231. *Kinetics and Mechanism of the Decomposition of Hyponitrous Acid.*

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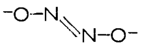
The kinetics of the decomposition of hyponitrous acid to nitrous oxide and water have been studied over the range pH 1—12·4 at several temperatures. The rate is of first order in hyponitrite and has a maximum at pH 9. The mechanism appears to be a unimolecular heterolysis of the (hydrogen hyponitrite) ion to nitrous oxide and hydroxide ion. The spectra of hyponitrous acid and its conjugate base have been obtained, together with values for the acid dissociation constants of both species at two temperatures. The results show that the mechanism previously suggested for the decomposition of hyponitrous acid, *i.e.*, the dehydration of the free acid, is wrong.

ALTHOUGH hyponitrous acid has been known for many years [1] there has been comparatively little work on its properties.[2] The sodium salt $Na_2N_2O_2$ can be made by the reduction of sodium nitrite with sodium amalgam.[3] The anion has the *trans*-structure (I).[4] The *cis*-form is not known.[5] Acidification of solutions of sodium hyponitrite produces hyponitrous acid, $H_2N_2O_2$. This is a weak acid with $pK_1 = 7$ and $pK_2 = 11$.[6] The acid is commonly supposed to be unstable.



(I)

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

Abel and Proisl [7] studied the decomposition in sodium hydroxide solution, and interpreted their results as showing that the rate-determining step in the decomposition is scheme (1). By assuming that $K_1 = 10^{-7}$, one can calculate that the first-order rate constant for scheme (1) is about 200 min.$^{-1}$ at 25°. Clearly hyponitrous acid should be very unstable. Abel and Proisl also calculated a value of 13 for pK_2 from the variation of rate with pH, two units higher than the value from indicator measurements.

However, Kortum and Finch [8] claim to have observed the absorption spectrum of hyponitrous acid in water, and Audrieth [9] to have isolated hyponitrite from a decomposing solution of hydroxylamine nitrite. This clearly suggests that hyponitrous acid is quite stable. The fact that the pK_1 value can be measured colorimetrically,[6] and that the free acid can be isolated as a white solid, point in the same direction.[2] Our interest in hyponitrous acid as a possible reaction intermediate [10] has led us to re-investigate the mechanism of its decomposition.

Spectra.—The spectra of dilute solutions of sodium hyponitrite have been measured in the range pH 1—13. The spectrum varies with pH, owing to the ionisation equilibria involving $H_2N_2O_2$, $HN_2O_2^-$, and $N_2O_2^{2-}$. In alkaline solutions, pH > 12, the spectra show a peak at 2480 Å ($\varepsilon = 3980$). This is characteristic of the anion $N_2O_2^{2-}$, and is in good agreement with previous work.[3]

In the pH range 12—10 the maximum shifts from 2480 Å to 2330 Å, and the intensity falls from $\varepsilon = 3980$ to $\varepsilon = 3310$. These values remain unchanged down to pH 8. We believe the peak at 2330 Å to be due to $HN_2O_2^-$, the spectrum of which does not seem to have been reported previously. The pH range 12—10 brackets the second pK_a value of

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[1] Divers, *Proc. Roy. Soc.*, 1871, **19**, 425.
[2] Mellor, " Inorganic and Theoretical Chemistry," Longmans, New York, 1928, Vol. 8, p. 404.
[3] Addison, Gamlen, and Thompson, *J.*, 1952, 338.
[4] Millen, Polydoropoulos, and Watson, *J.*, 1960, 687.
[5] Polydoropoulos and Watson, *Chimica Chronika*, 1961, **26***A*, 77.
[6] Latimer and Zimmerman, *J. Amer. Chem. Soc.*, 1939, **61**, 1550.
[7] Abel and Proisl, *Monatsh.*, 1938, **72**, 1.
[8] Kortum and Finckh, *Z. phys. Chem.*, 1941, *B*, **48**, 42.
[9] Audrieth, *J. Phys. Chem.*, 1930, **34**, 538.
[10] Bothner-By and Friedman, *J. Chem. Phys.*, 1952, **20**, 459.

hyponitrous acid, as expected. In more acid solutions, from pH 7·8 to 5 the intensity of the peak at 2330 Å falls, while a new peak appears at 2085 Å. Below pH 5 the spectra show only the peak at 2085 Å, $\varepsilon = 2740$, with a point of inflexion at 2425 Å, $\varepsilon = 122$. This new peak we identify as being due to hyponitrous acid. The pH range in which it appears brackets the first pK_a value for hyponitrous acid. Part of the spectrum has previously been reported by Kortum who found the point of inflexion at 2447 Å, $\varepsilon = 102$.

In acid and alkaline solutions, where the hyponitrite was present as $H_2N_2O_2$ and $N_2O_2^{2-}$, respectively, the spectra were unchanged during a period of hours. In the intermediate pH regions the solutions were unstable, and from pH 8 to pH 10 the intensity of the maximum decreased by about 11% in 5 minutes at *ca.* 20°. The shape of the absorption spectrum remained unchanged and no new peak appeared. From the rate of decrease of optical density with time at constant concentration of hyponitrite it appeared that the rate was only slightly dependent on pH in the range 8—10, suggesting that the decomposition took place through $HN_2O_2^-$, and that $H_2N_2O_2$ was quite stable.

Stability of Hyponitrous Acid.—To check further on the stability of hyponitrous acid, solutions of the sodium salt in excess of perchloric acid (0·1M) were kept for up to 20 hours at 25°. The maximum decomposition observed was 24% (for 20 hours). We conclude that hyponitrous acid is reasonably stable at room temperature.

Products.—Previous workers [7] reported that the products of decomposition in alkaline solutions were nitrous oxide and water. We found that solutions in which hyponitrite had completely decomposed showed no residual absorption. The gas evolved was completely condensable in liquid air, and was not absorbed by alkali or cold acidified ferrous sulphate. It seems that there is no appreciable amount of nitrogen or nitric oxide contaminating the nitrous oxide,[11] as found by Partington and Shah under other conditions. This was confirmed by mass-spectrometric analysis.

Kinetics.—The kinetics of decomposition were of first order in hyponitrite under all conditions studied. In a typical run, pH 8·33, ionic strength 0·1, $[\text{hyp}]_0 = 9{\cdot}7 \times 10^{-4}$M, $T = 45°$, the first four half-lives were 1·40, 1·43, 1·42, and 1·48, min., respectively. In another run, pH 7·38, ionic strength 0·1, $[\text{hyp}]_0 = 2{\cdot}56 \times 10^{-2}$M, $T = 25°$, successive half-lives were 25·5 and 28·0 min. The rate varied with pH and showed a maximum at pH 9. The rate constant was independent of buffer concentration, and the points for phosphate and borate buffers all fell on a common curve. Most of the results are summarised in Table 1.

TABLE 1.

First-order rate constants for decomposition of hyponitrite at 25°.

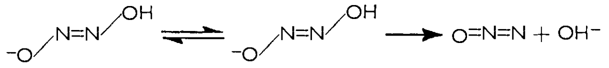
pH	10^4k_1	j	10^7K_1	pH	10^4k_1	j	$10^{11}K_2$
5·59	0·25	4·1	0·753	9·20	7·16	96·6	—
5·90	0·45	8·0	0·666	9·60	6·72	93·0	0·155
6·64	1·15	32·3	0·343	10·00	6·46	84·4	0·372
6·98	2·95	51·1	0·578	10·50	5·75	63·2	0·272
7·38	4·66	72·4	0·629	10·79	4·61	46·8	0·318
8·04	6·36	92·1	0·587	11·08	3·77	31·1	0·266
8·40	6·84	96·1	0·372	11·62	1·16	11·5	0·446
8·40	6·86 *	—	—	12·38	0·50	2·3	0·199
8·80	7·00	97·5	—				

k_1 in sec.$^{-1}$; $j = [HN_2O_2^-]/[\text{hyp}]$. * Half buffer concentration.

These results fit the rate equation $-d[\text{hyp}]/dt = k_*[HN_2O_2^-]$, where $[\text{hyp}] = [H_2N_2O_2] + [HN_2O_2^-] + [N_2O_2^{2-}]$. The mechanism appears to be a unimolecular heterolysis of the (hydrogen hyponitrite) ion. This reaction has been suggested by Latimer and Zimmerman,[6] but they did not present any kinetic evidence in its favour. There seems no reason to suppose that a solvent molecule is present in the transition state. Hyponitrites show no exchange of oxygen-18 with water in acid, alkaline, or neutral

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

conditions.[12] Nitrous oxide is linear, whereas the hyponitrite ion is bent. Presumably in the transition state the ONN angle is closer to 180°.


. . . . . (2)

The variation in rate with pH reflects the varying concentration of [$HN_2O_2^-$] which is in equilibrium with its conjugate acid and conjugate base. If we take the two pK values for hyponitrous acid to be 7·05 and 11 we can calculate the fraction of total hyponitrite present as $HN_2O_2^-$, at varying acidities. We call the ratio j. These figures are shown in the third and seventh columns in Table 1. The parallelism between [$HN_2O_2^-$]/[hyp] and k_1 is immediately obvious. Closer inspection of the figures shows that there are minor deviations. We ascribe this to either small errors in the literature values for K_1 and K_2, or to errors in the values taken for the activity coefficients of the three hyponitrite species.

A more satisfactory test is to calculate the values of K_1 and K_2 from the variation of k_1 with pH and observe the constancy of the values calculated at different pH's and to compare them with Latimer and Zimmerman's data. To do this we need to know the value of k_1, the rate constant for the heterolysis of the (hydrogen hyponitrite) ion by scheme (2). Below pH 8 the only hyponitrite species present in significant amount are $H_2N_2O_2$ and $HN_2O_2^-$ ([$N_2O_2^{2-}$]/[hyp] is less than 10^{-3}), and the rate of reaction is controlled by the equilibrium

$$H_2N_2O_2 \rightleftharpoons H^+ + HN_2O_2^-. \quad K_1 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

It can be shown that $1/k_1 = 1/k_* + [H^+]/K_1k_*$. A plot of $1/k_1$ against [H^+] gives a satisfactory straight line with an intercept of $1/k_* = 1380$ sec., $k_* = 7{\cdot}25 \times 10^{-4}$ sec.$^{-1}$. Similarly in the pH range above 10 the second ionisation,

$$HN_2O_2^- \rightleftharpoons H^+ + N_2O_2^{2-}, K_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

controls the value of [$HN_2O_2^-$], and hence the rate. It can be shown that here $1/k_1 = 1/k_* + K_2/k_*[H^+]$. A plot of this type can be extrapolated to $1/k_* = 1450$ sec., $k_* = 6{\cdot}89 \times 10^{-4}$ sec.$^{-1}$. A third value for k_* of $7{\cdot}24 \times 10^{-4}$ sec.$^{-1}$ can be obtained by multiplying the maximum value of k_1 (estimated to be $7{\cdot}1 \times 10^{-4}$ at pH 9) by 1·02, a correction factor for the small amount of ionisation to $H_2N_2O_2$ and $N_2O_2^{2-}$. This correction factor is calculated from the values of the ratio j in Table 1. The correction is small, so k_* calculated in this way is not very sensitive to errors in K_1 and K_2. We take a mean value of $7{\cdot}13 \times 10^{-4}$ sec.$^{-1}$ for k_*. K_1 and K_2 have been calculated on the assumptions that $k_1/k_* = [HN_2O_2^-]/[\text{hyp}]$ and $a_{H^+} = \text{antilog}\,(-\text{pH})$, and by use of activity coefficients calculated from the formula given by Davies.[14] The results are in the fourth and eighth columns of Table 1.

The values of K_1 are reasonably constant, with the exception of a single point at pH 6·64. The results for K_2 show more scatter, but there does not seem to be any trend with pH. In some cases the scatter is associated with the term $(k_* - k_1)$ which, in the range pH 8—10, is the small difference of two large numbers. The mean value of K_1 of $6{\cdot}1 \times 10^{-8}$ agrees satisfactorily with Latimer's value of $8{\cdot}9 \times 10^{-8}$. The mean value of K_2 of $2{\cdot}9 \times 10^{-12}$ is considerably lower than the published figure of 10^{-11}. In view of the activity-coefficient corrections that we have had to introduce, and the probable difficulties experienced by Latimer and Zimmerman in the colorimetric estimates of the pH of an unstable solution, we do not consider the difference between the two values to be significant.

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[12] Bigeleisen and Bonner, *J. Amer. Chem. Soc.*, 1952, **74**, 4944.
[13] "International Critical Tables," McGraw-Hill, New York, 1933, Vol. 1, p. 81.
[14] Davies, *J.*, 1938, 2093.

Effect of Temperature.—We have investigated the variation of rate with pH in some detail at 45° and more briefly at 15° and 35°. At pH > 9, we found that the pH values measured directly with a temperature-compensated pH-meter were rather lower than the literature values. At 25° there was good agreement between the two pH's. In our calculations we have used the literature values. The results are summarised in Table 2.

TABLE 2.

Variation of rate with temperature.

pH	$10^4 k_1$	pH	$10^4 k_1$	pH	$10^4 k_1$	pH	$10^4 k_1$
15°		45°		45°		45°	
6·98	0·66	5·59	6·91	7·79	83·2	9·45	83·2
8·50	1·74	5·90	9·54	7·89	80·4	9·40	80·7
		6·64	28·4	8·34	84·3	9·66	71·4
35°		6·92	46·0	8·40	84·7	9·78	72·8
6·98	11·7	7·17	58·5	8·52	84·4	10·56	50·2
8·50	25·3	7·34	64·8	8·70 *	84·9	11·0	28·8
				9·05	81·8	11·55	7·48

k_1 in sec.$^{-1}$; I, 0·1. * At $\frac{1}{3}$ buffer concentration.

The general pattern of results is clearly the same at 45° as at 25°. The maximum is shifted from pH 9 to 8·8. From the variation in rate K_1 and K_2 can be calculated to be $1{\cdot}2 \times 10^{-7}$ and $1{\cdot}25 \times 10^{-11}$. The measurements at 15° and 35° give K_1 values of $0{\cdot}48 \times 10^{-7}$ and $0{\cdot}67 \times 10^{-7}$, respectively. Latimer and Zimmerman [6] have calculated $\Delta H^\circ_{298\cdot2}$ for the complete ionisation of hyponitrous acid to be 11·1 kcal. mole^{-1}. Using values that they estimated for the entropy of hyponitrous acid and the (hydrogen hyponitrite) ion, one can calculate that $\Delta H^\circ_{298\cdot2}$ for the first and second ionisations, schemes (3) and (4), are 4·2 and 6·9 kcals. mole^{-1}, respectively. Our results for K_1 at 15°, 25°, and 35° show that for the first ionisation $\Delta H^\circ_{298\cdot2}$ is 3 ± 1 kcal. mole^{-1} and for the second ionisation (by difference) 8 ± 1 kcal. mole^{-1}. Within the limited accuracy of the present work, our results are consistent with those of Latimer and Zimmerman. If the temperature dependence of the rate is expressed in the form $k_* = (\boldsymbol{k}T/\boldsymbol{h})\exp(\Delta S/\boldsymbol{R})\exp(-\Delta H/\boldsymbol{R}T)$ then $\Delta S = 3{\cdot}0$ e.u. and $\Delta H = 22{,}670$ cal. mole^{-1}. The small value of ΔS is very reasonable for a unimolecular reaction.

Kinetics of Decomposition in Sodium Hydroxide Solutions.—We have briefly investigated the decomposition in excess of sodium hydroxide at 45°. The kinetics are of first order in hyponitrite and the rate decreases with increasing concentration of hydroxide. The results are summarised in Table 3.

TABLE 3.

Decomposition of hyponitrite in sodium hydroxide at 45°.

$10^2[OH^-]$ (M)	1	2	5	10	0·87	1·3	6·5	13·0
I	0·1	0·1	0·1	0·1	0·0087	0·013	0·065	0·13
$10^3 k_1$ (sec.$^{-1}$)	1·80	0·95	0·41	0·23	2·85	2·14	0·49	0·21
$10^{12} K_2$	8·3	8·8	8·7	8·0	7·7	7·5	6·4	7·8

The values of K_2 calculated from these results are satisfactorily constant for the first four experiments, done at constant ionic strength. The rather lower values in the last four results probably reflect errors in the values assumed for the activity coefficients of the bivalent ion $N_2O_2^{2-}$. The mean value of K_2 of $0{\cdot}79 \times 10^{-11}$ is rather lower than the value obtained from the experiments in borate and glycine buffers, but these were based on rather old literature values of pH. The difference corresponds to about 0·2 unit of pH. We do not think this has any mechanistic significance.

Salt Effects.—We have investigated the effect of a large concentration of added sodium chloride (1·67M) upon the rate at several values of pH, at 25°. The maximum still occurs at pH 9; but the value of k_1 drops from $7·1 \times 10^{-4}$ sec.$^{-1}$ to $6·5 \times 10^{-4}$ sec.$^{-1}$. This may reflect the somewhat greater spread of charge in the transition state, with a slightly larger value for the activity coefficient compared with that of the (hydrogen hyponitrite) anion.

Discussion of Abel's Work.—These results differ in both form and interpretation from those of Abel and Proisl.[7] They investigated the reaction at about 2·0M-sodium hydroxide and found a rate equation $v = k[\text{hyp}]/[\text{OH}^-](k' + [\text{OH}^-])$. Now above pH 12 one would expect, on the basis of our results, that the rate would be proportional to $[\text{OH}^-]^{-1}$. At these high ionic strengths, salt effects vary significantly with the nature of the electrolyte. If such a specific salt effect were superposed on this rate equation, the overall effect might be that the rate would vary inversely with $[\text{OH}^-]$ to a power appreciably greater than unity. This could easily be mistaken for the more complex rate equation suggested by Abel and Proisl and such a formulation would be very attractive in view of the very reasonable mechanism suggested to account for it. Whether or not this is the correct explanation, it is clear that Abel's mechanism is wrong. There is ample evidence from the present investigation that hyponitrous acid is quite stable in aqueous solution up to 45°.

EXPERIMENTAL

Materials.—Sodium hyponitrite was prepared by the method recommended by Addison.[3] The purity, based upon the ultraviolet spectrum and on permanganate titration, was better than 99%. The other materials were " AnalaR " chemicals.

Buffer Solution.—The buffer solutions used, phosphate, borate, and glycine, were made up according to literature specifications. pH's were checked with a Radiometer (Copenhagen), type T.T.T1 a, and with an E.I.L. instrument, model 23A.

At 25° the measured pH's were in good agreement with literature values.[13] At higher temperature, with borate buffers, the measured pH values were sometimes rather lower than literature values.

Kinetic Runs.—Standard methods were used in the kinetic runs. Reaction was started by adding either solid sodium hyponitrite, or a solution in alkali, to the appropriate volume of buffer solution. Samples were removed at regular intervals and run into excess of sodium hydroxide to convert all of the hyponitrite into stable $N_2O_2^{2-}$. The concentration was determined from the light absorption at 2480 Å, $\varepsilon = 3980$ being assumed. Some runs were carried out in a thermostatically controlled cell-holder and followed directly on a Unicam S.P. 500; these gave rate constants in good agreement with those obtained above. Rate constants were reproducible to within ±3%.

Spectrophotometric Measurements.—Complete spectra were run on an Optica C.F. 4 instrument. Optical density measurements needed for extinction coefficients were made on the Unicam S.P. 500 spectrometer.

Activity Coefficients.—These were calculated from the formulæ quoted by Davies.[14]

The authors are indebted to the D.S.I.R. for a grant (to M. N. H.), and to Dr. C. A. Bunton for mass-spectrometric analyses.

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[*Received, April 19th*, 1962.]