99. *The Reaction between Amines and* 1-*Chloro*-2 : 4-*dinitrobenzene.*

By O. L. Brady and F. R. Cropper.

The reaction of a number of alkylamines and dialkylamines with chlorodinitrobenzene has been studied kinetically, and it has been found that there is a remarkable difference between the rate constants for different amines which is not directly related to their basic strength; for example, the rate constant for dimethylamine is more than 30,000 times that for di*iso*propylamine though the latter is the stronger base.

Evidence is adduced that a steric effect plays an important part in determining the rate constant.

The reaction between primary and secondary amines and 1-chloro-2 : 4-dinitrobenzene

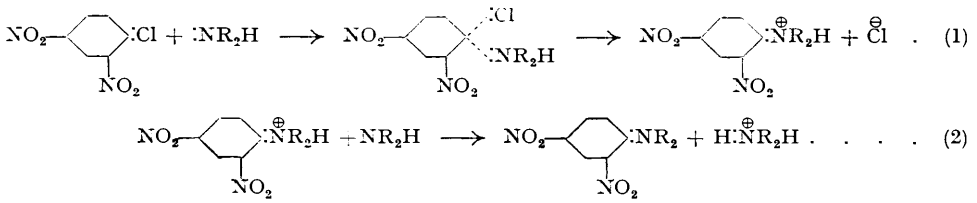
$$2NHRR' + C_6H_3Cl(NO_2)_2 \longrightarrow C_6H_3(NO_2)_2 \cdot NRR' + NH_2RR'Cl$$

produces only the substituted dinitroaniline and amine hydrochloride. The dinitrophenylalkylamine or dinitrophenyldialkylamine does not react further with the chlorodinitrobenzene,

and the hydrolysis or alcoholysis of the last-named compound is not appreciable. The reaction, therefore, has advantages for the study of the reactivity of amines.

A concentration of amine twice that of the chlorodinitrobenzene being used, the reaction, in alcohol, was found to be of the second order, and good rate constants (k_2) were obtained for all amines used except those which reacted very slowly.

The simplest method of representing the reaction is as a heterolytic, nucleophilic one of type (*b*) in Ingold's classification of the mechanisms of substitution at a saturated carbon atom (1) (Hughes, *Trans. Faraday Soc.*, 1941, **37**, 604), followed by loss of proton from the first product to a second molecule of amine.



Since the dinitrophenyldialkylamines are very weak bases the rate-determining reaction will be (1).

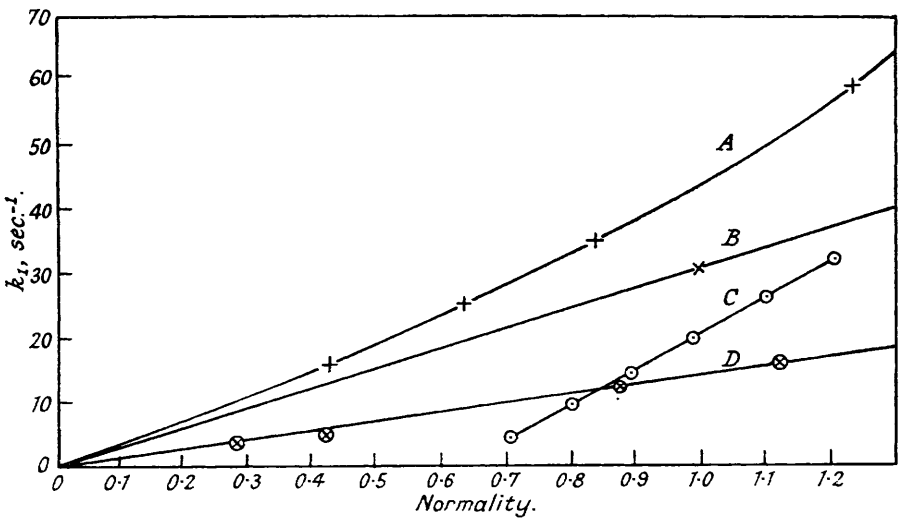
Possible secondary reactions are the following:

$$NHR_2 + HOEt \rightleftharpoons \overset{\oplus}{N}H_2R_2 + \overset{\ominus}{O}Et$$

$$(NO_2)_2C_6H_3Cl + \overset{\ominus}{O}Et \longrightarrow (NO_2)_2C_6H_3{\cdot}OEt + \overset{\ominus}{Cl}$$

$$(NO_2)_2C_6H_3{\cdot}OEt + NHR_2 \longrightarrow (NO_2)_2C_6H_3{\cdot}NR_2 + HOEt$$

Although alkoxyl ions act readily on 1-chloro-2 : 4-dinitrobenzene (Holleman and ter Weel, *Rec. Trav. chim.*, 1915, **35**, 1), their concentration under the conditions used cannot be sufficiently high for interference except in the cases of very slow-acting, fairly strongly basic amines such as *tert.*-butylamine or di*iso*propylamine (see Table I) since with a concentration of triethylamine ($K_b = 6{\cdot}4 \times 10^{-4}$) some twenty times that of the amine used in the study of the second-order reaction the liberation of chloride ion is exceedingly slow.



A, B, C, *Concn. of* NH_2Me. D. *Concn. of* NEt_3 *added to* 0·64N-NH_2Me.

When the concentration of amine was far greater than that of the chlorodinitrobenzene the reaction became one of the first order or pseudo-unimolecular. The plot of the rate constant against concentration of amine is, however, not linear, the rate constant increasing more rapidly at higher concentrations of amines. The figure shows the plot of k_1^{25} against concentration of methylamine (*A*), the concentration of chlorodinitrobenzene being 0·329N., and of k_1' calculated

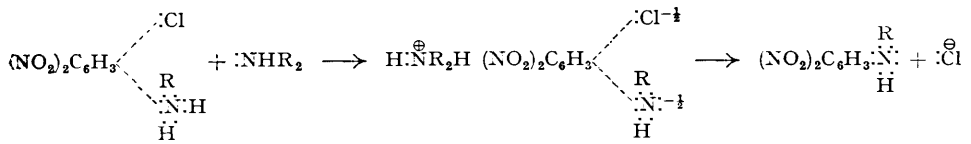
from the second-order rate constant k_2^{25} by putting b, the concentration of methylamine, equal to unity (B).

Above 0·4N-methylamine the difference between the observed rate constant k_1 and the extrapolated value k_1' is proportional to the excess of methylamine over 0·4N. Curve C shows the plot of $k_1 - k_1'$ against concentrations of methylamine. One would expect this proportionality not to hold for concentrations of methylamine much below 0·4N., since this represents only six times the equivalent concentration of amine (0·0658N.) for the chlorodinitrobenzene, and the assumption necessary for using first-order kinetics is becoming of doubtful validity.

Triethylamine, which does not react to an appreciable extent with chlorodinitrobenzene under the conditions of experiment, also increases the rate constant when added to a reaction mixture containing 0·64N-methylamine, and the increase in the rate constant ($k_1'' - k_1$) is proportional to the concentration of triethylamine. Curve D shows $(k_1'' - k_1)$/(concn. of NEt_3).

It is clear, therefore, that the velocity is influenced by a proton acceptor. Since the dinitrophenylalkylamines are very weak bases whose salts are practically completely hydrolysed in aqueous or alcoholic solution, reaction (2) is probably extremely rapid and we have to look elsewhere for the influence of the proton acceptor.

In the intermediate stage of (1) the presence of a proton acceptor will increase the electron availability of the nitrogen and facilitate its attachment to the carbon with the accompanying extrusion of the chloride ion :



This effect will be appreciable, probably, only when the concentration of amine is relatively high as in the pseudo-unimolecular reaction.

If the mechanism suggested for the bimolecular reaction be correct, the rate constant should depend upon the electron-availability at the nitrogen of the reacting amine, and electron-donating groups therein should increase the rate constant, which one would expect to bear a direct relation to the dissociation constants of the amine. The bimolecular rate constants (k_2^{25}) of the interaction between a number of amines with 1-chloro-2 : 4-dinitrobenzene in alcohol at 25° have been obtained by measuring the rate of liberation of chloride ion; the results are given in Table I, Col. 3.

The experimental part of this work was completed in 1935 and it was not until the results for the second-order reaction had been practically completed that it was discovered that Blanksma and Schreinemakers (*Rec. Trav. chim.*, 1933, **52**, 498) had published the rate constants for the reaction between 1-chloro-2 : 4-dinitrobenzene and a number of amines also in alcohol at 25° as measured by the rate of disappearance of amine. These are given in Table I, Col. 2, calculated to sec.$^{-1}$ from Blanksma and Schreinemakers's figures to min.$^{-1}$. Where the same amines were employed the results in Col. 2 and Col. 3 were obtained by different methods quite independently and the agreement in most cases is close. Even where there are appreciable discrepancies, *e.g.*, for piperidine, it does not affect the order of reactivity of the amines.

From a consideration of these results certain peculiarities are at once apparent. First, although the replacement of hydrogen by methyl, with the corresponding increase in basicity of the amine, leads to an increase in the rate constant ($k_2 \times 10^4$, $NH_3 = 0·04$, $NH_2Me = 31·6$, $NHMe_2 = 355$), yet in other cases the rate constants bear no obvious relation to the dissociation constants (K_b) of the amines. [The dissociation constants taken from the literature and given in Table I are for aqueous solutions, but it has been shown that their relative order is unchanged in passing from water to alcohol although their magnitude is greatly reduced (Goodhue and Hixon, *J. Amer. Chem. Soc.*, 1934, **56**, 1329).]

Secondly, one notices the high rate constant for methylamine ($k_2 \times 10^4 = 31·6$) compared with ethylamine ($k_2 \times 10^4 = 9·1$), for dimethylamine ($k_2 \times 10^4 = 355$) compared with diethylamine ($k_2 \times 10^4 = 1·9$), and for piperidine ($k_2 \times 10^4 = 153$) compared with ethyl-*n*-propylamine ($k_2 \times 10^4 = 1·7$) and α-pipecoline ($k_2 \times 10^4 = 0·22$).

Thirdly, whereas the rate constant for dimethylamine is about ten times that for methylamine, the rate constant for diethylamine is about one-fifth of that for ethylamine, and that for di*iso*propylamine about one-hundredth of that for *iso*propylamine.

TABLE I.

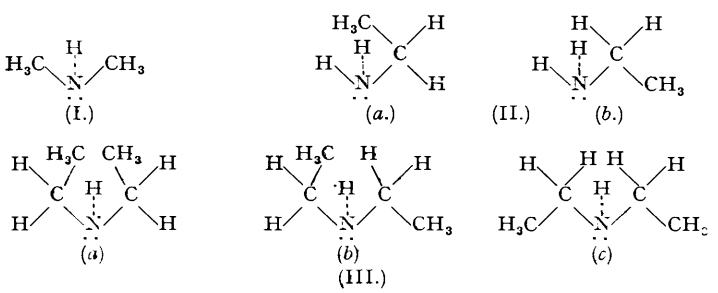
Amine.	$10^4 k_2^{25}$, sec.$^{-1}$, B. & Schr.	$10^4 k_2^{25}$, sec.$^{-1}$, B. & C.	$10^4 K_b$.	pK_H (25°).*
Dimethylamine	348	355	5·0	10·71
Piperidine	191	153	12·5	11·13
Methylamine	31·3	31·6	4·0	10·64
n-Heptylamine	10·2	10·0	—	—
n-Amylamine	10·1	—	—	10·64
n-Butylamine	9·5	10·0	—	10·61
n-Propylamine	8·9	9·6	3·9	10·58
Ethylamine	8·6	9·2	4·6	10·67
*iso*Butylamine	—	6·8	2·6	10·42
Diethylamine	1·8	1·9	10·0	10·98
Di-*n*-butylamine	—	1·8	—	11·31
Di*iso*amylamine	1·7	—	—	11·00
Ethyl-*n*-propylamine	—	1·7	—	—
Di-*n*-propylamine	1·6	1·6	8·2	10·91
*iso*Propylamine	1·1	1·0	4·3	10·63
sec.-Butylamine	0·92	0·91	3·6	10·56
Di*iso*butylamine	0·67	0·58	3·9	10·82
α-Pipecoline	—	0·22	—	10·98
Ethyl*iso*propylamine	—	0·18—0·033	—	—
Ammonia	0·04	0·04	0·18	9·27
tert.-Butylamine	—	0·038	3·4	10·45
Di*iso*propylamine	—	0·011—0·007	—	11·05
αα-Lupetidine	—	0·011—0·006	—	—
Tetrahydroquinoline	—	0·068—0·004	—	—
Tetrahydroquinaldine	—	0·004—0·002	—	—

* Negative log of hydrolysis constant (Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469).

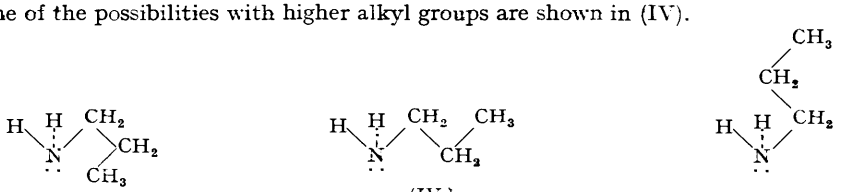
Fourthly, branching of the chain of the alkyl radical at the first carbon atom greatly reduces the rate constant ($k_2 \times 10^4$, *n*-propylamine = 9·6, *iso*propylamine = 1·0; *n*-butylamine = 10·0, *sec.*-butylamine = 0·92, *tert.*-butylamine = 0·038), but there is much less difference between *n*-butylamine ($k_2 \times 10^4$ = 10·0 and *iso*butylamine ($k_2 \times 10^4$ = 6·8).

In the light of these results it seems that the arrangement in space of the atoms of the alkyl groups in the amines plays an important part in determining their reactivity towards chlorodinitrobenzene.

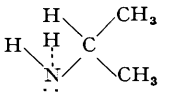
If one considers the stereochemistry of methylamine and ethylamine it will be seen that, whereas in methylamine and dimethylamine (I) there is at all times ample room for the approach of the large chlorodinitrobenzene molecule to the exposed part of the nitrogen atom, yet in the case of ethylamine, if there is free rotation about the carbon–nitrogen bond, at some time the methyl group can interfere with the approach of the chlorodinitrobenzene (II*b*). With diethylamine the time during which this steric hindrance will be effective will be greater (III*b*, III*c*).



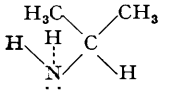
Some of the possibilities with higher alkyl groups are shown in (IV).

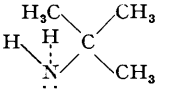


Branching at the first carbon atom of the alkyl chain will increase the time during which steric hindrance is effective; in *iso*propylamine (V) the time at which a methyl will exert a steric hindrance will be twice that in ethylamine, whilst in *tert.*-butylamine (VI) a methyl group will at all times interfere.



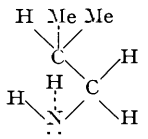
(V.)



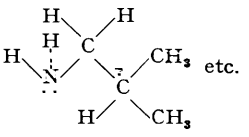


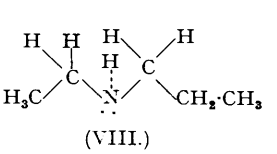
(VI.)

The effect of two *iso*propyl groups would be greater than that of one. The methyl in the *iso*butyl group would not have the same effect (VII), and *iso*butylamine might be expected to show similar results to *n*-butylamine.



(VII.)



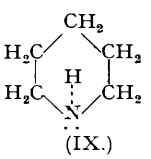


(VIII.)

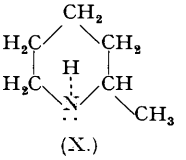
Since the basicity of the amine depends on the position of the equilibrium $NH_2R + \overset{\oplus}{H} \rightleftharpoons \overset{\oplus}{N}H_3R$, it would not be affected by steric influences.

The rate constants are all in agreement with the above views.

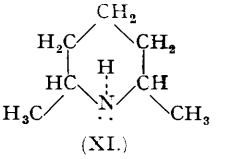
Confirmation is afforded by a consideration of ethyl-*n*-propylamine (VIII), piperidine (IX), pipecoline (X), and lupetidine (XI).



(IX.)



(X.)



(XI.)

In the first case the rate constant is low ($k_2 \times 10^4 = 1{\cdot}7$) and of the order of that for diethylamine, since at some time a steric effect can be exerted; when the carbon atoms take part in ring formation the state of affairs shown in (VIII) cannot occur and the rate constant for piperidine ($k_2 \times 10^4 = 153$) is of the same order as that of dimethylamine; the introduction of a permanently hindering methyl group results in a greatly reduced rate constant for α-pipecoline ($k_2 \times 10^4 = 0{\cdot}22$). Lellmann (*Ber.*, 1890, **23**, 1388; 1891, **24**, 2104) observed qualitatively the abnormally slow rate of reaction of α-pipecoline with 1-chloro-2 : 4-dinitrobenzene compared with that of piperidine or β-pipecoline (the β-methyl group could not interfere sterically). Finally, the rate constant for αα-lupetidine, where there are two permanently hindering methyl groups, is so low ($k_2 \times 10^4 = 0{\cdot}011$—$0{\cdot}006$) as to prevent accurate measurement at the temperature employed for the other amines.

The foregoing explanation has been put forward on the assumption that perfectly free rotation exists about the carbon–nitrogen bond, but the study of the Raman spectra of, *e.g.*, such a compound as 1 : 2-dichloroethane, has suggested that there is some restriction of rotation even between two singly bound carbon atoms. The possibility that the terminal methyl group in ethylamine is preferentially situated near the exposed part of the nitrogen atom cannot be rejected; it might certainly be so if the polarity of the C–H bond in the alkylamines is in the direction $\overset{\ominus}{C}$–$\overset{\oplus}{H}$ but, as stated by Gent (*Quart. Reviews*, 1948, **2**, 381), knowledge of the polarity of the C–H bond in various situations is still small, so it would be unprofitable to speculate in this direction.

The rate constants for the bimolecular reaction between chlorodinitrobenzene and methylamine and dimethylamine have been determined at 25°, 30°, 35°, and 40°, and it was found that the plot of log k against $1/T$ was, in both cases, a straight line, so it was assumed that the Arrhenius equation held for the interaction of the other amines with chlorodinitrobenzene. The energies of activation and collision frequencies are given in Table II. With the exception of

those for methylamine and dimethylamine, the results are probably not very accurate, as measurements were made at only two temperatures.

TABLE II.

Amine.	E, cals.	$B \times 10^{-5}$, sec.$^{-1}$.	Amine.	E, cals.	$B \times 10^{-5}$, sec.$^{-1}$.
Dimethylamine	9,340	1·7	Ethylpropylamine ...	13,000	5·8
Piperidine	10,200	4·7	Di-*n*-butylamine ...	14,200	48
Methylamine	10,700	2·3	*sec.*-Butylamine	14,800	67
Ethylamine	11,700	3·6	Di*iso*butylamine	14,800	42
n-Butylamine	11,700	3·9	*iso*Butylamine	15,500	1600
Diethylamine	12,650	3·7	*iso*Propylamine	15,900	475

The energies of activation are low and rise with the decline in the rate constant, but *iso*butylamine and to a smaller degree *iso*propylamine are exceptions.

EXPERIMENTAL.

Materials.—The amines were mostly purchased and purified by careful fractionation; methylamine, ethylamine, and dimethylamine were purified by recrystallisation of their hydrochlorides; the bases were liberated by concentrated potassium hydroxide, dried by passing through tubes packed with sodium hydroxide, and absorbed in the solvent.

Ethylpropylamine was prepared by heating 33% aqueous ethylamine with *n*-propyl chloride in a rotating autoclave at 125—150° for 24 hours and distilling the oil liberated by alkali; the fraction, b. p. 84—86°, was used. Ethyl*iso*propylamine was prepared similarly by using *iso*propyl bromide at 120—160° for 120 hours, the fraction of b. p. 70—74° being used. *tert.*-Butylamine was prepared by the Hofmann reaction on pivalamide and purified through the hydrochloride and by distillation, the fraction, b. p. 45—46°, being used. α-Pipecoline, αα-lupetidine, and tetrahydroquinaldine were prepared by reduction of α-picoline, αα-lutidine, and quinaldine; α-pipecoline was purified through the thiocarbamate (Ladenberg, *Annalen*, 1888, **247**, 62) and collected at 199°; αα-lupetidine was purified through its hydrochloride and collected at 127°; tetrahydroquinaldine was purified by the method of Pope and Peachey (*J.*, 1899, **75**, 1089) and collected at 154°/43 mm.

The 1-chloro-2 : 4-dinitrobenzene was crystallised from benzene. No attempt was made to employ alcohol completely free from water owing to the difficulty in preventing absorption of small quantities of water during the experiments. It was thought that changes in velocity would be greater as the alcohol approached purity, so one batch was employed for all experiments; this had a density of 0·788 at 25°, corresponding to 99% of alcohol.

Procedure.—The amine was dissolved in alcohol, and the strength and the concentration checked by titration with acid. Solutions of 1-chloro-2 : 4-dinitrobenzene were prepared by dissolving a weighed quantity in alcohol and dilution to the correct volume. The concentrations of chlorodinitrobenzene at time 0 were 0·0329N. or 0·0148N., obtained by using 25 c.c. of 0·986N- or 0·0444N-chlorodinitrobenzene. The concentrations of the amines at time 0 were 0·0658N. or 0·0296N., obtained by using 50 c.c. of 0·0986N or 0·0444N-amine. In these cases the concentration of amine was twice that of the chlorodinitrobenzene. Where excess of amine was used the concentrations varied from 0·2N. to 1·5N., obtained by using 50 c.c. of 0·3N- to 2N-amine.

In carrying out the reaction, 50 c.c. of the amine solution at 25° were mixed with 25 c.c. of the chlorodinitrobenzene solution, also at 25°, and the mixture was kept in a closed vessel in a thermostat. At known intervals 10 c.c. of the reaction mixture were removed with a pipette and run into a mixture of 5 c.c. of nitric acid and 25 c.c. of 0·017N-silver nitrate in a 100-c.c. measuring flask. The volume was made up to 100 c.c. with water, the whole filtered, and 50 c.c. of the filtrate were titrated with a standard solution of potassium thiocyanate, ferric alum being used as indicator.

For tetrahydroquinoline and tetrahydroquinaldine the above method could not be used owing to the formation of an intense red colour with ferric alum and nitric acid, so the excess of silver nitrate was titrated with potassium iodide, starch–nitrite indicator being used.

Results.

The Bimolecular Reaction.—Figures are given below for the bimolecular reaction, in some detail for methylamine, dimethylamine, and ethylamine, to indicate the agreement between the values found, and in summarised form for the other amines (Table III). In each case samples were taken at five or six time intervals and the variation in the constant was small in the more rapid reactions. In the very slow reactions, *e.g.*, *tert.*-butylamine, the constant diminished with time, and greater detail is given of this determination as an example.

Since two moles of amine to one of chlorodinitrobenzene were used and two moles of amine react with one mole of chlorodinitrobenzene, if a = concn. of chlorodinitrobenzene, $2a$ = concn. of amine then $dx/dt = k_2(a - x)(2a - 2x) = 2k_2(a - x)^2 = K(a - x)^2$; hence $K = x/ta(a - x)$, where $K = 2k_2$.

Methylamine.

0·0658N-NH_2Me, 0·0329N-$C_6H_3Cl(NO_2)_2$; 25°; in 99% alcohol.

Time (secs.)	630	1800	3600	6030	9960	17,460
Decompn., %	13·56	27·76	43·83	57·12	68·49	79·39
$k_2 \times 10^4$	34·6	32·5	34·1	33·6	33·2	33·5

50% Decompn. at 4620 secs. Average $k_2 = 33{\cdot}6 \times 10^{-4}$ sec.$^{-1}$.

0·0296N-NH_2Me, 0·0148N-$C_6H_3Cl(NO_2)_2$; 25°; in 99% alcohol.

Time (secs.)	1500	3150	4980	5790	12,810	84,240
Decompn., %	12·1	22·2	31·2	35·0	54·2	88·8
$k_2 \times 10^4$	31·0	30·6	30·7	31·4	31·2	31·8

50% Decompn. at 10,620 secs. Average $k_2 = 31·1 \times 10^{-4}$ sec.$^{-1}$.
$t_{\frac{1}{2}}/t'_{\frac{1}{2}} = 2·3$; ratio of concentrations 0·0329/0·0148 = 2·22.
The average of four determinations gave $k_2 = 31·6 \times 10^{-4}$ sec.$^{-1}$.

0·0658N-NH_2Me, 0·0329N-$C_6H_3Cl(NO_2)_2$, in 99% alcohol.

At 30°.			At 35°.			At 40°.		
Time, secs.	Decompn., %.	$k_2 \times 10^4$.	Time, secs.	Decompn., %.	$k_2 \times 10^4$.	Time, secs.	Decompn., %.	$k_2 \times 10^4$.
900	20·7	44·2	1005	28·06	58·9	660	25·3	78·1
1800	33·76	43·1	1500	36·75	59·1	900	31·66	78·3
3000	46·0	43·2	3615	57·91	57·9	1200	38·41	79·1
4200	54·88	44·1	5820	69·41	59·3	1920	50·24	80·0
5400	60·36	42·2	8925	77·68	59·3	3006	61·63	81·3
7380	67·96	43·7				4500	70·49	80·7
	Average =	43·4		Average =	58·9		Average =	79·6

Dimethylamine.

0·0658N-$NHMe_2$, 0·0329N-$C_6H_3Cl(NO_2)_2$; 25°; in 99% alcohol.

Time, secs.	240	360	600	1686	2490
Decompn., %	35·23	45·67	58·72	80·11	85·85
$k_2 \times 10^4$	345	355	360	363	372

50% Decompn. at 435 secs. Average $k_2 = 359 \times 10^{-4}$ sec.$^{-1}$.

0·029N-$NHMe_2$, 0·0148N-$C_6H_3Cl(NO_2)_2$; 25°; in 99% alcohol.

Time, secs.	555	1290	2160	4890
Decompn., %	36·5	56·2	69·0	84·1
$k_2 \times 10^4$	352	337	348	366

50% Decompn. at 975 secs. Average $k_2 = 351 \times 10^{-4}$ sec.$^{-1}$.
Ratio $t_{\frac{1}{2}}/t'_{\frac{1}{2}} = 2·24$; ratio of concentrations = 2·22.

0·0658N-$NHMe_2$, 0·0329N-$C_6H_3Cl(NO_2)_2$, in 99% alcohol.

At 30°.			At 35°.			At 40°.		
Time, secs.	Decompn., %.	$k_2 \times 10^4$.	Time, secs.	Decompn., %.	$k_2 \times 10^4$.	Time, secs.	Decompn., %.	$k_2 \times 10^4$.
180	35·09	45·6	90	22·06	57·5	90	31·66	78·2
240	42·20	46·2	105	28·46	57·6	162	45·16	77·3
306	48·54	46·9	225	46·41	58·4	210	50·24	78·7
390	54·44	46·6	270	52·38	62·0	240	55·31	78·4
570	63·74	46·9	300	54·69	61·2	303	60·78	77·8
774	70·08	46·1	480	65·26	59·6	420	68·38	78·3
	Average	46·4		Average	59·4		Average	78·1

Ethylamine.

0·0658N-NH_2Et, 0·0329N-$C_6H_3Cl(NO_2)_2$; 25°; in 99% alcohol.

Time, secs.	3825	9825	17,685	26,820	40,170	87,780
Decompn., %	19·16	37·69	50·93	62·42	69·9	83·72
$k_2 \times 10^4$	9·4	9·3	8·9	8·8	8·8	8·9

50% Decompn. at 12,620 secs. Average $k_2 = 9·1 \times 10^{-4}$ sec.$^{-1}$.

0·0296N-NH_2Et, 0·0148N-$C_6H_3Cl(NO_2)_2$; 25°; in 99% alcohol.

Time, secs.	6885	21,420	38,430	84,605	258,420
Decompn., %	16·0	36·5	50·6	69·7	87·6
$k_2 \times 10^4$	9·3	9·2	9·0	9·2	9·2

50% Decompn. at 36,600 secs. Average $k_2 = 9·2 \times 10^{-4}$ sec.$^{-1}$.
Ratio $t_{\frac{1}{2}}/t'_{\frac{1}{2}} = 2·20$; ratio of concentrations = 2·22.

0·0658N-NH_2Et, 0·0329N-$C_6H_3Cl(NO_2)_2$; 35°; in 99% alcohol.

Time, secs.	1850	4500	6770	10,440	14,100	17,700
Decompn., %	17·9	34·0	47·33	54·68	62·04	66·64
$k_2 \times 10^4$	17·2	17·4	17·6	17·6	17·6	16·7

Average $k_2 = 17·4 \times 10^{-4}$ sec.$^{-1}$.

tert.-Butylamine.

0·0296N-NH_2Bu^t, 0·0148N-$C_6H_3Cl(NO_2)_2$; 25°; in 99% alcohol.

Time, hours	172·3	312·2	552·7	1296·2	1802·1	2502·2
Decompn., %	8·27	16·4	19·2	32·8	38·9	49·1
$k_2 \times 10^4$	0·0049	[0·0059]	0·0040	0·0035	0·0033	0·0034

Average $k_2 = 0·0038 \times 10^{-4}$ sec.$^{-1}$.

Time, hours	165·8	378·1	594	1483·8	2130·4	4027
Decompn., %	8·27	16·43	21·4	36·9	44·0	59·4
$k_2 \times 10^4$	0·0051	0·0049	0·0043	0·0037	0·0035	0·0034

Average $k_2 = 0·0041 \times 10^{-4}$ sec.$^{-1}$.

Diisopropylamine.

0·0658N-$NHPr^i_2$, 0·0329N-$C_6H_3Cl(NO_2)_2$; 25°; in 99% alcohol.

Time, mins.	15,880	30,223	67,940	85,117	110,860	286,689
Decompn., %	6·86	11·46	17·00	19·76	23·89	43·19
$k_2 \times 10^4$	0·012	0·011	0·0078	0·0073	0·0072	0·0067

Lupetidine.

0·0658N-Lupetidine, 0·0329N-$C_6H_3Cl(NO_2)_2$; 25°; in 99% alcohol.

Time, mins.	15,774	34,537	70,629	92,240	136,808	156,852
Decompn., %	6·41	12·86	18·73	20·66	25·66	32·15
$k_2 \times 10^4$	0·011	0·011	0·0082	0·0072	0·0064	0·0063

In the case of amines which react less rapidly than ammonia, *e.g.*, *tert.*-butylamine, di*iso*propylamine, and lupetidine (cf. above), there is a fall in the rate constant, rapid at first but then much slower. Probably these amines contain small amounts of more reactive amines which are removed in the first period of the reaction. With these very slowly reacting amines very small quantities of impurities would have a large effect in the first stage.

The Pseudo-unimolecular Reaction.—The results obtained are summarised in Table IV.

Addition of Triethylamine.—With 0·0329N-chlorodinitrobenzene and N-triethylamine in alcohol at 25° less than 2% of chloride ion was liberated after 6180 secs., and less than 10% after 1,737,000 secs.

The results of addition of triethylamine in the first-order reaction are summarised in Table V.

TABLE III.

0·0658N-Amine, 0·0329N-$C_6H_3Cl(NO_2)_2$ in 99% alcohol.

	Temp. = 25°.		Temp. = 35°.		Average values.	
Amine.	Time, secs. $\times 10^{-1}$.	$k_2 \times 10^4$, sec.$^{-1}$, extremes.	Time, secs. $\times 10^{-1}$.	$k_2 \times 10^4$, sec.$^{-1}$, extremes.	$k_2^{25} \times 10^4$, sec.$^{-1}$.	$k_2^{35} \times 10^4$, sec.$^{-1}$.
n-Propylamine	396—7,418	9·4—9·8	—	—	9·6	—
n-Butylamine	160—3,543	9·8—10·1	540—1,746	18·8—19·5	10·0	19·2
n-Heptylamine	408—3,804	9·7—10·0	—	—	10·0	—
Diethylamine	1,575—17,340	1·9—1·9	780—9,426	3·7—4·0	1·9	3·8
Di-*n*-propylamine	1,620—43,638	1·5—1·7	—	—	1·6	—
Di-*n*-butylamine	1,746—28,182	1·8—1·9	1,326—10,974	3·9—4·1	1·8	4·0
Ethyl-*n*-propylamine	1,884—34,560	1·6—1·7	1,155—19,380	3·3—3·6	1·7	3·4
*iso*Butylamine	360—11,320	6·6—7·1	300—1,790	14·9—16·0	6·8	15·6
*iso*Propylamine	1,929—42,072	0·98—1·0	1,248—17,688	2·3—2·5	1·0	2·4
sec.-Butylamine	2,826—60,546	0·88—0·95	2,826—17,022	2·0—2·1	0·91	2·1
Di*iso*butylamine	630—61,020	0·56—0·60	8,940—26,710	1·3—1·4	0·58	1·3
Piperidine	42—219	153—158	22·5—136·5	264—275	153	269
α-Pipecoline	4,291 min.—44,673	0·21—0·25	—	—	0·22	—
Ammonia	4,090 min.—100,600	0·037—0·046	—	—	0·04	—
Ethyl*iso*propylamine	6,140 min.—105,066	0·014—0·0032 *				
,, ,,	4,266 min.—126,780	0·019—0·0031 *				
Tetrahydroquinoline	3,012 min.—109,657	0·068—0·006 *				
,, ,,	17,149 min.—161,517	0·021—0·0045 *				
Tetrahydroquinaldine	23,061 min.—119,654	0·004—0·002 *				

* In these cases there was a progressive fall of k_2 with time.

TABLE IV.

0·0329N-$C_6H_3Cl(NO_2)_2$; 25°; 99% alcohol.

Amine.	Concn., N.	Time, secs.	Extremes of $k_1 \times 10^4$.	Average $k_1 \times 10^4$.
Methylamine	0·424	99—960	15·4—16·5	16·1
	0·634	90—1,026	25·3—26·3	25·6
	0·833	120—605	35·0—35·9	35·6
	1·227	60—420	58·2—62·8	59·4
Ethylamine	0·583	126—4,260	6·13—6·95	6·35
	0·840	150—3,120	10·3—10·8	10·5
	1·350	245—1,170	20·1—21·1	20·5
n-Propylamine	0·553	345—3,000	5·96—6·45	6·15
	0·687	630—3,570	7·51—7·85	7·66
	0·790	720—2,790	9·07—9·35	9·26
n-Butylamine	0·573	615—3,270	7·08—7·24	7·12
	0·730	330—2,850	9·08—9·84	9·37
	0·753	375—1,890	9·62—9·92	9·75
n-Heptylamine	0·700	330—2,430	9·53—9·72	9·61
Dimethylamine	0·450	64—190	177—191	183 *
	0·500	57—180	206—218	214 *
	0·580	60—180	252—260	256 *
Diethylamine	0·491	1,935—18,300	0·99—1·05	1·03
	0·573	1,935—17,280	1·21—1·28	1·22
Di-*n*-propylamine	0·347	1,575—39,060	0·53—0·55	0·54
	0·566	1,440—21,300	1·02—1·04	1·03
Di-*n*-butylamine	0·400	4,500—18,630	0·76—0·82	0·78
	0·483	2,835—24,672	0·92—0·98	0·96
	0·560	2,646—20,820	1·11—1·18	1·13
Ethyl-*n*-propylamine	0·373	2,340—15,750	0·67—0·71	0·69
	0·453	3,600—28,980	0·80—0·89	0·85
	0·555	3,006—20,160	1·02—1·09	1·07
*iso*Butylamine	0·640	303—1,815	5·45—5·93	5·75
	0·813	270—1,170	7·85—8·25	8·04
	1·000	1,860—4,260	10·4—11·1	10·7
*iso*Propylamine	0·647	1,515—19,110	0·86—0·93	0·88
	0·947	3,426—15,666	1·36—1·45	1·40
sec.-Butylamine	0·400	5,220—40,950	0·42—0·45	0·44
	0·600	9,000—25,200	0·50—0·52	0·52
Di*iso*butylamine	0·520	3,300—37,890	0·33—0·35	0·34
	0·650	2,703—34,260	0·44—0·46	0·45
	0·0148N-$C_6H_3(NO_2)_2Cl$; 25°.			
Methylamine	0·634	180—1,020	25·0—26·4	25·6
	0·833	126—636	36·5—38·0	37·5
	1·227	60—360	62·0—79·5	69·3

* Approximate, as the reaction is too fast at 25° for satisfactory measurements.

TABLE V.

0·0329N-$C_6H_3Cl(NO_2)_2$; 25°; in 99% alcohol.

Amine.	Concn. of amine, N.	Concn. of NEt_3.	Time, secs.	Extremes of $k_1 \times 10^4$.	Average $k_1 \times 10^4$.
Methylamine	0·64	0·28	90—600	28·2—29·6	29·1
	,,	0·329	90—450	30·8—31·8	31·4
	,,	0·873	150—480	36·3—40·5	38·4
	,,	1·12	66—420	38·3—43·2	42·2
	,,	1·33	75—465	44·0—46·0	44·9
	,,	2·00	66—450	56·3—59·3	58·0
Ethylamine	0·84	0·607	165—1,800	13·7—13·9	13·9
n-Propylamine	0·687	0·633	180—2,895	10·1—10·8	10·4
n-Butylamine	0·730	0·633	360—2,580	10·7—10·8	10·8
Dimethylamine	0·500	0·660	65—180	256—275	268 *
Diethylamine	0·573	0·807	930—16,020	1·64—1·85	1·72
Di-*n*-propylamine	0·347	0·677	3,075—39,060	0·66—0·69	0·68
Di-*n*-butylamine	0·483	0·660	5,820—20,820	1·13—1·16	1·15
*iso*Butylamine	0·813	0·687	420—840	9·55—10·8	10·0
*iso*Propylamine	0·947	0·647	2,580—9,210	1·85—1·96	1·91
sec.-Butylamine	0·400	0·440	8,460—30,810	0·51—0·53	0·52
Ammonia	1·093	0·647	21,546—211,620	0·082—0·099	0·088

* Approximate.

A number of derivatives of dinitroaniline have been prepared in the course of the work. The residual solutions obtained from the interaction of *tert.*-butylamine and 1-chloro-2 : 4-dinitrobenzene were mixed, heated in the water-bath, cooled, and diluted with water. The precipitate on crystallisation from dilute alcohol gave yellow crystals of N-tert.-*butyl*-2 : 4-*dinitroaniline*, m. p. 119° (Found : C, 50·0; H, 5·5. $C_{10}H_{13}O_4N_3$ requires C, 50·2; H, 5·5%). Chlorodinitrobenzene (5 g.) and di*iso*propylamine (5 g.) were heated in a sealed tube at 100° for 30 days. The black mass was extracted with boiling alcohol, and the solid which separated on cooling after being twice crystallised from alcohol gave N-*diiso*propyl-2 : 4-*dinitroaniline* as golden-yellow needles, m. p. 127° (Found : C, 53·9; H, 6·2. $C_{12}H_{17}O_4N_3$ requires C, 53·9; H, 6·4%). Mulder (*Rec. Trav. chim.*, 1906, **25**, 109, 113) failed to obtain this compound by this method. Alcoholic solution of α-pipecoline (100 c.c. of N/3) and chlorodinitrobenzene (75 c.c. of N/10) were mixed and kept for 14 days. The solution was evaporated to small bulk and the solid which separated on crystallisation from alcohol gave orange-red crystals of N-α-*pipecolyl*-2 : 4-*dinitroaniline*, m. p. 67° (Found: C, 54·3; H, 5·6. $C_{12}H_{15}O_4N_3$ requires C, 54·1; H, 5·7%); Lellman (*loc. cit.*) described an impure specimen as an oil. Alcoholic solutions of tetrahydroquinoline (60 c.c. of N.) and chlorodinitrobenzene (250 c.c. of N/10) were heated to 100° and kept for two days, evaporated to small bulk, and the solid which separated crystallised from alcohol–benzene; N-*tetrahydroquinolyl*-2 : 4-*dinitroaniline* was obtained as yellow crystals, m. p. 155·5°, which became red on exposure to light (Found : C, 60·6; H, 4·4. $C_{15}H_{13}O_4N_3$ requires C, 60·2; H, 4·4%).

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