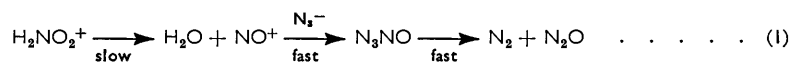


342. Mechanism of the Azide-Nitrite Reaction. Part IV.<sup>1</sup>

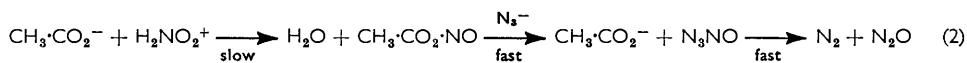
By G. STEDMAN.

Reaction between nitrous acid and hydrazoic acid in an acetate buffer occurred by two mechanisms. Nitrosyl acetate was formed by a nucleophilic attack by the acetate ion on the nitrous acidium ion, and then reacted either with the azide ion, to form nitrosyl azide, or with the nitrite ion, to form dinitrogen trioxide, which in turn either reacted with the azide ion, to form nitrosyl azide, or was hydrolysed. The rates of these processes were similar. The nitrosyl azide subsequently rapidly decomposed to nitrogen and nitrous oxide. The rate of formation of nitrosyl acetate was found from the rate variation with azide concentration by extrapolation; it was similar to the rate of other substitutions by anions at the nitrous acidium ion. The mechanism of the diazotisation of aniline in acetate buffers was studied. An explanation of reported apparently contradictory results for this reaction is suggested.

THE present investigation was commenced in order to explain a discrepancy between some results reported by Seel and Schwaebel<sup>2</sup> in a study of the kinetics of the azide-nitrite reaction in acetate buffers, and the work of Hughes, Ingold, and Ridd<sup>3</sup> on the diazotisation of aromatic amines in mildly acidic media. Seel and Schwaebel reported that the rate equation was of the form  $v \propto [H^+][HNO_2]$  and they interpreted this as showing a rate-determining formation of the nitrosonium ion:



Hughes, Ingold, and Ridd, on the other hand, were unable to find any evidence for nitrosation by the nitrosonium ion in acetate buffers, or in mildly acidic aqueous media (pH > 2). Bunton, Llewellyn, and Stedman<sup>4</sup> showed that Seel and Schwaebel's results could also be interpreted as a rate-determining formation of nitrosyl acetate:



A number of authors<sup>5-7</sup> have studied the kinetics of reactions of nitrous acid in solutions buffered with acetate or phosphate, and have interpreted their results in terms of mechanisms involving the nitrosonium ion as an intermediate in mildly acidic conditions. Hughes, Ingold, and Ridd showed that the nature and concentration of carboxylate buffers can have a profound effect on the kinetics and mechanism of reactions of nitrous acid. It was therefore essential to study first the mechanism of reaction in the absence of such buffers. Thus previous papers in this series were devoted to a study of the azide-nitrite reaction in excess of perchloric acid,<sup>8</sup> and in azide buffers.<sup>9</sup> The present paper describes an extension of this work to a system containing an acetate buffer.

## EXPERIMENTAL

*Materials.*—Buffers were made from stock solutions of "AnalaR" acetic acid and sodium acetate. Aniline was purified by distillation. Solutions of aniline perchlorate were prepared

<sup>1</sup> Part III, *J.*, 1959, 3466.

<sup>2</sup> Seel and Schwaebel, *Z. anorg. Chem.*, 1953, **274**, 169.

<sup>3</sup> Hughes, Ingold, and Ridd, *J.*, 1958, 58.

<sup>4</sup> Bunton, Llewellyn, and Stedman, *Chem. Soc. Spec. Publ.*, 1957, No. 10, p. 113.

<sup>5</sup> Anbar and Taube, *J. Amer. Chem. Soc.*, 1954, **76**, 6243.

<sup>6</sup> Dusenbury and Powell, *J. Amer. Chem. Soc.*, 1951, **73**, 2269.

<sup>7</sup> Edwards, Abbott, Ellison, and Nyberg, *J. Phys. Chem.*, 1959, **63**, 359.

<sup>8</sup> Stedman, *J.*, 1959, 2943.

<sup>9</sup> Stedman, *J.*, 1959, 2949.

by adding the calculated amount of standard perchloric acid to aniline. 3-Hydroxynaphthalene-2,7-disulphonic acid was purified by the method of Hughes *et al.*<sup>3</sup> Other materials used were as described in previous papers.

*Kinetic Runs.*—For the azide-nitrite reaction the procedure and analytical method were essentially the same as described earlier.<sup>8,9</sup> For the diazotisation of aniline the methods used were similar to those of Hughes *et al.*<sup>3</sup>

*Buffer Solutions.*—In many runs the quantity of sodium azide added was sufficient to affect significantly the pH of the buffer, by reaction to form undissociated hydrazoic acid. A calculated quantity of standard perchloric acid was always added with the azide, sufficient to correct for this disturbance.

*Calculation of Results.*—First-order rate constants were obtained from the initial slopes of plots of  $\log$  [nitrite] against time. For the diazotisation of aniline the reaction-time relation was linear, and the slope gave the rate of reaction directly. The value of  $[H^+]$  was calculated from the buffer composition, a value of  $1.65 \times 10^{-5}$  being used for the dissociation constant of acetic acid at  $0^\circ$ .<sup>10</sup> The values of  $[HN_3]$  and  $[N_3^-]$  were calculated from the total azide concentration, the value of  $[H^+]$  was calculated as above, a value for the dissociation constant of hydrazoic acid of  $1.0 \times 10^{-5}$  mole l.<sup>-1</sup> being used.  $[HNO_2]$  and  $[NO_2^-]$  were calculated by using a dissociation constant of nitrous acid of  $3.2 \times 10^{-4}$  mole l.<sup>-1</sup>.<sup>11</sup>

In this paper the term [nitrite] means stoichiometric nitrite concentration, *i.e.*,  $[\text{nitrite}] = [HNO_2] + [NO_2^-]$ ; similarly  $[\text{azide}] = [HN_3] + [N_3^-]$ .

## RESULTS AND DISCUSSION

Preliminary experiments indicated that, with azide and nitrite concentrations of approximately 0.002M, and 0.1M-acetate buffer, the rate of reaction was of first order in nitrite and between zero and first order in azide. This is consistent with Seel and Schwaebel's<sup>2</sup> results. The non-integral dependence on azide concentration made it difficult to calculate rate constants. The procedure used was to calculate initial first-order rate constants with respect to nitrite; these were then compared for a series of runs in which only one factor was varied. This is essentially a comparison of initial rates of reaction, but it is more convenient to use this procedure than to determine initial rates of reaction directly.

The order with respect to nitrite was determined from a series of experiments in which buffer and azide concentrations were kept constant, and only the initial nitrite concentration was varied. The results are given in Table 1. The initial first-order rate constant with respect to nitrite does not vary with the initial nitrite concentration; clearly reaction is of first order in nitrite.

TABLE I. *Effect of nitrite concentration on the rate of the azide-nitrite reaction at  $0^\circ$ .*

$10^3[CH_3 \cdot CO_2H]$ (M) .....	5.90	5.90	12.6	12.6	12.6	23.6	23.6
$10^3[CH_3 \cdot CO_2^-]$ (M) .....	13.2	13.2	6.54	6.54	6.54	6.54	6.54
$10^3[\text{azide}]$ (M) .....	5.45	5.45	5.45	5.45	5.45	2.73	2.73
$10^3[\text{nitrite}]$ (M) .....	1.60	6.40	0.80	1.60	6.40	1.60	6.40
$10^3k_1$ (sec. <sup>-1</sup> ) .....	4.13	3.87	35.3	37.2	35.0	80.5	80.8

The order with respect to azide was determined from experiments in which the buffer and nitrite concentrations were kept constant, and only the azide concentration was varied. The results are given in Table 2. The rate increases with azide concentration, but the rate of increase with azide is much less than corresponds to a first-order law. A value of the "order" with respect to azide was obtained from the slope of a plot of  $\log k_1$  against  $\log$  [azide]; the values ranged from *ca.* 0.2 to *ca.* 0.5. These values have only an approximate quantitative significance, because for the experiments listed in the third column of Table 2, the plot of  $\log k_1$  against  $\log$  [azide] was slightly curved, while for the experiments listed in the second column, the graph showed a very pronounced curvature.

<sup>10</sup> Harned and Ehlers, *J. Amer. Chem. Soc.*, 1932, **54**, 1350.

<sup>11</sup> Klemmens and Hayek, *Monatsh.*, 1929, **54**—**55**, 407.

TABLE 2. Effect of azide concentration on the rate of the azide-nitrite reaction in acetate buffers at 0°.

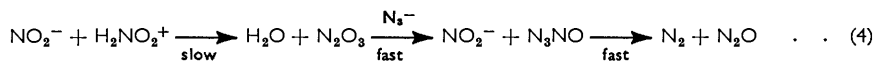
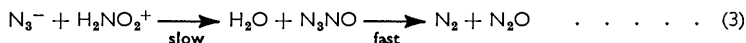
$10^2[\text{CH}_3\cdot\text{CO}_2\text{H}]$ (M):	2.95	5.90	12.6	23.6
$10^2[\text{CH}_3\cdot\text{CO}_2^-]$ (M):	6.82	6.82	6.54	6.82
$10^3[\text{azide}]$ (M)	$10^5k_1$	$10^5k_1$	$10^5k_1$	$10^5k_1$
0.545	1.12	4.29	—	42.2
0.682	—	—	15.8	—
1.36	1.65	5.92	21.6	58.5
		4.87		
2.05	—	—	24.3	—
2.73	2.02	6.98	27.3	80.5
		6.93		
3.41	—	—	32.3	—
5.45	2.10	—	37.2	—
6.82	2.15	8.28	—	102.5
		7.83		
$10^5k_a$ :	0.613	2.09	7.73	20.8

$k_a[\text{nitrite}] = d[\text{N}_2\text{O}_3]/dt$ , see page 1706.  
 $k_1$  and  $k_a$  in  $\text{sec}^{-1}$ ;  $[\text{nitrate}] = 0.0016\text{M}$  in all experiments.

TABLE 3. Effect of buffer concentration on the rate of azide-nitrite reaction in acetate buffers at 0°.

$10^2[\text{CH}_3\cdot\text{CO}_2\text{H}]$ (M)	$10^2[\text{CH}_3\cdot\text{CO}_2^-]$ (M)	$10^3[\text{azide}]$ (M)	$10^3[\text{nitrite}]$ (M)	$10^5k_1$ ( $\text{sec}^{-1}$ )
2.95	6.82	6.82	1.60	2.15
5.90	13.64	6.82	1.60	3.77
2.95	6.82	5.45	1.60	2.10
5.90	13.64	5.45	1.60	4.13
2.95	3.41	2.73	1.60	3.7
5.90	6.82	2.73	1.60	6.93
5.90	6.82	2.73	1.60	6.98
11.8	13.6	2.73	1.60	12.7
12.6	6.54	5.45	1.60	37.2
25.3	13.1	5.45	1.60	69.0
11.8	3.41	2.73	1.60	45.2
23.6	6.82	2.73	1.60	80.5

The effect of buffer concentration on the rate of reaction at constant azide and nitrite concentrations was investigated in a series of experiments summarised in Table 3. The rate is approximately proportional to the acetate buffer concentration, although there is a small component of the rate equation that is independent of buffer concentration. This is very probably due to a small part of the reaction occurring by mechanisms (3) and (4):

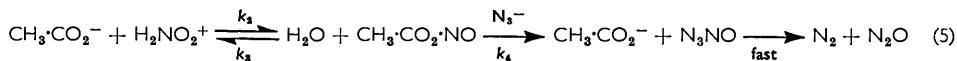


Previous work on the kinetics of the azide-nitrite reaction in excess of perchloric acid has shown the existence of these mechanisms.<sup>8,9</sup>

It is not possible to determine the dependence of the reaction rate upon acidity by directly comparing the results from different buffers, because the order with respect to azide varies with acidity. The reason for this is that the reactive azide species is the ion  $\text{N}_3^-$ , and it is the value of  $[\text{N}_3^-]$  that determines the order with respect to azide. In the acetate buffers, the values of  $[\text{N}_3^-]$  and  $[\text{HN}_3]$  were comparable, and solutions with the same value of  $[\text{azide}]$  and different values of  $[\text{H}^+]$  therefore had different values of  $[\text{N}_3^-]$ . Values of  $k_1$  corresponding to  $[\text{N}_3^-] = 0.5, 1.0, 1.25,$  and  $2.5 \times 10^{-3}\text{M}$  were obtained by interpolation. Fig. 1 shows a typical graph of  $\log k_1$  against  $\log [\text{H}^+]$ . The slopes obtained were 2.1, 2.1, 2.2, and 2.0. Clearly the rate is proportional to the square of  $[\text{H}^+]$ .

The complete rate equation is thus  $v \propto [\text{H}^+]^2[\text{CH}_3\cdot\text{CO}_2^-][\text{NO}_2^-][\text{N}_3^-]^x$ , where  $0 < x < 1$ ; this can be rewritten as  $v \propto [\text{H}^+][\text{HNO}_2][\text{CH}_3\cdot\text{CO}_2^-][\text{N}_3^-]^x$ . This expression

ignores the small term in the full rate equation which is independent of buffer concentration. A mechanism that is consistent with this rate equation is given by:



In the most alkaline buffer, the value of  $[\text{N}_3^-]$  was sufficiently high for  $k_4[\text{N}_3^-]$  to be much greater than  $k_3[\text{H}_2\text{O}]$ . In this case nearly all the nitrosyl acetate molecules formed react to give nitrosyl azide, and very few are hydrolysed back to the initial reactants. The rate of reaction is then the rate of formation of nitrosyl acetate, and is of zero order in azide, *i.e.*,  $x = 0$ . In the more acid buffers the concentration of the azide ion was lower, and the ions were not able to compete so effectively with the solvent for nitrosyl acetate.

FIG. 1. Dependence of rate of the azide-nitrite reaction upon acidity. Values interpolated for  $[\text{N}_3^-] = 5 \times 10^{-4}\text{M}$ .  $[\text{CH}_3\cdot\text{CO}_2^-] = 6.82 \times 10^{-2}$ .

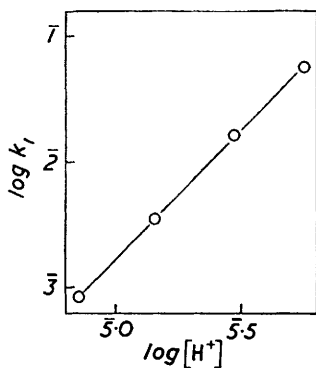
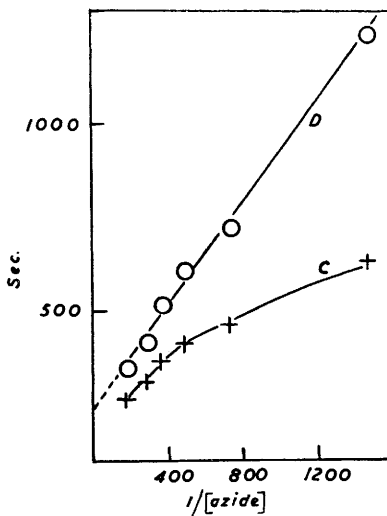


FIG. 2. Dependence of the rate of the azide-nitrite reaction upon azide concentration (runs 8-14, Table 2).  $[\text{H}^+] = 3.2 \times 10^{-5}\text{M}$ .



C.  $1/k_1$  against  $1/[\text{azide}]$ .  
D.  $1/(k_1 - k_2)$  against  $1/[\text{azide}]$ .

Under these conditions, the order of reaction, with respect to azide, rises from nearly zero to a higher value between zero and one.

The above mechanism is believed to be correct so far as it goes, but it is inadequate to explain all of the results. If the steady-state treatment is applied to the mechanism in reaction (5), the rate equation takes the form:

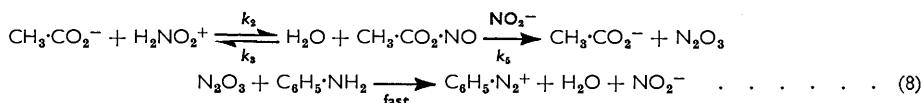
$$v = k_2[\text{H}^+][\text{HNO}_2][\text{CH}_3\cdot\text{CO}_2^-] \cdot \frac{k_4[\text{N}_3^-]}{k_4[\text{N}_3^-] + k_3[\text{H}_2\text{O}]} \quad (6)$$

This can be rearranged to:

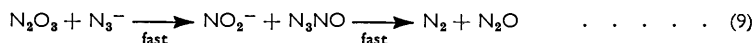
$$\frac{1}{v} = \frac{1}{k_2[\text{H}^+][\text{HNO}_2][\text{CH}_3\cdot\text{CO}_2^-]} + \frac{k_3[\text{H}_2\text{O}]}{k_2[\text{H}^+][\text{HNO}_2][\text{CH}_3\cdot\text{CO}_2^-] \times k_4[\text{N}_3^-]} \quad (7)$$

A plot of the reciprocal of the initial rate against the reciprocal of the azide-ion concentration should be linear, with a positive intercept on the  $1/[\text{azide}] = 0$  axis. (This holds at constant buffer concentration, acidity, and stoichiometric nitrite concentration.) When the results in Table 2 are plotted in this manner, curves are obtained, and not straight lines (see graph C, Fig. 2).

The explanation of this is that there is another reaction mechanism that is also important. Hughes, Ingold, and Ridd<sup>3</sup> showed that the formation of dinitrogen trioxide from nitrous acid is strongly catalysed by acetate buffers:



Previous work showed that at a very low concentration, *ca.*  $10^{-7}\text{M}$ , azide ions can compete on equal terms with water for dinitrogen trioxide, the products being nitrosyl azide, nitrite ions, and molecular nitrous acid. In the present work, the concentration of azide ions was far above this critical value, so that every molecule of dinitrogen trioxide formed by mechanism (8) would react to form nitrosyl azide:



A number of kinetic runs on the diazotisation of aniline was carried out. The conditions were identical with those used in the experiments on the azide-nitrite reaction, save that the azide was replaced by aniline perchlorate. The results, discussed in detail later, show that the rate of formation of dinitrogen trioxide by (8) varies from 15 to 50% of the total rate of the azide-nitrite reaction. Equation (7) makes no allowance for this important reaction path, and hence is inadequate, the plot of  $1/k_1$  against  $1/[\text{N}_3^-]$  being curved. It is possible to allow for this additional reaction path by replacing  $1/k_1$  by  $1/(k_1 - k_a)$ , where  $k_a[\text{nitrite}] = d[\text{N}_2\text{O}_3]/dt$ . There is then a linear relation between  $1/(k_1 - k_a)$  and  $1/[\text{N}_3^-]$ . Values of  $k_a$  are given at the bottom of Table 2, and they can be compared with the corresponding values of  $k_1$ , the initial first-order rate constant for the total azide-nitrite reaction. Graph *D* in Fig. 2 is a plot of  $1/(k_1 - k_a)$  against  $1/[\text{N}_3^-]$  for runs 8-14, and it can be seen that this gives a much better fit to the results than does a plot of  $1/k_1$  against  $1/[\text{N}_3^-]$  (graph *C*). In correcting the total rate of the azide-nitrite reaction for reaction *via* dinitrogen trioxide, it is necessary to express both rates in the same form; the total rate has been expressed as a first-order rate constant,  $k_1$ , and so, therefore, the rate of dinitrogen trioxide formation has been expressed as  $k_a$ , which, from the definition above, is a formal first-order rate constant. We might equally well have expressed each as an instantaneous rate, and have obtained a similar dependence upon azide-ion concentration. The dependence of rate upon azide-ion concentration can be deduced as follows.

Using the steady-state treatment we can write the rate equation for the total reaction as eqn. (11):

$$v = k_2[\text{H}^+][\text{HNO}_2][\text{CH}_3\cdot\text{CO}_2^-] \frac{(k_4[\text{N}_3^-] + k_5[\text{NO}_2^-])}{(k_3[\text{H}_2\text{O}] + k_4[\text{N}_3^-] + k_5[\text{NO}_2^-])} \quad \dots \quad (10)$$

If the dissociation constant of nitrous acid is  $K_{\text{HNO}_2}$ , then

$$[\text{nitrite}] = [\text{HNO}_2] + [\text{NO}_2^-] = [\text{HNO}_2](1 + K_{\text{HNO}_2}/[\text{H}^+]) \quad \dots \quad (11)$$

On substitution and rearrangement, it follows that eqn. (10) is equivalent to eqn. (12):

$$\frac{v}{[\text{nitrite}]} = k_1 = \frac{k_2[\text{H}^+]^2[\text{CH}_3\cdot\text{CO}_2^-]}{([\text{H}^+] + K_{\text{HNO}_2})} \cdot \frac{(k_4[\text{N}_3^-] + k_5[\text{NO}_2^-])}{(k_3[\text{H}_2\text{O}] + k_4[\text{N}_3^-] + k_5[\text{NO}_2^-])} \quad (12)$$

Similarly, for the formation of dinitrogen trioxide by mechanism (8), it can be shown that the rate equation is given by eqn. (13):

$$\frac{v}{[\text{nitrite}]} = k_a = \frac{k_2[\text{H}^+]^2[\text{CH}_3\cdot\text{CO}_2^-]}{([\text{H}^+] + K_{\text{HNO}_2})} \cdot \frac{k_5[\text{NO}_2^-]}{(k_3[\text{H}_2\text{O}] + k_5[\text{NO}_2^-])} \quad \dots \quad (13)$$

From eqns. (12) and (13) it can be shown that:

$$\frac{1}{k_1 - k_a} = \frac{([H^+] + K_{HNO_2})}{k_2[H^+]^2[CH_3 \cdot CO_2^-]} \cdot \frac{(k_3[H_2O] + k_5[NO_2^-])}{k_3[H_2O]} \cdot \left(1 + \frac{k_3[H_2O] + k_5[NO_2^-]}{k_4[N_3^-]}\right) \quad (14)$$

For a given acidity, buffer concentration, and stoichiometric concentration of nitrite, a plot of  $1/(k_1 - k_a)$  against  $1/[N_3^-]$  should be linear, with a positive intercept on the  $1/[N_3^-] = 0$  axis. Graph *D* in Fig. 2 shows that a relation of this type fits the exceptional results satisfactorily.

The above treatment takes no account of reaction occurring by the non-buffer-catalysed paths (3) and (4). The fact that the rate of the azide-nitrite reaction in acetate buffer is nearly proportional to the buffer concentration shows that the total rate of reactions (3) + (4) is small compared to the buffer-catalysed rate, and hence these reactions have been neglected in this work. It is a little surprising that, as an appreciable fraction of the azide-nitrite reaction proceeds *via* dinitrogen trioxide as an intermediate, the order of the total reaction, with respect to nitrite, is not slightly greater than unity. No sign of such an effect was found.

*The Rate of Formation of Nitrosyl Acetate.*—In the above experiments, the rate of reaction was always less than the rate of formation of nitrosyl acetate, because there was not a sufficiently high concentration of azide ion to trap effectively all the nitrosyl acetate formed; some was hydrolysed back to nitrous and acetic acid. To obtain the rate of formation of nitrosyl acetate it is necessary to extrapolate the results to a much higher concentration of azide ion. This could not be realised experimentally, without adding so much azide that the nature of the buffer was changed. The linear relation between  $1/(k_1 - k_a)$  and  $1/[N_3^-]$  enables this extrapolation to infinite azide concentration, *i.e.*,  $1/[N_3^-] = 0$ , to be made. A second estimate can be obtained by extrapolating a graph of  $1/k_1$  against  $1/[N_3^-]$  to  $1/[N_3^-] = 0$ . Although the graph is curved, it approximates to a straight line as  $1/[N_3^-]$  tends to zero, and a fairly reliable extrapolation can be made.

TABLE 4. Rate constants for the formation of nitrosyl acetate at 0°.

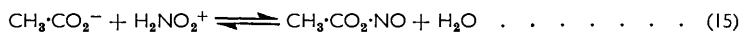
$10^2[CH_3 \cdot CO_2H]$ (M) .....	2.95	5.90	12.6	23.6
$10^2[CH_3 \cdot CO_2^-]$ (M) .....	6.82	6.82	6.54	6.82
$k_a$ , I .....	2230	2150	2750	2220
$k_a$ , II .....	2193	2149	2534	2137

$k_a$  in mole<sup>-2</sup> l.<sup>2</sup> sec.<sup>-1</sup>; values in row I were obtained by extrapolation of  $1/(k_1 - k_a)$  against  $1/[N_3^-]$  to  $1/[N_3^-] = 0$ . Values in row II were obtained by extrapolation of  $1/k_1$  against  $1/[N_3^-]$  to  $1/[N_3^-] = 0$ . [Nitrite] = 0.0016M in all experiments.

The values obtained by the two methods are given in Table 4. They are in good agreement. The rate constant  $k_2$  is defined by the equation:

$$\text{Rate of formation of nitrosyl acetate} = k_2[H^+][HNO_2][CH_3 \cdot CO_2^-].$$

It is of interest to compare this result with those of other workers. Bunton, Llewellyn, and Stedman<sup>4</sup> reported preliminary studies on the exchange of oxygen atoms between nitrous acid and water in acetate buffers. Their results suggest that exchange is of first order in nitrite, consistently with the idea that it occurs by the formation and hydrolysis of nitrosyl acetate:

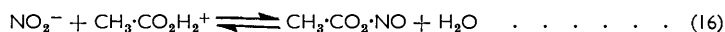


A more detailed study by Bunton and Masui<sup>12</sup> confirms this early result. The numerical value of the rate constant  $k_2$  is in satisfactory agreement with the values of the rate constants for the attack of nucleophilic anions on the nitrous acidium ion, obtained from other

<sup>12</sup> Bunton and Masui, personal communication.

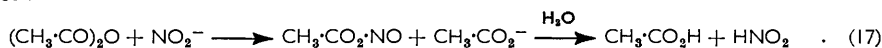
kinetic studies. The chloride, bromide, thiocyanate, iodide, nitrite, and azide ions all substitute at the nitrous acidium ion to form the corresponding nitrosyl compounds with rate constants varying from 975 to 2340 mole<sup>-2</sup>l.<sup>2</sup>sec.<sup>-1</sup>. The value for the acetate ion falls within this range. Because the calculated value of  $k_2$  depends upon the dissociation constant of nitrous acid, and on the value of  $[H^+]$ , which was calculated from the buffer composition and the dissociation constant of acetic acid, there is some uncertainty about its absolute numerical value. For this reason it is not possible to decide where the acetate ion fits into the reactivity sequence of the other anions.

These conclusions differ somewhat from those recorded by Seel, Wölffe, and Zwarg<sup>13</sup> in a recent paper, in which the earlier theory of Seel and Schwaebel appears to have been abandoned, *i.e.*, that the azide-nitrite reaction in acetate buffers occurs *via* the nitrosonium ion as an intermediate. The view is now apparently accepted that nitrosyl acetate is involved. However, they state that acetate buffers have an extraordinarily large catalytic effect on the rate of the azide-nitrite reaction, which they consider to be much too large to be accounted for by mechanism (5) alone. They suggest an additional mechanism for the formation of nitrosyl acetate:



The present results show that the rate of formation of nitrosyl acetate, by attack of a nucleophilic anion on the nitrous acidium ion, is very similar to the rates of formation of other nitrosyl compounds, and is in no way abnormally high. Bunton, Llewellyn, and Stedman have shown, by oxygen-18 tracer experiments, that there is no exchange of oxygen atoms between acetic acid and water in the presence of nitrous acid. Thus, in the hydrolysis of nitrosyl acetate bond fission must occur between the acetate and nitroso-groups, and not between the acetyl and nitrite groups. Thus, for mechanism (16) we may conclude, from the principle of microscopic reversibility, that in nitrosyl acetate only the oxygen of the terminal nitroso-group comes from the nitrite ion, and that the other oxygen atoms in nitrosyl acetate are those in the original acetic acidium ion. In this case mechanism (16) differs from that used in the present paper, (5), only in the positions assigned to the mobile protons, and it is difficult to see how a distinction could be made experimentally.

Saville and Lees<sup>14</sup> have reported a study of the nitrite-catalysed solvolysis of acetic anhydride in aqueous acetone, and interpret their results in terms of nitrosyl acetate as an intermediate:



They could find no evidence for bond fission between the acetyl and nitrite groups by a nucleophilic attack of the acetate ion on nitrosyl acetate to re-form acetic anhydride, *i.e.*, the reverse of the first step in mechanism (17).

*The Diazotisation of Aniline in Acetate Buffers.*—A number of experiments were carried out on the diazotisation of aniline in acetate buffers. These have some bearing on the interpretation of similar investigations by Hughes, Ingold, and Ridd,<sup>3</sup> and by Edwards *et al.*<sup>7</sup> The results are given in Table 5.

Hughes, Ingold, and Ridd showed that in phthalate buffers (0.05M) and with low concentrations of nitrite (0.005—0.015M), the diazotisation of aniline (0.0005M) was a reaction of second order in nitrite, and of zero order in aniline. Similar results were obtained for diazotisation in acetate buffers, but in this case Hughes *et al.* did not specifically establish the order of reaction with respect to nitrite by varying the initial concentration of nitrite. Edwards and his co-workers found that under similar conditions, but with higher concentrations (0.01—0.08M) of nitrite, reaction was of first order in nitrite and of zero order in

<sup>13</sup> Seel, Wölffe, and Zwarg, *Z. Naturforsch.*, 1958, **13b**, 136.

<sup>14</sup> Saville and Lees, *J.*, 1958, 2262.

amine. A comparison of runs 21 and 22, 26 and 35, 48 and 49, given in Table 5, shows that in acetate buffers, and under conditions similar to those used by Hughes, Ingold, and Ridd, reaction is indeed of second order in nitrite. The exact order obtained is 1.8. The

TABLE 5. *Diazotisation of aniline in acetate buffers at 0°.*

Run	$10^2[\text{CH}_3\cdot\text{CO}_2\text{H}]$ (M)	$10^2[\text{CH}_3\cdot\text{CO}_2^-]$ (M)	$10^3[\text{Nitrite}]$ (M)	$10^4[\text{C}_6\text{H}_5\cdot\text{NH}_2\cdot\text{HClO}_4]$ (M)	$10^8v_0$
21	12.6	6.54	1.60	1.17	12.4
22	12.6	6.54	0.533	1.17	1.65
26	5.90	6.82	1.60	2.34	3.34
35	5.90	6.82	0.533	2.34	0.478
48	23.6	6.82	1.60	2.34	33.3
49	23.6	6.82	0.533	2.34	4.51
34	2.95	6.82	1.60	2.34	0.98

$v_0$  is the initial rate in mole  $\text{l}^{-1} \text{sec}^{-1}$ .

different result obtained by Edwards *et al.* appears to be associated with their use of a much higher concentration of nitrite ion. It is suggested that Edwards *et al.* used a sufficiently high concentration of nitrite ion to trap nearly every molecule of nitrosyl acetate formed, and to convert it into dinitrogen trioxide, which then diazotised aniline in a further fast step. This means that  $k_5[\text{NO}_2^-] \gg k_3[\text{H}_2\text{O}]$  [see mechanism (8)], and that the rate of diazotisation is the rate of formation of nitrosyl acetate. To confirm this explanation it would be desirable to carry out parallel studies of the diazotisation of aniline, and of the azide-nitrite reaction over a wide range of azide, nitrite, amine, and buffer concentrations, so that the rates of the two reactions could be compared under identical conditions. Such a comparison cannot be made from the present results and those in the literature.

When the results of the present studies on the azide-nitrite reaction and the diazotisation of aniline are compared, it is found that the rate of diazotisation is an appreciable fraction of the corresponding rate of formation of nitrosyl acetate. For diazotisation, the order with respect to nitrite was 1.8, while in phthalate buffers, under similar conditions, the order was 1.7.<sup>3</sup> This suggests that, even with concentrations of nitrite ion as low as 0.0005M,  $k_5[\text{NO}_2^-]$  is of comparable magnitude to  $k_3[\text{H}_2\text{O}]$ , and that an appreciable fraction of the nitrosyl acetate molecules formed are converted into dinitrogen trioxide, so that nitrosyl acetate is not formed in a true pre-equilibrium. These conclusions underline the complexity of the reaction mechanisms of nitrous acid in carboxylate buffers, and show that great care is needed in the interpretation of the results.