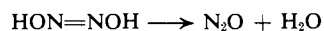# The Decomposition of Hyponitrous Acid.
II. The Chain Reaction

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Berkeley 4, California. Received January 22, 1965

The disproportionation of hyponitrous acid, $5HON=NOH \rightarrow 4N_2 + 2NO_3^- + 2H^+$, proceeds in two stages: in the first HNO_2 is produced; in the second HNO_2 is consumed. The second-stage reaction has a rate law of the form $(HON=NOH)(HNO_2)(k_1 + k_2h_0)$, corresponding to a nitrosation of hyponitrous acid. In view of the scavenging evidence for OH and NO_2, it is proposed that the O-nitrosation produces these ($HNO_2 + HON=NOH \rightarrow NO_2 + N_2 + OH + H_2O$) with subsequent chain-propagating steps involving them. The first-stage reaction is interpreted as an induced oxidation of hyponitrous acid by OH radicals resulting from the O-nitrosation. OH radicals alone are ineffective in the oxidative cleavage of hyponitrous acid, by comparison with their effectiveness in the presence of the ions of Cu, Ag, Tl, Hg, Co, Ni, or chloride, nitrate, or sulfate; such ions are suggested to act as oxidation transfer agents.

In an earlier paper,[1] we reported a kinetic study of the dehydration of hyponitrous acid to N_2O. Independently, and almost simultaneously, the same investigation was under way in the laboratories of Hughes and Stedman,[2] of Anderson,[3] and of Polydoropoulos and Pipinis.[4] The observations of the four groups of investigators are in quite satisfactory agreement.

$$HON=NOH \longrightarrow N_2O + H_2O$$

We noted[1] that we had to take the precaution of adding 0.1 mole % of ethanol to all acidic solutions if reproducible rate measurements were to be obtained. Otherwise, after an induction period of erratic length, a rapid decomposition reaction set in. Its products are, besides N_2O, nitrogen and nitrate ion in amounts corresponding to the disproportionation

$$5HON=NOH \longrightarrow 4N_2 + 2NO_3^- + 2H^+$$
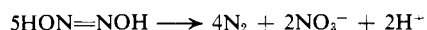
On account of the erratic induction period and the sensitivity to inhibition by traces of various organic compounds, we conjectured that the reaction is a chain reaction with radical-chain carriers. A more direct line of evidence is that decomposing hyponitrous acid solutions cause polymerization of added acrylonitrile and rather rapidly decolorize added diphenylpicrylhydrazyl.

The chemical nature of at least some of the chain carriers is demonstrated as follows. If benzene is added to a decomposing acidic solution of hyponitrous acid, the reaction becomes somewhat slower but does not stop. Both the aqueous layer and the benzene layer take on a yellow-brown color, which becomes red in alkaline solution (suggesting nitrophenols). Upon paper chromatography with 2-butanol saturated with 5 M NH_4OH as the moving phase,[5] the colored material is separated into five spots, of which the largest is yellow and has R_f 0.57, closely matching that of authentic specimens of nitrophenols. When the experiment is repeated on a larger scale, using a cellulose powder column, enough material is isolated from the yellow spot to permit its vacuum distillation at 10^{-4} mm.; the visible and ultraviolet spectra of the volatile material match those of o-nitrophenol; the spectra of the residue match those of p-nitrophenol, with a small shoulder possibly indicating a little m-nitrophenol. This formation of nitrophenols from benzene suggests that OH radicals and NO_2 are intermediates in the decomposition. Halfpenny and Robinson[6] found that peroxynitrous acid, presumably after homolytic fission into OH and NO_2, reacts with benzene to produce nitrophenols among other products.

Accordingly, in the interpretation of our kinetic data reported below, we have proposed a number of radical-chain sequences, including some which account for the presence of OH and of NO_2 in the reaction mixture.

Experimental

Hyponitrous acid solutions were prepared from $Na_2N_2O_2$, which was prepared by Addison's method.[7] This involves precipitating the $Na_2N_2O_2$ with ethanol, which was removed by keeping the sample at 10^{-5} mm. for a week or more.

The rate of reaction was measured in a Beckman Model DU spectrophotometer as previously described.[1] The concentrations of $H_2N_2O_2$, HNO_2, or NO_3^-, or all of these, were followed. Gas analysis was by gas chromatography with a silica gel column.

Results and Discussion

A. The Stoichiometric Sequence. As it turns out, the radical decomposition of $H_2N_2O_2$ will not take place at all unless there are present certain kinds of anions (e.g., Cl^-) or of cations (e.g., Cu^{2+}) in the solution; we return later to the question of their role. But even in solutions where they are present, the reaction proceeds in two stages as Figure 1 illustrates. In the early stage, which corresponds to the "induction period," HNO_2 is formed; and, in fact, the induction period can easily be wiped out by the initial addition of a little HNO_2. In the later stage, HNO_2 and $HON=NOH$ are disappearing simultaneously, with the formation of nitrate. The two stages of stoichiometry are

(1) J. R. Buchholz and R. E. Powell, J. Am. Chem. Soc., 85, 509 (1963).
(2) M. N. Hughes and G. Stedman, J. Chem. Soc., 1239 (1963); 163 (1964).
(3) J. H. Anderson, Analyst, 88, 494 (1963).
(4) C. N. Polydoropoulos and M. Pipinis, Z. physik. Chem. (Frankfurt), 40, 322 (1964).
(5) M. Lederer, Australian J. Sci., 11, 208 (1949).
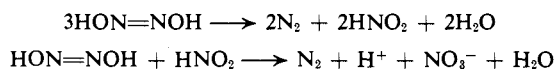(6) E. Halfpenny and P. L. Robinson, J. Chem. Soc., 928 (1952).
(7) C. A. Addison, C. A. Gamlen, and R. Thompson, ibid., 338 (1952).

$$3HON{=}NOH \longrightarrow 2N_2 + 2HNO_2 + 2H_2O$$

$$HON{=}NOH + HNO_2 \longrightarrow N_2 + H^+ + NO_3^- + H_2O$$

The over-all kinetics of the decomposition is therefore complex and does not correspond to a reaction of any simple kinetic order. However, the second stage can be studied in the absence of the first, using solutions of $H_2N_2O_2$ and HNO_2 from which Cu^{2+}, Ag^+, Hg^{2+}, Hg_2^{2+}, Ni^{2+}, and Co^{2+}, as well as Cl^-, NO_3^-, and SO_4^{2-}, have been excluded. Ordinary laboratory distilled water contains little enough of these metals so that it is satisfactory; distilled water de-ionized with a cation-
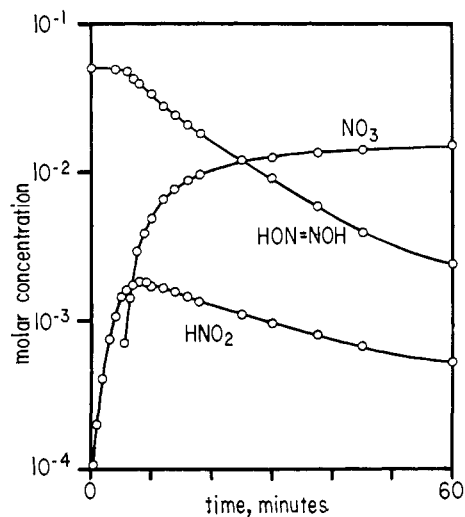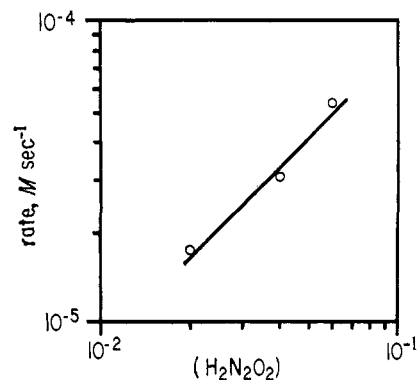
Figure 2. Initial rate as a function of initial hyponitrous acid concentration (25°, 0.04 M H_2SO_4, 0.004 M HNO_2).

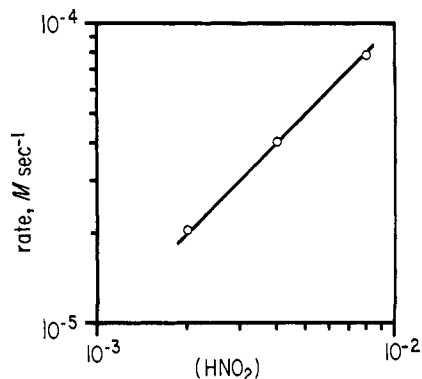Figure 3. Initial rate as a function of initial nitrous acid concentration (25°, 1 M H_2SO_4, 0.02 M $H_2N_2O_2$).

Figure 1. The course of decomposition of 0.05 M hyponitrous acid at 25° (H^+ 0.7 M, 2.0 M Cl^-).

exchange resin is somewhat better in suppressing the first-stage reaction, but the suspicion arises that traces of organic matter washed off the resin may be responsible for the suppression. The undesired anions can be excluded, at least in the early portion of the reaction, by using solutions made up with $HClO_4$. Nitrate ion is a product of the reaction, so that one cannot prevent its presence in the later portion of the reaction, especially if concentrated solutions are under investigation; however, its effectiveness in bringing about the first-stage reaction is not great, and it does not significantly interfere with the kinetic investigation of solutions made up with $HClO_4$.

Hughes and Stedman[2] have remarked that only in a few (about 10%) of their runs on the kinetic study of the nonradical reaction did they encounter interference from the very fast, presumably free-radical, reaction; and that "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." We now know the reason: namely, that in our earlier study, we had no suspicion of the effect of chloride ion, so that we made up our reaction mixtures from $Ag_2N_2O_2$ and HCl and moreover used $NaCl$ to adjust the ionic strength; thus all of our runs were made in the presence of what we now know to be a potent agent for the first-stage free-radical reaction (and some of them may have contained a trace of Ag^+, which is even more potent). On the other hand, Hughes and Stedman made up their reaction mixtures from $Na_2N_2O_2$ and $HClO_4$, so it is probable that in

those few cases they encountered the free-radical reaction they had either adventitious traces of heavy metals or considerable nitrate ion.

B. The Reaction between Nitrous Acid and Hyponitrous Acid. After our experimental work on this reaction was finished, a study of the same reaction by Hughes and Stedman[8] was published. To the extent that our experimental conditions and theirs overlap, our observations agree with theirs.

Under the conditions of our kinetic study (0.02–0.06 M hyponitrous acid and 0.002–0.008 M nitrous acid) the stoichiometry corresponded 98–99% to the reaction

$$HON{=}NOH + HNO_2 \longrightarrow N_2 + NO_3^- + H^+ + H_2O$$
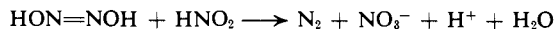
Aside from a trace of NO presumably arising from the decomposition of the HNO_2, the remaining gaseous product consisted of 1–2% N_2O. Hughes and Stedman[8] also observe N_2O as a product of the reaction, particularly at high hyponitrous acid concentration. Since NO_3^- is one of the agents bringing about the first-stage reaction, and since the first-stage reaction is always accompanied by the formation of some N_2O, we ascribe most, if not all, the N_2O production to this side reaction. In any event it does not interfere seriously with the kinetic study.

The dependence of rate on initial concentrations indicates that the reaction is kinetically first order with respect to hyponitrous acid (Figure 2) and first order with respect to nitrous acid (Figure 3). Up to an

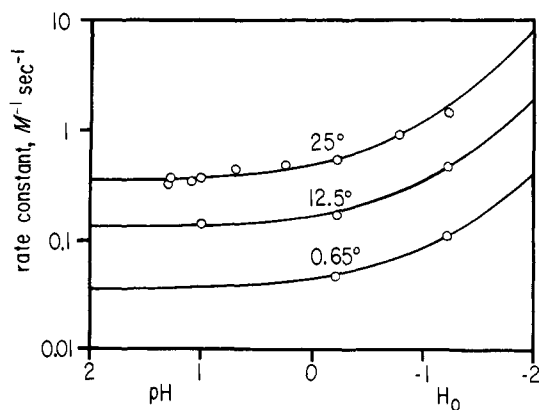(8) M. N. Hughes and G. Stedman, J. Chem. Soc., 4230 (1963).

Figure 4. Second-order rate constant for the reaction of hypo-nitrous acid with nitrous acid as a function of pH or H_0. The curve through each set of data represents a function of the form $k_1 + k_2 h_0$.

acidity somewhat less than 1 M H^+ there is little kinetic dependence on acidity, but at higher acidity the rate increases in a way best fitted by a first-order dependence of Hammett acidity h_0 (Figure 4).[9]

The corresponding rate law is

$$d(N_2)/dt = (k_1 + k_2 h_0)(H_2N_2O_2)(HNO_2)$$

From the data shown in Figure 4, the constants k_1 and k_2 at the several temperatures have been calculated, as given in Table I. The corresponding activation parameters are: for k_1, $\Delta H^* = 15.6$ kcal. and $\Delta S^* = -12$ cal. deg.$^{-1}$; for k_2, $\Delta H^* = 21.6$ kcal. and $\Delta S^* = +5$ cal. deg.$^{-1}$.

Table I. Temperature Effect on the Reaction Rate between Hyponitrous and Nitrous Acids

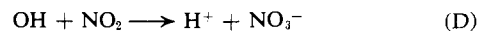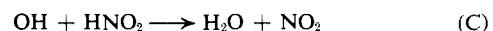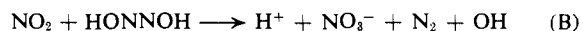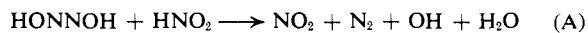| Temp., °C.	k_1, sec.$^{-1}$ M^{-1}	k_2, sec.$^{-1}$ M^{-2}
0.65	0.023	0.0037
12.5	0.14	0.017
25.0	0.37	0.078

This kind of rate law, including the h_0 dependence at high acidities, is familiar for nitrosations (cf. the O-nitrosation of ascorbic acid).[10] It is plausible, therefore, to interpret the rate law as Hughes and Stedman have, namely as arising from the rate-determining O-nitrosation of the HONNO$^-$ ion and of HONNOH, respectively. The nitrosating agent is NO$^+$ (or, as the Ingold school prefer it, $H_2NO_2^+$) formed in a rapid pre-equilibrium

$$NO^+ + {}^-ONNOH \longrightarrow ONONNOH$$

$$NO^+ + HOHHOH \longrightarrow ONONNOH + H^+$$
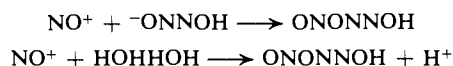
The transient product, ONONNOH, must then decompose rapidly to yield the final products, namely N_2 and NO$_3^-$. Bearing in mind the qualitative evidence for OH radicals and NO$_2$ in these reaction mixtures, we suggest that this does not occur in a single step, but in a free-radical chain initiated by the fission into NO$_2$ + N$_2$ + OH. Thus

(9) Professor Stedman has kindly informed us that he and Hughes have likewise observed this dependence on acidity.
(10) H. Dahn and L. Loewe, *Helv. Chim. Acta*, 43, 294 (1960).

$$HONNOH + HNO_2 \longrightarrow NO_2 + N_2 + OH + H_2O \quad (A)$$

$$NO_2 + HONNOH \longrightarrow H^+ + NO_3^- + N_2 + OH \quad (B)$$

$$OH + HNO_2 \longrightarrow H_2O + NO_2 \quad (C)$$

$$OH + NO_2 \longrightarrow H^+ + NO_3^- \quad (D)$$

Upon making a steady-state approximation with respect to OH and NO$_2$, one obtains from this chain

$$d(N_2)/dt = (HONNOH)(HNO_2)\left[k_A + \sqrt{\frac{k_A k_B k_C}{k_D}}\right]$$

In other words, the chain reaction does not change the rate law, but it can considerably increase the rate by a factor whose numerical magnitude depends on four rate constants. We have omitted as a chain-breaking step the hydrolysis of NO$_2$, namely

$$NO_2 + NO_2 + H_2O \longrightarrow HNO_2 + H^+ + NO_3^-$$
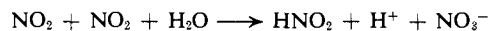
chiefly because in the limit it would lead to a rate law of the form $(HNO_2)^{1/2}(HONNOH)^{3/2}$, and we see no substantial evidence of such a trend in our kinetic data. No doubt it should be included in any full treatment of the kinetics.

An estimate of the chain length can be obtained by adding scavengers to react with OH or with NO$_2$; if OH only were scavenged, the specific rate would be expected to drop to $2k_A$; if NO$_2$ only, to k_A. We observe that the addition of 1.4% ethanol to a reaction mixture reduces the rate by a factor of 4.5. If ethanol scavenges only OH radicals, this indicates that the chain length is 8, which must be considered a lower limit, since the scavenging is probably not perfect.

As a referee has pointed out, reactions C and D are likely to be diffusion controlled, so that k_C and k_D are approximately equal. Then a chain length of 8 corresponds to a k_B/k_A ratio of 49. In an attempt to estimate experimentally the rate of the chain-propagating step B, we allowed NO$_2$ gas (at about 0.5 atm.) to pass directly into stirred 0.1 M hyponitrous acid at 25°. After 1-min. contact time, 10% of the hyponitrous acid had reacted. The gaseous product was 99% N$_2$ and 1% N$_2$O, and the solution contained 0.014 M HNO$_2$ and 0.024 M NO$_3^-$. Since the simple hydrolysis of NO$_2$ yields equimolar HNO$_2$ and NO$_3^-$, we attribute the excess of NO$_3^-$ to reaction B. The rate of reaction B is therefore comparable to the rate of hydrolysis of NO$_2$.[11] A more numerical conclusion does not seem warranted, inasmuch as the principal gaseous species in our experiment is actually N$_2$O$_4$, and moreover the rate is undoubtedly mass-transfer controlled so that the concentration of aqueous NO$_2$ is not spatially uniform.

C. *The Nitrous Acid Forming Reaction.* Two observations are crucial in elucidating the mechanism of the first-stage reaction. One is that nitrous acid is required; *i.e.*, that the formation of nitrous acid is autocatalytic. The other is that certain cations or anions must be present. We have examined in some detail only the reactions with Cu^{2+} and with Cl$^-$, but among the other cations which will bring about reaction are Ag$^+$, Tl$^+$, Co^{2+}, Ni^{2+}, and both Hg$_2^{2+}$ and Hg^{2+}; and among anions NO$_3^-$, and SO$_4^{2-}$. Moreover, the dependence of rate on the concentration of these additives is unusual, in that it levels off and becomes independent of concentrations as that increases (Figure 5).
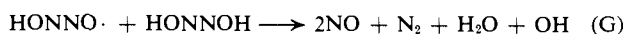
(11) M. M. Wendel and R. L. Pigford, *A.I.Ch.E. J.*, 4, 249 (1958).

An induced-oxidation mechanism is generally consistent with these observations. The mechanism would begin with reaction A, producing OH and NO_2. It would be followed by the oxidation of a species X by OH radical

$$X + OH \longrightarrow X^+ + OH^-$$
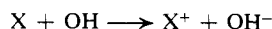
The NO_2 could either oxidize the species X directly, or the OH radical resulting from its reaction with hyponitrous acid could do so; in either case, two of the species X^+ would be produced each time reaction A proceeded. In support of this hypothesis, we note that the ionic species which are effective in bringing about the first-stage reaction are those which can plausibly be oxidized to higher oxidation states; we propose that they thereby serve as oxidation transfer agents. The ceiling on rate as their concentration is increased is easily understandable, since the rate of oxidation transfer cannot exceed the rate of OH production. The final step, according to this mechanism, would be the oxidative attack of X^+ on hyponitrous acid.

The following sequence is proposed to account for the oxidative cleavage of hyponitrous acid. Reaction F

$$X^+ + HONNOH \longrightarrow X + HONNO\cdot + H^+ \quad (E)$$

$$HONNO\cdot \longrightarrow N_2O + OH \quad (F)$$

$$HONNO\cdot + HONNOH \longrightarrow 2NO + N_2 + H_2O + OH \quad (G)$$

$$NO + HONNOH \longrightarrow HNO_2 + N_2 + OH \quad (H)$$

accounts for the N_2O which is always a product, and reactions G and H account for the HNO_2 produced. Reaction H is proposed as the fate of NO, rather than a chain-breaking reaction such as

$$NO + X^+ + H_2O \longrightarrow HNO_2 + X + H^+$$
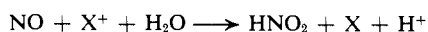
because the latter would not give a rate law in which the nitrous acid concentration initially rises. Moreover, we have observed that NO is rapidly absorbed by hyponitrous acid solutions at 1 M H^+.

The yield of N_2 relative to N_2O is roughly proportional to the speed of reaction. Thus, if the half-life of hyponitrous acid at 25° is 25 min., the $N_2:N_2O$ ratio is 0.5–0.7; if 10 min., 1–2; if 2 min., 7–8. This generalization is based on only a dozen observations of product composition, involving six different oxidation transfer agents, so it must be subject to later refinement. It does, however, suggest that among the N_2-producing reactions there be included one which is bimolecular in
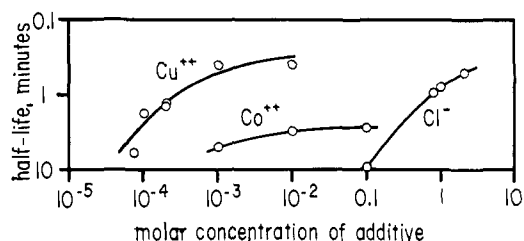

Figure 5. The effect of various additives on the rate of decomposition of hyponitrous acid, subsequent to the induction period (25°); the experiments with cupric and cobaltous ions had H^+ 0.16 M and initial $H_2N_2O_2$ 0.2 M, and those with chloride had H^+ 0.7 M and initial $H_2N_2O_2$ 0.05 M; the half-lives plotted have been multiplied by the respective initial concentrations of $H_2N_2O_2$, so that they correspond to the half-lives of 1 M hyponitrous acid with the indicated additives.

radical species, such as

$$HONNO\cdot + X^+ \longrightarrow X + 2NO + H^+ \quad (I)$$

This whole sequence E–I is admittedly speculative, and we set it down primarily as a guide to future investigation. A direct kinetic study of the reaction of hyponitrous acid with various oxidizing species will give far more reliable rate constants than those we might infer from the data at hand.

If the first-stage reaction is a branching chain, as we have here proposed, then a very small rate of free-radical initiation will suffice to bring it about. It is plausible that an azo-type homolytic fission of hyponitrous acid is responsible for those first few OH radicals

$$HON{=}NOH \longrightarrow HO + N_2 + OH$$
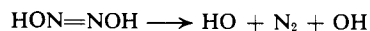
Analogous fission has been proposed for hyponitrite esters in the gas phase[12] and liquid phase.[13] We attempted to identify this process by carrying out the decomposition of acidified hyponitrous acid at room temperature with 1–5 mole % added ethanol or allyl alcohol. The product was at least 99.5 % N_2O arising from the simple dehydration of hyponitrous acid.[1] Since that reaction has a half-life of 2 weeks, the half-life of the homolytic fission appears to be at least 5 years. It may well be that the requisite few radicals do not arise from homolytic fission at all, but from adventitious traces of other reactants such as molecular oxygen.

(12) H. W. Holden and K. O. Kutschke, *Can. J. Chem.*, **39**, 1552 (1951).
(13) S. K. Ho and J. B. de Souse, *J. Chem. Soc.*, 1788 (1961).