17. *Nitrosation, Diazotisation, and Deamination. Part V.* Catalysis by Anions of Strong Acids in the Diazotisation of Aniline and of* o-*Chloroaniline in Dilute Perchloric Acid.*

By E. D. Hughes and J. H. Ridd.

Perchlorate and nitrate ions do not catalyse diazotisation, and apparently fluoride ions do not, though chloride, bromide, and iodide ions do, with an importance increasing in this order.

The catalytic effect of chloride and bromide ions was first investigated by Schmid, who elucidated its kinetics as of first order each in hydrogen ion, amine, nitrous acid, and halide ion. We have tried so to adjust conditions that the reactions become of zeroth order in amine, whilst remaining of first order in each of the other reactants, by building up a sufficiently high concentration of a sufficiently reactive free-amine in the acid required by the catalysis. We failed for chloride-catalysis. For bromide-catalysis, we failed with aniline, but succeeded with the weaker base *o*-chloroaniline. And for iodide-catalysis we succeeded easily even with aniline.

It is shown that the process made rate-controlling in this way is completely independent of the process made rate-controlling when the kinetics of the uncatalysed reactions are similarly modified (Part II).

(1) *Survey of Anion Catalysis.*—The background against which we have to consider the catalysis of diazotisation by inorganic anions is that of two normally concurrent processes of diazotisation, the first uncatalysed and involving kinetics limited by the rate-laws (1) and (2), and the second catalysed by hydrogen ion and following the kinetic law (3):

$$\text{Uncatalysed}\begin{cases}\text{Rate} = k_3''[\text{Ar·NH}_2][\text{HNO}_2]^2 & (1)\\ \text{Rate} = k_2''[\text{HNO}_2]^2 & (2)\end{cases}$$

$$\text{H}^+\text{-catalysed Rate} = k_3^{\text{H}}[\text{H}^+][\text{Ar·NH}_2][\text{HNO}_2] \qquad (3)$$

We have sought catalytic effects of added sodium perchlorate, nitrate, fluoride, chloride, bromide, and iodide. Up to concentrations of the order 0·1M, added sodium perchlorate and nitrate have no noticeable catalytic effect. This was expected for the perchlorate, because nitrosyl perchlorate does not exist in covalent form. But it could not have been confidently anticipated for the nitrate, since nitrosyl nitrate does exist in the form of dinitrogen tetroxide. However, this molecule seems to be a relatively poor nitrosating agent for primary aromatic amines (cf. Part I, section 1b). Fluoride appears to have no catalytic effect.

Added sodium chloride, bromide, and iodide exert catalytic effects, increasing in importance in this order, on the diazotisation of aniline or *o*-chloroaniline. This observation in itself is not new, because Schmid and Muhr[1] have described the catalytic effects

---

* Part IV, preceding paper.

[1] Schmid and Muhr, *Ber.*, 1937, **70**, 421; Schmid, *Z. Elektrochem.*, 1937, **43**, 626.

of chloride and bromide ion on the diazotisation of aniline, in the moderately strongly acid conditions in which the background rate for uncatalysed diazotisation is governed by equation (1). They showed that the kinetic effect of the halide ion is to add to the background rate a new rate-term of fourth order, as follows:

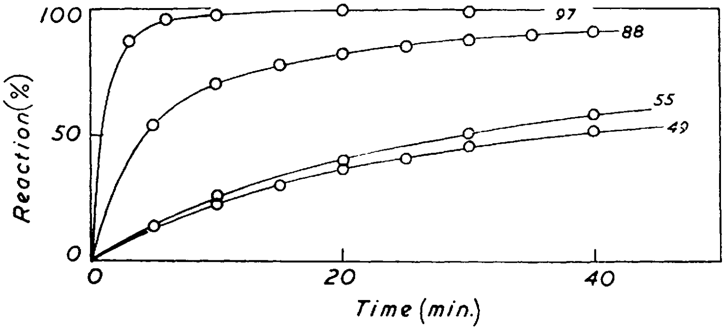
$$\text{Hal}^-\text{-Catalysed rate} = k_4^{\text{Hal}}[\text{H}^+][\text{Ar}\cdot\text{NH}_2][\text{HNO}_2][\text{Hal}^-] \quad . \quad . \quad . \quad (4)$$

Our object has been to discover whether equation (4) is really a limiting law, like equation (1). We had to try, either by cutting down the acidity, or by reducing the basicity of the amine, or by both devices, to break down the dependence of the catalytic rate on amine concentration, so carrying the kinetics, through a transitional situation, to another limiting form, possibly that of equation (5), which, analogously to equation (2), would represent the control of diazotisation rate by some purely inorganic process:

$$\text{Hal}^-\text{-Catalysed rate} = k_3^{\text{Hal}}[\text{H}^+][\text{HNO}_2][\text{Hal}^-] \quad . \quad . \quad . \quad . \quad (5)$$

So far, we have had no success in this attempt in the case of chloride-catalyses, but we have succeeded in that of bromide-catalyses, and more easily in that of iodide-catalyses.

FIG. 1. *Diazotisation of aniline. Runs illustrating bromide-catalysis, and its persistent dependence on amine, at such acidity that the uncatalysed reaction has become insensitive to amine.* (For details see Table 1.)



There can be no doubt that all these catalysed processes of diazotisation depend on preliminary inorganic-chemical reactions, which can be rate-controlling in principle, though in practice the conditions for such rate-control are not always easily fulfilled. The main condition is that a sufficient concentration of a sufficiently reactive amine shall be furnished in free-basic form to intercept completely the normal hydrolytic reversal of the formation in the preliminary process of the catalytic nitrosating agent. This condition becomes progressively easier to satisfy as we pass from chloride-, through bromide-, to iodide-catalysis.

(2) *Bromide-catalysis.*—Some experiments were first made in order to discover whether bromide-catalysis was to be thought of as an elaboration of the uncatalysed reaction, the basic kinetic form of which is comprised within equations (1) and (2). In this reaction, a preliminary, inorganic-chemical process occurs, which (we might suppose) bromide ions might extend to form a new nitrosating substance. Now the basic inorganic process becomes rate-controlling when acidity is so reduced that a concentration of free amine is built up which suffices to consume all the product of the process. When this happens, the kinetics change from those of equation (1) to those of equation (2). If the product of the same inorganic-chemical process were required for interaction with bromide ions in order to generate the active agent of bromide-catalysed diazotisation, then bromide-catalysis should disappear when the product of the basic process is wholly drawn off by amine, that is, when the uncatalysed kinetic form changes from that of equation (1) to that of

equation (2). We have shown that this does not happen; and we conclude that the bromide-catalysed reaction is not an elaboration of the uncatalysed reaction.

As evidence we may consider two pairs of runs on the diazotisation of aniline. They are specified as to conditions in Table 1, and compared as to results in Fig. 1. In all four runs, the initial concentration of nitrous acid is the same; and so is the concentration of free acid. The runs of the first pair are uncatalysed, whilst those of the second pair are catalysed by the same amount of sodium bromide. In the first run of each pair the initial concentration of aniline is the same; and in the second of each pair it is ten times greater than in the first. Now the acidity is at such a level that the uncatalysed reaction is proceeding essentially in accordance with equation (2). This is shown by the lower two curves in Fig. 1, which depict quite similar rates, though one run has ten times more amine than the other. The effect of bromide-catalysis is seen in the upper two curves in Fig. 1. They show that both the catalysed runs are greatly accelerated, and that the one with the larger amount of amine is much more accelerated than the other. Evidently, when the uncatalysed reaction goes over from kinetic form (1) to form (2), bromide-catalysis is preserved. Moreover, it is preserved in its amine-dependent kinetic form (4).

TABLE 1. *Bromide-catalysis in the diazotisation of aniline at low acidity at* 0°.

Initially added, $[HNO_2] = 0{\cdot}001$M, and [excess of $HClO_4$] $= 0{\cdot}002$M, throughout.

Run	49	55	88	97
$[Ph{\cdot}NH_3^+ClO_4^-]$	0·001	0·01	0·001	0·01
[NaBr]	—	—	0·01	0·01

(The reaction–time curves are shown in Fig. 1.)

If, then, there is a preliminary inorganic-chemical process in bromide-catalysis, it is one which short-circuits, rather than extends, the preliminary process of the uncatalysed reaction: obviously, we have to go to greater lengths in order to isolate kinetically the suspected new process by the provision of a good organic-chemical trap for its product. This suggests recourse to a weaker base than aniline.

If the bromide-catalysed reaction is not to be regarded as an elaboration of the uncatalysed reaction, the most obvious alternative is to picture it as an extension of the hydrogen-ion catalysed process. The correspondences in equations (3) and (4) suggest this. Now the hydrogen-ion reaction of equation (3) was successfully investigated with *o*-chloroaniline as the diazotised amine (Part IV), and we therefore continued our study of bromide-catalysis in this example.

With *o*-chloroaniline as the diazotised amine, we can cut out the uncatalysed reaction of kinetic equations (1) and (2) practically completely by using very low concentrations of nitrous acid. When, as in these experiments, the initial stoicheiometric concentration of nitrous acid is 0·0001M, the only background reaction of which we have to take serious account is the hydrogen-ion reaction of equation (3). We know the rate of this at 0° (Part IV), and therefore we know what to subtract from diazotisation rates observed at 0° under bromide-catalysis, in order to isolate the catalytic rate term.

In all the runs now to be described, the amine was stoicheiometrically in large excess, and the acidity was large enough to remain substantially constant during a run. The bromide ions were not consumed. Thus the only concentration which was variable within a run was that of nitrous acid. By plotting the reaction–time curves in the usual semi-logarithmic way, it was found that the reaction including bromide-catalysis, just like the reaction without added bromide, was of first order in nitrous acid. This held for all the amine concentrations, acidities, and bromide concentrations investigated. A few examples are shown in Fig. 2.

From the slope of any such curve, we obtained a stoicheiometric, observed first-order rate-constant, $\bar{k}_1^{obs}$. By the use of Table 3 of Part IV (or, in some cases, of an extension of such a Table), we can compute from this a molecular, observed, first-order rate-constant,

k_1^{obs}. This is the overall rate-constant of equation (6), which applies when the only variable concentration is that of nitrous acid:

$$\text{Rate} = k_1^{obs}[HNO_2] = (k_1' + k_1^{Br})[HNO_2] \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The rate-constant k_1^{obs} is the sum of a background constant k_1' and a catalytic constant k_1^{Br}. The background constant is the product of certain factors taken from equation (3), as follows:

$$k_1' = k_3^{H}[H^+][Ar{\cdot}NH_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

From Part IV, section 3, we know that, for *o*-chloroaniline at 0°, k_3^H is 175 sec.$^{-1}$ mole^{-2} l.^{2}. Hence, from this figure, the hydrogen-ion concentration applying to the run, and the concentration of stoicheiometric amine, in constant excess, during the run, together with the proportion in which the amine is present in molecular form, as given by Table 3 of Part IV, or a similar Table, we can compute the background first-order rate-constant k_1'. Thus we may obtain the catalytic first-order rate-constant, k_1^{Br} by subtraction of k_1' from the observed constant k_1^{obs}.

Now we know that the background rate-constant k_1' depends on the amine concentration, as in equation (7), and the point to be determined is whether the catalytic rate-constant k_1^{Br} similarly depends on the concentration of the amine, or whether, by a sufficient raising of the concentration of free-basic amine, this constant has been, or can be, made independent of that concentration. At a fixed acidity, the molecular amine concentration is a constant fraction of the stoicheiometric amine concentration. Several runs at a common fixed acidity, but with a range of concentrations of stoicheiometric amine in constant excess, are cited in Table 2, where the observed, molecular first-order rate-constants, k_1^{obs}, are split up, by the method described above, into their background and catalytic components, k_1' and k_1^{Br}. One sees that, when the amine concentration is high enough,

FIG. 2. *Diazotisation of* o-*chloroaniline in the presence of bromide ions. Plot of the logarithm of the concentration of nitrous acid* versus *the time, for various constant concentrations of amine, hydrogen ion, and bromide ion* (*cf.* *Tables* 2—4).

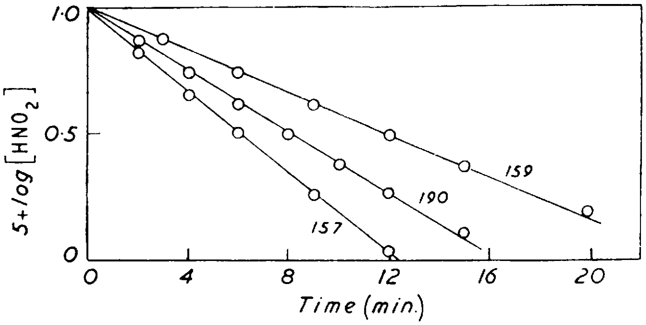


TABLE 2. *Bromide-catalysed diazotisation of* o-*chloroaniline with a low concentration of nitrous acid at* 0°. *Effect of amine concentration on the background and catalytic rates.*

Initially, $[H^+] = 0{\cdot}0051$, $[Br^-] = 0{\cdot}0004$, and [stoicheiometric HNO_2] = 0·0001M. All rate-constants in sec.$^{-1}$.

Run	[Stoich. amine]	$10^3k_1^{obs}$	$10^3k_1'$	$10^3k_1^{Br}$
156	0·001	2·05	0·22	1·83
155	0·002	2·65	0·43	2·22
163	0·003	2·97	0·65	2·31
157	0·004	3·33	0·87	2·46

the catalytic rate-constant k_1^{Br} is almost independent of it. Thus, when the stoicheiometric amine concentration is doubled, between 0·001M and 0·002M, the catalytic constant is raised by only 20%; and when the concentration is again doubled, between 0·002M and 0·004M, the constant is raised further by only 10%. At higher concentrations the rates become somewhat too great for accurate measurement, because the background rate continues to go up, even though the catalytic rate does not. However, there can be no doubt that, even over the concentration range explored, the catalytic rate is substantially of zeroth order in amine.

The summary of this finding is that, whilst the background term in equation (6) is under the restriction that the only variable concentration shall be that of nitrous acid, the catalytic term holds when the concentrations of nitrous acid and amine are both variable. It is therefore convenient to break up equation (6), and consider further only the catalytic part, now rewritten as equation (8):

$$\text{Br}^-\text{-Catalysed rate} = k_1^{Br}[HNO_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The remaining problem is to determine how k_1^{Br} depends on the other two possibly variable concentrations, those of bromide ions and of hydrogen ions, when the concentration of free amine is large enough not to appear in the rate equation.

The answer with respect to bromide-ion concentration is contained in Table **3**, which records rate-constants for a series of runs, all with a sufficiently high concentration of amine, and with a fixed acidity, but with various concentrations of bromide ion. The observed, molecular, first-order rate-constants are split up as before into their background and catalytic parts. The catalytic first-order constant is then seen to be directly proportional to the bromide-ion concentration, wherefore the ratio of these quantities, which is the second-order constant k_2^{Br} of equation (9), is constant:

$$\text{Br}^-\text{-Catalysed rate} = k_2^{Br}[HNO_2][Br^-] \quad . \quad . \quad . \quad . \quad . \quad (9)$$

TABLE 3. *Bromide-ion dependence of the bromide-catalysed diazotisation of* o-*chloroaniline at* 0°.

Initially, $[H^+] = 0·0051$, [stoicheiometric amine] = 0·0040, and [stoicheiometric HNO_2] = 0·0001M. All first-order rate-constants in sec.$^{-1}$, and the second-order constants k_2^{Br} in sec.$^{-1}$ mole^{-1} l.

Run	$[Br^-]$	$10^3k_1^{obs}$	$10^3k_1'$	$10^3k_1^{Br}$	k_2^{Br}
188	0·0001	1·47	0·87	0·60	6·00
189	0·0002	2·08	0·87	1·21	6·05
190	0·0003	2·63	0·87	1·76	5·87
157	0·0004	3·33	0·87	2·46	6·15

TABLE 4. *Hydrogen-ion dependence of the bromide-catalysed diazotisation of* o-*chloroaniline at* 0°.

Initially, [stoicheiometric HNO_2] = 0·0001M, throughout; k_1^{obs} and k_1^{Br} are in sec.$^{-1}$, k_2^{Br} is in sec.$^{-1}$ mole^{-1} l., and k_3^{Br} is in sec.$^{-1}$ mole^{-2} l.^{2}.

Run	$[H^+]$	[Stoich. amine]	$[Br^-]$	$10^3k_1^{obs}$	$10^3k_1'$	$10^3k_1^{Br}$	k_2^{Br}	$10^{-3}k_3^{Br}$
158	0·0017	0·002	0·0010	2·28	0·28	2·00	2·00	1·18
159	,,	0·001	,,	2·13	0·15	1·98	1·98	1·17
160	0·0034	0·003	0·0004	2·17	0·58	1·58	3·95	1·16
161	,,	0·002	,,	1·97	0·38	1·58	3·95	1·16
157	0·0051	0·004	,,	2·33	0·87	2·46	6·15	1·21
163	,,	0·003	,,	2·97	0·65	2·31	5·78	1·13
190	,,	0·004	0·0003	2·63	0·87	1·76	5·87	1·15
189	,,	,,	0·0002	2·08	0·87	1·21	6·05	1·19
188	,,	,,	0·0001	1·47	0·87	0·60	6·00	1·18

The final question is that of the dependence of the second-order catalytic constants k_2^{Br} on acidity. To settle this, several sets of runs were done, each set characterised by a different acidity. The results are in Table **4**. From them, we see that the second-order catalytic constants are directly proportional to the hydrogen-ion concentration. It follows that the full kinetic equation for the catalysed reaction is the third-order equation (10), the rate-constant of which, as the last column of the Table shows, remains constant under variations in the concentrations of all substances involved in the reaction:

$$\text{Br}^-\text{-Catalysed rate} = k_3^{\text{Br}}[\text{H}^+][\text{HNO}_2][\text{Br}^-] \quad . \quad . \quad . \quad . \quad (10)$$

The mean rate-constant, k_3^{Br}, at 0° is 1170 sec.$^{-1}$ mole^{-2} l.^{2}.

Equation (10) is a specialised form of equation (5). It is the kinetic equation of a purely inorganic-chemical process, preliminary to bromide-catalysed diazotisation, and of such a nature that it can become rate-controlling. When the amine draws off the product of this first process much more slowly than the process itself becomes reversed, then the catalytic reaction has the kinetic form observed by Schmid and Muhr, and represented by equation (4). But when a sufficiently reactive amine is supplied in sufficient concentration as free base wholly to trap the product of the preliminary process, then the catalytic rate ceases to depend on the amine, and so the kinetics become simplified to those of equation (5). As will be shown in Part VI, a kinetic transition such as this fully establishes the chemical mechanism.

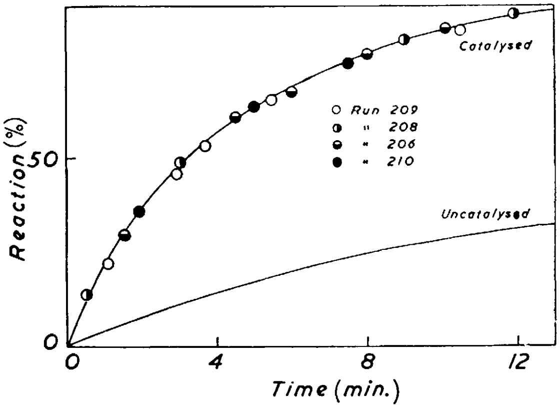


FIG. 3. *Diazotisation of aniline. Runs illustrating iodide-catalysis, and its independence of amine at such acidity that the uncatalysed reaction is also insensitive to amine.*
The lower curve represents an uncatalysed run. The upper curve is common to a series of runs, catalysed with the same concentration of iodide ion, but differing with respect to amine concentration over a 23-fold range.

The data of Table 4 leave no room for a bromide-catalysed rate term which does not depend on hydrogen ions; and nowhere in this work has any sign of such a rate-term been encountered.

(3) *Iodide-catalyses.*—The transition of kinetic form, in which the factor dependent on amine disappears from the rate equation, is much easier to observe with the iodide-catalysis of diazotisation than with its bromide-catalysis. It is not necessary to resort to the diazotisation of any weaker base than aniline in order to demonstrate this effect in iodide-catalysis. If the diazotisation of aniline in aqueous perchloric acid, with such a concentration of nitrous acid that the uncatalysed reaction is almost the only background process, is followed at progressively reduced acidities, then, even before the transition from kinetic form (1) to form (2) in the background process is complete, the transition from form (4) to form (5) in a superposed iodide-catalysed reaction is quite complete. The total rate is now essentially independent of the amine, and is expressed by equation (11):

$$\text{Rate} = k_2''[\text{HNO}_2]^2 + k_3^{\text{I}}[\text{H}^+][\text{HNO}_2][\text{I}^-] \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Details are given in support of the main conclusion here summarised by citation of the series of runs specified as to conditions in Table 5, and compared as to results in Fig. 3. All these runs were started with a common stoicheiometric concentration of nitrous acid and a common acidity. An uncatalysed run is included as a standard of reference: it is a close reproduction of some of the second-order runs recorded in Part II. All the other runs of the set are catalysed by the same concentration of sodium iodide. They differ widely with respect to concentration of amine, and yet the kinetic course of all these runs

TABLE 5. *Iodide-catalysis in the diazotisation of aniline at low acidity at* 0°.

Initially, [stoicheiometric HNO_2] = 0·001, and [excess of $HClO_4$] = 0·002M, throughout.

Run	201	209	208	206	210
$[Ph{\cdot}NH_3^+ClO_4^-]$	0·010	0·001	0·005	0·010	0·023
[NaI]	—	0·001	0·001	0·001	0·001

(The reaction–time curves are shown in Fig. 3.)

is described by a common curve. Further analysis of such runs shows them to be consistent with equation (11). The third-order rate-constant k_3^{I} has the value 1370 sec.$^{-1}$ mole^{-2} l.^{2}. This is evidently the rate-constant of a preliminary inorganic-chemical process, which, at the low acidities used in these measurements, is rate-controlling for iodide-catalysed diazotisation.

It may be noted that the iodide-catalysed diazotisations went to completion as accurately as did the uncatalysed diazotisations. Thus, no decomposition of nitrous acid by iodide ions could be noticed in these experiments.

The help of Dr. K. G. Oldham and of Dr. J. Wilby in making some of these measurements is gratefully acknowledged.

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

[*Received, June* 12*th*, 1957.]