

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY 4, CALIF.]

The Decomposition of Hyponitrous Acid. I. The Non-chain Reaction<sup>1</sup>

BY JERRY R. BUCHHOLZ AND RICHARD E. POWELL

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With addition of a trace of ethanol to suppress a free-radical side reaction, the kinetics of decomposition of  $\text{H}_2\text{N}_2\text{O}_2$  to  $\text{N}_2\text{O}$  is reproducibly measurable over the range from  $\text{pH}$  14 to  $H_0 - 6$ . Four pathways are identified: one involving  $\text{HN}_2\text{O}_2^-$ , one  $\text{H}_2\text{N}_2\text{O}_2$  and two protonated  $\text{H}_2\text{N}_2\text{O}_2$ , the latter involving the activity of  $\text{H}_2\text{O}$  to different extents. Activation energies, salt effects and deuterium isotope effects are reported.

The previously published kinetic study of the decomposition of hyponitrous acid is that of Abel and Proisl.<sup>2</sup> On the basis of rate measurements at  $\text{pH}$  13–14, they concluded that the molecular species which decomposes is  $\text{H}_2\text{N}_2\text{O}_2$ . Their conclusion is, however, suspect on two counts: first, that they were forced to assume for the second ionization of hyponitrous acid  $\text{p}K_2 = 13.54$ , in serious disagreement with the directly measured value of  $11.0 \pm 0.1$  or  $10.8 \pm 0.1$ <sup>3a,b</sup>; and second, that their rate law would assign to dilute aqueous hyponitrous acid at room temperature a half-life of about one-tenth second, whereas such a solution is actually stable enough to permit calorimetric study.<sup>3a</sup> Accordingly, it appeared worthwhile to reinvestigate the reaction.

Preliminary experiments showed that the decomposition in solutions more acidic than  $\text{pH}$  5 is highly erratic. Some preparations decomposed rapidly, others slowly; upon occasion, the decomposition would proceed slowly for hours, then suddenly become so fast that it was complete in a few minutes. The same sort of behavior was noted by Latimer and Zimmermann<sup>3a</sup>: "A series of experiments disclosed, however, that at 25° a 0.1  $M$  solution was practically completely decomposed in one hour while a 0.01 or 0.001  $M$  solution did not change noticeably in two hours. The decomposition of the 0.1  $M$  solution was quite slow at first but became faster as time went on." We have observed that whenever the erratic reaction occurs, the products include a large proportion of  $\text{N}_2$  and  $\text{NO}_3^-$ ; and that the erratic reaction in 0.1  $M$  hyponitrous acid is suppressed completely by 0.05 to 1 mole % of acrylonitrile, allyl alcohol or even ethanol. These observations suggest that the erratic reaction is caused by a radical chain, whose initiating step is the homolytic fission of hyponitrous acid



In the present study the radical reaction was purposely suppressed by the addition of 0.1 mole % of ethanol to all runs more acidic than  $\text{pH}$  5. Analysis of the product gas (by freezing out  $\text{N}_2\text{O}$  and mass spectrometry of any residual gas) at  $\text{pH}$  9,  $\text{pH}$  1,  $H_0 - 2$  and  $H_0 - 5$  showed it to consist of at least 99.9%  $\text{N}_2\text{O}$  in all cases; nor did the solutions contain appreciable  $\text{NO}_3^-$ , since they were transparent to wave lengths less than 2100 Å. Accordingly, the stoichiometry of the decomposition under these conditions is at least 99.9%



## Experimental

Hyponitrite was prepared by essentially the method of Divers<sup>4</sup>:  $\text{NaNO}_2$  (Baker analyzed 98.8%) was reduced by sodium amalgam, prepared by dropping mercury onto heated sodium under a stream of dry nitrogen. The hyponitrite was precipitated as the silver salt, which was purified by dissolving in 6  $M$   $\text{NH}_4\text{OH}$  and reprecipitating with  $\text{HNO}_3$ , then dissolving in 2  $M$   $\text{HNO}_3$  and

reprecipitating with  $\text{NH}_4\text{OH}$ , all at ice temperature. *Anal.* Found: Ag, 77.86; N, 10.00. *Calcd.*: Ag, 78.24; N, 10.16. Excess of  $\text{Ag}_2\text{N}_2\text{O}_2$  was added to ice-cold dilute  $\text{HCl}$ , and after filtering off the silver chloride the  $\text{H}_2\text{N}_2\text{O}_2$  solution was made 0.5  $M$  in  $\text{NaOH}$  and stored at ice temperature until needed.

The rate of decomposition was followed by the decrease in ultraviolet absorption of hyponitrite, using a Beckman model DU spectrophotometer equipped with a thermostated copper block. Each run was made on a separate solution. In the highly alkaline region the wave length used was 2470 Å., the  $\lambda_{\text{max}}$  for  $\text{N}_2\text{O}_2^{--}$ ; in the  $\text{pH}$  range 7–11, 2320 Å., the  $\lambda_{\text{max}}$  for  $\text{HN}_2\text{O}_2^-$ ; and in acidic solutions, the lowest wave length obtainable with the instrument (around 2150 Å.), since the  $\lambda_{\text{max}}$  for  $\text{H}_2\text{N}_2\text{O}_2$  is 2070 Å. Reactions were usually followed for at least three half-lives, and all were clean first order.

The initial concentration of hyponitrous acid was  $10^{-4}$   $M$  for each run, the concentration of buffer approximately  $10^{-2}$   $M$ , and, except for those runs otherwise noted, enough  $\text{NaCl}$  was added to bring the ionic strength up to 1.0  $M$ . The reagents used for control of  $\text{pH}$  were:  $\text{pH}$  12–14,  $\text{NaOH}$ ;  $\text{pH}$  10–12,  $\text{K}_2\text{HPO}_4$  plus  $\text{NaOH}$ ;  $\text{pH}$  7–9,  $\text{H}_3\text{BO}_3$  plus  $\text{NaOH}$ ;  $\text{pH}$  4–7,  $\text{KH}_2\text{PO}_4$  plus  $\text{NaOH}$ ;  $\text{pH}$  0–3,  $\text{HClO}_4$ ; all  $\text{pH}$ 's were measured with a Beckman model H  $\text{pH}$  meter. In the  $H_0$  region  $\text{H}_2\text{SO}_4$  was used for all solutions, the  $H_0$  being calculated from the data of Long and Paul.<sup>5</sup> All solutions more acidic than  $\text{pH}$  5 contained 0.1 mole % ethanol; *vide supra*.

## Results and Discussion

The dependence of the rate on acidity, from  $\text{pH}$  14 to  $H_0 - 6$ , is shown in Fig. 1. These data can be analyzed conveniently by considering four regions of acidity, in each of which a separate mechanism of decomposition predominates: (a) In solutions more alkaline than  $\text{pH}$  4, decomposition of  $\text{HN}_2\text{O}_2^-$ ; (b) from  $\text{pH}$  4 to  $H_0 - 1$ , uncatalyzed decomposition of  $\text{H}_2\text{N}_2\text{O}_2$ ; (c) from  $H_0 - 1$  to  $-4$ , acid-catalyzed decomposition of  $\text{H}_2\text{N}_2\text{O}_2$ , dependent on the activity of  $\text{H}_2\text{O}$ ; and (d) in more acidic solutions than  $H_0 - 4$ , acid-catalyzed decomposition not dependent on the activity of  $\text{H}_2\text{O}$ .

The smooth curve of Fig. 1 is calculated from the corresponding four-term rate law

$$d \text{N}_2\text{O}/dt = k_a[\text{HN}_2\text{O}_2^-] + k_b[\text{H}_2\text{N}_2\text{O}_2] + \frac{k_c[\text{H}_2\text{N}_2\text{O}_2]k_0[\text{H}_2\text{O}]^2}{k_1 + [\text{H}^+]} + k_d[\text{H}_2\text{N}_2\text{O}_2]k_0$$

**Decomposition of the Anion.**—Between  $\text{pH}$  7.5 and 10.5, where the species  $\text{HN}_2\text{O}_2^-$  accounts for most of the hyponitrous acid in solution, the rate exhibits a plateau with  $k_a(25^\circ) = 5.0 \times 10^{-4} \text{ sec}^{-1}$  (half-life 23 minutes). In more acidic or more basic solutions, in which the population of  $\text{HN}_2\text{O}_2^-$  is depleted by the formation of  $\text{H}_2\text{N}_2\text{O}_2$  or  $\text{N}_2\text{O}_2^{--}$ , respectively, the observed rate follows closely the population of the species  $\text{HN}_2\text{O}_2^-$ ; the apparent rate constant is given by

$$\frac{k_a}{1 + \frac{[\text{H}^+]}{K_1} + \frac{K_2}{[\text{H}^+]}}$$

where our data are fitted by  $\text{p}K_1 = 6.75$  and  $\text{p}K_2 = 10.85$  at ionic strength 1.0  $M$ . These values are in satisfactory agreement with the literature<sup>3a,b</sup> values (at infinite dilution), namely,  $7.0 \pm 0.1$  and  $10.9 \pm 0.1$ , respectively.

No significant kinetic salt effect would be anticipated in the plateau region, since the activated complex has

(5) F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 1 (1957).

(1) Presented at the 142nd Natl. Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 14, 1962.

(2) E. Abel and J. Proisl, *Monatsh.*, **72**, 1 (1938).(3) (a) W. M. Latimer and H. W. Zimmermann, *J. Am. Chem. Soc.*, **61**, 1550 (1939); (b) C. N. Polydoropoulos, *Chim. Chronika*, **24**, 147 (1959).(4) E. Divers, *J. Chem. Soc.*, **75**, 95 (1899).

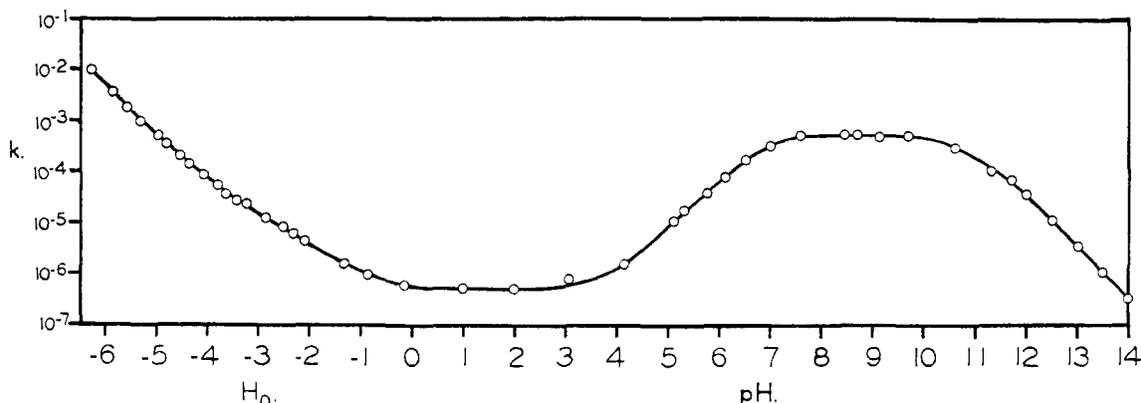


Fig. 1.—Decomposition of hyponitrous acid at 25°, as a function of acidity.

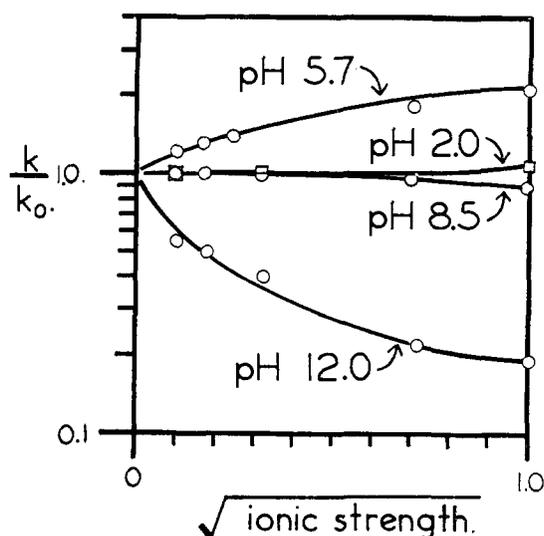


Fig. 2.—Salt effects on the decomposition of hyponitrous acid.

the same charge as the reactant; on the other hand, there ought to be a pronounced positive salt effect on the acid side of the plateau, and a negative effect on the basic side, because of the salt effects on the first and second ionizations of hyponitrous acid. These are in fact just the salt effects observed (Fig. 2). The magnitudes of the salt effects are approximately those expected on the basis of the activity coefficients of  $\text{N}_2\text{O}_2^{2-}$  and  $\text{HN}_2\text{O}_2^-$ , although here one can only proceed by analogy with activity coefficients of known salts, the activity coefficients of hyponitrites not having been measured.

It was on this point that Abel and Proisl went astray. They worked with 0.1  $M$  to 1  $M$  NaOH, without maintaining constant ionic strength or taking activity coefficients into account. Consequently, a negative salt effect was superimposed on the inverse-first power dependence on  $[\text{OH}^-]$  in this region, leading to a false result for the dependence of rate on  $p\text{H}$ .

**Decomposition of the Molecule.**—Between  $p\text{H}$  0 and  $p\text{H}$  3, where  $\text{H}_2\text{N}_2\text{O}_2$  is the principal species and neither the decomposition of  $\text{HN}_2\text{O}_2^-$  nor of protonated  $\text{H}_2\text{N}_2\text{O}_2$  contributes significantly to the rate, there is a plateau with  $k_b(25^\circ) = 4.9 \cdot 10^{-7} \text{ sec.}^{-1}$  (half-life 16 days). As this small rate of decomposition indicates, an aqueous solution of hyponitrous acid can be stored at this acidity for a number of days without extensive loss, provided the free-radical decomposition has been suppressed. There is no significant salt effect on the rate of decomposition of  $\text{H}_2\text{N}_2\text{O}_2$  (Fig. 2).

**Acid-catalyzed Decomposition.**—Over much of the  $H_0$  range, the curve of  $\log k$  vs.  $H_0$  has a slope consider-

ably less than unity. Bunnett<sup>6</sup> has examined a large number of such cases, interpreting them in terms of the number of additional water molecules implicated in the activated complex. Following Bunnett, we plot our data in the form  $\log k/h_0$  vs.  $\log a(\text{H}_2\text{O})$ ; Fig. 3. The

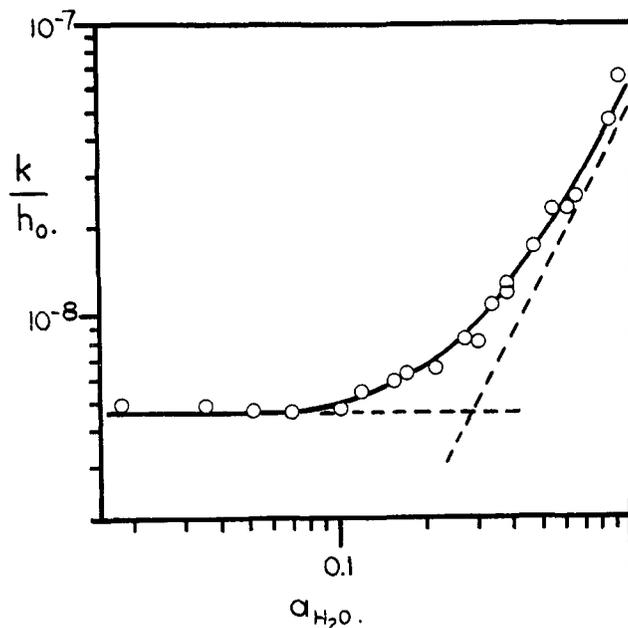


Fig. 3.—Bunnett plot for the decomposition of hyponitrous acid in the  $H_0$  region.

points fall well on a curve representing the sum of the two dotted lines in Fig. 3, the one at moderate acidities having a slope (Bunnett's  $w$ ) of 2, the one at high acidities a slope of zero. On a somewhat literal interpretation, these results indicate one mechanism in which a proton is transferred to 2 water molecules, plus another in which it is donated to solvent (presumably to  $\text{H}_2\text{SO}_4$ ) without the requirement of water molecules. The corresponding terms in the rate law are

$$k_c[\text{H}_2\text{N}_2\text{O}_2]h_0[a(\text{H}_2\text{O})]^2 + k_d[\text{H}_2\text{N}_2\text{O}_2]h_0$$

with  $k_c(25^\circ) = 1.67 \cdot 10^{-5}$  and  $k_d(25^\circ) = 6.4 \cdot 10^{-5} \text{ sec.}^{-1}$ .

At the time this work was completed, the authors were not aware of another instance of a reaction in which a pathway involving water molecules is superseded at high acidities, as the activity of water is reduced, by another pathway not involving water. Professor D. S. Noyce has kindly informed us that it has recently been observed<sup>7</sup> in the isomerization of *cis*-2-methoxychalcone.

(6) J. F. Bunnett, *J. Am. Chem. Soc.*, **83**, 4956, 4968, 4972 (1961).

(7) D. S. Noyce and M. J. Jorgenson, *ibid.*, **84**, 4312 (1962).

TABLE I  
 TEMPERATURE EFFECT ON DECOMPOSITION RATES OF HYPONITROUS ACID<sup>a,b</sup>

Temp., °C.	Raw $k$ , sec. <sup>-1</sup>		
18.6	$2.78 \times 10^{-4}$	$k_a = 2.78 \times 10^{-4}$	$pH\ 8.5\ \Delta H^\ddagger = 23.5 \pm 1.5\ \text{kcal.}$
25.3	6.42	6.42	$\Delta S^\ddagger = 6 \pm 5\ \text{e.u.}$
32.2	17.9	17.9	
39.9	44.6	44.6	
25.0	$5.01 \times 10^{-7}$	$k_b = 4.93 \times 10^{-7}$	$pH\ 2.05\ \Delta H^\ddagger = 24.7 \pm 0.2\ \text{kcal.}$
44.0	63.5	62.5	$\Delta S^\ddagger = -5.8 \pm 0.7\ \text{e.u.}$
60.0	448	441	
25.0	$3.72 \times 10^{-5}$	$k_c k_0 [a(\text{H}_2\text{O})]^2 = 1.67 \times 10^{-5}$	$H_0\ -3.65\ \Delta H^\ddagger = 22 \pm 2\ \text{kcal.}$
40.0	23.1	9.1	$\Delta S^\ddagger = -24 \pm 6\ \text{e.u.}$
55.0	136	54	
0.7	$0.665 \times 10^{-4}$	$k_d k_0 = 0.643 \times 10^{-4}$	$H_0\ -5.69\ \Delta H^\ddagger = 22.9 \pm 0.2\ \text{kcal.}$
25.0	17.7	17.1	$-5.57\ \Delta S^\ddagger = -21.2 \pm 0.7\ \text{e.u.}$
34.4	52.1	50.4	$-5.52$

<sup>a</sup>  $k_a$ ,  $k_b$ ,  $k_c$  and  $k_d$  have been calculated from the raw  $k$ -values by subtracting the contribution of pathways other than that under consideration. In calculating  $\Delta S^\ddagger$  for  $k_b$ ,  $k_c$  and  $k_d$ , the basis has been  $k/2$  in order to take into account the statistical factor of 2 in these pathways. <sup>b</sup> The experiments for determination of  $k_a$  were carried out at ionic strength 0.05  $M$ ; for  $k_b$ , at ionic strength 0.01  $M$ . Because of the comparatively small salt effect, these differ only slightly from the values at ionic strength 1.0  $M$ .

**Temperature Dependence.**—The data on the temperature dependence of the rate constants are collected in Table I.

**Deuterium Isotope Effect.**—The effects of carrying out the reaction in 99%  $\text{D}_2\text{O}$  are given in Table II.

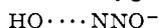
 TABLE II  
 RELATIVE RATES OF DECOMPOSITION OF HYPONITROUS ACID IN  $\text{D}_2\text{O}$  AND  $\text{H}_2\text{O}$ 

	$k(\text{D}_2\text{O})$	$k(\text{H}_2\text{O})$	$k(\text{H}_2\text{O})/k(\text{D}_2\text{O})$
$pH\ 8.5, 25^\circ$ , ionic strength 0.05 $M$	$4.96 \times 10^{-4}$	$6.42 \times 10^{-4}$	1.30
$pH\ 1, 60^\circ$ , ionic strength 0.1 $M$	$2.30 \times 10^{-5}$	$4.48 \times 10^{-5}$	1.95
45.2% $\text{D}_2\text{SO}_4$ vs. 47.3% $\text{H}_2\text{SO}_4, 25^\circ$ <sup>a</sup>	$1.13 \times 10^{-5}$	$1.62 \times 10^{-5}$	1.43
44.4% $\text{D}_2\text{SO}_4$ vs. 46.5% $\text{H}_2\text{SO}_4, 25^\circ$	$0.972 \times 10^{-5}$	$1.41 \times 10^{-5}$	1.45
63.8% $\text{D}_2\text{SO}_4$ vs. 65.7% $\text{H}_2\text{SO}_4, 25^\circ$	$4.76 \times 10^{-4}$	$6.75 \times 10^{-4}$	1.41
65.2% $\text{D}_2\text{SO}_4$ vs. 67.1% $\text{H}_2\text{SO}_4, 25^\circ$	$6.34 \times 10^{-4}$	$9.52 \times 10^{-4}$	1.50

<sup>a</sup> In comparing  $\text{D}_2\text{SO}_4$  with  $\text{H}_2\text{SO}_4$ , solutions of equal mole fractions are considered.

**Interpretation.**—Although the assignment of structures to activated complexes is naturally speculative, our observed rate laws and the associated salt, temperature and isotope effects do suggest certain plausible structures.

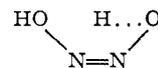
The decomposition of  $\text{HN}_2\text{O}_2^-$  probably takes place by the simple scission of the oxygen–nitrogen bond



since this would lead at once to the products  $\text{OH}^-$  and  $\text{N}_2\text{O}$ , and the observed  $\Delta S^\ddagger$  is reasonable for a unimolecular decomposition. The observed isotope effect can, no doubt, be rationalized *a posteriori* as a

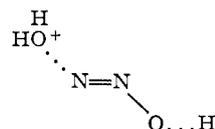
secondary or solvent effect; we are not, however, able to claim that it would have been predicted on the basis of current theory.<sup>8,9</sup>

In the decomposition of  $\text{H}_2\text{N}_2\text{O}_2$ , the isotope effect suggests that an  $\text{O} \cdots \text{H}$  bond is being broken in the activated complex, and the somewhat negative  $\Delta S^\ddagger$  suggest that it has a somewhat restricted geometrical structure. The internal hydrogen transfer in *cis*-hyponitrous acid would be consistent with these descriptions



the subsequent decomposition of the zwitterion  $\text{H}_2\text{O}^+ \cdots \text{NNO}^-$  being rapid. It is implausible that the fission of the zwitterion is itself the slow process, since this would be expected to have the opposite isotope effect and to have a salt effect considerably greater than that observed.<sup>10</sup>

The acid-catalyzed decompositions probably proceed as do acid-catalyzed enolizations, the addition of a proton to one end of the molecule facilitating the loss of a proton from the other



The observed  $H_0$  dependence, as well as that on  $a(\text{H}_2\text{O})$ , are typical of enolizations. The observed isotope effect, interpreted as a primary isotope effect on the leaving proton, partially compensated by the isotope effect of the catalyzing proton, is also consistent with this model.

(8) C. G. Swain and R. F. W. Bader, *Tetrahedron*, **10**, 182 (1960).

(9) C. A. Bunton and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **83**, 42, 3207, 3214 (1961).

(10) Cf. L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 974 (1940).