16. *Nitrosation, Diazotisation, and Deamination. Part IV.** *Hydrogen-ion Catalysis in the Diazotisation of* o-*Chloroaniline in Dilute Perchloric Acid.*

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

Diazotisation rates were sometimes observed which were greater than those prescribed by the kinetic equations of the preceding papers; a study of the discrepancies revealed that they were due to an additional diazotisation process, which could be made dominating with an amine of suitable basicity, by operating in a suitable range of acidity, with a very low concentration of nitrous acid. This new process was examined in detail for *o*-chloroaniline in perchloric acid in 0·005—0·020M-excess, with nitrous acid in concentrations below 0·0001M. The reaction was shown to be of first order each in hydrogen ions, in amine, and in nitrous acid.

(1) *The Detection of Acid-catalysis.*—When the concentration of aniline in free-basic form is increased by a progressive reduction of acidity, the rate of diazotisation, with a constant concentration of molecular nitrous acid, at first increases proportionally to the concentration of free base, then begins to increase more slowly, and finally attains a constant maximum. The first situation is represented by equation (1), and the last by equation (2), where the bracketed quantities mean molecular, rather than stoicheiometric, concentrations:

$$\text{Rate} = k_3''[\text{Ar·NH}_2][\text{HNO}_2]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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

This was established in Part II particularly. It follows from it that other aromatic amines should be diazotised at rates, which at low acidities rise to the same upper limit, represented by equation (2). This conclusion was shown in Part III experimentally to have a certain range of validity. However, when the experimental work of Part II was repeated with other aromatic amines, the rates obtained were sometimes greater than the expected maximum rate given by equation (2). These discrepancies arose, or became more marked, when (*a*) the acidity was not excessively low, (*b*) the aromatic amine was a considerably weaker base than aniline, and (*c*) the concentration of molecular nitrous acid was excessively low. This suggests the incursion of another mechanism of diazotisation, one unconnected with kinetic equations (1) and (2). One can tentatively assign kinetic characteristics to the new mechanism: (*a'*) it is probably acid-catalysed; (*b'*) it probably has a kinetic order greater than zero in the aromatic amine; (*c'*) it certainly has a kinetic order less than two in the nitrous acid.

There is, of course, an interplay between effects (*a*) and (*b*), and between conclusions (*a'*) and (*b'*), an interplay expected to lead to optima. For example, if the new reaction were of first order in acid and first in amine, the acidity, which has to be low enough to give significance to the reference rate of equation (2), cannot be made indefinitely low if the new reaction is to appear, because even a maximum liberation of free-basic amine will be unable to compensate the kinetic effect of a vanishing acidity. Again, whilst it is important that the amine should be a weak enough base to be liberated appreciably at the allowable acidities, it must not be so weak, and hence so unreactive, that, even if liberated quantitatively, it produces a vanishing reaction rate by the new mechanism. Obviously the new reaction has to be of order lower than two in nitrous acid, so that it will be left in relative prominence, as the reaction of equation (2) dies out, when the concentration of nitrous acid is reduced.

It is implied in these conclusions that the " old " reaction, that governed by the limiting equations (1) and (2), and by the transitional kinetics bounded by them, and the

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* Part III, preceding paper.

" new " reaction, that detected as described, must in principle go on together. Under the conditions of the experiments described in Parts II and III, the new reaction must have accounted for only a small proportion of the total rate, with the result that the old reaction stood sufficiently alone for kinetic elucidation. Our object was now to reverse these relations; *i.e.*, to reduce the old reaction to relative insignificance, and so kinetically to isolate the new reaction.

(2) *Isolation of Acid-catalysed Diazotisation.*—A preliminary survey, guided by these considerations, of the diazotisation of various aromatic amines led us to select for detailed study the diazotisation of *o*-chloroaniline, a base about 65 times weaker than aniline. We found it convenient to work in the acidity range 0·005—0·02M, maintained by suitable excesses of perchloric acid, and to employ nitrous acid initially in the very small stoicheiometric concentration 0·0001M.

Some explanation is necessary of the method of controlling acidity, since it was not, and could not be, the same as in the previously described experiments, on the diazotisation of aniline in perchloric acid. In those experiments, the concentration of hydrogen ions could be taken with sufficient approximation as equal to the stoicheiometric excess of perchloric acid. This was a legitimate simplification, because, at the relevant acidities, nitrous acid was too weak, and the anilinium ion much too weak, as an acid, to supply any important proportion of the hydrogen ions. However, the *o*-chloroanilinium ion is a considerably stronger acid, pK_a 2·77, and, in our acidity range, pH 1·7—2·3, it will be a significant contributor of hydrogen ions. Nitrous acid will remain negligible in this regard, largely because stoicheiometrically so little of it is present. Therefore, in order to keep a fixed hydrogen-ion concentration in a series of runs characterised by successively increased initial concentrations of *o*-chloroaniline, we have to compensate for the increased supply of hydrogen ions on account of increases in the concentration of *o*-chloroanilinium ion, by providing successively decreased stoicheiometric excesses of perchloric acid. The example given in Table 1 will make the method clear.

TABLE 1. *Control of hydrogen-ion concentration* (M) *in the diazotisation of* o-*chloroaniline.*

Run	151	154	124	123
[Stoicheiometric *o*-$Cl{\cdot}C_6H_4{\cdot}NH_3^+$]	0·0020	0·0040	0·0060	0·0080
[,, HNO_2]	0·0001	0·0001	0·0001	0·0001
[Neutralised * $HClO_4$]	0·0021	0·0041	0·0061	0·0081
[Excess of $HClO_4$]	0·0046	0·0041	0·0036	0·0031
[H^+]	0·0051	0·0051	0·0051	0·0051

* By initially added *o*-chloroaniline and sodium nitrite.

We have next to show that, under the conditions selected, the old reaction can indeed be made so subordinate as to leave the new reaction in isolation. Three runs with different stoicheiometric concentrations of *o*-chloroaniline, but with the same concentration of nitrous acid, and at the same acidity, are recorded in Table 2. It is clear from inspection of the plots in Fig. 1, that these runs have a finite kinetic order in *o*-chloroaniline. From the rate constant k_2'' of equation (2), as determined in Part II, and the molecular concentration of nitrous acid used in the present experiments, we can calculate the maximum rate, given by equation (2), of diazotisation by the old reaction, acting alone. This is represented by the full-line curve near the bottom of the diagram. Of course, it is the curve which would express reaction progress by this mechanism, if there were no other way than that of using up nitrous acid. In order to obtain a curve representing the extent to which the old reaction accompanies the new, we must reduce the slope of the curve for the old reaction in proportion to the square of the concentration of nitrous acid surviving the new. This is done for run no. 138, the run in which the old reaction has its greatest importance, in the broken line in Fig. 1. Clearly the old reaction is only of small importance (total 8%) even in this case. It will be negligible in most cases, and thus we can proceed to study the kinetics of the new mechanism with almost complete disregard of the old.

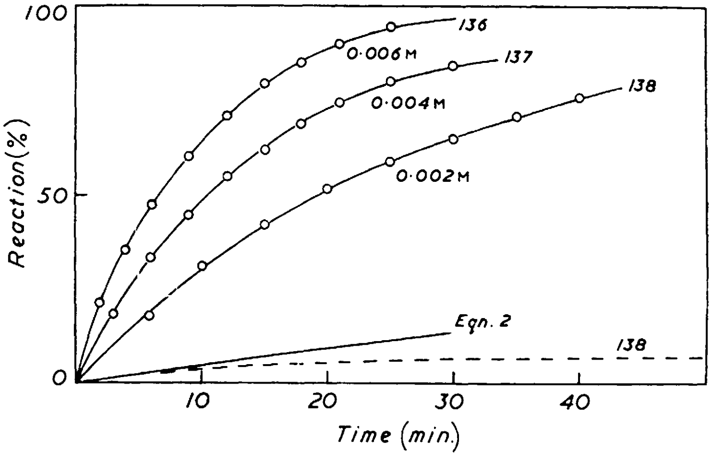
TABLE 2. *Course of the diazotisation of* o-*chloroaniline in water at* 0°.

Initially, $[HNO_2]$ = 0·0001, and $[H^+]$ = 0·0204M, throughout; whilst [stoicheiometric amine] is as follows: Run 136, 0·006M; run 137, 0·004M; run 138, 0·002M.

Run:	136	137	138
	Reaction (%)		
Time (min.)			
2	21·0	—	—
3	—	18·0	—
4	35·0	—	—
5	—	—	17·0
6	47·3	33·7	—
9	60·0	44·5	—
10	—	—	31·5
12	71·0	54·2	—
15	79·5	61·5	42·5
18	85·3	68·5	—
20	—	—	51·3
21	90·0	74·3	—
25	94·5	80·0	58·5
30	—	84·5	65·0
35	—	—	71·2
40	—	—	76·0

(3) *Kinetics of Acid-catalysed Diazotisation.*—The data obtained for this purpose constitute a generalisation of those in Table 2. In all runs, the initial concentration of stoicheiometric nitrous acid was 0·0001M, and the amine was stoicheiometrically in constant excess. In the set of runs illustrated in Table 2, the initial stoicheiometric concentration of amine was changed from run to run, whilst the acidity was kept constant in the set. Several other sets of runs were done, within each of which the amine concentration was varied, whilst the acidity was kept constant within each set but was varied from set to set.

FIG. 1. *Diazotisation of* o-*chloroaniline with three initial stoicheiometric concentrations of amine (entered against the curves), and a common initial concentration of nitrous acid* 0·0001M *and a common acidity* (0·0204M). (*For interpretation of the bottom two lines see text.*)



Since acid-catalysis is found to be involved in the new reaction, we have to keep clear the distinction between stoicheiometric and molecular rate-constants (Part I, section 3c). For the purpose of computing the latter from the former, we need to know the proportions in which nitrous acid and *o*-chloroaniline are present in molecular form at the different acidities used. Taking the acidity constant of nitrous acid as 4·5 × 10^{-4} mole $l.^{-1}$ and that of the *o*-chloroanilinium ion as 3·6 × 10^{-3} mole $l.^{-1}$, we obtain the values shown in Table 3, which have been used in the calculations.

TABLE 3. *Proportions in which nitrous acid and* o-*chloroaniline are present in molecular form at various acidities.*

$[H^+]$	0·0051	0·0102	0·0153	0·0204
Nitrous acid, non-ionised (%)	92	96	97	98
o-Chloroaniline as base (%)	25·0	14·3	10·0	7·7

The results of these experiments are assembled in Table 4, where they are expressed in terms of rate-constants of various types, calculated as described below, with the aid, in some cases, of the data of Table 3.

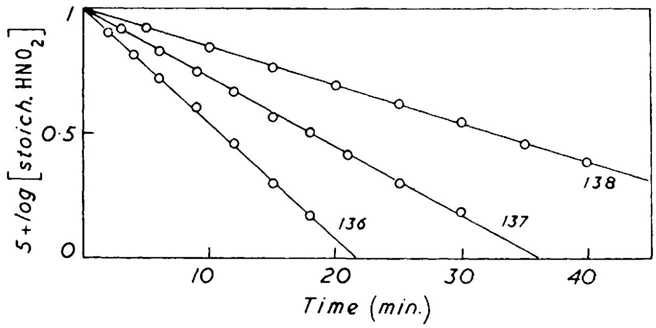
TABLE 4. *Rate-constants for the diazotisation of* o-*chloroaniline with a low concentration of nitrous acid in dilute aqueous perchloric acid at* 0°.

(Initial stoicheiometric concentration of nitrous acid 0·0001M throughout. Units: $\bar{k}_1'$ and k_1' in sec.$^{-1}$; $\bar{k}_2'$ and k_2' in sec.$^{-1}$ mole^{-1} l.; k_3^{H} in sec.$^{-1}$ mole^{-2} l.^{2}.)

Set	Run	[H$^+$]	[Stoich. amine]	Stoich. $10^3\bar{k}_1'$	Molr. $10^3k_1'$	Stoich. $10\bar{k}_2'$	Molr. $10k_2'$	Molr. $10^{-2}k_3^{\text{H}}$
1	123	0·0051	0·008	1·53	1·67	1·91	8·3	1·63
1	124	0·0051	0·006	1·15	1·25	1·86	8·1	1·59
1	154	0·0051	0·004	0·80	0·87	2·00	8·7	1·71
1	151	0·0051	0·002	0·47	0·50	2·35	10·6	2·08
2	132	0·0102	0·006	1·42	1·48	2·37	17·3	1·70
2	133	0·0102	0·004	0·97	1·00	2·42	17·6	1·73
2	134	0·0102	0·002	0·52	0·53	2·60	18·9	1·86
3	128	0·0153	0·006	1·52	1·57	2·53	26·0	1·70
3	130	0·0153	0·004	1·00	1·03	2·50	25·7	1·68
3	131	0·0153	0·002	0·53	0·55	2·65	27·2	1·78
4	136	0·0204	0·006	1·68	1·72	2·81	37·1	1·81
4	137	0·0204	0·004	1·08	1·10	2·70	35·8	1·76
4	138	0·0204	0·002	0·58	0·60	2·90	38·4	1·92

When the reaction–time data for any of these runs are plotted semilogarithmically, linear graphs are obtained as shown for the runs of set 4 in Fig. 2. This establishes that the new diazotisation process is of first order in nitrous acid. The slopes of the graphs give the stoicheiometric first-order rate-constants, $\bar{k}_1'$. From these, with the aid of Table 3, we can calculate the molecular first-order constants, k_1', that is, the true rate-constants of equation (3), which apply when the nitrous acid concentration is the only variable.

FIG. 2. *Diazotisation of* o-*chloroaniline: Plot of the logarithm of nitrous acid concentration* versus *the time for three runs at the same acidity but with different concentrations of amine in constant excess.*



$$\text{Rate} = k_1'[\text{HNO}_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

When the stoicheiometric first-order rate-constants for any single set of runs are plotted against the (constant-excess) stoicheiometric concentrations of amine, a straight line is obtained, which passes through the origin. Similarly plotted, the data for the different sets of runs give different straight lines, all passing through the origin. This establishes that the reaction is of first order in amine. The slopes of the lines give the stoicheiometric second-order rate-constants $\bar{k}_2'$, and from these, by further use of Table 3, we can compute the molecular second-order constants k_2', that is, the true rate-constants of equation (4), which applies when the variable concentrations are those of the nitrous acid and the amine:

$$\text{Rate} = k_2'[\text{Ar·NH}_2][\text{HNO}_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Alternatively, we may plot the molecular first-order rate-constant k_1' against the molecular concentration of amine, deduced with the help of Table 3, so obtaining a family of straight lines, one line for each set of runs, all lines going through the origin. They are shown in Fig. 3, and their slopes directly measure the molecular second-order constant k_2'. In passing, we may note that equation (4) is the second-order rate-equation which so many of the earlier investigators thought they were observing (Part I, section 2), when in fact they were observing kinetics according to the other second-order equation (2), with the rate-constant k_2'' (Part II, section 2).

Molecular rate-constants are so constituted that they do not suffer change reflecting any effects of acidity on the acid–base equilibrium in which arylammonium and nitrite ions are involved. If these constants vary with acidity, then that means that the transition state, after the indicated amine and nitrous acid molecules have been supplied, requires added or subtracted protons, wherefore the concentration of hydrogen ions appears to the appropriate positive or negative power in the complete kinetic equation. It is clear from Fig. 3 that the molecular second-order constants k_2' do vary with a positive power of the acidity; and indeed, if we plot the slopes of the curves against the hydrogen-ion concentration, we again get a straight line passing through the origin, as shown in Fig. 4. This establishes that one extra proton is required in the transition state of the reaction, and that the complete kinetic equation is (5):

FIG. 3.

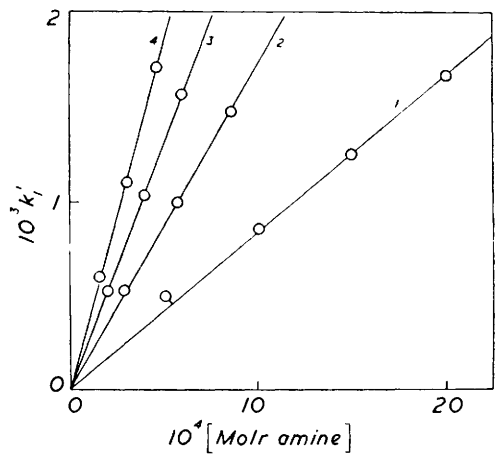


FIG. 3. *Diazotisation of* o-*chloroaniline*: *Plot of the molecular first-order rate-constant in nitrous acid* versus *the molecular concentration of amine. The different curves correspond to the different sets of runs, each set characterised by a different acidity. The hydrogen-ion concentrations are proportional to the figures used to number the sets, as noted beside the curves.*

FIG. 4.

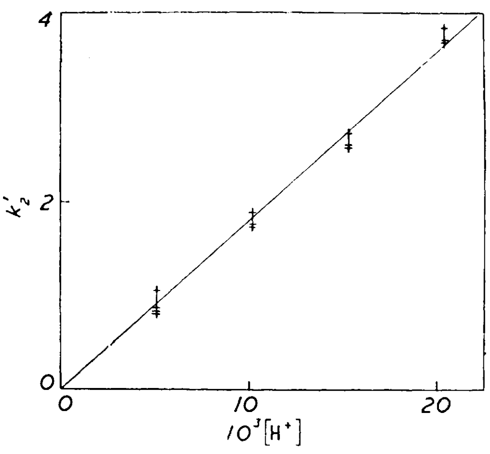


FIG. 4. *Diazotisation of* o-*chloroaniline*: *Plot of the molecular second-order rate-constant* versus *the concentration of hydrogen ions.*

$$\text{Rate} = k_3^{\text{H}}[\text{H}^+][\text{Ar·NH}_2][\text{HNO}_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The rate-constant k_3^{H} of this third-order reaction of *o*-chloroaniline at 0° is 175 sec.$^{-1}$ mole^{-2} l.^{2}.

In Fig. 4, points are entered for the second-order constants of the individual runs, because the errors show a significant trend. Among the set of points belonging to each acidity, the highest point always corresponds to the lowest amine concentration. Also, the absolute spread of points is about the same at each acidity, and therefore it is proportionally greater at the lower acidities. In considering our experiments as illustrating equation (5), it has to be remembered that $[\text{HNO}_2]$ varies only during runs, whereas

[H$^+$] and [amine] are varied from run to run. Our errors suggest, then, that observed rates are raised above the rates required by equation (5), by a roughly constant amount, which makes a proportionally greater difference when [amine] is low, and, after that, when [H$^+$] is low. This is just what would happen if the reaction according to equation (5) were not quite kinetically pure, but were accompanied by a small amount of reaction according to equation (2). This latter process does not kinetically depend either on [amine] or on [H$^+$], and it is therefore not retarded, as reaction by equation (5) is retarded, when we cut down the concentrations of amine and hydrogen ions.

William Ramsay and Ralph Forster Laboratories,
University College, Gower St., London, W.C.1.

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