respect to sulfamate and hydrogen ion concentrations, and to be accompanied by a primary salt effect of the expected magnitude.

A mechanism is proposed for the hydrolysis, in which the formation of an intermediate dipolar ion in equilibrium with the reactants is postulated. With the aid of this mechanism it is possible to explain the high values found for the energy and entropy of activation.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Rates of Ionization of Pseudo-acids. III. Forward and Reverse Reactions for Nitroethane

BY RALPH G. PEARSON AND ROBERT L. DILLON

The rate of the water-catalyzed ionization of nitroethane has now been measured over a range of temperatures[1] by following the rates of bromination and iodination in aqueous solution. These rates have turned out to be the same showing that the rate determining step in each case is the ionization.

$$C_2H_5NO_2 + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_2H_4NO_2^- + H_3O^+ \qquad (1)$$

The rates were measured both by the usual titration technique and by the conductimetric method mentioned in paper II of this series.[2] A range of temperatures from 15 to 35° enables us to calculate the heat and entropy of activation. Moreover, from the relationship $k_1/k_2 = K_{eq} = K_{ion}$, one can calculate the rate constant k_2 for the recombination of ions and the attendant heat and entropy of activation. The value of K_{ion} is known from 18 to 30° by the work of Turnbull and Maron,[3] being 3.50×10^{-9} at 25°.

It is of interest to extrapolate the calculated value of k_2 down to 0° since Maron and La Mer[4] attempted a direct measurement of this quantity at that temperature. The procedure used by Maron and La Mer was to make a solution of the barium salt of nitroethane and to acidify it with an equivalent amount of sulfuric acid. This produced the aci-form which isomerized to the nitro-form at a measurable rate. Since the aci-form is a stronger acid than the nitro-form, the isomerization is accompanied by a decrease in the ionic concentration and an increase in resistance. Maron and La Mer measured the resistance and found it to be linear with the time. By several assumptions they were able to justify this linearity as being consistent with the mechanism

$$H_2O + C_2H_4NO_2H \rightleftharpoons C_2H_4NO_2^- + H_3O^+ \xrightarrow{k_2} C_2H_5NO_2 + H_2O \qquad (2)$$

The aci-form is in mobile equilibrium with its ions which react together slowly to give the nitro compound. They then calculated a value of 144 for k_2 at 0°. From measurements at 5° they also computed the heat and entropy of activation. Tables I and II give a compilation of the data gathered in this work and by Maron and La Mer.

The discrepancy between a rate constant of 26 and 144 is not too alarming since the values depend upon an extrapolation of several quantities (including the ionization constant of the aci-form of nitroethane) from room temperature down to 0°. The disagreement between the heats and entropies of activation is serious, however, since these quantities should be nearly independent of temperature over a small range.

Accordingly the data of Maron and La Mer were re-examined and it became evident that they had incorrectly identified the conductance with the concentration of unreacted aci-nitroethane. The conductance, of course, should be identified with the concentration of the ions resulting from the aci-compound. Since the latter is a weak acid comparable to acetic acid, $K_A = 3.6 \times 10^{-5}$ at 0° (ref. 3), one can derive the equation

$$[H_3O^+] = [C_2H_4NO_2^-] = K_A^{1/2}[C_2H_4NO_2H]^{1/2} = K_A^{1/2}(a - x)^{1/2} \qquad (3)$$

where K_A is the ionization constant of the aci-form and $(a - x)$ has its usual kinetic meaning. Since the reciprocal of the resistance is proportional to the concentration of ions, the experimental fact that the resistance is linear with the time is equivalent to saying that $1/(a - x)^{1/2}$ is linear with the time. This corresponds to a rate expression of the form

$$dx/dt = k\,(a - x)^{3/2} \qquad (4)$$

which is satisfied by either of the two mechanisms

$$H_3O^+ + C_2H_4NO_2H \xrightarrow{k_3} H_3O^+ + C_2H_5NO_2 \qquad (5)$$

$$C_2H_4NO_2^- + C_2H_4NO_2H \xrightarrow{k_4} C_2H_5NO_2 + C_2H_4NO_2^- \qquad (6)$$

Mechanism (5) can be ruled out by the principle of microscopic reversibility since there is no acid catalysis for the ionization of nitroethane (the reverse of reaction (5) would be an acid-catalyzed ionization). The mechanism shown in (6), however, is a reasonable and indeed an expected one

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(1) Junell, *Arkiv. Kemi, Mineral. Geol.*, **11B**, 30 (1934), has measured the rate of ionization at 69.85° in 1 molar hydrochloric and hydrobromic acids.

(2) Pearson and Mills, THIS JOURNAL, **72**, 1692 (1949).

(3) Turnbull and Maron, *ibid.*, **65**, 212 (1943).

(4) Maron and La Mer, *ibid.*, **61**, 692 (1939).

since the isomerization of aci-nitroethane is known to be subject to general acid catalysis.[5] One concludes then that the main reaction studied by Maron and La Mer is between the anion of nitroethane and a neutral aci-nitroethane molecule.

A complete rate expression, however, will include the reaction with the anion by all acids present in the system (ref. 5) giving rise in this case to

$$dx/dt = k_4K_A^{1/2}(a - x)^{3/2} + k_2K_A\,(a - x) \qquad (7)$$

where the first term is due to the acid, $C_2H_4NO_2H$, and the second term to the acid, H_3O^+. The integration of (7) in the case where the second term is small compared to the first gives the result

$$\frac{1}{(a - x)^{1/2}} - \frac{1}{a^{1/2}} = \left[\frac{k_4K_A^{1/2}}{2} + \frac{k_2K_A}{2a^{1/2}}\right]t \qquad (8)$$

An inspection of Maron and La Mer's results shows that their experimental constant "k_2" is equal to

$$``k_2" = \frac{k_4K_A^{1/2}}{2a^{1/2}} + \frac{k_2K_A}{2a} \qquad (9)$$

Actually their values of "k_2" vary with initial concentration in the approximate way shown in (9) but the internal consistency is not good enough to evaluate k_4 and k_2.

Accordingly it was decided to study the isomerization reaction at 0° under conditions where the reaction with hydrogen ion is negligible. This can be done by preparing a solution of the sodium or barium salt of nitroethane and adding to it enough acid to convert only a fraction of it to the aci-form. This produces a solution where the hydrogen ion concentration is very low and only reaction (6) is important. The change from aci- to nitro-form was followed by titrating the unchanged aci-form with bromine water. Since the rate expression (7) under these conditions gives pseudo-first order kinetics

$$dx/dt = k_4[C_2H_4NO_2^-](a - x) + k_2K_A(a - x) \qquad (10)$$

where $[C_2H_4NO_2^-]$ is constant, a plot of the log of the concentration of unchanged aci-nitroethane against the time gave straight lines. From the slope and the concentration of unchanged nitroethane anion, k_4 can be calculated if the term in k_2K_A is neglected.

The experiments of Maron and La Mer were also repeated using equivalent amounts of the sodium salt[6] and acid and the bromine titration method. A plot of the reciprocal of the square root of the concentration of aci-nitroethane against the time gave good straight lines. From the slope the quantity $(k_4K_A^{1/2}/2 + k_2K_A/2a^{1/2})$ was calculated. This enabled a calculation of k_2 to be made since k_4 and K_A are known.

Knowing the approximate value of k_2 now enables a better estimate of k_4 to be made by going back to equation (10). This in turn enables a better calculation of k_2 to be made. Since k_2 changes by only 10% in the second approximation a further correction of k_4 is not necessary. Tables III and IV show the results giving the first and second approximations for the rate constants.

One experimental detail was noted. An extrapolation of the experimental curves back to zero time did not give a value of the initial concentration agreeing with the theoretical, always being less. Very careful control of the temperature on mixing still left an error of about 3%. Since the results of Maron and La Mer[4,7] indicate rather conclusively that there is no decomposition on adding equivalent amounts of acid to salts of nitroethane, an effect of this kind could not be blamed. We are forced to the conclusion that the equilibrium in equation (2) is not established instantaneously but requires several minutes. This leaves a rather high concentration of ions for a time which can, of course, react together to give the nitro-form. Titrations during the first few minutes after mixing actually showed a high rate of reaction. Since the half life of the main reaction studied is about 100 minutes, the error would be small in any event, but was eliminated by using the extrapolated value of the concentration in calculating the rate constants. This slowness in establishing an ionic equilibrium of the type shown in (2) is surprising but is in agreement with the results obtained by Branch and Jaxon-Deelman.[8] These investigators measured the conductance change when hydrochloric acid was added to the sodium salts of nitromethane and phenylnitromethane at 0° in methanol–water solvent. They found an initial rapid drop in conductance, lasting for several minutes, followed by a slow decrease due to the usual isomerization. Their explanation for the initial sharp drop was the same as given here.

The data of Maron and La Mer were also used to solve for k_2 by means of equation (8) and a value of 4.90 for k_4. The average value of k_2 turns out to be 167. However, all of the values in Table IV are too high since the approximation made in integrating (7), that the first term is much larger than the second, is not very good. Actually the second term, depending upon the concentration, is very nearly as large as the first. Accordingly, equation (7) was integrated exactly and k_2 solved for by trial for a number of our experimental points. Fairly constant values of about 110 (±10%) were obtained compared to 125 using the approximate solution. The exact integration of (7) gives

$$\ln\left[\frac{k_2K_A^{1/2}}{k_4(a - x)^{1/2}} + 1\right] - \ln\left[\frac{k_2K_A^{1/2}}{k_4a^{1/2}} + 1\right] = \frac{k_2K_At}{2} \qquad (11)$$

Unfortunately the value of k_2 is very sensitive

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[5] Junell, *Svensk. Kem. Tid.*, **46**, 125 (1934).

[6] Hass and Bender, THIS JOURNAL, **71**, 1767 (1949), suggest the name sodium ethanenitronate, etc., for the salts of the nitroparaffins. It is assumed throughout that only one anion exists for these salts whether they be derived from the aci- or the nitro-compound.

[7] Maron and La Mer, *ibid.*, **60**, 2588 (1938). The authors are indebted to Dr. Maron for calling these data to our attention.

[8] Branch and Jaxon-Deelman, *ibid.*, **49**, 1765 (1927).

to changes in K_A which is known experimentally only between 18–30°. A 50% error in K_A at 0° would cause a 100% error in the calculated k_2 for example. It seems then that the best estimate we can make is that $k_2 \simeq 110$ for the recombination of hydrogen ion and the anion of nitroethane at 0°. The heat of activation is 20.6 kcal. and the entropy of activation is + 14.5 E.U. for this process at 25° and not too much different at 0°. This positive entropy term for the recombination of ions is consistent with what has been observed before.[2,9] The heats and entropies of activation reported by Maron and La Mer do not refer to any simple reaction.

Experimental

The preparation of materials and the general experimental technique have been described previously.[2,7] Stock solutions of nitroethane were made fresh for each run or two since decomposition to hydroxamic acid occurs even in the cold room. The rates of ionization were measured with the nitroparaffin in large excess and followed as a pseudo-zero order reaction. The rate of bromination was followed by the conductance change. The rate of iodination was followed by titrating the unreacted iodine directly with thiosulfate. This procedure is possible because nitroethane differs from other pseudo acids in that iodine on the α-carbon atom either does not react with thiosulfate or does so very slowly. Good zero order kinetics were found by both methods of analysis. The rate constants were calculated on the basis that only monobromination occurred. A correction can readily be made for dibromination if we take Junell's value[1] of ten to one for the relative rates of ionization of α-bromonitroethane and nitroethane. At the concentrations of nitroparaffin and halogen used here, the error turns out to be one or two per cent. That is, the results in Table I are high by that amount.

TABLE I

RATE OF IONIZATION, $C_2H_5NO_2 + H_2O \longrightarrow C_2H_4NO_2^- + H_3O^+$

T, °C.	Nitroethane, moles/l.	Halogen, moles/l.		k, min.$^{-1}$
34.86	0.270	0.00194	Bromine	7.39×10^{-6}
34.86	.319	.00203	Iodine	7.60×10^{-6}
25.6	.287	.00194	Bromine	2.46×10^{-6}
25.6	.321	.00145	Iodine	2.38×10^{-6}
15.2	.258	.000725	Iodine	5.87×10^{-7}
15.2	.299	.000725	Iodine	5.59×10^{-7}
14.7	.338	.00145	Iodine	4.96×10^{-7}
69.85	...	......	......	2.65×10^{-4}[a]

$E_{act.} = 22.9$ kcal. $\Delta H_1^{\ddagger} = 22.3$ kcal. $\Delta S_1^{\ddagger}$ -18.4 E. U.

[a] This value given by Junell, ref. 1, falls on the same plot of log k *vs.* $1/T$ as our data.

TABLE II

RATE OF ION RECOMBINATION, $C_2H_4NO_2^- + H_3O^+ \longrightarrow C_2H_5NO_2 + H_2O$

	This work	Maron and La Mer
k_{25}, l./mole-min.	626	....
k_0, l./mole-min.	26	144
$\Delta H_2^{\ddagger}$, kcal.	20.6	10.4
$\Delta S_2^{\ddagger}$, e. u.	14.5	−18.5

TABLE III

ISOMERIZATION OF ACI-NITROETHANE AT 0°, $C_2H_4NO_2^- + C_2H_4NO_2H \longrightarrow C_2H_5NO_2 + C_2H_4NO_2^-$

$C_2H_4NO_2H$, mole/l.	$C_2H_4NO_2^-$, mole/l.	k_4 l./mole-min. first approx.	second approx.
0.01109	0.00668	5.58	4.88
.01109	.00668	5.60	4.90
.00776	.00534	5.66	4.80

TABLE IV

$C_2H_4NO_2^- + H_3O^+ \longrightarrow C_2H_5NO_2 + H_2O$

$C_2H_4NO_2H$, mole/l.	$\frac{k_4 K_A{}^{1/2}}{2} + \frac{k_2 K_A}{2a^{1/2}}$	k_2, l./mole-min. first approx.	second approx.
0.0167	0.0327	114	129
.0131	.0345	113	126
.0174	.0308	103	118
Data of Maron and La Mer			
0.0383	0.0258	98	121
.0383	.0266	107	129
.0361	.0304	144	165
.0361	.0320	160	183
.0340	.0336	172	194
.0319	.0350	181	200
.0289	.0349	171	190
.0232	.0331	138	155
.0218	.0340	141	158
.0218	.0354	153	170
.0217	.0348	147	165
.0203	.0359	151	167
.0180	.0402	174	190

For the isomerization reactions samples were converted completely to the sodium salt by adding an excess of sodium hydroxide and allowing to stand at room temperature for several hours. After cooling to 0° enough hydrochloric acid solution to change any desired fraction of the anion to free aci-form was added and timing begun. To determine the total concentration of aci-form and anion at any time, a known excess of bromine water was added followed by potassium iodide. The excess iodine was then titrated with thiosulfate. One sample was always allowed to stand for a long enough time to verify the stoichiometry (one mole of bromine for one mole of nitro compound).

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Summary

The rate of ionization of nitroethane in water has been measured at a series of temperatures.

The isomerization of aci-nitroethane to nitroethane in the absence of added acids occurs principally through the reaction of the anion with a molecule of aci-nitroethane acting as an acid.

The rate constants for this reaction and the reaction between hydrogen ion and the anion at 0° have been measured.

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(9) Pearson, THIS JOURNAL, **70**, 204 (1948).