14. *Nitrosation, Diazotisation, and Deamination. Part II.* Second- and Third-order Diazotisation of Aniline in Dilute Perchloric Acid.*

By E. D. Hughes, C. K. Ingold, and J. H. Ridd.

The overall kinetic order of the diazotisation of aniline in dilute perchloric acid falls, as the excess of acid is reduced, from 3 to near 2, and finally rises to about 2·6 as the last of the excess of acid is removed. The rise is due to easily understood but uninteresting causes, whereas the fall is mechanistically significant. It is due to a fall of order in aniline from 1 to 0, the kinetic order in nitrous acid being always 2. These kinetics account for nearly all the reaction, though signs of a small acid-catalysed component can be seen.

As noted in Part I * (section 2), the diazotisation of aniline and other aromatic amines has been found to be kinetically of second order by some previous investigators and of third order by others. No one had brought these observations together, treating the two sets with equal seriousness, as presenting a problem in reconciliation. Our first objective, on taking up the subject in 1949, was to try to verify the suggested kinetic duplexity, and, if it were confirmed, to trace the variations in experimental conditions which produce the change of kinetic form. In these experiments, aniline was employed as the amine, and the temperature was 0·0° throughout. A comparison of the conditions applying to to the previously recorded observations had suggested that the difference of kinetic result might be connected with the acidity; and we soon found that this was correct. The acid employed in common by the previous investigators had been hydrochloric acid, but, for reasons which will be clear from the preliminary theoretical considerations in Part I (section 1), we preferred, at this stage of our work, to use perchloric acid.

(1) *Two Kinetic Orders and the Transition between Them.*—An overall kinetic order, even when non-integral, can be determined by the variation in the time of half-reaction with dilution of an initial reaction mixture. The relation is

$$\log t_{\frac{1}{2}} = C - (n - 1) \log a$$

where n is the overall kinetic order, a is the initial concentration of each reactant, $t_{\frac{1}{2}}$ is the half-life of the reactants, and C is a constant. This equation has been used to determine the overall reaction order for the diazotisation of aniline in various concentrations of excess of perchloric acid. By the excess of acid is meant the excess over what is required to convert the aniline into anilinium perchlorate and to liberate nitrous acid from the supplied sodium nitrite. For each excess of acid, runs were done at various dilutions of a reaction mixture containing stoicheiometrically equivalent concentrations of aniline and nitrous acid. The results are in Table 1, and a logarithmic plot of them is shown in Fig. 1. The slopes of the graphs are values of $(1 - n)$. The resulting values of the reaction order n are plotted against the concentration of excess of acid in Fig. 2.

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* Part I, preceding paper.

It appears that the overall reaction order falls from almost 3 to near 2, as the acidity is reduced from 0·050 to 0·002M; but that the order rises again to about 2·6, when the excess of acid is removed altogether. These conclusions are confirmed by examination of the behaviour of integrated, stoicheiometric, second- and third-order rate-constants, $\bar{k}_2$ and $\bar{k}_3$, calculated at successive stages of individual runs. Three contrasting illustrations are given in Table 2. Of course, this is an insensitive method of determining kinetic order, but it serves as a simple check of the large differences here under consideration. With no excess of acid, $\bar{k}_2$ falls and $\bar{k}_3$ rises in the course of the run. With 0·002M-acid, $\bar{k}_2$ remains constant, whilst $\bar{k}_3$ rises strongly. With 0·050M-acid, $\bar{k}_2$ falls strongly, whilst $\bar{k}_3$ remains steady.

FIG. 1. *Diazotisation of aniline: logarithmic plot of reactant half-life* versus *reactant concentration, at various concentrations of excess of perchloric acid. (The figures are the millimolarities of the excess of acid in the several sets of experiments.)*

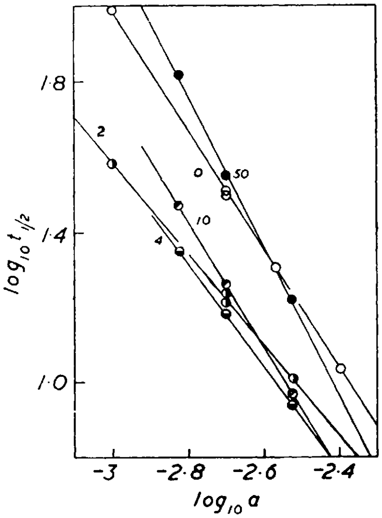
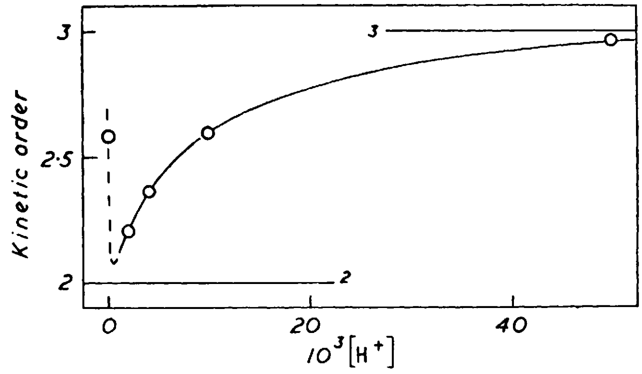


FIG. 2. *Diazotisation of aniline: overall kinetic order as a function of the excess of perchloric acid concentration.*



We interpret these results as follows. At all acidities from 0·050M down to 0·002M, the concentrations of hydrogen ion can be taken as approximately constant throughout any one run. Hence the concentration of either reactant in its uncharged molecular form will be a constant fraction of the stoicheiometric concentration of the reactant throughout any one run. It follows that the stoicheiometric second- or third-order rate-constants calculated

TABLE 1. *Diazotisation of aniline in dilute perchloric acid at 0°. Reactant half-life (min.) as a function of initial reactant concentration.*

Run	Free $[H^+]$	Stoicheiometric $[Ar{\cdot}NH_3^+] = [HNO_2]$	Half-life	Run	Free $[H^+]$	Stoicheiometric $[Ar{\cdot}NH_3^+] = [HNO_2]$	Half-life
47	0·000	0·0010	97·5	25	0·004	0·0015	22·2
21	,,	0·0020	31·5	26	,,	0·0020	15·2
45	,,	0·0020	32·5	27	,,	0·0030	8·6
20	,,	0·0027	20·0	28	0·010	0·0015	29·3
19	,,	0·0040	10·8	29	,,	0·0020	18·0
49	0·002	0·0010	38·3	30	,,	0·0030	9·4
44	,,	0·0020	16·1	182	0·050	0·0015	65·0
23	,,	0·0020	17·1	180	,,	0·0020	35·5
48	,,	0·0030	10·1	181	,,	0·0030	16·6

for any run are proportional to the corresponding molecular rate constants (cf. Part I, section 3c): constancy or drift in the molecular rate-constants will be reproduced faithfully in the stoicheiometric constants. It follows also that the reaction orders, computed as they have been from the manner of diminution of the stoicheiometric concentrations of the reactants, are the same as if they had been computed from the rates of disappearance of the reactants in their uncharged molecular forms. We conclude that the fall of reaction order, which can be traced over the greater part of Fig. 2, from approximately 3 at 0·050M-acid to near 2 at 0·002M-acid, owes nothing to the acid–base equilibria to which the reactants are subject. It must therefore be of primary significance for the mechanism of diazotisation.

On the other hand, when the excess of perchloric acid is removed completely, the concentration of hydrogen ions does not remain constant in a run: two weak acids, the anilinium ion and nitrous acid, are being replaced by a neutral diazonium ion and water; and hence the pH will rise. Of the two weak acids, nitrous acid is the stronger, and hence will be neutralised first. And thus the first effect of the rising pH will be to replace nitrous acid by nitrite ion in increasing proportions. The concurrent replacement of anilinium ion by molecular aniline has no comparable, countervailing, kinetic effect for a reason which will appear below. Hence the shift in the acid–base equilibria as reaction progresses will lead to a growing retardation, and this will show itself as an enhancement of kinetic order. It is possible thus to account for the rise of overall order to about 2·6 as the last of the excess of strong acid is removed. Therefore this change, shown on the extreme left of Fig. 2, has no primary significance for the mechanism of diazotisation.

TABLE 2. *Diazotisation of aniline in aqueous perchloric acid at 0°. Variations of integrated stoicheiometric, second- and third-order rate-constants during the progress of runs at different acidities.*

Run 47 [Reactants] = 0·001M. [Acid] = nil.				Run 49 [Reactants] = 0·001M. [Acid] = 0·002M.			
t (min.)	Reaction (%)	$\bar{k}_2$ (sec.$^{-1}$ mole^{-1} l.)	$\bar{k}_3$ (sec.$^{-1}$ mole^{-2} l.^{2})	t (min.)	Reaction (%)	$\bar{k}_2$ (sec.$^{-1}$ mole^{-1} l.)	$\bar{k}_3$ (sec.$^{-1}$ mole^{-2} l.^{2})
0	7·0	—	—	0	13·0	—	—
15	20·0	0·195	222	5	21·5	0·417	503
25	26·5	0·190	230	10	29·5	0·448	583
35	32·0	0·188	238	15	35·3	0·440	593
45	37·5	0·195	260	20	40·0	0·430	608
55	40·0	0·178	245	25	44·5	0·435	640
75	46·0	0·172	252	35	51·0	0·423	677
95	50·3	0·163	253	45	55·0	0·397	672
115	54·0	0·157	258	55	60·0	0·410	745
				65	63·5	0·408	793

Run 181
[Reactants] = 0·003M. [Acid] = 0·050M.

t (min.)	Reaction (%)	$\bar{k}_2$ (sec.$^{-1}$ mole^{-1} l.)	$\bar{k}_3$ (sec.$^{-1}$ mole^{-2} l.^{2})
0	21·0	—	—
3	31·7	0·367	167
6	39·1	0·348	167
9	43·8	0·315	158
12	47·9	0·303	162
17	53·3	0·287	153
22	57·4	0·272	163
27	60·4	0·258	163
32	63·2	0·255	168
37	65·1	0·242	168
42	66·9	0·230	163

(2) *Detailed Kinetics of the Second-order Reaction.*—Concerning the distribution of kinetic order between the reactants, the third-order reaction has already been examined by Schmid (cf. Part I, section 2), who found its kinetic form to be identical with that previously established by Taylor for the reaction of nitrous acid with other types of amine. With

our convention (Part I, section 1c) of attaching a literal rather than an analytical meaning to bracketed symbols, this equation takes form (1):

$$\text{Rate} = k_3''[\mathrm{Ar{\cdot}NH_2}][\mathrm{HNO_2}]^2 \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

As to the second-order reaction, Hantzsch and Schumann originally assigned a unit of kinetic order to each reactant, but without experimental proof, and presumably because they could imagine no alternative (cf. Part I, section 2). This assignment, represented in our terminology by equation (2), had been neither proved, nor specifically questioned, since then:

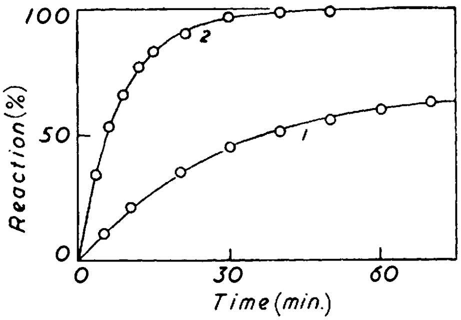


FIG. 3. *Effect of nitrous acid concentration on the rate of second-order diazotisation in aqueous perchloric acid at 0°.*

Stoicheiometric concentrations:

1, *Initially,*
$[\mathrm{Ar{\cdot}NH_3^+}] = 0{\cdot}001$, $[\mathrm{HNO_2}] = 0{\cdot}001$, $[\mathrm{H^+}] = 0{\cdot}002\text{M}$.

2, *Initially,*
$[\mathrm{Ar{\cdot}NH_3^+}] = 0{\cdot}001$, $[\mathrm{HNO_2}] = 0{\cdot}002$, $[\mathrm{H^+}] = 0{\cdot}002\text{M}$.

$$\text{Rate} = k_2'[\mathrm{Ar{\cdot}NH_2}][\mathrm{HNO_2}] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

Therefore we next took up experimentally the matter of the distribution of order in this reaction.

A series of experiments with the same initial stoicheiometric concentration of nitrous acid, 0·001M, and the same excess of perchloric acid, 0·002M, but with initial concentrations of anilinium perchlorate varying over a 10-fold range, gave reaction rates which were, to within 20%, the same, as shown in Table 3. Obviously, the kinetic order in aniline was zero substantially, and therefore the order in nitrous acid had to be two. We concluded that the correct equation for the second-order reaction was (3):

$$\text{Rate} = k_2''[\mathrm{HNO_2}]^2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

This was confirmed by duplicating two of the runs (nos. 49 and 50), but with a doubled initial concentration of nitrous acid: the runs then went four times as fast, as illustrated for one case in Fig. 3.

TABLE 3. *Effect of aniline concentration on rate of second-order diazotisation in aqueous perchloric acid at 0°.*

	Run:	49	50	56	55
Stoich. initial concns.	$[\mathrm{Ar{\cdot}NH_3^+}]$	0·001	0·002	0·005	0·010
	$[\mathrm{HNO_2}]$	0·001	0·001	0·001	0·001
	$[\mathrm{H^+}]$	0·002	0·002	0·002	0·002
Time (min.)		Percentage reaction			
10		21·5	24·0	25·3	26·0
20		35·3	38·4	41·0	41·0
30		44·5	48·3	50·7	51·0
40		51·0	55·4	57·5	58·0
50		55·0	61·0	63·0	63·7
60		60·0	65·0	67·2	68·0
70		63·5	69·0	70·8	71·0

Final confirmation of the need to change the older view of the second-order reaction was obtained by calculating integrated, stoicheiometric, second-order rate-constants, $\bar{k}_2'$ and $\bar{k}_2''$, corresponding to equations (2) and (3), respectively. The behaviour of these constants in the course of a run, one of such a kind that the choice of equation is critical, inasmuch as the reactants are out of stoicheiometric equivalence, is illustrated in Table **4**: obviously, equation (2) is invalid, whilst equation (3) is valid.

(3) *The Absence of Hydrogen-ion Catalysis.*—Equation (3) is a correct expression of the second-order reaction, but it remains to be proved that it is complete. What has not yet been discussed is the dependence of the second-order rate-constant on acid, a question not raised by an examination of the kinetics of any one run, or by comparisons of rates among different runs at the same acidity. Obviously the degree of acidity must affect the rate by its control of acid–base equilibria (Part I, section 3c) in which the reactants are involved in particular, nitrous acid, the kinetically significant reactant for the second-order reaction. But the point to be determined is whether, when this has been allowed for, a dependence on acid remains, which should be expressed by some definite kinetic order in hydrogen ions.

TABLE 4. *Stoicheiometric rate-constants* (*sec.*$^{-1}$ *mole*$^{-1}$ *l.*), *calculated according to alternative second-order equations, for the diazotisation of aniline in aqueous perchloric acid at* 0°.

Run 50.—Stoicheiometric initial concentrations: $[Ar\cdot NH_3^+] = 0{\cdot}002$, $[HNO_2] = 0{\cdot}001$, $[H^+] = 0{\cdot}002$M.

t (min.)	Reaction (%)	$\bar{k}_2'$ (eqn. 2)	$\bar{k}_2''$ (eqn. 3)	t (min.)	Reaction (%)	$\bar{k}_2'$ (eqn. 2)	$\bar{k}_2''$ (eqn. 3)
0	24·0	—	—	40	61·0	0·180	0·517
10	38·4	0·208	0·513	50	65·0	0·170	0·513
20	48·3	0·198	0·513	60	69·0	0·167	0·512
30	55·4	0·195	0·512	70	71·5	0·158	0·522

Experiments have therefore been carried out to determine the dependence of the second-order rate-constants on acid concentration, and the results are in Table 5. The stoicheiometric rate-constants $\bar{k}_2''$ show an appreciable positive dependence on acidity, though it is very much less than would correspond to a unit of kinetic order in hydrogen ions. When we calculate the more significant molecular rate-constants k_2'', the greater part of the dependence on acid drops away, leaving only 15% of change for a 10-fold change in acidity. It is therefore clear that equation (3) is complete as it stands, and that it represents a process which is not catalysed by hydrogen ions.

TABLE 5. *Acid-dependence of the second-order* (*equation* 3) *stoicheiometric* ($\bar{k}_2''$) *and molecular* (k_2'') *rate-constants* (*sec.*$^{-1}$ *mole*$^{-1}$ *l.*) *for the diazotisation of aniline in aqueous perchloric acid at* 0°.

Initially added, $[Ph\cdot NH_3^+ClO_4^-] = 0{\cdot}01$, and $[HNO_2] = 0{\cdot}001$M, throughout. (Molecular rate-constants are calculated by assuming the acidity constant of nitrous acid to be $4{\cdot}5 \times 10^{-4}$ mole l.$^{-1}$. The above stoicheiometric concentration of aniline is sufficient to secure second-order kinetics at all the following acidities.)

Run	55	183	184	185
$[H^+]$	0·002	0·009	0·014	0·019
$\bar{k}_2''$	0·583	0·837	0·923	0·938
k_2''	0·867	0·925	0·983	0·983

The cause of the small increase in the molecular rate-constant with increasing acidity cannot be settled unambiguously on the basis of the data in this paper. The drift as calculated depends on the value taken for the acidity constant of nitrous acid, and also on the changes in activity coefficients with ionic strength. However, we may be seeing signs here of a small acid-catalysed component of the observed reaction. For this reason, the true value of the second-order rate-constant k_2'' is a little uncertain, but, given that the acidity constant of nitrous acid may be taken as $4{\cdot}5 \times 10^{-4}$ mole l.$^{-1}$, the data of Table 5 allow us to assign to k_2'' the approximate value 0·85 sec.$^{-1}$ mole^{-1} l.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, GOWER ST., LONDON, W.C.1.

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