15. *Nitrosation, Diazotisation, and Deamination. Part III.* Zeroth-order Diazotisation of Aromatic Amines in Carboxylic Acid Buffers*

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The diazotisation of aniline in acetate and phthalate buffers near pH 5, with a constant excess of nitrous acid, follows linear reaction–time curves until the falling concentration of aniline approaches 10^{-5}M. At higher aniline concentrations, the kinetic order is 0 in aniline; and, by comparisons among different runs, it is shown to be 1·8 in nitrous acid, the defect below 2 being explicable as a buffer disturbance. The zeroth-order law applies, not only to aniline, but also to substituted anilines with pK_a greater than about 4, which all undergo diazotisation at the same absolute rate. But for more weakly basic aniline derivatives the rate falls, and a non-zero order in amine enters, these effects increasing as the basic strength is diminished. Analogies with previous investigations on nitration and chlorination are pointed out.

In first approximation, acetate and phthalate buffers do not change the kinetic orders in amine or nitrous acid, but a part of the rate in their presence is represented by a catalytic term of first order in buffer anion. There is probably a superposed small disturbance, of a type serious with some other buffers and characterised by a loss of kinetic order in nitrous acid in substitution for an introduced non-zero order in buffer acid (cf. halide catalysis, Part V of this series).

In the experiments recorded in Part II * on the diazotisation of aniline in dilute aqueous perchloric acid, it was not possible to bring the overall kinetic order from 3 completely down to 2 by progressively reducing the concentration of the excess of perchloric acid, because, when this excess became reduced below 0·002M, the acid–base equilibria in which the reactants are involved become shifted as reaction progresses in such a way as to produce an appreciable increase in apparent kinetic order. For the purpose of setting a steady acidity much lower than the rough limit indicated, one has to have recourse to buffers.

A further consideration indicated the need for work in this direction. As we shall see in Part VI, the group of kinetic results assembled in Part II contains one finding of outstanding importance, *viz.*, that the second-order reaction is of zeroth order in aniline. This proves that a purely inorganic reaction of nitrous species is involved, which is of such a nature that it can become rate-controlling; and this in turn proves the nitrosation mechanism, just as, in the past, observations on nitration, and on chlorination, of zeroth order in what was being nitrated or chlorinated, established mechanisms of substitution by the nitronium ion and the chlorinium ion. Obviously it was important to demonstrate the zeroth order clearly, and, having in mind particularly the model provided by the previous demonstration concerning nitration,[1] we wished to exhibit zeroth-order diazotisation by having nitrous acid in constant excess and obtaining a rectilinear reaction–time curve, which should be the same for all sufficiently reactive amines, though this uniform simplicity should break down in a characteristic way as the reactivity of the amine is reduced. The difficulty of fulfilling this programme, by the technique of Part II, is that, in excess of perchloric acid, the nitrous acid is nearly all in non-ionised form, and the necessary excessive concentration of it, 0·01M or more, is so large as to render diazotisation too rapid for easy measurement. Now this difficulty can be overcome by carrying out diazotisations in solutions buffered at about pH 5. At this pH, most of the nitrous acid is in ionised form, with the result that a considerable stoicheiometric concentration involves only a small molecular concentration, wherefore, even with 0·01M stoicheiometric nitrous

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* Part II, preceding paper.

[1] Benford and Ingold, *J.*, 1938, 929; Hughes, Ingold, and Reed, *Nature*, 1946, **158**, 448; *J.*, **1950**, 2400.

acid, the rate of diazotisation can be kept down to easily measurable values. At the same time, by virtue of the buffering, the molecular concentration of nitrous acid remains a constant fraction of its stoicheiometric concentration, so that if the latter is in constant excess, the former is constant.

A decision to use buffers involves an investigation into the suitability of possible buffers. For we must expect that, in general, buffer anions will disturb diazotisation, and it is therefore necessary to ensure that any such disturbance does not upset what is to be demonstrated. Now a buffer anion might conceivably disturb diazotisation kinetics in either of two ways. First, it might catalyse the formation of that nitrosating entity which would have operated in its absence, and *a fortiori* operates also in its presence. Secondly, it might produce a new and more active nitrosating entity. The problem, then, is to choose a buffer which does not act in the second of these ways, or, to put it more practically, one which, even if it catalyses the measured reaction, does not otherwise change its kinetic form. The required conditions were found to be fulfilled by acetate and phthalate buffers. (They are not fulfilled by phosphate buffers, which have, uncircumspectly, been employed in related reactions by other workers—cf. Part VI.) Some further details of this ancillary investigation are given in section 4.

(1) *Diazotisation of Aniline: Kinetic Order with Respect to Aniline.*—When acetate and phthalate buffers are used near pH 5 and in 20-fold stoicheiometric excess of nitrous acid over amine, zeroth-order reaction–time curves have been obtained for aniline and for several other aromatic amines. Some data for aniline are recorded in Table 1, and the graphs obtained are shown in Fig. 1.

TABLE 1. *Diazotisation of aniline in aqueous buffers at 0°.*

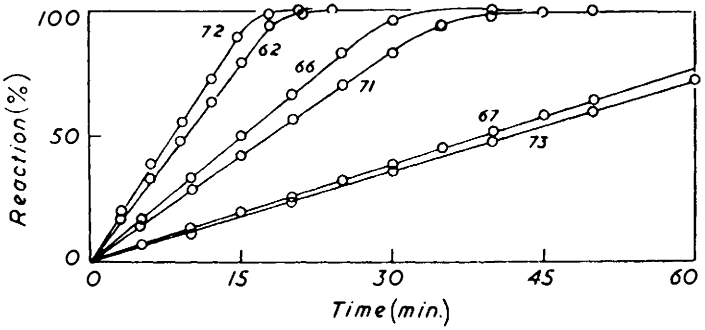
Initially added, $[Ph{\cdot}NH_3^+ClO_4^-] = 0{\cdot}0005$, $[NaNO_2] = 0{\cdot}01$, and either [sodium acetate + acetic acid] or [sodium potassium phthalate + potassium hydrogen phthalate] = 0·05M.

	Acetate buffer			Phthalate buffer		
Run	62	66	67	72	71	73
pH	4·63	4·77	5·02	4·80	5·00	5·20
Time (min.)	Reaction (%)					
3	16·0	—	—	19·8	—	—
5	—	16·8	—	—	14·6	6·4
6	33·2	—	—	38·2	—	—
9	47·8	—	—	56·2	—	—
10	—	33·4	12·0	—	28·8	13·0
12	63·4	—	—	73·0	—	—
15	78·8	50·0	—	88·6	42·0	20·0
18	92·8	—	—	98·6	—	—
20	—	66·0	24·2	—	56·8	26·2
21	99·8	—	—	100	—	—
24	100	—	—	100	—	—
25	—	82·8	—	—	70·4	33·4
27	—	—	—	—	—	—
30	—	95·2	36·4	—	83·0	39·0
35	—	—	—	—	93·0	45·8
40	—	100	47·2	—	97·0	52·2
45	—	—	—	—	99·2	58·8
50	—	—	59·2	—	99·2	64·2
60	—	—	70·4	—	—	—

It is clear that, over nearly the whole of these runs, the kinetic order in aniline is zero. A deviation occurs above 95% reaction, when the concentration of aniline is becoming very low. At pH 5, the aniline is present almost entirely in the form of free base, and at 95% reaction, both the stoicheiometric and (what really matters) the molecular concentration of aniline is approaching 10^{-5}M. We can understand the kinetic deviation in this region as the onset of transition from overall second-order to third-order kinetics (Part II). It is to be compared with what happens when, in the experiments on diazotisation in perchloric acid (Part II), we increase the excess of acid, thereby cutting down the concentration of molecular aniline. Here also the kinetic transition takes place when the concentration of molecular aniline becomes reduced to the order of magnitude 10^{-5}M.

(2) *Diazotisation of Aniline: Kinetic Order with Respect to Nitrous Acid.*—It is necessary to check the order in nitrous acid, and since nitrous acid is in constant excess, this has to be done by comparing one run with another. We can change the concentration of molecular nitrous acid from run to run by changing the pH, and keeping constant the stoicheiometric concentration of nitrous acid. In our pH range, a few units per cent. of the stoicheiometric nitrous acid are present in molecular form, and we change this percentage when we change the pH. The data for a test of this nature are in Table 1. Because of the specific effect of the buffer components, we must compare runs with the same buffer in the same concentrations, and such comparisons lead, as will be illustrated, to a kinetic order in molecular nitrous acid of approximately 2. However, this result alone would leave a sense of doubt, because, in changing the pH, we have to change the buffer ratio, and this might modify the specific kinetic effect of the buffer.

FIG. 1. *Zeroth-order reaction–time curves for the diazotisation of aniline with excess of nitrite in acetate or phthalate buffers at* pH 4·6—5·2. (*The figures against the curves are run numbers as in Table* 1.)



It seems a safer plan to vary the concentration of molecular nitrous acid by holding the pH constant and changing the stoicheiometric concentration of nitrous acid. A series of experiments have been conducted on these lines. In them the pH was buffered at 5·0 with 0·05M-phthalate buffer, and the concentration of initially added sodium nitrite was changed from run to run. The results are given in Table 2, along with those of the previously mentioned experiments in phthalate buffer in which the pH was changed and the concentration of added sodium nitrite was kept constant.

TABLE 2. *Dependence of zeroth-order rates* (*mole l.*$^{-1}$ *sec.*$^{-1}$) *of diazotisation of aniline in* 0·05M-*phthalate buffer at* 0° *on the concentration of molecular nitrous acid.*

Run	pH	Added $[NaNO_2]$ (10^{-3}M)	Added $[Ph{\cdot}NH_3^+ClO_4^-]$ (10^{-3}M)	Molecular $[HNO_2]$ * (10^{-3}M)	10^6k_0
73	4·8	10	0·5	0·138	0·108
71	5·0	,,	0·5	0·218	0·240
72	5·2	,,	0·5	0·340	0·530
82	5·0	5	0·1	0·109	0·061
94	,,	10	0·5	0·218	0·247
93	,,	13·3	0·5	0·290	0·325
95	,,	15·4	0·5	0·336	0·485

* Calculated by taking the acidity constant of nitrous acid to be 4·5 × 10^{-4} mole l.$^{-1}$.

When the sets of figures in the last two columns of Table 2 are plotted on a logarithmic scale, the points, no matter whether they are related through variations of pH, or through variations in the stoicheiometric concentration of nitrous acid, lie about a common straight line of slope 1·8, as is shown in Fig. 2. This slope represents the kinetic order with respect to nitrous acid.

The observed small defect below the integral kinetic order of two may be real, and may be the measure of one's failure to find buffers which would not produce specific nitrosating agents of reactivity appreciable in comparison with that of those nitrous species which effect nitrosation in the absence of buffers and are still of main importance in the buffers. If nitrosyl acetate or nitrosyl phthalate were to be formed, and were to become dominating nitrosating agents, the kinetic order in nitrous acid should fall to unity; and if such buffer-derived nitrosating agent were formed sufficiently quickly, the kinetic order in aniline should rise to unity. In fact, the order in aniline remains zero, and that in nitrous acid falls only a little below two. This shows that we are at least not changing the main nitrosating agent when we work in these particular buffers.

(3) *Diazotisation of Various Aromatic Amines.*—The kinetic order of zero with respect to aniline must mean that the aniline is reacting instantly with a slowly formed nitrosating agent. When we follow overall second-order diazotisation, we measure the purely inorganic process leading to this reagent. Therefore any amine which (*a*) is present in sufficient concentration, and (*b*) has a sufficient specific activity to take up the reagent as fast as it is produced, should react according to the same kinetic law, and at the same absolute rate, as aniline. This statement should hold generally for primary and secondary, aliphatic and aromatic, amines: indeed, it need not be confined to amines. In relation to the conditions of the present diazotisations in buffers, aromatic primary amines are in a simple position as regard supply, inasmuch as their molecular concentrations are practically equal to their stoicheiometric concentrations, which one may directly control and keep comparable. As regards specific reactivity, basic strength will serve as a qualitative guide. The pK_a values of the conjugate acids of the amines to be compared in this section, are given below:

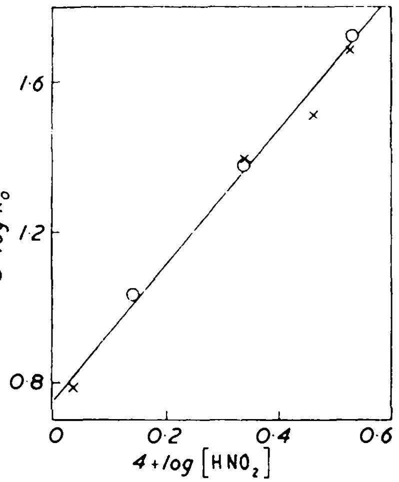


FIG. 2. *Logarithmic plot of the zeroth-order rate of diazotisation of aniline in phthalate buffers* versus *the concentration of molecular nitrous acid.*

○, *Points related by variation of* pH. × *Points related by variation in the stoicheiometric concentration of nitrous acid. The straight line has the slope* 1·8.

R in $R{\cdot}C_6H_4{\cdot}NH_2$	*p*-Me	*m*-Me	H	*o*-Me	*p*-Br	*m*-Br	*o*-Br
pK_a	5·07	4·69	4·58	4·39	3·94	3·51	2·60

The identity of diazotisation rate for aniline and the three toluidines is shown in Table 3. All these diazotisations follow the same reaction-time curve; and this common curve is a straight line up to 95% reaction, like the curves shown in Fig. 1. In these experiments, as in those of Table 1 and Fig. 1, the initial amine concentration was 0·0005M.

On going to successively weaker bases, we must expect sooner or later to reach a point at which this simple relation breaks down, because the aromatic amine is insufficiently reactive to take up the nitrosating agent as fast as the latter is formed. Such a point is reached when the pK_a value of the conjugate acid of the amine drops below about 4.

This is shown in the experiments recorded in Table 4. In these the initial amine concentration was lowered to 0·0001M, and because of this more restricted supply of amine, the linear law for aniline now holds up to about 75% reaction. However, the restricted supply brings into greater relief the effects of base-weakness, as seen in Fig. 3. *p*-Bromoaniline is diazotised appreciably more slowly than aniline, though one can only with difficulty in this case detect the incipient change of kinetic form. But *m*-bromoaniline, and still more *o*-bromoaniline, are diazotised much more slowly, and their reaction–time curves depart detectably from linearity, even up to 40—50% of reaction.

FIG. 3. *Reaction–time curves for the diazotisation of aniline and the three bromoanilines with excess of nitrite in a phthalate buffer at* pH 5.

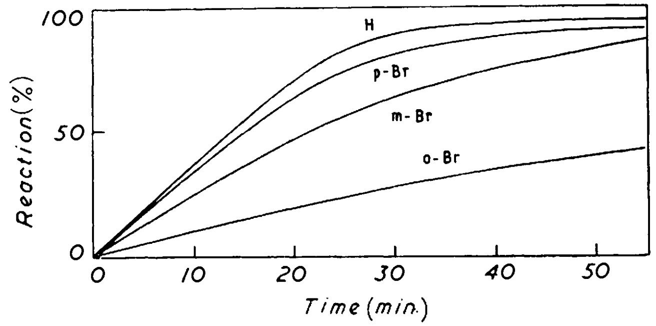


TABLE 3. *Illustrating the identical diazotisation rates of aromatic amines, having* pK_a *values greater than 4, in a* 0·05M-*phthalate buffer of* pH 5 *at* 0°.

(Initially added, $[Ar{\cdot}NH_3^+ClO_4]^-$ = 0·0005, and $[NaNO_2]$ = 0·01M throughout.)

Time (min.)	Reaction (%)			
	Run 71 Aniline	Run 76 *o*-Toluidine	Run 75 *m*-Toluidine	Run 74 *p*-Toluidine
5	14·6	14·8	14·4	14·4
10	28·8	29·4	29·6	28·4
15	42·0	44·0	43·0	42·8
20	56·8	57·2	57·4	56·8
25	70·4	70·6	70·6	70·4
30	83·0	82·4	82·6	82·8
35	93·0	92·6	93·8	93·8
40	97·0	98·8	99·0	99·0
45	99·2	100·0	100·0	100·2
50	99·2	99·8	99·8	99·8

TABLE 4. *Deviations from the common diazotisation rate, represented by that of aniline, shown by amines with* pK_a *values less than 4, in a* 0·05M-*phthalate buffer of* pH 5 *at* 0°.

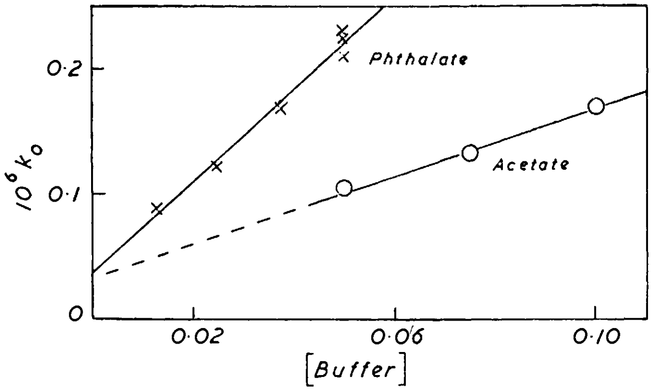
(Initially added, $[Ar{\cdot}NH_3^+ClO_4^-]$ = 0·0001 and $[NaNO_2]$ = 0·005M, throughout.)

Time (min.)	Reaction (%)			
	Run 82 Aniline	Run 83 *p*-Bromo-	Run 85 *m*-Bromo-	Run 84 *o*-Bromo-
5	18·1	17·1	12·8	—
10	36·8	34·2	25·0	9·1
15	53·5	50·8	36·4	—
20	69·5	64·0	46·6	17·4
25	80·5	74·0	56·0	—
30	88·0	80·5	63·5	25·8
35	91·5	84·0	69·5	—
40	91·5	87·5	74·2	32·6
45	92·5	89·5	78·4	—
50	94·0	90·0	82·4	40·0

The phenomenon under observation here is of the kind already known in aromatic nitration with excess of nitric acid: when the reactivity of the aromatic compound is progressively reduced, the previously coincident and rectilinear reaction–time curves (*a*) lose slope, (*b*) separate from one another, and (*c*) bend, as a reaction of zeroth order in the aromatic compound goes over into a reaction of first order.[1] The interpretation is the same in that case as in the present one of diazotisation. It is that a preliminary inorganic-chemical process is required to produce the effective agent, and that this process is just sufficiently slow enough for it to be rate-controlling or not, according to the reactivity of what is available to interact with the reagent formed.

(4) *Catalysis of Diazotisation by Buffer Components.*—Although the buffers here used do not change the kinetic order, either in the amine or in the nitrous acid, they do supply a catalysis. This is evident from the fact that, at the same pH, diazotisation in a phthalate buffer is faster than in an acetate buffer (cf. the curves for runs 67 and 73 in Fig. 1); and also from the fact that, in both these buffers, diazotisation is faster than it is in the absence of a buffer, but in perchloric acid of such low concentration as to produce the second-order reaction (Part II). Presumably the specific acceleration in buffers is due to catalysis by the buffer anion of the rate-controlling step of second-order diazotisation, or, in other words, catalysis of the formation of the same nitrosating agent as would have been effective in the absence of the buffer. A considerable fraction of the rate in the buffer solutions is due to such catalysis.

FIG. 4. *Catalysis by buffer components, at constant ionic strength, of the zeroth-order diazotisation of aniline at* 0° *by* 0·01M-*sodium nitrite at* pH 5.



It is not necessary to describe the routine examination for specific effects of all the buffers considered, but in Table 5 some data are recorded for the buffers used, because the figures allow rate-equations and rate-constants to be deduced for both the uncatalysed and the buffer-catalysed processes. Some of the figures are zeroth-order rates of diazotisation of aniline by nitrous acid in the constant stoicheiometric concentration 0·01M, in a series of acetate buffers, all at pH 5, but with various concentrations of buffer, yet all at the constant ionic strength 0·1M, made up as necessary by the addition of sodium perchlorate. The rest of the figures refer to similar experiments with phthalate buffers, also at pH 5, but with various buffer concentrations, and made up to an ionic strength of 0·1M by means of sodium perchlorate. This method standardises the general salt effect,

TABLE 5. *Zeroth-order rates* (*mole* $l.^{-1}$ $sec.^{-1}$) *of diazotisation of aniline by a constant excess of nitrous acid in buffers at* pH 5 *but in various concentrations and at* 0°.

Initially added, [$Ph{\cdot}NH_3^+ClO_4^-$] = 0·0005, and [$NaNO_2$] = 0·01M, in all runs. Acetate and phthalate buffers were made up with $NaClO_4$ to ionic strength 0·10M.

Acetate	[Buffer]	0·050		0·075	0·100		
	$10^6 k_0$	0·100	0·104	0·130	0·168		
Phthalate	[Buffer]	0·0125	0·0250	0·0375	0·0500		
	$10^6 k_0$	0·089	0·124	0·168	0·211	0·222	0·229

which is probably retarding, and isolates the specific accelerating effects of the buffer components.

As can be seen from the graphs of these results in Fig. 4, buffer catalysis is linear in buffer concentration. Neither the uncatalysed nor the catalysed part of the rate is negligible.

We have to combine this result with those reported in the preceding sections. It was there shown that, for the diazotisation of aniline, and of other primary aromatic amines of similar or greater basic strength, in carboxylate buffers at or near pH 5, the overall rate is of zeroth order in aromatic amine and of second order in nitrous acid. These findings must apply to both the uncatalysed and the catalysed part of the rate. Thus we can summarise the combined results of this paper in equations (1) and (2):

$$\text{Uncatalysed rate} = k_2''[\mathrm{HNO_2}]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{Catalysed Rate} = k_3^{\mathrm{OAcyl}}[\mathrm{OAcyl^-}][\mathrm{HNO_2}]^2 \quad . \quad . \quad . \quad . \quad (2)$$

In equation (2), the dependence of the catalysed rate on buffer is expressed in terms of buffer anion, because the alternatives of dependence on buffer acid can be excluded on the evidence of Parts II and IV. In Part II it was shown that in the diazotisation of aniline in much more strongly acid conditions than those of the present experiments, there is no appreciable acid catalysis. In Part IV it will be shown that hydrogen-ion catalysis in diazotisation can be observed, but only with amines considerably less basic than aniline, and only then provided that the concentration of nitrous acid is so reduced as to suppress kinetic forms dependent on its square. It is thus clear that, in the diazotisation of bases at least as strong as aniline, in the conditions of quadratic dependence of rate on nitrous acid, there is no substantial hydrogen-ion catalysis, and therefore, *a fortiori*, there can be no general acid catalysis.

We can compute the constants of equations (1) and (2). First, as to equation (1), the experiments in phthalate buffers were carried to sufficiently low buffer concentrations to justify an extrapolation to zero concentration of the buffer, though the relevant ionic strength will still be the common ionic strength in this series of experiments, *viz.*, 0·1M. The extrapolated zeroth-order rate is $0{\cdot}037 \times 10^{-6}$ mole $\mathrm{l.^{-1}}$ $\mathrm{sec.^{-1}}$. This figure applies to diazotisation by a concentration of molecular nitrous acid determined jointly by the stoicheiometric concentration of the nitrous acid and the pH. If we may take the acidity constant of nitrous acid as $4{\cdot}5 \times 10^{-4}$ mole $\mathrm{l.^{-1}}$, the concentration of molecular nitrous acid is calculated to be $0{\cdot}218 \times 10^{-3}$M. By dividing the zeroth-order constant by the square of this concentration, we obtain the second-order rate-constant k_2'' for diazotisation according to equation 1. The value is 0·78 $\mathrm{sec.^{-1}}$ $\mathrm{mole^{-1}}$ l. This applies to an ionic strength of 0·1M.

From the dependence on acid of the stoicheiometric second-order rate-constants, observed for diazotisation in small excesses of perchloric acid, it was computed in Part II, again on the assumption that the acidity constant for nitrous acid may be taken as $4{\cdot}5 \times 10^{-4}$ mole $\mathrm{l.^{-1}}$, that the molecular second-order rate-constant k_2'' is close to 0·85 $\mathrm{sec.^{-1}}$ $\mathrm{mole^{-1}}$ l. This applies to low ionic strengths. The agreement with the constant deduced by extrapolation from rates in buffers is satisfactory.

In order to obtain the values of the constant k_3^{OAcyl} of equation (2), we have to divide the slopes of the curves in Fig. 4, first by the mole-fraction of anion in the acetate buffer, or of bivalent anion in the phthalate buffer, and then by the square of the concentration of molecular nitrous acid, calculated as before. The result for acetate ion is 38 $\mathrm{sec.^{-1}}$ $\mathrm{mole^{-2}}$ $\mathrm{l.^2}$; and for phthalate ion it is 160 $\mathrm{sec.^{-1}}$ $\mathrm{mole^{-2}}$ $\mathrm{l.^2}$.

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