25. *Kinetics and Mechanism of the Decomposition of Hyponitrous Acid. Part II.*[1]

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The kinetics of decomposition of hyponitrous acid in perchloric acid at 70° have been investigated. The rate is of first order in hyponitrous acid. Reaction occurs by two mechanisms; in one the first-order rate constant is independent of acidity, while in the second it is proportional to h_0. Under some conditions decomposition by a free-radical mechanism occurs. The mechanism of these reactions is discussed briefly.

IN a previous paper [1] it was shown that decomposition of hyponitrous acid in the range pH 5—13 occurs by heterolysis of the hydrogen hyponitrite ion $^-ON{:}N{\cdot}OH \longrightarrow N_2O + OH^-$. The p$K_a$ values of hyponitrous acid are approximately 7 and 11, so decomposition by this mechanism should be very slow in solutions more acid than pH 3. Partington and Shah [2] have, however, reported that at 50° solutions of sodium hyponitrite in 3M-sulphuric, -nitric, or -hydrochloric acid decompose to form mixtures of nitrogen, nitrous oxide, and nitric oxide. It therefore seemed likely that there were additional mechanisms for the decomposition of hyponitrous acid, and the kinetic studies were extended to higher acidities. Recently, after the present work was completed, Powell and Buchholz [3] reported a detailed study of the mechanism of decomposition of hyponitrous acid: their results are referred to below.

RESULTS

Kinetics.—Preliminary experiments showed that at low acidities (pH 1) hyponitrous acid decomposed slowly at room temperature and it was necessary to raise the temperature to 70° for the rate of reaction to be conveniently measurable. At constant acidity, and with hyponitrous acid concentrations 10^{-2}—10^{-3}M, the rate equation was $-d[H_2N_2O_2]/dt = k_1[H_2N_2O_2]$. In a typical run, with $[H_2N_2O_2]_0 = 4{\cdot}2 \times 10^{-3}$M, $[H^+] = 1{\cdot}24$M, and $[NaClO_4] = 2{\cdot}26$M, successive half-lives were 51, 53, and 52 min., respectively. In a group of runs in 1·24M-perchloric acid with $10^3[H_2N_2O_2]_0 = 1{\cdot}35$, 1·53, 6·00, and 10·0M, values of 10^4k_1 were 1·65, 1·62, 1·70, and 1·63 sec.$^{-1}$, respectively. The reaction is acid-catalysed, and values of k_1 were measured at several acidities up to 4·5M-perchloric acid. The effect of added sodium perchlorate was investigated at several different acid concentrations. The results are summarised in the Table and the Figure. It is clear that the rate equation is made up of two terms, one independent of

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[1] Part I, Hughes and Stedman, *J.*, 1963, 1239.

[2] Partington and Shah, *J.*, 1931, 2071.

[3] Powell and Buchholz, *J. Amer. Chem. Soc.*, 1963, **85**, 509.

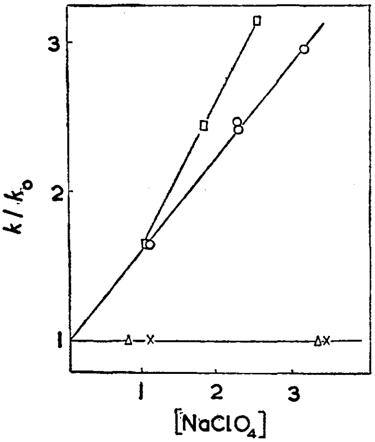
acidity, and the other involving acid-catalysis. The rate constant for the former, k_2, is the limiting value of k_1 obtained by extrapolation to $[H^+] = 0$. The rate constant for the latter, k_3, is given by $k_1 - k_2$. Clearly k_3 increases with acidity.

First-order rate constants for the decomposition of hyponitrous acid at 70°.

$[H^+]$ (M)	0·12	0·41	1·24	2·30	3·36	4·45
10^4k_1 (sec.$^{-1}$) *	1·26	1·32	1·63	2·69	4·54	9·54
10^4k_3 (sec.$^{-1}$) †	—	—	0·37	1·43	3·28	8·28
10^4k_4 (sec.$^{-1}$) ‡	1·26	1·34	2·32	2·96 §	4·99	9·54

* These values are each the mean of 3—5 runs. † $k_3 = k_1 - 1{\cdot}26 \times 10^{-4}$ sec.$^{-1}$. ‡ Values of k_1 corrected to an ionic strength of 4·45M. § Interpolated for $[H^+] = 2{\cdot}15$M.

Results of Powell and Buchholz.—It is convenient to consider at this point some results recently reported by Powell and Buchholz on the kinetics of decomposition of hyponitrous acid. They found that at 25° " the decomposition in solutions more acid than pH 5 is highly erratic. Some preparations decomposed rapidly, others slowly; upon occasions the decomposition would proceed slowly for hours, then suddenly so fast that it was complete in a few minutes." These authors found that the erratic reaction was completely suppressed by a small amount of ethanol. Whenever the erratic reaction occurred the products contained a large proportion of nitrogen and nitrate ion. In the absence of the erratic reaction the products were 99·9% nitrous oxide. These observations lead Powell and Buchholz to suggest that the erratic reaction was due to a free-radical mechanism, and that in its absence the stoicheiometry is



Salt effects upon the rate of decomposition of hyponitrous acid.

k_2 values: ×, $[H^+] = 0{\cdot}12$; Δ, $[H^+] = 0{\cdot}41$.
k_3 values: ○, $[H^+] = 1{\cdot}35$; □, $[H^+] = 2{\cdot}15$.

$$H_2N_2O_2 \longrightarrow N_2O + H_2O \qquad (1)$$

This provides a reasonable explanation of the observations of Partington and Shah.

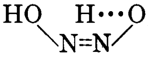
In our kinetic studies we found little interference from this free-radical mechanism. The results fell into two classes. Most of the runs (~90%) gave good plots for first-order rates over 2—3 half-lives, and the values of k_1 were constant over a ten-fold change in initial hyponitrous acid concentration. The same rates were obtained with several preparations of sodium hyponitrite. In a very limited number of runs, mostly at 25°, reaction occurred much faster than expected, and in these cases decomposition was often complete by the time the first sample was taken. It seems likely that this was due to the free-radical mechanism. For the runs at 70° very few difficulties of this type were experienced. The reason why this mechanism was of only minor significance in our work, whereas it seems to have been much more important for Buchholz and Powell, is not known.

DISCUSSION

As the rate equation is made up of two terms, one of which is independent of acidity and the other of which involves acid-catalysis, there are thus at least two mechanisms concerned. This is confirmed by the salt effects, shown graphically. At low acidities where the rate equation is $v = k_2[H_2N_2O_2]$, the addition of up to 3·5M-sodium perchlorate does not affect the rate. At higher acidities, where acid-catalysis is important, addition of M-sodium perchlorate markedly increases the rate.

Non-acid-catalysed Reaction.—The value of k_2 at 70° is $1{\cdot}26 \times 10^{-4}$ sec.$^{-1}$, in good agreement with the figure of $1{\cdot}4 \times 10^{-4}$ sec.$^{-1}$ that can be calculated from Buchholz and Powell's values for $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ for the same rate law. The very small salt effect indicates that the initial and the transition state have almost the same polarity. A likely reaction mechanism is:

$$trans\text{-HO}\cdot\text{N}{:}\text{N}\cdot\text{OH} \xrightarrow[\text{a}]{} cis\text{-HO}\cdot\text{N}{:}\text{N}\cdot\text{OH} \xrightarrow[\text{b}]{} N_2O + H_2O$$

Buchholz and Powell suggest, on the basis of a solvent isotope effect of $k(H_2O)/k(D_2O) = 1{\cdot}95$ and of the entropy of activation of $-5{\cdot}8$ e.u., that the transition state has the structure  and they ascribe the isotope effect to " the internal hydrogen transfer in *cis*-hyponitrous acid." This implies that the breakdown of *cis*-hyponitrous acid is the slow step, and hence that *cis*-hyponitrous acid has a certain stability. Now there is evidence from isotopic experiments on the nitrous acid–hydroxylamine reaction that *cis*-hyponitrous acid may occur as a transient intermediate,[4] and it has been suggested that the product of the empirical formula $(NaNO)_x$ obtained by treating sodium in liquid ammonia with nitric oxide contains sodium *cis*-hyponitrite, which is immediately hydrolysed in water.[5] However, there is no direct physical evidence for the existence of *cis*-hyponitrous acid in aqueous solution. We therefore think it more likely that the slow stage is the isomerisation, step (a), and that the breakdown of the *cis*-acid in step (b) is very fast.

Acid-catalysed Reaction.—The first-order rate constants for this mechanism, k_3, were obtained by subtracting $1{\cdot}26 \times 10^{-4}$ from the values of k_1 and are in the third line of the Table. They increase much more rapidly than $[H_3O^+]$. If the k_3 values are corrected to a constant ionic strength of 4·45M, the values in the fourth line of Table 1, k_4, are obtained. These also increase more rapidly than $[H_3O^+]$. A more satisfactory correlation is obtained by plotting log k_3 against H_0. This gives a straight line with a slope of 0·80. Powell and Buchholz found a similar result for sulphuric acid solutions. Bunnett [6] has suggested a plausible explanation for low slopes of this sort in terms of solvation of the transition state. The increase of rate with added sodium perchlorate is probably due to the salt effect upon H_0. Ridd and Challis [7] have shown that over the range 0·5—2·5M-perchloric acid the addition of one mole of sodium perchlorate per l. decreases H_0 by $\sim$0·25 unit. These salt effects, measured at 25°, are only slightly larger than the salt effects upon k_3 that we observe at 70°. The mechanism thus appears to be

$$H^+ + H_2N_2O_2 \underset{\text{Fast}}{\rightleftharpoons} H_3N_2O_2^+ \xrightarrow[\text{Slow}]{} N_2O + H_3O^+.$$

It is difficult to make a quantitative comparison between the present results and those of Powell and Buchholz because they investigated the variation of rate with temperature in much more acid solutions. From their results one can calculate that k_3 in 4·45M-perchloric acid at 70° should be $\sim 5 \times 10^{-4}$ sec.$^{-1}$, compared with the observed value of $8{\cdot}3 \times 10^{-4}$ sec.$^{-1}$. The differences in conditions are such that it is doubtful whether the difference in k_3 values is significant.

EXPERIMENTAL

Materials.—Sodium hyponitrite was prepared as described in Part I. Other chemicals were " AnalaR " materials.

[4] Hughes and Stedman, *J.*, 1963, 2824.

[5] Polydoropoulos and Watson, *Chimica Chronika*, 1961, **26***A*, 77.

[6] Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956.

[7] Ridd and Challis, *J.*, 1962, 5208.

Kinetic Measurements.—Solutions were made up from sodium hyponitrite and perchloric acid. Samples were removed at suitable time intervals, and reaction was stopped by addition to an excess of cold sodium hydroxide solution. The concentration of sodium hyponitrite was estimated spectrophotometrically from the peak at 2480 Å.

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