

spectra of 3-ethylpentane and 3-methylpentane are surprisingly different.

We wish to thank the Physics Department for the use of a traveling microscope.

Summary

The Raman spectra of the five hexanes and the nine heptanes are described.

CHICAGO, ILLINOIS

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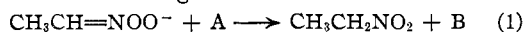
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Kinetics of Isomerization of Aci to Nitro Forms of Nitroethane in H₂O and D₂O

BY SAMUEL H. MARON¹ AND VICTOR K. LA MER

In a preceding paper² were reported kinetic studies in H₂O and D₂O on the isomerization of nitro- to aci-nitroparaffins in presence of hydroxyl and deuterioxy ions. In this paper are described kinetic measurements of the reverse process, namely, the conversion of aci-nitroethane to nitro-nitroethane in presence of H₃O⁺ in H₂O at 0 and 5°, and in presence of D₃O⁺ in D₂O at 5°.

The kinetics and mechanism of regeneration of nitroethane from the aci form were first studied quantitatively by Junell³ in various buffer mixtures in H₂O at 0°. He showed that the reaction proceeds according to the scheme



where A and B are acids and bases in general, as defined by Brönsted.⁴ The specific rate constants for the various acids used obey the Brönsted relation between catalytic constant and acid strength,

$$\frac{k_A}{p} = G \left(\frac{q}{p} K_A \right)^\alpha$$

The rate constant for the isomerization in presence of H₃O⁺ was not measured directly, but was inferred from the kinetics of the reaction in buffered solutions in which the hydrogen ion concentration was appreciable. The course of the reaction was followed by bromination of the aci-nitroethane.

Because of certain discrepancies observed between the results of the bromination and conductance methods,² and because of the indirect nature of Junell's result for H₃O⁺, it was deemed desirable to investigate directly the reaction with H₃O⁺ at 0° by conductance, and to extend the measurements to 5° and to D₂O as solvent.

Experimental

The chemicals, apparatus, and general procedure

(1) Present address: Department of Chemical Engineering, Case School of Applied Science, Cleveland, Ohio.

(2) Maron and La Mer, *THIS JOURNAL*, **60**, 2588-2596 (1938).

(3) Junell (a) *Arkiv Kemi, Mineral. Geol.*, **11B**, No. 30 (1934);

(b) *Svensk Kem. Tid.*, **46**, 125-136 (1934); (c) Dissertation, University of Uppsala, Sweden, 1935, pp. 99-110.

(4) Brönsted, *Chem. Rev.*, **5**, 231 (1928).

have been described.² The reaction was initiated by adding to barium nitroethane in a conductivity cell an equivalent quantity of H₂SO₄ (in H₂O) or D₂SO₄ (in D₂O). The rate of isomerization of the liberated acid of aci-nitroethane was followed by measuring the variation of resistance of the solutions with time.

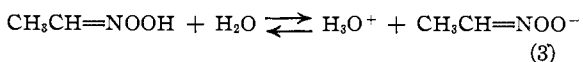
A relation between resistances observed and the rate constants can be obtained as follows. Let:

- a = total initial concentration of aci-nitroethane
- $(a - x)$ = total concentration of aci-nitroethane at time t
- (N^-) = concentration in equivalents per liter of the anion of aci-nitroethane at time t
- (HN) = concentration of un-ionized aci-nitroethane at time t
- K_H = Ionization constant of $\text{CH}_3\text{CH} = \text{NOOH}$

Then

$$(\text{HN}) + (N^-) = (a - x) \quad (2)$$

Since the equilibrium



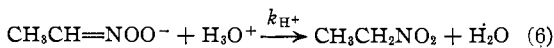
is always maintained

$$K_H = \frac{(\text{H}_3\text{O}^+)(N^-)}{(\text{HN})} \quad (4)$$

where K_H is expressed in terms of concentrations rather than activities. At the low ionic strengths used in the experiments described here, this assumption introduces no serious error. Eliminating (HN) between (2) and (4), it follows that

$$(N^-) = \frac{(a - x)K_H}{(\text{H}_3\text{O}^+) + K_H} \quad (5)$$

From Junell's work³ it may be expected that the isomerization with H₃O⁺ should proceed according to



and with the rate equation

$$\begin{aligned} \frac{-d(a - x)}{dt} &= k_{H^+}(N^-)(\text{H}_3\text{O}^+) \\ &= k_{H^+}(N^-)^2 \end{aligned} \quad (7)$$

since $(N^-) = (\text{H}_3\text{O}^+)$ in the experiments in ques-

tion, and both are removed at an equal rate. Inserting (5) in (7)

$$\frac{dx}{dt} = \frac{k_H + K_H^2(a-x)^2}{[(H_3O^+) + K_H]^2} \quad (8)$$

Again, if it be assumed that $[(H_3O^+) + K_H]$ remains sensibly constant during the course of a given experiment, (8) becomes

$$\frac{dx}{dt} = k_2(a-x)^2 \quad (9)$$

where

$$k_2 = \frac{K_H^2 k_{H^+}}{[(H_3O^+) + K_H]^2} \quad (10)$$

Equation (9) becomes on integration

$$k_2 a t = \frac{x}{(a-x)} \quad (11)$$

It can be shown readily that $x = Z'(\kappa_0 - \kappa_t) = Z\left(\frac{1}{R_0} - \frac{1}{R_t}\right)$ and $(a-x) = Z'\kappa_t = Z/R_t$, where Z' and Z are proportionality constants, κ_0 and κ_t the specific conductances at $t = 0$ and $t = t$, respectively, and R_0 and R_t the corresponding resistances. Inserting these values in (11)

$$k_2 a t = \frac{R_t - R_0}{R_0} \quad (12)$$

and

$$R_t = R_0 + (R_0 k_2 a) t \quad (13)$$

A plot of R_t vs. t should yield a straight line with slope $S = R_0 k_2 a$ and y -intercept $b = R_0$. Then

$$k_2 = S/ba \quad (14)$$

Figure 1 shows the plots for several typical runs, and shows that equation (13), and hence also (7), is obeyed. It also shows that the assumption made in equation (10) is justified.

The results obtained in this manner in H_2O at 0 and 5° are to be found in Table I, while those in D_2O at 5° are given in Table II. The time is in minutes, while the concentrations are in equivalents per liter. Although k_2 is constant within any one run, its value differs from experiment to experiment, being larger the lower the initial concentration. This variation in k_2 must be ascribed to the (H_3O^+) term in equation (10), which is different for each different initial concentration, and which was assumed to be sensibly constant only within a run. Because of the latter assumption, (H_3O^+) is given essentially by

$$(H_3O^+)_0(N^-)_0 = K_H(HN)_0 \quad (15)$$

or

$$(H_3O^+)_0^2 = K_H[a - (N^-)_0] \quad (16)$$

since $(H_3O^+)_0 = (N^-)_0$ and $[(HN)_0 + (N^-)_0] = a$. The subscript zero refers to the initial concentra-

tions. As K_H is of the order of 10^{-5} , $(N^-)_0$ will be small compared to a , and equation (16) becomes

$$(H_3O^+)_0 = (H_3O^+)_0 = K_H^{1/2} a^{1/2} \quad (17)$$

Inserting (17) into (10) we get

$$k_2 = \frac{K_H^2 k_{H^+}}{[K_H^{1/2} a^{1/2} + K_H]^2} = \frac{K_H k_{H^+}}{[a + 2a^{1/2} K_H^{1/2} + K_H]} \quad (18)$$

Because K_H is very small compared to a

$$k_2 = \frac{K_H k_{H^+}}{[a + 2a^{1/2} K_H^{1/2}]}$$

and

$$K_H k_{H^+} = k_2 [a + 2a^{1/2} K_H^{1/2}] \quad (19)$$

$K_H k_{H^+}$ given by (19) should be a constant independent of concentration and pH in H_2O . A corresponding equation with k_{D^+} for k_{H^+} and K_D for K_H should hold in D_2O .

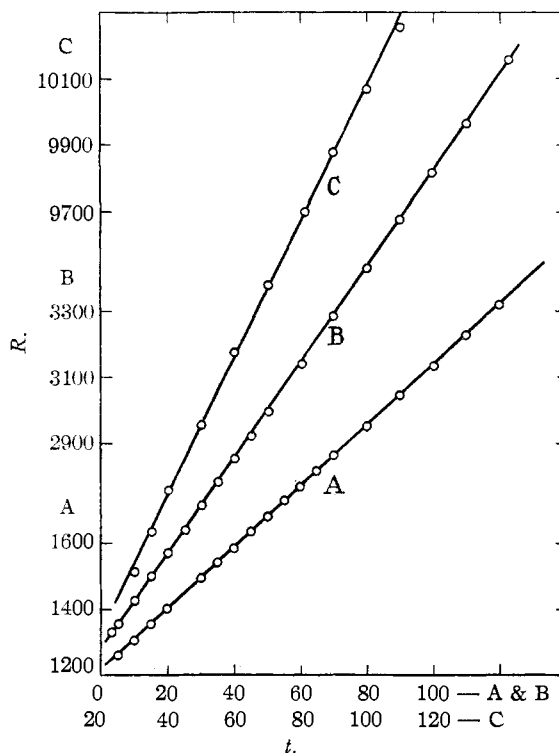


Fig. 1.—Plot of R vs. t for aci-nitroethane: A, 0.0191 N in H_2O at 5° ; B, 0.0319 N in H_2O at 0° ; C, 0.0166 N in D_2O at 5° .

The ionization constant of aci-nitroethane calculated from kinetic data is given by Junell⁵ as 7×10^{-5} . Because of the questionable accuracy of this value, K_H was determined directly with a glass electrode⁶ and shown to be $(4.1 \pm 0.1) \times 10^{-5}$ at 23° . Assuming K_H to be sensibly con-

(5) See ref. 3b; ref. 3c, p. 107.

(6) Maron and Shedlovsky, *THIS JOURNAL*, **61**, 753 (1939).

stant with temperature $K_H k_{H^+}$ values for nitroethane in H_2O at 0 and 5° were calculated and are tabulated in the last column of Table I. Unlike k_2 , values of $K_H k_{H^+}$ show acceptable constancy, and justify the assumptions made in deriving equation (19). From the mean values in Table I $k_{H^+} = 144$ at 0° and $k_{H^+} = 207$ at 5°.

TABLE I
KINETICS OF THE REACTION $CH_3CH=NOO^- + H_3O^+$ IN H_2O

Expt.	a	k_2 0°	$K_H k_{H^+}$
19-A	0.0383	0.132	0.0054
20-A	.0383	.136	.0056
26-A	.0361	.160	.0062
25-A	.0361	.163	.0063
21-A	.0340	.182	.0066
27-A	.0319	.196	.0067
7-A	.0289	.205	.0064
17-A	.0232	.217	.0055
22-A	.0218	.230	.0055
23-A	.0218	.240	.0057
24-A	.0217	.236	.0056
8-B	.0203	.252	.0056
24-B	.0180	.299	.0059
			0.0059 ± 0.0004
5°			
74-A	0.0328	0.250	0.0088
53-A	.0279	.294	.0088
72-A	.0257	.282	.0078
51-A	.0249	.325	.0088
75-A	.0232	.363	.0091
73-A	.0191	.396	.0083
76-A	.0138	.510	.0078
			0.0085 ± 0.0004

Attention should be directed to Runs 8B and 24B in Table I. In Run 8B nitroethane was neutralized with barium hydroxide, reconverted to nitroethane with sulfuric acid, neutralized again with barium hydroxide, and then sulfuric acid added and the kinetics of the reaction followed. In Run 24B the same procedure was employed but the kinetics were measured during both conversions of aci- to nitro-nitroethane (Runs 24A and 24B). In all cases the same result was obtained, showing that in absence of excess acid or alkali the isomerizations proceed smoothly in both directions, and without decomposition.

To obtain K_D in D_2O , the graphical relation between the ratio K_H/K_D and $-\log K_H$ given by Rule and La Mer⁷ was employed. Although aci-nitroethane is an acid of a somewhat different type than usually dealt with, no serious objection can

be envisaged to the use of the graphical relationship in this case. The relationship suggested by Rule and La Mer involves such different acids as chloroacetic, primary phosphoric, and hydroquinone, and hence may be expected to hold for aci-nitroethane as well. From the plot referred to, $K_H/K_D = 3.20$ for an acid of the strength of aci-nitroethane, and hence $K_D = 4.1 \times 10^{-5}/3.20 = 1.3 \times 10^{-5}$. With this value of K_D were calculated the products $K_D k_{D^+}$ by equation (19), as given in the last column of Table II. The mean gives $k_{D^+} = 208$ at 5° as compared with $k_{H^+} = 207$ at the same temperature.

TABLE II
KINETICS OF THE REACTION $CH_3CH=NOO^- + D_3O^+$ IN D_2O

Expt.	a	k_2	$K_D k_{D^+}$
55-A	0.0259	0.119	0.0032
46-A	.0233	.127	.0031
59-A	.0189	.122	.0024
56-A	.0189	.123	.0024
48-A	.0186	.156	.0031
57-A	.0166	.152	.0027
58-A	.0148	.149	.0023
			0.0027 ± 0.0003

Discussion

The value $k_{H^+} = 144$ at 0° in H_2O is in very good agreement with Junell's estimate of $k_{H^+} = 150$, an estimate based on the kinetics of isomerization of aci-nitroethane in sodium acetate-acetic acid, sodium chloroacetate-chloroacetic, and sodium β -chloropropionate- β -chloropropionic acid buffered solutions. However, instead of Junell's value $K_H = 7 \times 10^{-5}$, we use the direct⁶ experimental value $K_H = 4.1 \times 10^{-5}$. A recalculation of Junell's data for the sodium acetate-acetic acid buffered solutions, the only ones for which a fair test can be made, with $K_H = 4.1 \times 10^{-5}$ gives values for k_{HAc} , the catalytic constant of acetic acid, which are not as good as those obtained with $K_H = 7 \times 10^{-5}$. The discrepancy may be reconciled by taking into consideration the effect of the fairly high ionic strengths at which Junell worked.

The full rate equation for the isomerization of aci-nitroethane in acetic acid is

$$-\frac{dx}{dt} = [k_{HAc}(HAc) + k_{H^+}(H_3O^+)] \left(\frac{K_H}{K_H + (H_3O^+)} \right) (a - x) \quad (20)$$

No appreciable primary salt effect is to be expected for the acetic acid-nitroethane ion reaction, but a substantial one may be expected for the

(7) Rule and La Mer, THIS JOURNAL, 60, 1981 (1938).

hydrogen-ion reaction. Since the magnitude of the latter is only of the order of a correction to the former, the primary salt effect can make no serious difference in the rate constants.

A secondary salt effect may, however, be significant because of the presence of K_H in the rate equation. At very low ionic strengths K_H is essentially the thermodynamic ionization constant while at higher ionic strengths K_H may differ considerably from the thermodynamic constant. Although it is difficult to predict *a priori* how K_H will vary with $\sqrt{\mu}$ over a considerable range of ionic strengths, still it may be assumed as a first approximation that

$$\log K_H = \log K_a + \sqrt{\mu} = \log (4.1 \times 10^{-5}) + \sqrt{\mu} \quad (21)$$

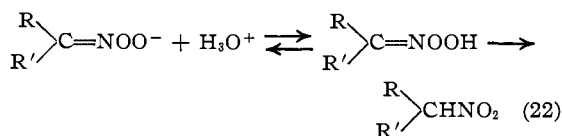
If now for each ionic strength that Junell used, a value of K_H be calculated by (21) and along with $k_{H^+} = 144$ used to evaluate k_{HOAc} , results almost identical with Junell's are obtained, as may be seen from Table III. It may be concluded, therefore, that although Junell properly neglected the small primary salt effect, he was not justified in ignoring the secondary salt effect.

TABLE III

THE SECONDARY SALT EFFECT IN ISOMERIZATION OF ACI-NITROETHANE IN NaOAc-HOAc BUFFERED SOLUTIONS

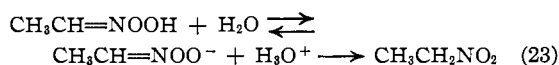
Expt.	$\sqrt{\mu}$	$\frac{k_{HOAc}}{K_H} = 7 \times 10^{-5}$	$\frac{k_{HOAc}}{K_H}$ from (21)
14	0.0750	1.04	1.75
15	.1129	0.88	1.15
16	.1129	.93	1.20
17	.1766	.76	0.82
19	.2515	.71	.70
23	.2515	.69	.68
28	.2515	.74	.75
22	.2920	.66	.64
18	.3540	.66	.59
20	.3540	.66	.62
27	.3540	.66	.64
29	.3540	.67	.66
30	.3540	.66	.65
21	.3555	.66	.59
26	.3957	.67	.66
24	.5000	.60	.57
25	.5000	.61	.60

Ley and Hantzsch⁸ postulated that the conversion of an aci- to a nitro-nitroparaffin proceeds according to the scheme



(8) Ley and Hantzsch, *Ber.*, **39**, 3149 (1906).

However, the results of this paper confirm for nitroethane Junell's finding that the re-isomerization of aci-nitroethane proceeds through the nitroethane ion rather than the undissociated acid according to



Under the conditions described in this paper, the reaction involves in H_2O the transfer of a proton from H_3O^+ to the nitroethane ion, while in D_2O it involves the transfer of a deuteron from D_3O^+ to the same ion. Within the limits of experimental accuracy the rates of proton and deuteron transfer have been found to be equal at 5° , *i. e.*, $k_{H^+} = 207$, $k_{D^+} = 208$. As far as is known, this is the first instance where the rate of transfer of a proton from H_3O^+ to a substrate in H_2O has been found to be the same as the rate of transfer of a deuteron from D_3O^+ to the same substrate in D_2O . In every other case studied,⁹ with the exception of the mutarotation of glucose, the ratio k_{D^+}/k_{H^+} has been found to be greater than unity. For the mutarotation of glucose¹⁰ the ratio is 0.74.

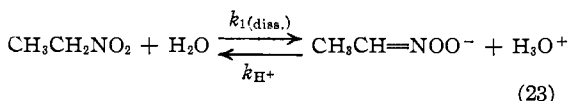
However, the reaction reported on here differs in one very important respect from those previously studied. Whereas all the H_3O^+ and D_3O^+ catalyzed reactions studied hitherto involved the transfer of a proton (or deuteron) from H_3O^+ (or D_3O^+) to an uncharged substrate, the re-isomerization of aci-nitroethane involves the transfer of a proton (or deuteron) to the *anion* of aci-nitroethane at the double bond. Once the proton (or deuteron) is transferred, the attendant electron shift stabilizes the final product, $\text{CH}_3\text{CH}_2\text{NO}_2$ (or $\text{CH}_3\text{CHDNO}_2$).

Since the electron shifts in the nitroparaffins are considered to be very rapid compared to the prototropic changes² (p. 2588), the measured rates of proton and deuteron transfer to the aci-nitroethane ion are the rates of association of the ions of the two acids, $\text{CH}_3\text{CH}_2\text{NO}_2$ and $\text{CH}_3\text{CHDNO}_2$, respectively. The equality of association rates for the proto and deutero acid observed in this paper raises the interesting and important question whether the association rates for all proto and their corresponding deutero acids are the same, or whether the instance of nitroethane represents an isolated case. The importance of this question is apparent from the following considerations.

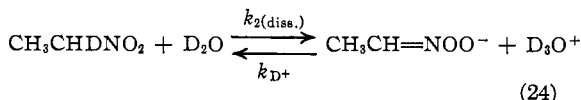
(9) See O. Reitz, *Z. Elektrochem.*, **44**, 72-81 (1938), for a summary of k_{D^+}/k_{H^+} values for various acid catalyzed reactions.

(10) Hamill and I. a Mer, *J. Chem. Phys.*, **4**, 395 (1936).

If the dissociation constant for the reaction



be defined as K_1 , then $K_1 = k_1(\text{diss.})/k_{\text{H}^+}$. Similarly, if the dissociation constant for



be defined as K_2 , then $K_2 = k_2(\text{diss.})/k_{\text{D}^+}$. For the ratio of dissociation constants of the proto and deuterio acids we get

$$\frac{K_1}{K_2} = \frac{k_1(\text{diss.})/k_{\text{H}^+}}{k_2(\text{diss.})/k_{\text{D}^+}} = \frac{k_1(\text{diss.})}{k_2(\text{diss.})} \quad (25)$$

since $k_{\text{H}^+} = k_{\text{D}^+}$. According to (25) the ratio of dissociation constants of the proto and deuterio acids depends only on the ratio of their dissociation rates, and is completely independent of their rates of association. If it can be shown that this conclusion applies to other acids besides nitroethane, then any theory of the variation of the ratio of proto to deuterio acids with acid strength need consider only the factors which determine the rates of protolytic transfer of the proton to H_2O and the deuteron to D_2O . The problem is being investigated further.

The variation of k_{H^+} with temperature in terms of the Arrhenius equation

$$\log_{10} k = -\frac{\Delta E^*}{2.303RT} + B$$

is

$$\log_{10} k_{\text{H}^+} = -\frac{2394.0}{T} + 10.925 \quad (26)$$

when k_{H^+} is expressed in equivalents per liter and minutes. The energy of activation for the reaction, ΔE^* , is then $\Delta E^* = 11,000$ cal./mole. This value of ΔE^* is lower than usually encountered for bimolecular reactions (*ca.* 20,000 cal./mole), and is lower again than the energy of activation

found for the isomerization of nitroethane to aci-nitroethane by OH^- -ion in H_2O (12,000 cal./mole)² (p. 2595).

If the variation of k_{H^+} with temperature be expressed in terms of Eyring's transition state theory of reaction velocity,¹¹ then

$$\log_{10} k = \log_{10} \frac{RT}{Nh} + \frac{\Delta S^*}{2.303R} - \frac{\Delta E^*}{2.303RT} \quad (27)$$

and

$$B = \log_{10} \frac{RT}{Nh} + \frac{\Delta S^*}{2.303R} = 14.54 + \frac{\Delta S^*}{2.303R} \quad (28)$$

at 2.5°, the average temperature for the interval 0–5°. Since $B = 10.925$ from (26), the entropy of activation for the reaction in H_2O , ΔS^* , is: $\Delta S^* = -16.5$ cal./degree/mole.

Summary

1. The rates of isomerization of aci-nitroethane to the nitro form of nitroethane have been studied by a conductance method in the presence of H_3O^+ in H_2O and in the presence of D_3O^+ in D_2O . Measurements are given in H_2O at 0° and 5° and in D_2O at 5°.

2. An equation for rate constants in terms of measured resistances is derived, and a graphical method for evaluating these constants from resistances is given.

3. The reaction is found to take place between the anion of aci-nitroethane and the acid, *i. e.*, H_3O^+ in H_2O and D_3O^+ in D_2O .

4. The rate constants for the reaction with H_3O^+ and with D_3O^+ are found to be the same at 5°, and certain deductions about the ratio of dissociation constants of proto and the corresponding deuterio acids are made.

5. The energy and entropy of activation for the reaction in H_2O are calculated.

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(11) Eyring, *Chem. Rev.*, **17**, 65 (1935); Wynne-Jones and Eyring, *J. Chem. Phys.*, **3** 492 (1935).