Kinetics of the Decomposition of Hyponitrous Acid: A Homogeneous Zeroth Order Reaction

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The rate determining step in the decomposition of hyponitrites in aqueous solution is shown to be the unimolecular decomposition $HN_2O_2^- \rightarrow N_2O + OH^-$. In buffered solutions the overall reaction is of the first order. The rate constant is very small at $pH = 4$ and increases rapidly with increasing pH.

In pure solutions of $H_2N_2O_2$ partially neutralized to $HN_2O_2^-$, but not buffered, the reaction proceeds at a constant rate which is shown to be proportional to the concentration of $HN_2O_2^-$.

The first dissociation constant (K_1) of hyponitrous acid is accurately determined over the range 0 to 30°C. Published data are reconsidered in order to evaluate K_2.

Es wird gezeigt, daß die geschwindigkeitsbestimmende Stufe beim Zerfall von Hyponitriten in wäßrigen Lösungen der monomolekulare Zerfall $HN_2O_2^- \rightarrow N_2O + OH^-$ ist. In gepufferten Lösungen ist die Gesamtreaktion von erster Ordnung. Die Geschwindigkeitskonstante ist sehr klein bei $pH = 4$ und wächst schnell bei steigendem pH.

In reinen nicht gepufferten Lösungen untersalpetriger Säure, partiell neutralisiert zu $HN_2O_2^-$, verläuft die Reaktion mit konstanter Geschwindigkeit, welche proportional der Konzentration des $HN_2O_2^-$ ist.

Die erste Dissoziationskonstante (K_1) der untersalpetrigen Säure wird im Bereich von 0 bis 30°C genau bestimmt. Zur Bestimmung der K_2 werden veröffentlichte Ergebnisse neu berechnet.

The properties of hyponitrous acid in acid solution have been studied very little. This is undoubtedly due to the widely accepted view that $H_2N_2O_2$ is unstable in acid solution[1]. Our own experience

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* C. N. P., Habilitation Thesis, University of Athens, 1963.
[1] E. ABEL, A. ORLICEK and J. PROISL, Wien. Mh. 72 (1938) 1.

however, as well as a careful consideration of the older literature could hardly be compromised with this assumption. Thus, to facilitate further research on the properties of hyponitrites, a systematic investigation of the supposed instability of hyponitrous acid seemed to be necessary[**]. While the completed work was in print, as a thesis of one of the authors[*], a paper by HUGHES and STEDMAN[2] appeared on the same subject. The conclusions of these authors coincide with ours, but their actual measurements and technique used do not. Thus a presentation of our results is justified because, we believe, a) they provide a more conclusive evidence and b) they allow for a direct and more accurate determination of the constants involved.

Experimental

Silver hyponitrite was precipitated from solutions of $Na_2N_2O_2$ prepared by the electrolytic method[3].

Pure solutions of $H_2N_2O_2$ were obtained by dropping into the desired amount of HCl an excess of $Ag_2N_2O_2$ freshly reprecipitated from dilute HNO_3 by $NaOH$ and thoroughly washed.

Kinetic runs were carried out by following the concentration of $H_2N_2O_2$ by the standardized precipitation method[4].

The pH-meter (Cambridge Portable) was standardized (by phthalate, phosphate and borate buffers) according to N.B.S. specifications[5]. The electrodes, buffers etc. were constantly kept at the temperature at which pH-measurements had to be made. The accuracy of the latter can be claimed to be ± 0.01.

Results and Discussion

Pure solutions of $H_2N_2O_2$, at a concentration around 0.05 mole/l, exhibit a pH of about 4.4, and they are quite stable at room temperature for the first few hours after their preparation. But afterwards they exhibit an acceleration of their decomposition as actually noticed

[2] M. N. HUGHES and G. STEDMAN, J. chem. Soc. [London] 1963, 1239.

[3] C. N. POLYDOROPOULOS, Chemistry & Industry 1963, 1686.

[4] C. N. POLYDOROPOULOS and M. PIPINIS, Chimika Chronika 28 A (1963) 107.

[5] R. G. BATES, "Electrometric pH determinations", J. Wiley and Sons, Inc. N. Y., 1954.

by earlier investigators[6]. This is accompanied by a drift of the pH to lower values. It should be noted, however, that such an autocatalysis has never been observed in solutions having a pH higher than 4.5*.

Decomposition in buffered solutions. Acetate buffer was added to pure solutions of $H_2N_2O_2$ and the reaction followed at 20.0°C. The reaction under these conditions is clearly of first order with respect to total hyponitrite concentration (C).

$$\log C = \log C_0 - \frac{k_1}{2.303} t \tag{1}$$

$$- \frac{dC}{dt} = k_1 C \tag{2}$$

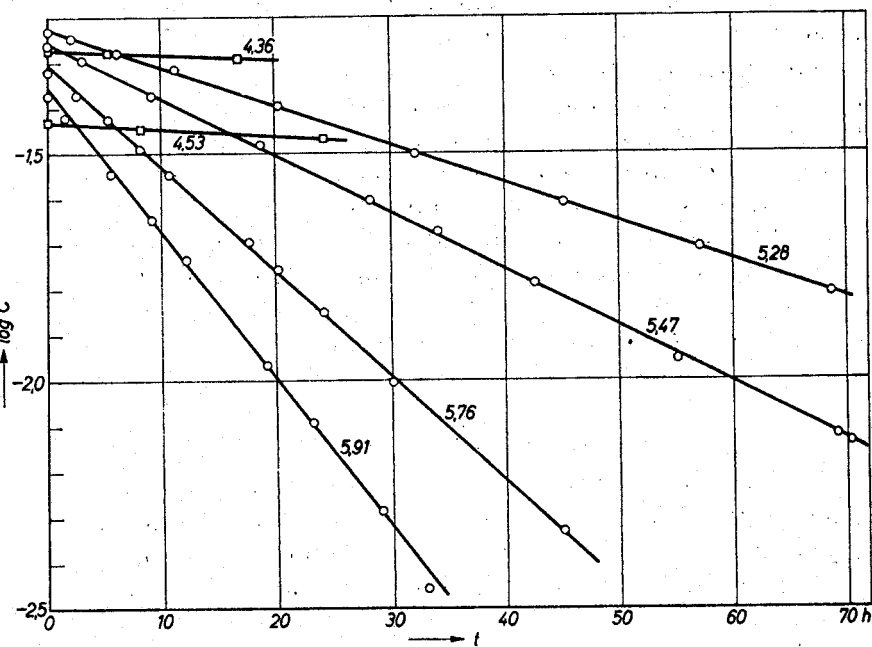Some of the runs are shown in Fig. 1. k_1 increases with increasing pH (Table 1).

Fig. 1. Illustration of the order of the reaction (first) under $pH =$ const. Acetate buffer, 20.0°C

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* This autocatalysis is very likely to be due to the formation of nitrous traces during the reaction. But this will be discussed in a future communication.

[6] W. M. LATIMER and H. W. ZIMMERMANN, J. Amer. chem. Soc. 61 (1939) 1550.

Table 1. *Dependence of the first order rate constant on the pH*

| pH	k_1	μ
	h^{-1}	
4.02	0.00181	0.003
4.36	0.00230	0.000
4.53	0.00368	0.000
4.67	0.00479	0.045
5.28	0.0196	0.200
5.47	0.0288	0.200
5.76	0.0527	0.200
5.91	0.0741	0.200

μ = ionic strength.

HUGHES and STEDMAN[2] have found similar results by using different buffers, at higher pH values and different temperatures. In terms of this experimental evidence they have discussed adequately the mechanism of the reaction.

We need only note that the dependence of k_1 on (H^+) is given* more precisely by (3)

$$\frac{1}{k_1} = \frac{1}{k_*} + \frac{f_-(H^+)}{K_1 k_*} \tag{3}$$

(where f_- is the activity coefficient of the ion $HN_2O_2^-$) and an extrapolation of the relative graph to obtain k_* is not sufficiently reliable because the intercept is small and the slope large. Instead k_* can be measured directly in acid solution as follows.

Decomposition in partially neutralized not buffered solutions. A small amount of $NaOH$ was added to pure solutions of $H_2N_2O_2$, so as to cause a neutralization, according to (4), by only a few percent.

$$H_2N_2O_2 + OH^- \rightleftharpoons HN_2O_2^- + H_2O \tag{4}$$
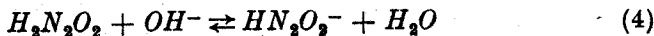
In these solutions the decomposition appears to be of zeroth order, showing a constant rate despite of the decrease of C down to the 1/5. Some of the runs are shown in Fig. 2. Similar results without exception were found at $0°$, $20°$, and $30°$.

These results are not surprising if the mechanism of the reaction is considered. The rate determining step is the decomposition:

$$HN_2O_2^- \rightarrow N_2O + OH^- \tag{5}$$
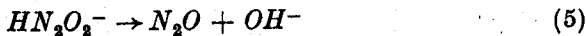
* Brackets stand for concentrations and parentheses for activities. All concentrations are expressed in moles/l.

Thus the overall rate should be

$$- dC/dt = k_* \, [HN_2O_2^-] \qquad (6)$$

Now it is obvious that from every $HN_2O_2^-$ decomposing an OH^- is set free, which is immediately neutralized, according to (4), and reproduces the $HN_2O_2^-$ lost. Therefore the concentration of $HN_2O_2^-$ remains constant and so does the rate.
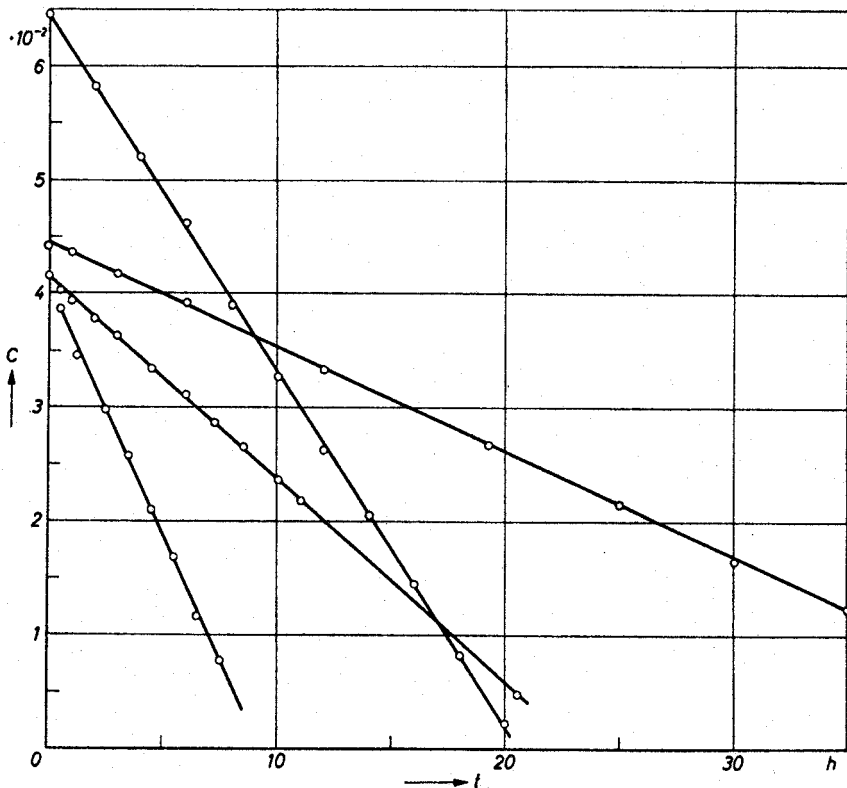

Fig. 2. Decomposition of hyponitrous acid partially neutralized by $NaOH$ without buffer, at $20.0\,^\circ C$

If so the rate should be directly proportional to the concentration of $HN_2O_2^-$ which in turn can be calculated from the amount of $NaOH$ added originally. This is actually shown in Fig. 3. Thus k_* is equal to $v/[HN_2O_2^-]$.

The mean values of k_* at $0.0\,^\circ$, $20.0\,^\circ$, and $30.0\,^\circ C$ are 0.058, 1.07, and $4.16\ h^{-1}$ respectively. A plot of log k_* against $1/T$ gives a slope of

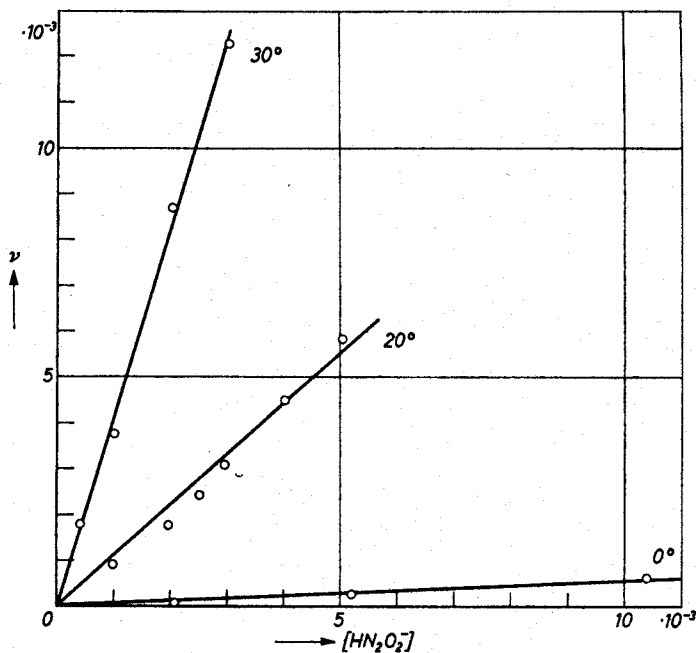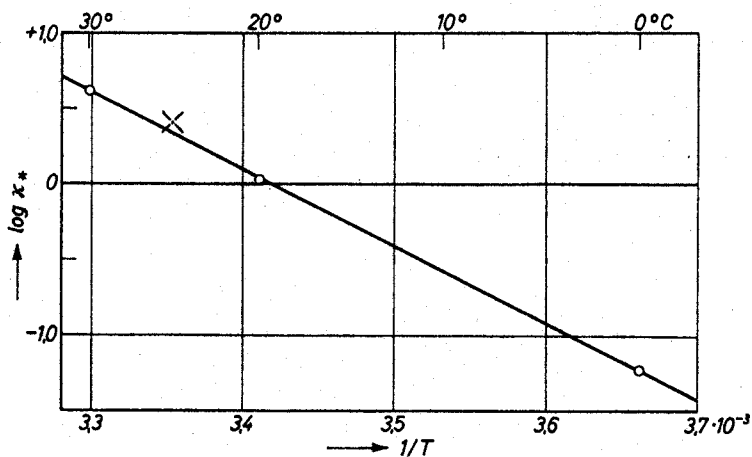Fig. 3. Dependence of the rate (v) on the concentration of $HN_2O_2^-$. The time in hours

Fig. 4. Dependence of k_* on temperature. $\times$ = value taken from ref. [2]. The time in hours

-5.16×10^3 (Fig. 4). From this an activation energy of 23.6 ± 0.5 kcal/mole is calculated. The frequency factor turns out to be 4.5×10^{17} h^{-1}, or 1.24×10^{14} sec^{-1}.

Comparison with the results of Hughes and Stedman[2] is difficult because these authors do not mention but a single value of k_*, i.e., the one shown by $\times$ in Fig. 4 (at 25°).

During the decomposition in these (unbuffered) solutions, since the concentration of $HN_2O_2^-$ remains constant, the pH should rise. The actual dependence of pH on time can provide a further support of mechanism (5).

Thus $dC/dt = d[H_2N_2O_2]/dt$ since, in weakly acid solution, $C = [H_2N_2O_2] + [HN_2O_2^-]$ and $[HN_2O_2^-] = $ const. Substitution of the rate from (6) and of the $[H_2N_2O_2]$ from the expression of K_1 (the first dissociation constant of $H_2N_2O_2$) yields
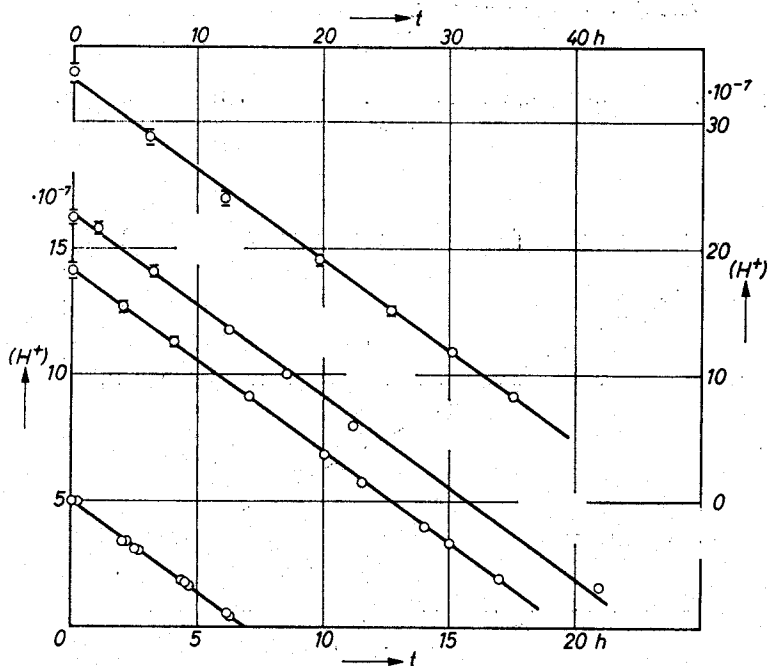
$$d(H^+)/dt = - k_* \, K_1/f_- \qquad (7)$$

Fig. 5. Dependence of pH on time in unbuffered solutions of $H_2N_2O_2$ partially neutralized by $NaOH$, at 20°. The runs correspond to those of Fig. 2

In these solutions the ionic strength is very small (equal to the concentration of $NaHN_2O_2$) and constant during each run, i.e., $f_- = $ const. Fig. 5 shows that eq. (7) is verified.

Similar straight lines were also found at 0° and 30°. From the slope of these lines K_1 can be calculated (see the Appendix).

Salt effect. No noticeable salt effect has been observed up to $\mu = 0.30$. The measurements were carried out (at 20°) as follows:

To pure solutions of $H_2N_2O_2$ was added a) a small amount of $NaOH$ ($[HN_2O_2^-] = 0.004$) and b) varying amounts of the salts $NaNO_3(0.10)$, $KNO_3(0.10)$, $Na_2SO_4(0.05)$, $K_2SO_4(0.04)$, $Ca(NO_3)_2(0.10)$, $Ba(NO_3)_2(0.025)$ up to the concentration indicated for each one. The hyponitrite concentration was followed from an original value of about 0.05 down to 0.005. The *pH* changed from 6 to 7. The reaction was still of zeroth order.

A blank experiment, without foreign electrolyte, was run in parallel. In no case a noticeable difference in the rate was observed.

HUGHES and STEDMAN [2] have also found null salt effect in buffered solutions with 1.67 M $NaCl$. The small difference in k_* they notice, should be attributed to experimental errors, because the shift of the value of k_* from 7.13×10^{-4} to 6.5×10^{-4} sec^{-1}, actually brings it nearer to the line defined by our measurements in Fig. 4.

A mechanism by which the activated complex $[HN_2O_2^-]^*$ is formed, might be as follows:

$$H^+ + N_2O_2^{--} \rightleftharpoons [HN_2O_2^-]^* \rightarrow .$$
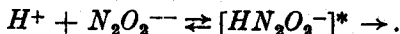
Apparently the salt effect measurements eliminate this possibility. Several other mechanisms, by which OH^- or H_2O would be involved in the transition state, are also excluded since hyponitrites show no exchange of O^{18} with water [7].

Thus the reaction seems to be a purely unimolecular decomposition of the species $HN_2O_2^-$.

Reconsideration of published data. The first thorough kinetic study of the decomposition of hyponitrites was published by ABEL, ORLICEK and PROISL [1]. These investigators contented themselves with measure-

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[7] F. BONNER and J. BIGELEISEN, J. Amer. chem. Soc. **74** (1952) 4944.

ments in highly alkaline solution ($NaOH$ $0.1 - 1.5$ M). They found a first order law

$$v = - dC/dt = \varkappa C \tag{8}$$

with $\varkappa$ decreasing as $[NaOH]$ increases.

The mechanism proposed by these authors (in which the rate determining step was the reaction $H_2N_2O_2 \rightarrow N_2O + H_2O$) requires that $1/\varkappa [OH^-]$ is a linear function of $[OH^-]$, and the illustrations they present do not seem to contradict this requirement.

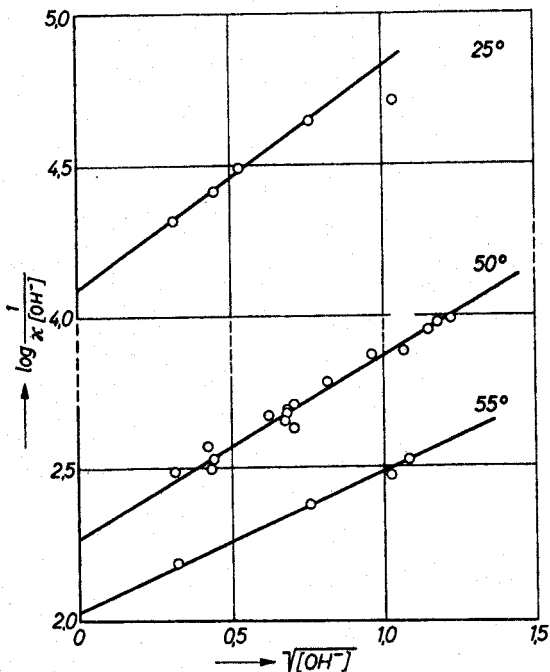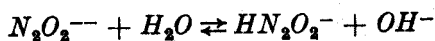Fig. 6. Recalculation of published data[1] on the decomposition of $Na_2N_2O_2$ in $NaOH$

The same measurements, however, can be interpreted, at least equally well, in terms of mechanism (5) as follows:

In highly alkaline solution the concentration of the ion $N_2O_2^{--}$ is practically equal to the total hyponitrite concentration (C). Consider the equilibrium

$$N_2O_2^{--} + H_2O \rightleftarrows HN_2O_2^- + OH^-$$

$$K_h = f \frac{[HN_2O_2^-][OH^-]}{[N_2O_2^{--}]}$$

where f is the fraction of the activity coefficients. By the substitutions $[N_2O_2^{--}] = C$ and $[HN_2O_2^-] = v/k_*$ one finds

$$v = \frac{k_* K_h}{f [OH^-]} \cdot C$$

from which, by putting the coefficient of C equal to the experimentally determined $\varkappa$ according to (8) and taking logarithms

$$\log (\varkappa [OH^-]) = \log (k_* K_h) - \log f . \tag{9}$$

Therefore the fact that $\varkappa [OH^-]$ does not remain constant can be attributed to the dependence of f on the ionic strength. In these solutions the ionic strength is practically equal to the concentration of OH^-.

The values of $\varkappa$ and $[OH^-]$ reported by ABEL and coworkers have been recalculated so as to express (9) as a function of the square root of the ionic strength, and they are shown in Fig. 6.

The series of measurements in Fig. 6 show a linearity at least equally good with that in the Figs. 4 and 5 of the original paper[1]. Thus mechanism (5) is not incompatible with ABEL's measurements.

Appendix
The dissociation constants of hyponitrous acid

1. K_1 can be estimated sufficiently accurately from the results shown in Fig. 5 in terms of eq. (7). k_* is taken from eq. (6).

The activity coefficient (f_-) of the ion $HN_2O_2^-$ was calculated from the DEBYE-HÜCKEL formula for an ion size parameter (α) 4.5 Å. Because of the low values of the ionic strength an uncertainty of ± 1.5 Å in α causes an error of the order of only 0.2%.

The mean values of K_1 are 3.09, 6.03, and 8.10×10^{-8} at $0.0°$, $20.0°$, and $30.0°$ respectively. They define a satisfactory straight line on a $\log K_1 - 1/T$ graph (Fig. 7, circles).

The points shown in Fig. 7 by squares refer to measurements reported in ref. 2(S), 6(L), and 8(P). Accuracy is claimed in none of these determinations.

The line defined by the present measurements in Fig. 7 can be expressed by

$$\log K_1 = - 3.26 - 1.16 \times 10^3 \frac{1}{T} .$$

From the slope, the enthalpy ($\Delta H_1°$) of the dissociation

$$H_2N_2O_2 \rightarrow H^+ + HN_2O_2^-$$
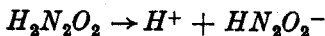
is found to be $\Delta H_1^\circ = 5.3$ kcal/mole. No thermochemical determination of ΔH_1° is available. The value 3 kcal/mole estimated by HUGHES and STEDMAN[2] from their measurements at 15, 25, and 35° (Fig. 7, points S) can no longer be considered.

Values of pK_1 (± 0.01) calculated by interpolation at selected temperatures are as follows:

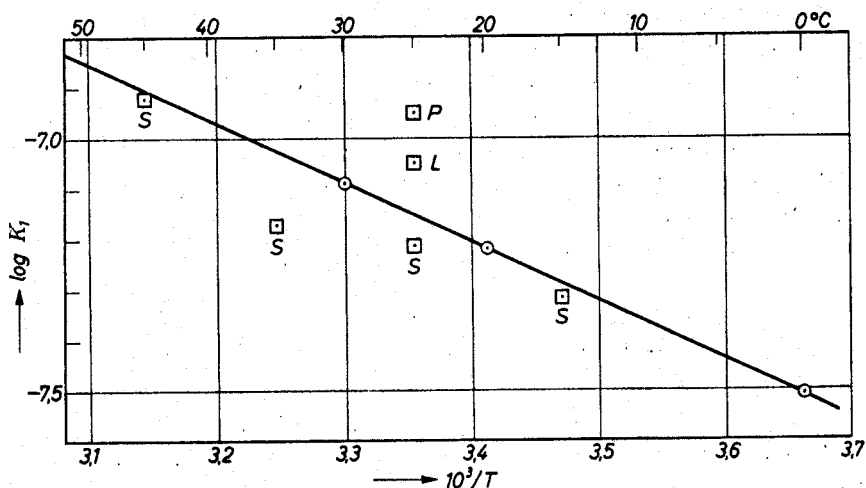| t°C	0	5	10	15	20	25	30	35
pK_1	7.51	7.44	7.36	7.29	7.22	7.15	7.09	7.03

Fig. 7. Temperature dependence of the first dissociation constant of hyponitrous acid

2. Fig. 6, apart from the support it lends to mechanism (5) in terms of eq. (9), also provides a means of estimating the second dissociation constant (K_2) of hyponitrous acid ($K_h = K_w/K_2$), at least approximately. In view of the lack of accurate data on K_2 this calculation is worth-while.

The values of $-\log(k_* K_h)$ found by extrapolations in Fig. 6 are 4.09, 2.27 and 2.03 at 25°, 50° and 55° respectively. The corresponding literature values[5] of $-\log K_w$ are 13.996, 13.262 and 13.137 and those of $\log k_*$ calculated by extrapolation of Fig. 4 are -1.4425, -0.1007 and $+0.1422$ (k_* in min^{-1}). This yields for pK_2 the values 11.35, 11.09 and 10.97 (at 25°, 50° and 55°).

Other values of pK_2 found in the literature are: 10.90 and 11.10 [2] at 45° and 11.54 [2], 11.00 [6], 10.84 [8] at 25°.

We have also found a value of 11.1 $\pm$ 0.2 at 18°, from determinations of the concentration (around 0.005) and of the pH (around 11.3, glass electr.) in pure solutions of $Na_2N_2O_2$.

Unfortunately a plot of all these data shows such a scattering that no precise conclusion can be drawn. It can only be said that, until it is more accurately determined, pK_2 may be taken as 11.2 $\pm$ 0.2 at ordinary temperatures.

[8] C. N. POLYDOROPOULOS, Chimika Chronika 24 A (1959) 147.