value obtained for fluoro compound is expected on general grounds. The greater strength of the C-F bond compared with that of the C-Cl bond and the fact that acetone solvates fluoride ions much less than chloride ions [39b] will reduce k_2, the rate constant for the uncatalysed decomposition of the intermediate formed by fluoro compounds relative to the corresponding value for chloro compound.

Even though reactions are at different temperatures, the value of k_{-1}/k_2 for piperidine reaction with the fluoro substrate is very much lower than that for the reaction of the same substrate with aniline as nucleophile. Assuming k_2 to be independent of amine, a change from an aliphatic amine such as piperidine to an aromatic amine such as aniline should result in an increase in the value of k_{-1}/k_2. The reason is that in the transition state for the reversion of the intermediate complex to reactants, represented by k_{-1}, by the principle of microscopic reversibility, there will be some conjugation of the nitrogen lone pair of electrons with the benzene ring when aniline is the nucleophile. This will stabilise the transition state with respect to that formed by piperidine.

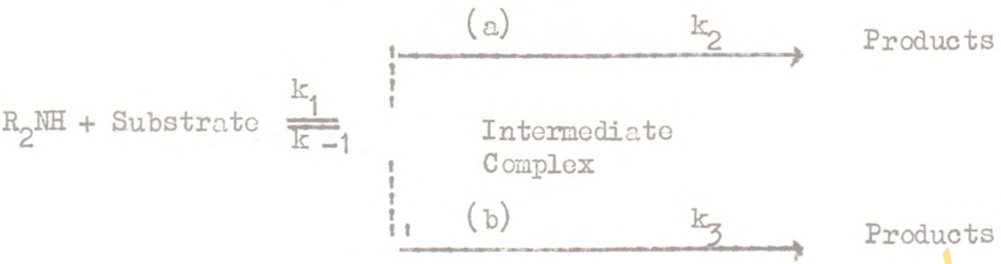
Where this effect is not possible, then the k_{-1}/k_2 ratios would be expected to be greater for aniline than for piperidine.

The ratio k_3/k_2 is the degree of base catalysis in the system. From Bunnetts' classification [45], systems where $k_3/K_2 \gg 50$ are said to be truly base catalysed. Where the value of the ratio falls appreciably below 50, these systems are said to be mildly catalysed. Thus according to this classification, the reaction of 2-F-5-nitropyridine with piperidine in acetone with $k_3/k_2 = 612$ is the only case of true base catalysis. The others are only mildly catalysed.

However, in all cases, the relation $k_1F > k_1Cl$ is observed, and the view is here held that all these cases are examples of the familiar intermediate complex mechanism in which the decomposition of the intermediate is base catalysed. To hold a different view is to say that the measured overall rate in acetone corresponds to the formation of the intermediate complex and one would then have to explain why the overall measured rate in the case of aniline is greater for the chloro substrate than for the fluoro [59], a sequence which has never been observed for the first step of the intermediate complex mechanism and which is contrary to the theoretical predictions already discussed.

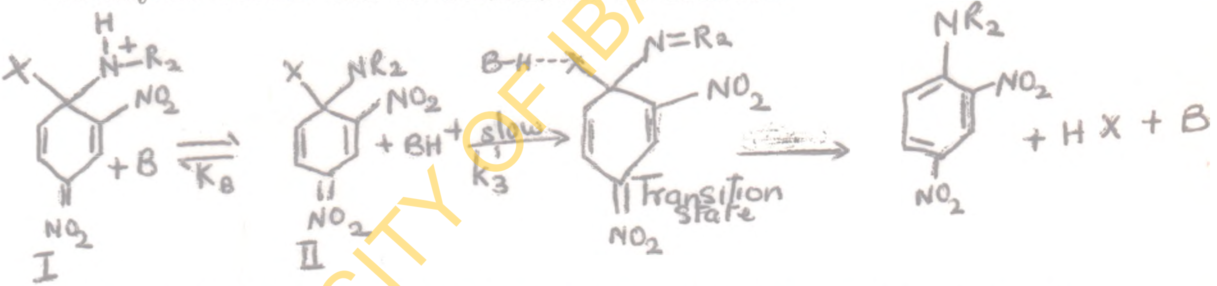
While the observed rate constants for the reactions in methanol are those for the formation of the intermediate complex, those for reactions in acetone are partly dependent on the rates of base assisted decomposition of the intermediate to products except for the reaction of 2-Cl-5-nitropyridine with piperidine where $k_o = k_1$.

In conclusion, the intermediate complex mechanism can be shown as



In methanol, the reactions of both fluoro and chloro substrates with both amines go via path (a) and there is apparently no base catalysis. In acetone, however, the rates of reaction are partly dependent on both paths; the path which overrides the other depends on the substrate, whether fluoro or chloro and the basic strength of the nucleophile.

The most favoured mechanism [17] proposed for the step in which base catalysis occurs can be formulated as follows:



This, in itself, comprises two steps - The intermediate I reacts reversibly with the base giving the second intermediate II and the conjugate acid of the base BH^+ In the second and rate determining step, the conjugate acid of the base B electro-philically assists the separation of the leaving group X from the intermediate II. Thus each K_3 (B) term of the equation 6I above really represents the product $k_3^1 K_B$ (B) where k_B is the equilibrium constant for the reaction of intermediate I with the base B to give intermediate

II and BH^+ and k_3^1 is the rate coefficient for the conjugate acid-catalysed expulsion of the leaving group X from the intermediate II.

It follows that when B is a good base, k_3 is very much greater than k_2 and hence k_3/k_2 for piperidine is much greater than for aniline. This trend has been confirmed for the fluoro substrate (table 6f) for the reaction of the fluoro compound with aniline, $\frac{k_{-1}}{k_2}$ is 31 but for reaction with piperidine, the ratio is much lower being only 0.7. For the reaction of the chloro compound with aniline, $\frac{k_{-1}}{k_2}$ is reduced to 1.5 i.e. approximately $\frac{1}{20}$th of the value for the fluoro compound. If the same reduction took place for the reaction with piperidine, then $k_{-1} \ll k_2$ i.e. it conforms to the condition when $k_{-1} \ll k_2 + k_3$ (B) and as explained earlier, no base catalysis will be observed as shown in table 6f.

II and BH^+ and k_3^1 is the rate coefficient for the conjugate acid - catalysed expulsion of the leaving group X from the intermediate II.

It follows that when B is a good base, k_3 is very much greater than k_2 and hence k_3/k_2 for piperidine is much greaterthan for aniline. This trend has been confirmed for the fluoro substrate (table 6f). For the chloro substrate however, k_3/k_2 for aniline is 4.95 while it is nil for Piperidine. Other factors, not presently known, must be responsible for this reversed order.

Also when X is a good leaving group, the catalytic ability of the base, if any, will not be manifested; but when X is a poor leaving group this catalytic effect can be more readily observed and hence for the same mucleophile,

$$\frac{k_3}{k_2}(F) > \frac{k_3}{k_2}(Cl)$$

This is true for both nucleophiles as shown in table of.

The reactions of 1-X-2, 4-dinitrobenzene (X= F, Cl) with:

(a) Piperidine in acetone

(b) n-butylamine in chloroform

(c) Piperidine in methanol

(d) n-butylamine in acetone

The reactions of 1-X-2, 4 - dinitrobenzene (X = F, Cl) with Piperidine in acetone

For the reactions of both fluoro and chloro substrates, the second-order rate constants increased with increasing amine concentrations: this increase was non-linear and the curvilinear plots 3 and 4 were obtained from the data in tables 3 and 4 respectively.

These reactions fall into the class where

$$k_{-1} \approx k_2 + k_3(\mathrm{B})$$

From the dissection of rate constants the results in table 6g were obtained. The reaction[59] of the fluoro substrate with piperidine at - 30°C is included for comparison. Also the reactions of both substrates[64] with aniline at 50°C are included.

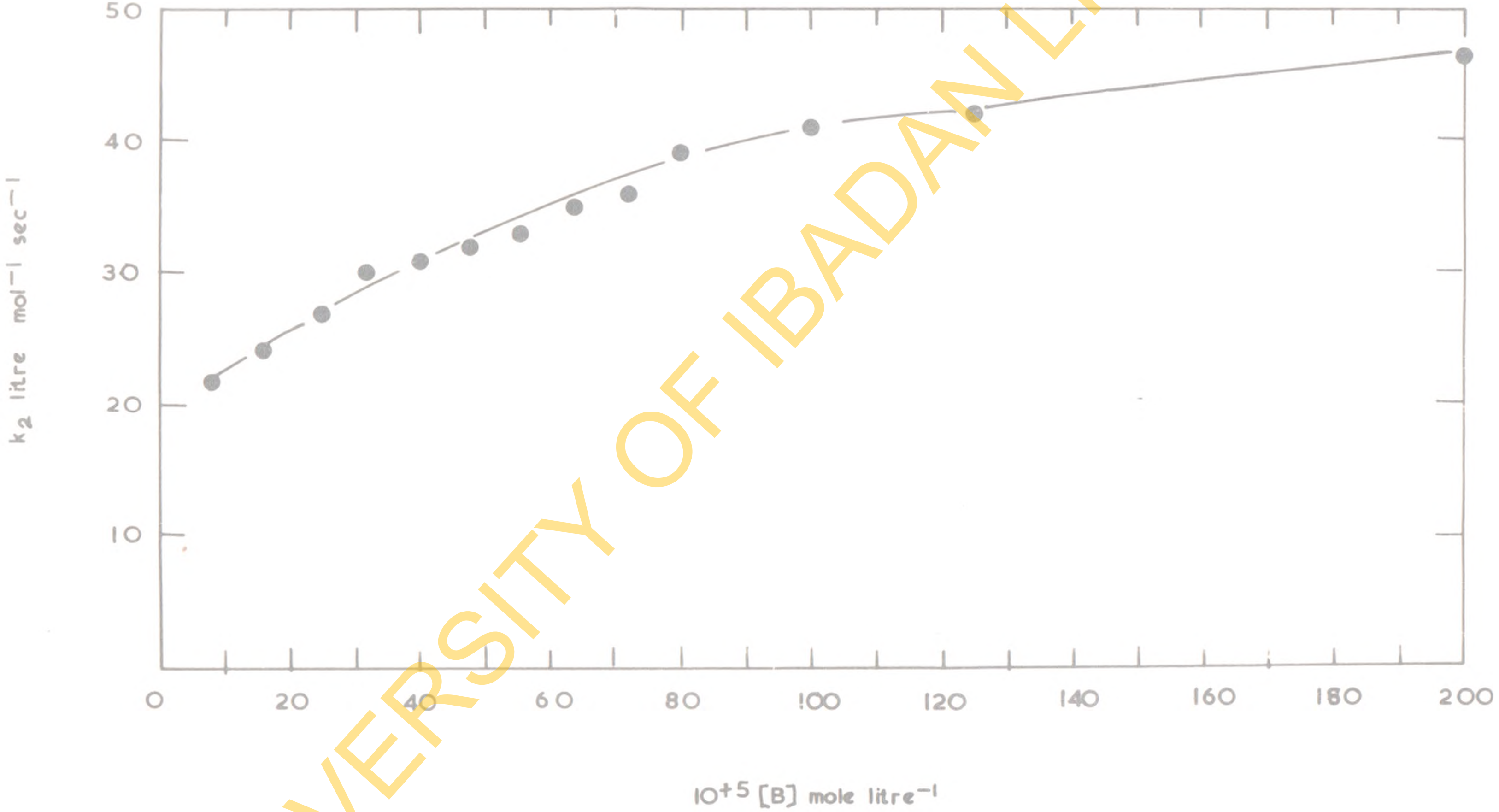
Table 6g

Partial rate constants for the reactions of 1-X-2, 4 - dinitrobenzene (X = F,Cl) with piperidine and aniline in acetone.

Substrate	Nucleophile	Temp °C	k_1	k_{-1}/k_3	k_{-1}/k_2	k_3/k_2
1-Cl-2-4-DNB	Piperidine	30	7.27×10^{-1}	8.31×10^{-3}	3.33	400
1-F,2-4-DNB	Piperidine	30	55.02	3.67×10^{-4}	22.1	6.06x10
1-F,2,4-DNB	Piperidine	-30	37.6	7.92×10^{-4}	1.27	1.61x10

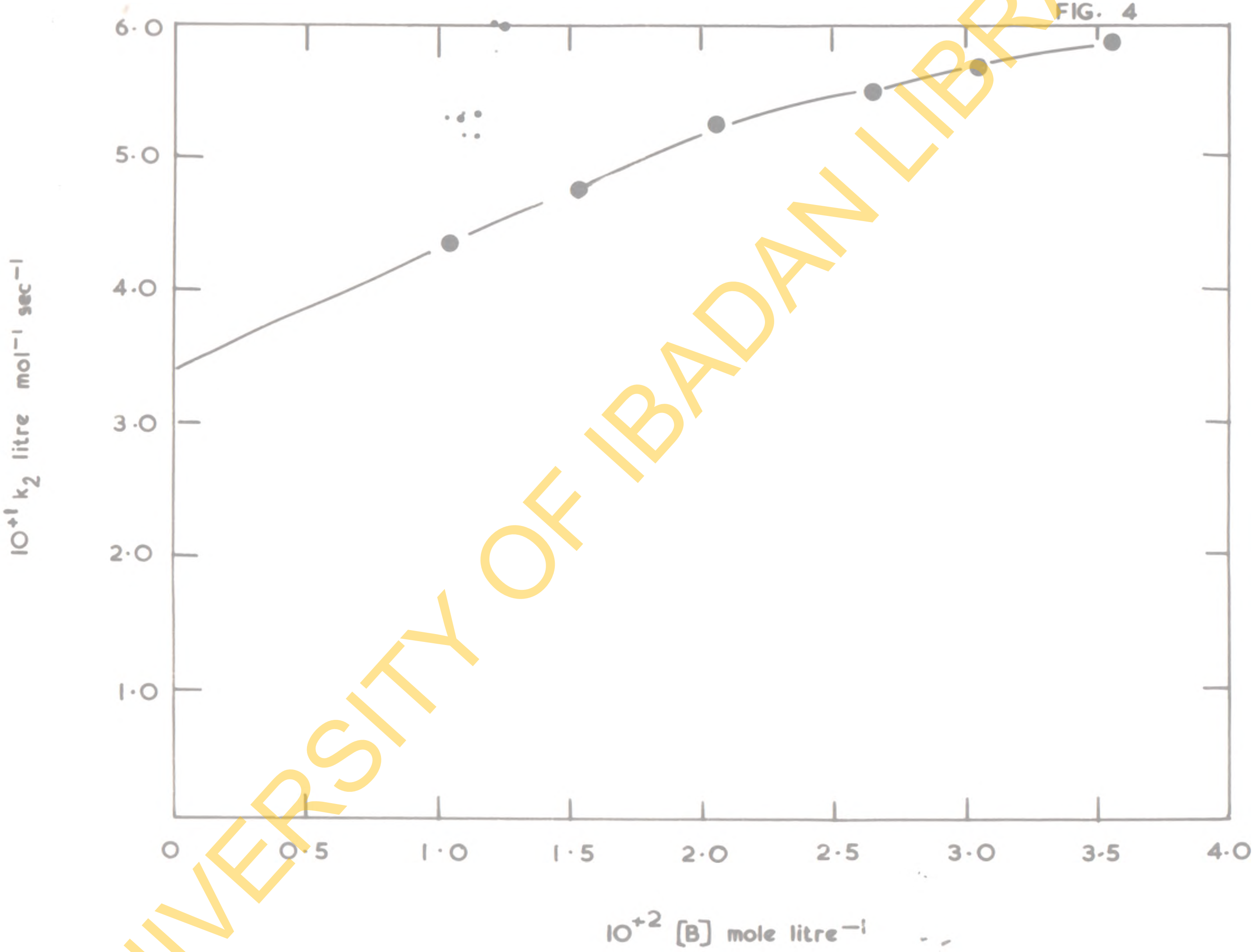
1-FLUORO-2, 4-DINITROBENZENE + PIPERIDINE IN ACETONE AT + 30°C

FIG. 3



I-CHLORO-2, 4-DINITROBENZENE WITH PIPERIDINE IN DRY ACETONE AT +30°C

FIG. 4



1-Cl-2,4-DNB	Aniline	50	6.54×10^{-5}	1.09×10^{-1}	5.04	46.5
1-F-2,4-DNB	Aniline	50	5.25×10^{-3}	1.60	-	-

$$\left(\frac{k_1F}{k_1Cl}\right)^{30^\circ C}_{\text{piperidine}} = 75.7 \qquad \left(\frac{k_1F}{k_1Cl}\right)^{50^\circ C}_{\text{Aniline}} = 80$$

There is base catalysis with both substrates at 30°Cwhen the nucleophile is piperidine as $k_3/k_2 > 50$ in both cases. The results obtained for the fluoro substrate with piperidine at -30°C compares favourably with those at +30°C except for k_1 values where one would have expected k_1 at + 30°C to be much greater than that at -30°C instead of the 1.5 increase observed.

The catalysis of the fluoro substrate is much greater than that of the chloro substrate as expectedon the basis of the proposed mechanism as discussed ealier on in this chapter.

The values of k_{-1}/k_2 are also in the expected sequence i.e. greater for fluoro than for chloro; because of the greater strength of the C-F bond compared with that of the C-Cl bond and the fact that acetone solvates fluoride ions much less than chloride ions [39b] will reduce k_2 the unimolecular rate constant for the decompositon of the intermediate formed by fluoro - compounds, relative to the corresponding value for the chloro - compounds.

The rate of formation of the intermediate, k_1, is greater for the fluoro substrates than for the chloro substrates with both nucleophiles. This is as expected, as earlier discussed, because of the greater activation by the fluorine atom.

The partial rate constant for the reactions of 2-X-5-nitropyridine

(X = F, Cl) with piperidine and aniline in acetone assembled in table 6f earlier on can be compared with those in table 6g.

Although the figures are not strictly comparable due to the wide spread of activity which precluded measurements of all the rates at the same temperature, some generalisationscan be made. Even though the values of F/Cl ratios for k_1 are expected to be temperature variable, this not withstanding, the figures indicate that for reactions with aniline, the ratio is higher in the 2,4 - dinitrobenzene than in the nitropyridine series. In the latter series, the value of this ratio is greater when the nucleophile is piperidine than when it is aniline.

In the former series, the present work gives about the same value for this ratio for aniline and piperidine. These results show that the greater the activation of the substrate, the greater is the F/Cl ratio for k_1. In contrast to an earlier notion [59], it does not appear unambiguously that there is a correlation of this ratio with base strength.

Effect of change of solvent from acetone to methanol/ethanol on the rate of formation of the intermediate can also be obtained with the aid of table 6h below. The useof the data obtained in methanol and ethanol is legitimate as Bamkole and Hirst have shown [59] that a change from methanol to ethanol has little or no effect on the activation parameters.

The figures in table 6h are already included in those of table 6c.

<u>Table 6h</u>

Rate of formation of the intermdiate complex for the reactions of 1-X-2, 4 - dinitrobenzene (X = Cl, F) with piperidine and aniline in methanol [63] and ethanol respectively.

Substrate	Nucleophile	Solvent	Temp °C	k_1
1-F-2,4-DNB	Piperidine	Methanol	50	11.94
1-Cl-2,4-DNB	Piperidine	Methanol	50	5.2×10^{-2}
1-F-2,4-DNB	Aniline	Ethanol	50	1.66×10^{-2}
1-Cl-2,4-DNB	Aniline	Ethanol	50	1.94×10^{-4}
1-F-2,4-DNB	Piperidine	Methanol	30	5.02
1-Cl-2,4-DNB	Piperidine	Methanol	30	1.55×10^{-2}

- DNB is abbreviation for -dinitrobenezene

$$\left(\frac{k_1F}{k_1Cl}\right)^{50}_{\text{Piperidine}} = 229.6 \qquad \left(\frac{k_1F}{k_1Cl}\right)^{50}_{\text{Aniline}} = 85.6$$

For the reactions in tables 6g and 6h, when the nucleophile is aniline, the rates of formation of the intermediate complex is faster in the hydroxylic solvent ethanol than in acetone. This is consistent with the theory of Hughes-Ingold which predicts that for reactions among neutral molecules, going through charged intermediates, a change to a more solvating solvent such as from acetone to methanol or ethanol, will result in an increase of rate of reaction.

But when the nucleophile is piperidine, the aprotic solvent acetone is much faster than the protic solvent methanol. In the case of piperidine, it would appear that solvation effects acting via hydrogen bonding favour acetone over methanol. This sequence has already been observed in the nitropyridine series earlier on and the discussion there also applies here.

Also, as in the nitropyridine series, in both solvents,

$$k_1 \, F > k_1 \, Cl$$

and also for both solvents

$$k_1 \text{ (Piperidine)} > k_1 \text{ (Aniline)}$$

From the results in tables 6f, 6g, and 6h, it will be gathered that the reactions of the 2-chloro-5-nitropyridine series are slower than those of the 2, 4 - dinitrobenzene series. This is easily explained as due to the greater activating effect of an ortho nitrogroup relative to an ortho cyclic nitrogen atom.

b. The reactions of 1-X-2, 4 -dinitrobenzene (X = F, Cl) with n-butylamine in stabilised and destabilised chloroform.

For both the fluoro and the chloro substrates, there is a small linear dependence of rate constants on amine concentration; tables 7 and 8 and the respective plots 7 and 8 illustrate this fact.

The data derived from these plots are given in table 6i below together with the result obtained [22] by S.D. Ross with the chloro substrate.

k^1 is the intercept i.e. the rate constant for the uncatalysed reaction and the unit is litre mol^{-1} sec^{-1};

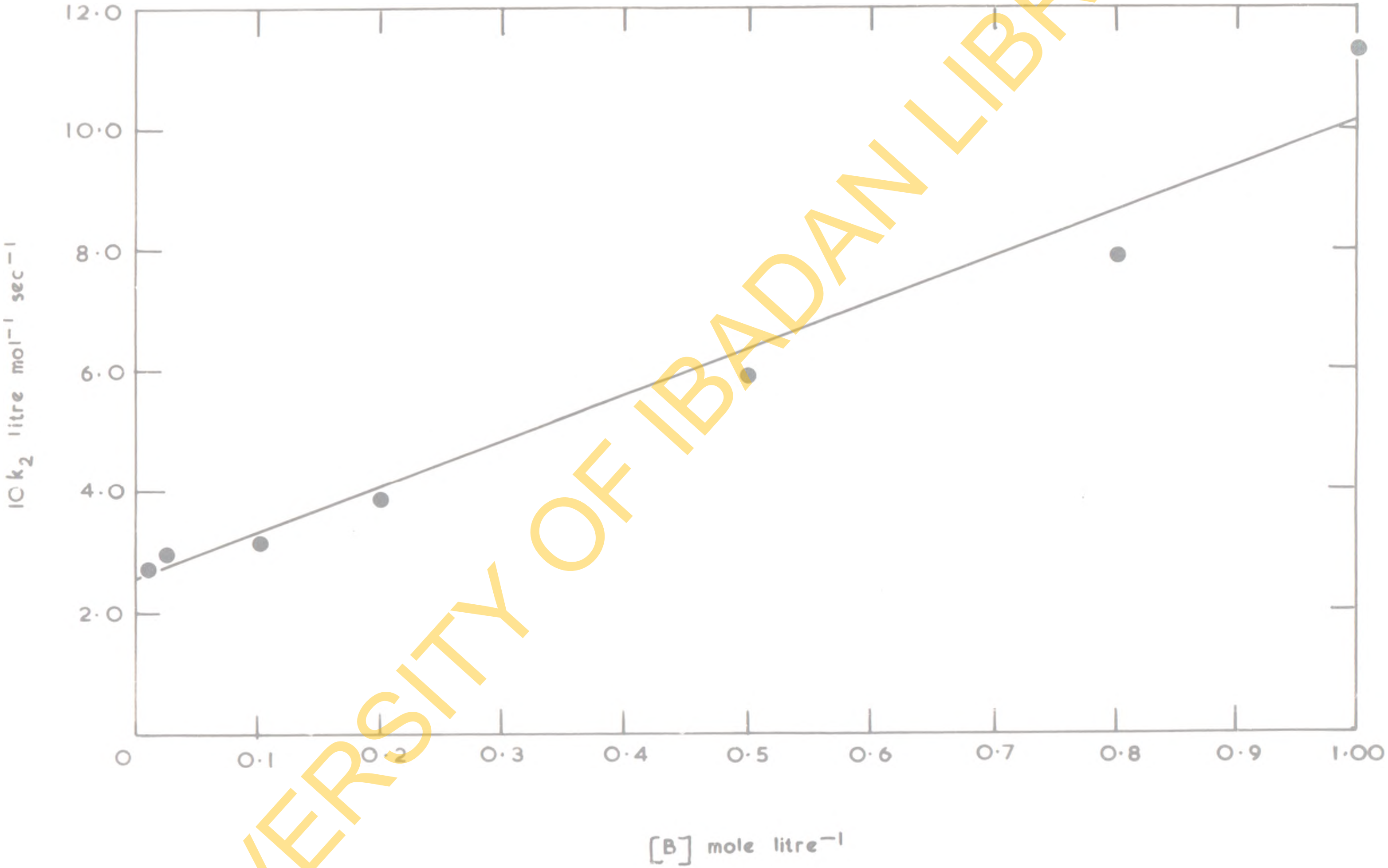
k^{11} is the slope i.e. the rate constant for the amine catalysed reaction and the unit is litre ^{2} mol^{-2} sec^{-1}. k^{11}/k^1 is therefore the extent of base catalysis in the system.

Table 6i

Summary of k^{11}, k^1 , k^{11}/k^1 for the reactions of 1-x-2,4-dinitrobenzene

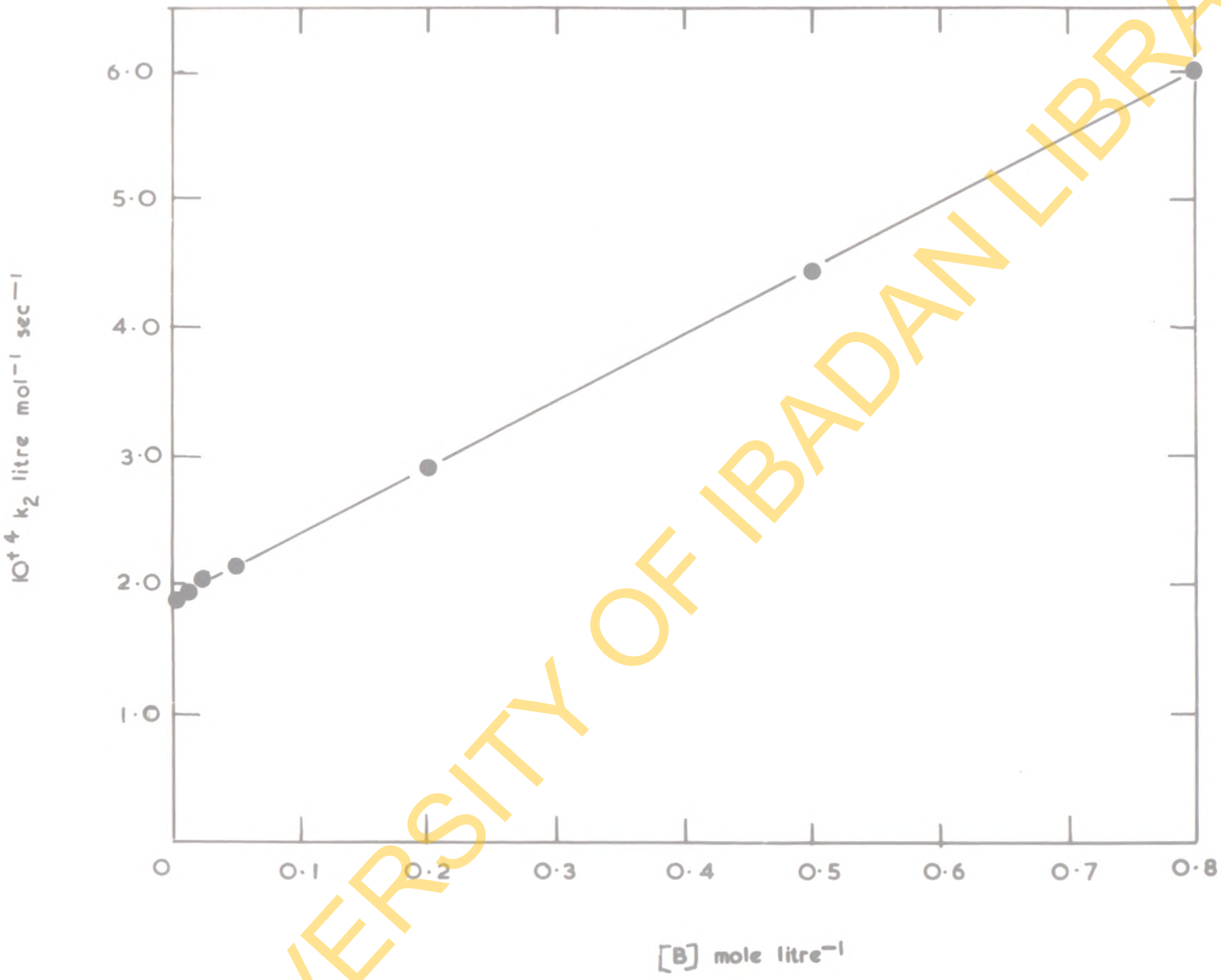
1-FLUORO-2,4-DINITROBENZENE WITH n-BUTYLAMINE IN STABILISED CHLOROFORM AT 24·82°C

FIG. 7



1-CHLORO-2,4-DINITROBENZENE WITH n-BUTYLAMINE IN STABILISED CHLOROFORM AT 24·82°C

FIG. 8



(X = F, Cl) with n-butylamine in stabilised chloroform.

Substrate	Nucleophile	Temp °C	k^{11}	k^{1}	$k^{11}/_{k}1$
1-Cl-2,4-DNB	n-butylamine	24.82	5.29×10^{-4}	1.90×10^{-4}	2.8
1-F-2,4-DNB	n-butylamine	24.82	7.63×10^{-1}	2.5×10^{-1}	3.1
1-Cl-2,4-DNB [22]	n-butylamine	24.82	5.63×10^{-4}	1.87×10^{-4}	3.0

These reactions show very mild base catalysis. For both substrates, stabilised and destabilised chloroform were used; the rate constants obtained were the same within thelimits of experimental error in both solvents - compare figures in tables 7 and 7a, 8 and 8a. For the fluoro substrate, when the stabilised chloroform is used, the molar concentration of the substra is 2.5 x 10^{-4} while that of ethanol, the stabilising agent is 2.00 x 10^{-2} M. The ethanol is therefore present in much larger concentration than the substrate. This makes it possible, from the hydrogen-bonding point of view, for the intermediate complex to be preferentially solvated by ethanol when stabilised chloroform is the solvent, and for the course of the reaction to follow essentially the same path as when ethanol is the solvent thus resulting in little or no catalysis. If this were so, then when the ethanol is removed, i.e. the chloroform is destabilised, a bigger response to the effect of increasing amine concentration may have been expected. But the results show that the removal of ethanol has no effect on the rate constants. This may mean that specific solvent effects such as hydrogen-bonding of the transition state by ethanol does not occur in these reactions or if it does, such specific effect is also equally possible with pure chloroform. Ross, in his own work, attributed[22] such mild accelerations in these reactions which involve a good leaving group and do not attain a limiting rate at high amine concentration as true base catalysis due to the presence of a hydrogen bond from the amine nucleophile to a suitable acceptor in the transition state for the intermediate formation. The acceptors can be a second amine molecule or an anion such as CH_3COO^- or OH^- or even any neutral molecule with groups that can act as hydrogen bond acceptor e.g. the NO_2 group in m - dinitrobenzene.[6]

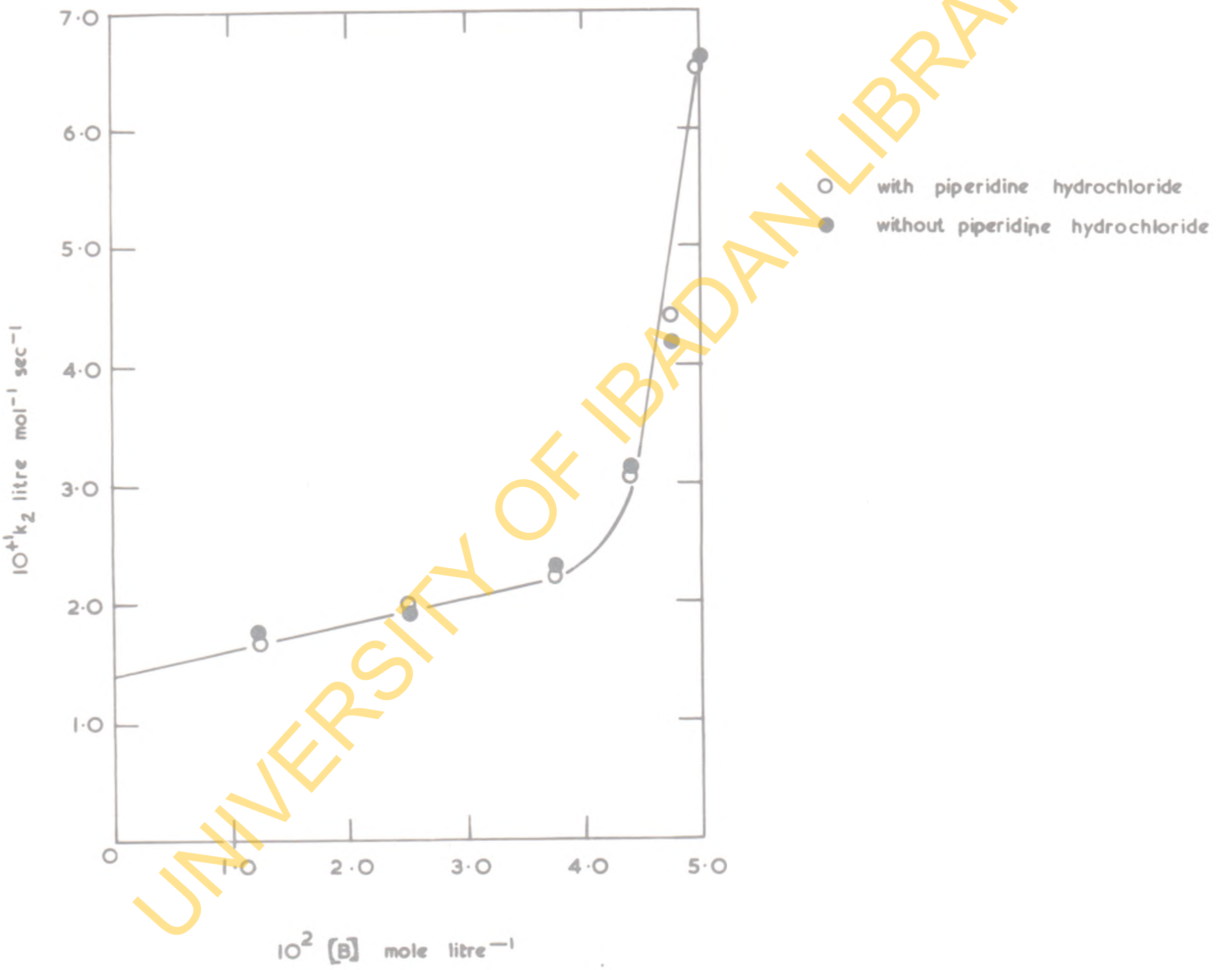
C. The reactions of 1-X-2, 4-dinitrobenzene (X = F, Cl) with Piperidine in methanol with and without Piperidine Hydrochloride.

The results obtained for these reactions are given in tables 1 and 2. For both the fluoro and the chloro substrates, there is an increase in rate constants with increasing amine concentration. The plot of rate constants versus amine concentration for the chloro substrate is linear with a single slope; for the fluoro substrate, however, there is first a gentle slope; then a steep slope see plots 1 and 2 respectively.

The addition of Piperidine hydrochloride did not seem to have had any appreciable effect on the rates of the reactions - see the plots of the values on the same graphs plots I and 2. If the presence of the hydrochloride had made any difference to the rates, this may have been attributed to electrophilic assistance by piperidine hydrochloride in the removal of F or Cl atom in the decomposition of the intermediate complex to products.

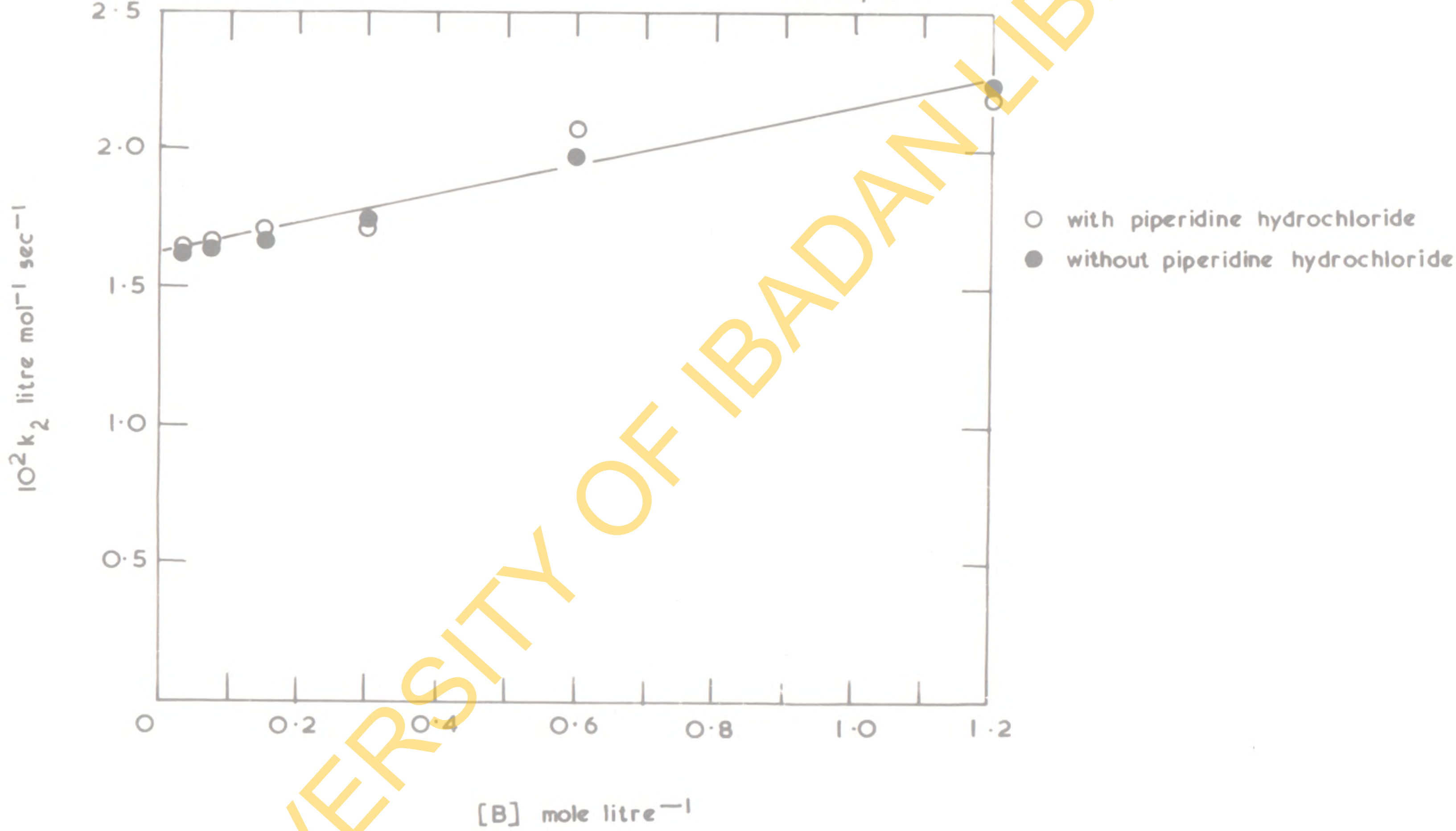
1- FLUORO-2, 4-DINITROBENZENE + PIPERIDINE IN METHANOL AT -29·6°C
WITH AND WITHOUT PIPERIDINE HYDROCHLORIDE

FIG. 1, 1a



1-CHLORO-2, 4-DINITROBENZENE WITH PIPERIDINE IN DRY METHANOL AT 30·20°C WITH PIPERIDINE HYDROCHLORIDE AND WITHOUT

FIG. 2, 2a



It is possible that the small rate increment with increasing amine concentration is due to the equilibrium

being established during reaction. The methoxide ion which is perhaps a stronger nucleophile may replace the nucleophile piperidine. Thus as the amine concentration is increased, so is the concentration of the MeO$^-$ and hence its catalytic effect. If this were so, then the addition of piperidine hydrochloride which will suppress further formation of MeO$^-$ ions will lead to a state where there is no rate dependence on amine concentration. Such addition of the hydrochloride has no effect on the rates of reaction so this possibility has to be discarded.

Assuming intermediate complex mechanism, these results suggest that the rate of formation of the intermediate complex is rate determining and the second step i.e. the decomposition of this intermediate to the products has no kinetic significance. Any variation of rate appears to be associated with the effect of increasing amine concentration in the medium on the first step of the reaction. Since electrophilic catalysis of the first step in this mechanism is not possible, this special effect is not electrophilic catalysis.[49a] It may be due to some special unknown medium effects.

For the chloro substrate, $k^{11} = 5.6 \times 10^{-3}$, $k^{1} = 1.6 \times 10^{-2}$, $k^{11}/k^{1} = 0.34$. In this system, one can say that there is virtually no base catalysis and that $k_o \simeq k_1$

The reaction of the fluoro substance which gave a doubly sloped curve was carried out at the very low temperature of -30°C. The slopes may merge as the temperature is increased but this was not done in this work.

Banjoko et al [64] carried out similar reactions in anhydrous acetone at 50°C and the fluoro substrate also gave a doubly sloped curve for the variation of rate constants versus amine concentrations. The explanation of electrophilic catalysis, valid for reactions in acetone, cannot be applied here.

d. The reactions of 1-X-2, 4-dinitrobenzene (X = F, Cl) with n-butylamine in acetone.

For these reactions, with both substrates, the second order rate constants increased linearly with increasing amine concentration - see tables 5 and 6 and the corresponding plots 5 and 6.

Data derived from these plots are given in table 6j.

Table 6j

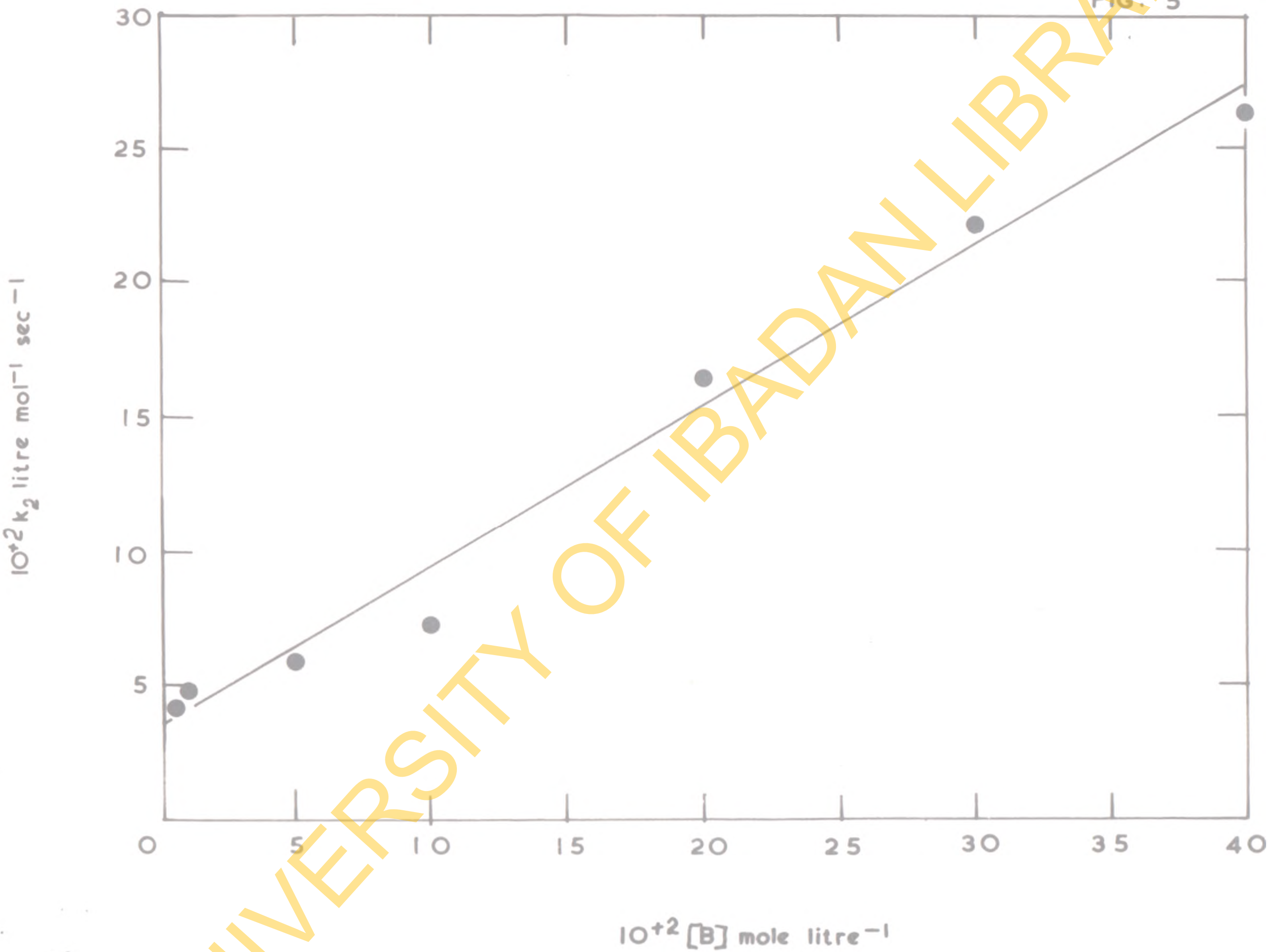
Summary of k^{11}, k^{1}, $k^{11}/_{k^1}$, for the reactions of 1-X-2, 4-dinitrobenzene (X = F, Cl) with n-butylamine in acetone.

Substrate	Nucleophile	Temp °C	k^{11}	k^{1}	$k^{11}/_{k^1}$
1-F-2,4-DNB	n-butylamine	24.82	$6.0\text{x}10^{-1}$	$3.5\text{x}10^{-2}$	17
1-Cl-2,4-DNB	n-butylamine	24.82	$1.0\text{x}10^{-3}$	$1.8\text{x}10^{-5}$	56

Both systems show a certain degree of base catalysis. [45] What is unusual in these reactions is that the chloro substrate is more prone to base catalysis than the fluoro substrate. This sequence is uncommon and the reason for it is at present obsure. The sequence is contrary to all those already discussed and needs more investigation.

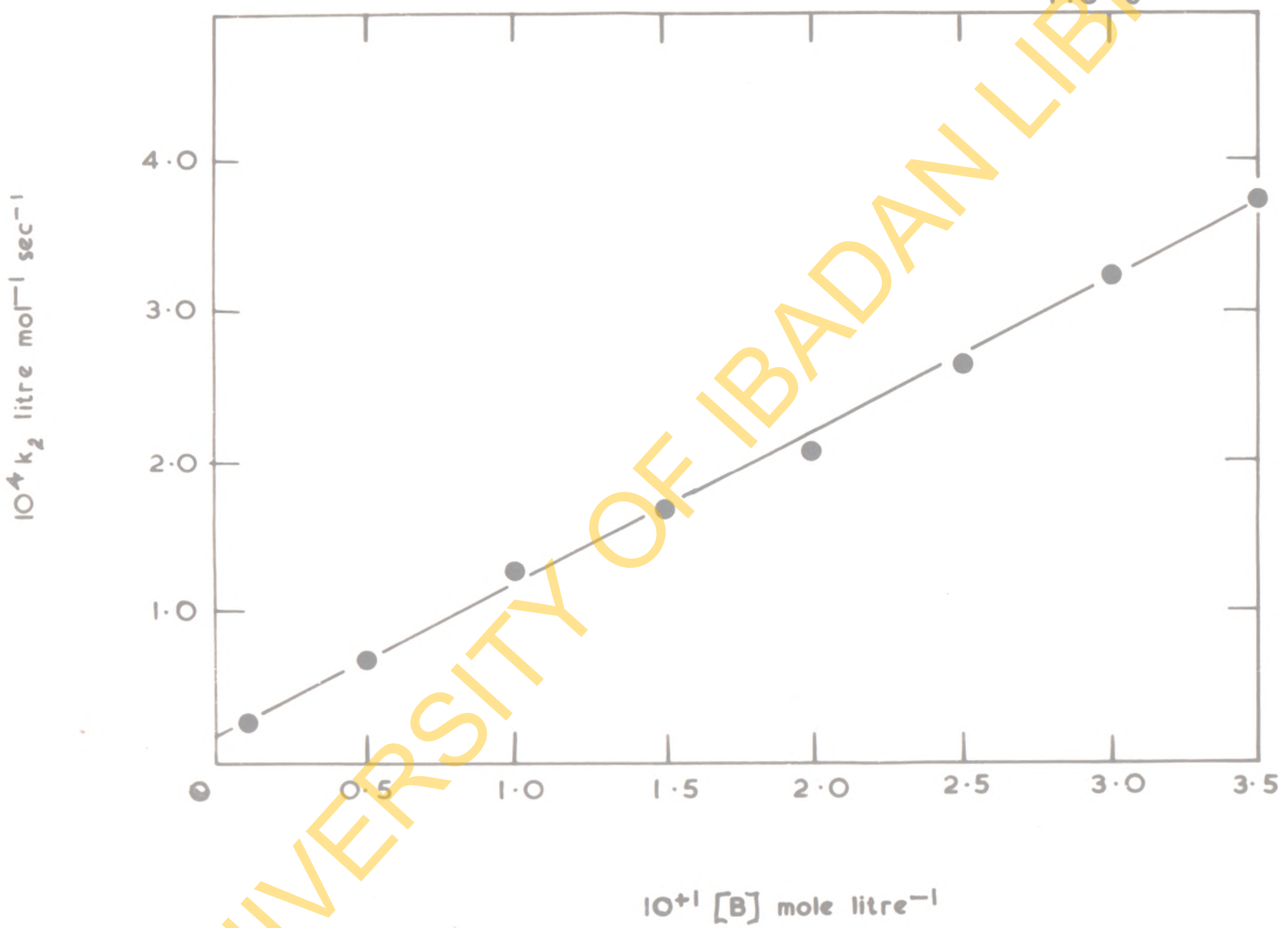
1- FLUORO-2,4-DINITROBENZENE WITH n-BUTYLAMINE IN DRY ACETONE AT 24.82°C

FIG. 5



1-CHLORO-2,4-DINITROBENZENE WITH n-BUTYLAMINE IN DRY ACETONE AT 30°C

FIG. 6



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