

670. Nitrosation, Diazotisation, and Deamination. Part VIII.¹
The Diazotisation of Weakly Basic Amines in Dilute Perchloric Acid.

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Diazotisation of *p*-nitroaniline, *o*-nitroaniline, and 2,4-dinitroaniline in dilute perchloric acid is of the first order in amine and in nitrous acid. The reactions are acid-catalysed, but can be studied kinetically with very low reactant concentrations in <0.5M-acid.

The relative reactivities of amines towards the nitrous acidium ion and dinitrogen trioxide are briefly discussed; and the kinetic results are considered in relation to preparative methods for diazotisation.

ANILINE, and amines of similar basicity, are diazotised by dinitrogen trioxide in dilute perchloric acid.^{1,2} The reactivities of amines towards dinitrogen trioxide decrease as their basicities are reduced; ¹ and, especially with the less basic amines, there is evidence of an acid-catalysed component of the reaction. By choosing suitable reactant concentrations in the diazotisation of *o*-chloroaniline it was possible to show that the acid-catalysed reaction obeyed rate equation (1),³ and arose from nitrosation by the nitrous acidium ion.⁴

$$\text{Rate} = k_3' [\text{Ar}\cdot\text{NH}_2][\text{HNO}_2][\text{H}^+] \quad \dots \quad (1)$$

The work described in this paper has been carried out to obtain further evidence of the importance of this mechanism, with particular reference to the variation of the reaction rate with the basicities, and hence reactivities, of aromatic amines.

The Diazotisation of p-Nitroaniline.—The overall reaction orders (in the perchloric acid concentrations listed in Table 1) have been determined by the half-life method.

TABLE 1. *Diazotisation of p-nitroaniline at 0°: overall reaction orders in various concentrations of perchloric acid in excess.*

[H ⁺]	0.00482	0.00964	0.0193	0.0606	0.0998	0.502
Reaction order	1.9	1.9	2.0	2.0	1.9	1.9

Different nitrosation carriers give rise to different rate equations,⁵ and the possible second-order rate equations are:

$$\text{Rate} = k_2''[\text{HNO}_2]^2 \quad \dots \quad (2)$$

and

$$\text{Rate} = k_2'[\text{Ar}\cdot\text{NH}_2][\text{HNO}_2] \quad \dots \quad (3)$$

Equation (1) reduces to equation (3) when runs are carried out in an excess of perchloric acid. Variation of the initial rate of reaction with reactant concentration has shown that equation (3) is obeyed throughout the range of acidity studied. This has been confirmed by the behaviour of the rate constants calculated from the alternative equations (2) and (3) for runs in which unequal concentrations of reactants were used. Two examples are given in the Experimental section (Table 4). In addition, runs carried out in an excess of amine were of the first order in nitrous acid.

From equations (1) and (3), equation (4) may be derived:

$$k_2' = k_3'[\text{H}^+] \quad \dots \quad (4)$$

Therefore, if equation (1) is the complete rate equation for the diazotisation of *p*-nitroaniline, k_2' should be proportional to [H⁺]. The Figure shows that this is true. The

¹ Part VII, preceding paper.

² Part II, Hughes, Ingold, and Ridd, *J.*, 1958, 65.

³ Part IV, *idem*, *J.*, 1958, 77.

⁴ Part VI, *idem*, *J.*, 1958, 88.

⁵ Part I, Hughes, Ingold, and Ridd, *J.*, 1958, 58.

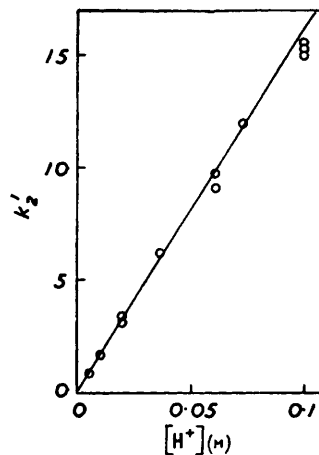
value of k_3' calculated from the slope of the straight line is $161 \text{ sec.}^{-1} \text{ mole}^{-2} \text{ l.}^2$. Therefore, throughout the acidity range $0.005\text{--}0.5\text{M}$, *p*-nitroaniline is diazotised according to equation (1).

The Diazotisation of o-Nitroaniline.—This amine has been found to diazotise readily in 0.01M -perchloric acid, in which the overall reaction order was 2, and the molecular third-order rate constant was $145 \text{ sec.}^{-1} \text{ mole}^{-2} \text{ l.}^2$. At pH 5 the order in amine was approximately unity, although the reaction was too slow to give accurate results. Larger concentrations of amine could not be used to increase the rate because the amine was insufficiently soluble. The kinetics of diazotisation seemed similar to those of *p*-nitroaniline, and so a more weakly basic amine was studied.

The Diazotisation of 2,4-Dinitroaniline.—Very dilute solutions of this amine could be obtained by prolonged boiling with water, but crystallisation soon occurred: standard solutions could be made up satisfactorily only if the amine was dissolved in 60% perchloric acid and the solution diluted with water until the excess of acid was about 6M . To obtain reasonable rates of reaction without using high concentrations of amine, runs have been carried out in a ten- or twenty-fold excess of nitrous acid. Under these conditions the reaction was found to be of the first order with respect to the amine. Values for the first-order stoichiometric rate constant are given in Table 2. In runs 16 and 19 the excess of nitrous acid was doubled. This increased the first-order rate constant by a factor of 1.9. Thus, the order in nitrous acid is one, and the rate follows equation (3) under these conditions.

Values for the stoichiometric second-order rate constants in several concentrations of acid are also given in Table 2. In all these acid concentrations the nitrous acid and the amine

($\text{p}K_a = -4.5$; ref. 6) can be considered to be present entirely as their non-ionic forms; the stoichiometric and molecular rate constants are therefore identical. The third-order



Diazotisation of *p*-nitroaniline at 0° : plot of molecular second-order rate constants versus concentration of hydrogen ions. The value of the rate constant in 0.5M -acid ($81.3 \text{ sec.}^{-1} \text{ mole}^{-1} \text{ l.}$) also lies on the line.

TABLE 2. Diazotisation of 2,4-dinitroaniline at 0° : rate constants in several concentrations of perchloric acid.

Run	[Amine]	[HNO ₂]	[H ⁺]	k_1' (sec. ⁻¹)	k_2' (sec. ⁻¹ mole ⁻¹ l.)	k_3' (sec. ⁻¹ mole ⁻² l. ²)
16	0.000221	0.00469	0.581	0.00153	0.325	5.60
17	0.000221	0.00469	0.313	0.000617	0.132	4.22
18	0.000111	0.00469	0.159	0.000277	0.059	3.71
19	0.000222	0.00235	0.581	0.000818	0.348	5.99

rate constants do not remain constant, but increase with the hydrogen-ion concentration. The reason for this is not yet clear. The complete rate equation is:

$$\text{Rate} = k_3'[\text{Ar}\cdot\text{NH}_2][\text{HNO}_2][\text{H}^+]^x$$

where x is slightly greater than unity.

DISCUSSION

Mechanism of Reaction.—In Table 3 are collected the third-order molecular rate constants for the amines which have been shown to be diazotised according to a rate of first order in nitrous acid and in amine. Kinetics of this form would be given by both the nitrous acidium ion and the nitrosonium ion when attack of the nitrosation carrier on the free amine is rate-controlling.⁵ The nitrosonium ion can be distinguished from the nitrous

acidium ion by the kinetic method described here if its formation can be made rate-controlling: the rate equation would then become independent of the amine and should be equation (2) or of the form:

$$\text{Rate} = k_2'[\text{HNO}_2][\text{H}^+]$$

according to whether the nitrosonium ion is produced by ionisation of dinitrogen trioxide or by dehydration of the nitrous acidium ion. For the formation of the nitrosonium ion to become rate-controlling it must be removed by the amine as soon as it is formed.

TABLE 3. *Third-order molecular rate constants for the diazotisation of weakly basic amines in dilute perchloric acid.*

Amine	$\text{p}K_a$	k_3' ($\text{sec.}^{-1} \text{ mole}^{-2} \text{ l.}^2$)	$[\text{H}^+]$ (M)
<i>o</i> -Chloroaniline	2.77	175 ^a	0.005—0.02
<i>p</i> -Nitroaniline	0.99 ^b	161	0.005—0.5
<i>o</i> -Nitroaniline	—0.29 ^b	145	0.01
2,4-Dinitroaniline	—4.5 ^b	3.7	0.159

To do this the amine must be reactive and present in large quantities as the free base. At the lowest acidities used, the three nitroanilines were almost entirely present in solution as the free bases. In spite of this the reaction remained fully amine-dependent; and it was therefore impossible to distinguish kinetically between the nitrous acidium and the nitrosonium ion mechanism. From investigations of the catalytic effect of bromide ions on the diazotisation of *o*-chloroaniline, and of the rate of oxygen exchange between nitrous acid and water, it has been deduced that the nitrous acidium ion is responsible for the diazotisation of *o*-chloroaniline; ⁴ presumably then this is true of the other amines in Table 3. Diazotisation by the nitrosonium ion should become more important as the acidity is increased and the basicity of the amine is reduced; nevertheless, the very slow reaction rate of 2,4-dinitroaniline does not suggest the incursion of a new mechanism of diazotisation.

Reactivities of Amines towards Dinitrogen Trioxide and the Nitrous Acidium Ion.—A notable feature of the results in Table 3 is the small reduction with diminishing basicity of the molecular third-order rate constants for the first three amines. This suggests that the nitrous acidium ion shows little discrimination in its reaction with the more basic amines; it is in marked contrast with the results obtained with dinitrogen trioxide, when, over a comparable decrease in $\text{p}K_a$ values, the molecular third-order rate constants were reduced by a factor of 50 (Table 4 of the preceding paper). A full discussion of the relative reactivities of amines towards different nitrosation carriers is deferred until studies being carried out on diazotisation by the nitrosonium ion are complete, but the results clearly imply that a decrease in basicity decreases the reactivities of amines towards dinitrogen trioxide far more than towards the nitrous acidium ion.

Correlation of Kinetic Results with Preparative Methods.—The practical value of a nitrosation carrier depends, not only on its reactivity towards a particular amine, but also on the equilibria governing its concentration. For any amine there is a critical nitrous acid concentration, different for each amine and lower for the more reactive amines, above which diazotisation by dinitrogen trioxide will supersede diazotisation by the nitrous acidium ion. This can be illustrated by reference to *p*-nitroaniline.

This amine is too unreactive to allow direct determination of the third-order molecular rate constant for its reaction with dinitrogen trioxide. However, its σ constant is 1.27,⁷ and extrapolation of the results in Table 4 of the preceding paper gives a value of $2.5 \times 10^3 \text{ sec.}^{-1} \text{ mole}^{-2} \text{ l.}^2$ for this rate constant. The molecular third-order rate constant k_3' for its

⁶ Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

⁷ Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, 1940, Chap. VII.

diazotisation by the nitrous acidium ion mechanism is $161 \text{ sec.}^{-1} \text{ mole}^{-2} \text{ l.}^2$. The contributions to diazotisation by dinitrogen trioxide and the nitrous acidium ion, in 0.01M-perchloric acid with 0.0001M-reactants, can be calculated by substitution in the appropriate terms of equation (5). They are found to be $0.000025[\text{Ar}\cdot\text{NH}_2]$ and $0.00016[\text{Ar}\cdot\text{NH}_2]$ mole sec.^{-1} respectively. The contribution by the nitrous acidium ion is more than six times

$$\begin{aligned} \text{Rate} &= k_3''[\text{Ar}\cdot\text{NH}_2][\text{HNO}_2]^2 + k_3'[\text{Ar}\cdot\text{NH}_2][\text{HNO}_2][\text{H}^+] \quad \dots (5) \\ &= [\text{Ar}\cdot\text{NH}_2]\{k_3''[\text{HNO}_2]^2 + k_3'[\text{HNO}_2][\text{H}^+]\} \end{aligned}$$

that by dinitrogen trioxide. It can readily be calculated that in concentrations of nitrous acid sufficient to exceed the critical concentration referred to in the previous paragraph, *e.g.*, 0.01M, the dinitrogen trioxide mechanism predominates because of its dependence on the square of the nitrous acid concentration, but in more concentrated perchloric acid, *e.g.*, 0.5M, still with 0.01M-nitrous acid, the nitrous acidium ion mechanism is again more important. The rate of diazotisation by dinitrogen trioxide is decreased in proportion to the fall in the free amine concentration in the more concentrated acid, but in diazotisation by the nitrous acidium ion, the fall in the free amine concentration is more than counter-balanced by the increased standing concentration of the nitrous acidium ion. It is evident that the most efficient way to diazotise *p*-nitroaniline is to use fairly concentrated acid and a high nitrous acid concentration, as is suggested in preparative methods.^{8a}

With the more basic amines, *e.g.*, aniline, the free amine concentration is so low that to obtain a reasonable rate of reaction the nitrous acid concentration has to be increased far beyond the critical value. As a result the specifically less reactive dinitrogen trioxide is the most important nitrosation carrier for the diazotisation of the more basic amines in dilute perchloric acid.

Many methods are used in the preparation of diazonium compounds, but, in general, strongly basic amines are diazotised in a slight excess of mineral acid, and weakly basic amines in concentrated acid.^{8a} The need for concentrated acid has led to the belief that the amine cation is the reactant:^{8b} yet the small quantities of these nitroanilines which dissolve can be diazotised in dilute perchloric acid. The function of the strong acid in large-scale preparative methods is to provide high concentrations of nitrosation carriers more electrophilic than dinitrogen trioxide, and to dissolve reasonable quantities of the amine.

EXPERIMENTAL

The kinetic method was identical with that reported in Part VII and the previous papers. Some examples of the kinetic results are given in Tables 4 and 5.

TABLE 4. Diazotisation of *p*-nitroaniline at 0°: stoichiometric second-order rate constants ($\text{sec.}^{-1} \text{ mole}^{-1} \text{ l.}$) calculated according to alternative rate equations (2) and (3).

Run 10				Run 42			
Stoichiometric initial concentrations:				Stoichiometric initial concentrations:			
[Ar·NH ₃ ⁺] = 0.0000972M, [HNO ₂] = 0.0000324M, [H ⁺] = 0.1M.				[Ar·NH ₃ ⁺] = 0.0000315M, [HNO ₂] = 0.0000630M, [H ⁺] = 0.502M.			
<i>t</i> (min.)	Reaction (%)	\bar{k}_2'' (eqn. 2)	\bar{k}_2' (eqn. 3)	<i>t</i> (min.)	Reaction (%)	\bar{k}_2'' (eqn. 2)	\bar{k}_2' (eqn. 3)
0	14.7	—	—	0	17.5	—	—
2.67	23.5	26.0	7.50	1.40	22.9	62.7	14.3
7.09	38.6	33.8	8.77	3.33	29.3	60.2	14.0
15.1	52.9	32.3	7.67	5.08	34.1	51.3	13.5
22.5	62.8	34.7	7.45	7.33	40.6	57.2	13.9
31.4	72.6	40.5	7.45	10.1	46.2	53.0	13.5
40.8	81.3	52.8	7.93	17.3	58.7	48.5	13.4
52.1	85.1	54.8	7.25	22.6	64.3	44.5	12.7
72.7	92.3	83.3	7.40				

⁸ Saunders, "The Aromatic Diazo-compounds," Edward Arnold and Co., London, 1949, (a) Chap. I, (b) p. 45.

TABLE 5. *Diazotisation of 2,4-dinitroaniline at 0°: examples of first-order rate constants during runs carried out in an excess of nitrous acid.*

Run 16			Run 19		
[Ar·NH ₂] = 0.000221M, [HNO ₂] = 0.00469M, [H ⁺] = 0.581M.			[Ar·NH ₂] = 0.000222M, [HNO ₂] = 0.00235M, [H ⁺] = 0.581M.		
<i>t</i> (min.)	Reaction (%)	<i>k</i> ₁ ' (sec. ⁻¹)	<i>t</i> (min.)	Reaction (%)	<i>k</i> ₁ ' (sec. ⁻¹)
0	25.8	—	0	13.0	—
1.55	35.8	0.00162	1.42	19.0	0.000827
2.80	44.3	0.00171	3.42	27.1	0.000852
5.05	54.0	0.00158	5.74	35.8	0.000880
7.55	62.3	0.00150	11.9	55.0	0.000760
9.65	69.0	0.00151	17.5	66.1	0.000782
12.1	74.5	0.00148	26.2	78.3	0.000805
22.1	86.6	0.00130			
Mean value of <i>k</i> ₁ ' = 0.00153 sec. ⁻¹ .			Mean value of <i>k</i> ₁ ' = 0.000818 sec. ⁻¹ .		

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