Kinetics of the Acid-Catalyzed Hydration of Isobutyraldehyde, Studied by Nuclear Magnetic Resonance Line-Broadening Techniques[1]

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In a study of catalysis of the deuterium exchange of isobutyraldehyde, determination of the rate of hydration of the aldehyde became desirable in order to learn whether the dehydration or hydration reaction would ever be slow enough to become the rate-determining step. Experimentally it was noted that the two separate sets of n.m.r. absorption lines due to the hydrate and the free aldehyde became broadened and then fused as increasing concentrations of strong acid were added to the aqueous solutions of the aldehyde studied. It was therefore decided to study the reaction rate by n.m.r. line-broadening techniques. After the completion of our experiments an investigation by Gruen and McTigue was published in which the kinetics of the hydration of isobutyraldehyde were studied by the maximum-temperature-rise method.[3]

Initially it was also intended to study the kinetics of the hydration of acetaldehyde in order to provide a test of the kinetic method used since the hydration of acetaldehyde had been studied by Bell and co-workers using dilatometric[4] and maximum-temperature-rise methods.[5,6] After carrying out preliminary experiments on acetaldehyde, however, our study was discontinued when it was learned that the reaction had already been studied by n.m.r. techniques by Evans, Kreevoy, and Miller.[7]

Results

The strongest lines in the n.m.r. spectra of aqueous solutions of isobutyraldehyde[8] are the doublets due to the methyl groups of the free aldehyde and its hydrate. When increasing concentrations of strong acid or strong base are added to such aqueous solutions, these doublets are broadened increasingly until they become unrecognizable; then a single merged doublet appears.

The height of an n.m.r. peak that is being broadened (and hence shortened) by chemical reaction is expressed by eq. 2 and 3 of Charman, Vinard, and Kreevoy[9-11] in terms of the reaction rate constant and various other parameters. By making approximations that should not lead to major errors in the present case the following simplified relation (eq. 1, CVK's eq. 5) is obtained

$$\frac{1}{\tau_B} = \frac{V_B^{\infty} - V_B}{V_B T_{2B}} \tag{1}$$

where V_B is the height of the absorption peak under the given set of conditions, V_B^{∞} is the height of the peak under conditions such that the rate of chemical reaction is negligible, T_{2B} is the transverse relaxation time ($1/T_{2B}$ is equal to one-half the width of the peak[13] at half-height under nonreacting conditions), and $1/\tau_B$ is the first-order rate constant for the transformation of the species B to species A in the equilibrium being studied. In our case

$$\mathrm{RCHO} + \mathrm{H_2O} \underset{k_A}{\overset{k_B}{\rightleftharpoons}} \mathrm{RCH(OH)_2}$$

where both k_B and k_A are treated as first-order rate constants.

We were not able to determine V_B^{∞} and T_{2B} reliably since we were not able to obtain reaction conditions under which the hydration rate is really negligible. Aldehyde hydration is catalyzed by acids and our purification procedures did not succeed in removing all of the acidic impurities in our aldehyde samples. Since hydration is also catalyzed by bases, including salts of weak acids, it was not enough to "neutralize" our acidic impurities. Furthermore even uncatalyzed hydration proceeds at an appreciable rate. However, by crude measurements of the hydration rate of aldehyde samples to which no acid had been added, we were able to show that the first-order rate constant for hydration under such conditions is no more than 0.2 sec.$^{-1}$. This proves that V_B^a, the height, and T_{2B}^a, the reciprocal of the half-width at half-height of the n.m.r. peak in solutions containing purified aldehyde and no added acid, are not too far from V_B^{∞} and T_{2B}. If the product of the peak height and half-width remains constant (as it would be expected to do and as it can be seen to do over a considerable range of reaction rates) over the range of rates from zero to the rate at which V_B^a and T_{2B}^a were measured, then V_B^{∞}/T_{2B} will be equal to V_B^a/T_{2B}^a. Equation 1 may then be rewritten as eq. 2. The second-order rate constant for the hydrogen ion catalyzed reaction is equal to the rate of change of the first-order rate constant k_B with respect to the hydrogen ion concentration (eq. 3). Therefore no error in the determination of k_{H^+} will result from the use of V^a and T_{2B}^a instead of V_B^{∞} and T_{2B}, although the k_B values that would result will be in error by a constant amount and

$$k_B = \frac{1}{\tau_B} = \frac{V_B^{\infty}}{V_B T_{2B}} - \frac{1}{T_{2B}} = \frac{V^a{}_B}{V_B T_{2B}^a} - \frac{1}{T_{2B}} \tag{2}$$

$$k_{H^+} = \frac{dk_B}{d[H^+]} = \left(\frac{V_B^{\infty}}{T_{2B}}\right)\frac{d(1/V_B)}{d[H^+]} = \left(\frac{V_B^a}{T_{2B}^a}\right)\frac{d(1/V_B)}{d[H^+]} \tag{3}$$

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(2) National Defense Education Act Fellow, 1960-1963.

(3) L. C. Gruen and P. T. McTigue, *J. Chem. Soc.*, 5224 (1963).

(4) R. P. Bell and B. d. B. Darwent, *Trans. Faraday Soc.*, **46**, 34 (1950).

(5) R. P. Bell and J. C. Clunie, *Proc. Roy. Soc.* (London), **212A**, 33 (1952).

(6) R. P. Bell, M. H. Rand, and K. M. A. Wynne-Jones, *Trans. Faraday Soc.*, **52**, 1093 (1956).

(7) Private communication from R. P. Bell.

(8) J. Hine, J. G. Houston, and J. H. Jensen, *J. Org. Chem.*, **30**, 1184 (1965).

(9) H. B. Charman, D. R. Vinard, and M. M. Kreevoy, *J. Am. Chem. Soc.*, **84**, 347 (1962).

(10) In order to conserve space these equations will not be repeated here. However, certain typographical errors should be pointed out. In the last two terms in the numerator in eq. 2, 2A and 2B should be τ_{2A} and τ_{2B}, respectively. In the denominator of eq. 3 a plus sign is missing just before $\Delta\omega^2$.

(11) According to Alexander, the classical McConnell equations, upon which Charman, Vinard, and Kreevoy's derivation is based, are valid as long as the rate constant for exchange is small compared to the difference in chemical shifts between the two environments of the exchanging species (13 c.p.s. in our case). The Solomon-Bloembergen correction factor, which would never introduce a correction of as much as 4% into any of our data, is said to be generally valid.[12]

(12) S. Alexander, *J. Chem. Phys.*, **38**, 1787 (1963).

(13) In radians per second, not cycles per second.

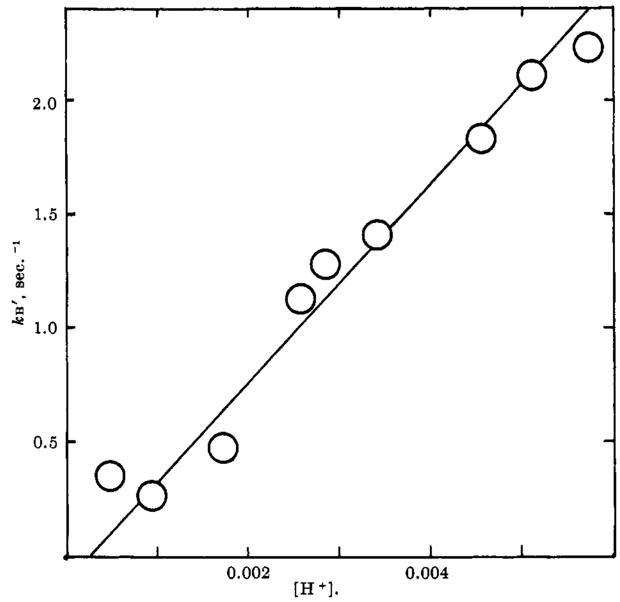

Figure 1.—Plot of k_B' calculated from the data of Table I using eq. 4 *vs.* [H$^+$].

will hence be denoted k_B'. Since V_B values were not so reproducible as desired they were measured by reference to a standard, *t*-butyl alcohol, added in known concentrations (*cf.* CVK[9]) so that we actually used eq. 4,

$$k_B' = \frac{V_B^a/V_r^a - V_B/V_r}{T_{2B}^a\, V_B/V_r} \qquad (4)$$

were the V_r terms are the heights of the reference peaks. Plots of the values of k_B' thus obtained *vs.* the hydrogen ion concentration gave a straight line from as low a hydrogen ion concentration as could be obtained (without added base) to about 0.006 *M*, after which the slope decreased. The data obtained in solutions containing more than 0.006 *M* acid were neglected since the decrease in slope is presumably due to the overlap of one peak with another, a factor not allowed for in the equation used.

To assess the validity of the assumptions that led to eq. 1, the rate constants were calculated analogously using CVM's complete eq. 3. The values thus obtained differed from those obtained using the simpler equation by less than 1%.

A plot of a set of data obtained at 35° is shown in Figure 1. From the slope of the line shown a second-order rate constant of 438 M^{-1} sec.$^{-1}$ may be calculated for the acid-catalyzed hydration of isobutyraldehyde in aqueous solution. Combination of this value with those obtained in several other such plots led to an average k_{H^+} value of 440 ± 40 M^{-1} sec.$^{-1}$.

Discussion

The rate constant we have obtained for the acid-catalyzed hydration of isobutyraldehyde in aqueous solution at 35° (440 M^{-1} sec.$^{-1}$) is larger than that obtained at 25° by Gruen and McTigue (370 M^{-1} sec.$^{-1}$)[3] using a different method. However our value is about 50% smaller than the value at 35° that would be calculated from the rate constant of Gruen and McTigue at 25° and an activation energy (16.2 kcal./mole) equal to that which may be calculated for the hydration of acetaldehyde.[5,6] We have no explanation for this discrepancy but note that the rate constant for the acid-catalyzed hydration of acetaldehyde at 25° reported by Bell, Rand, and Wynne-Jones[6] is 31% smaller than that reported by Gruen and McTigue.

Inasmuch as isobutyraldehyde is 30% hydrated at equilibrium in aqueous solution at 35°,[8] a value of 1.0 × 10^3 M^{-1} sec.$^{-1}$ may be calculated for the second-order rate constant for the acid-catalyzed dehydration of isobutyraldehyde hydrate.

Experimental

The n.m.r. spectra of isobutyraldehyde and its aqueous solutions were described earlier.[8,14] In typical kinetic experiments 0.50-ml. samples of a 3% aqueous isobutyraldehyde solution were added to each of a number of n.m.r. tubes containing 0.25 ml. of aqueous perchloric acid of known concentration under nitrogen. The n.m.r. spectrum of each sample was determined in the vicinity of the absorption due to the methyl groups at a sweep width of 50 cycles and a sweep time of 500 sec. The spectra thus obtained were not changed significantly when the sweep time was changed to 250 sec., showing that the slow sweep assumption is valid. The results obtained in a typical run are shown in Table I. There was no significant difference in the rate constants obtained at a different radiofrequency field strength; therefore, apparently the results are not complicated by saturation effects.

Table I

N.m.r. Measurements on Aqueous Isobutyraldehyde[a]

[H$^+$] × 10^4	V_B	V_r	k_B'
4.74	20.35	15.81	0.35
9.33	19.80	14.85	0.26
17.17	17.00	13.80	0.47
25.8	16.50	16.75	1.13
28.5	14.90	15.80	1.28
34.4	14.45	15.90	1.41
45.8	13.02	16.00	1.83
51.2	12.00	15.70	2.10
57.3	12.30	16.60	2.23

[a] The values of V_B^a, V_r^a, and T_{2B}^a are 21.20, 14.20, and 0.455, respectively.

Crude measurements on the rate of hydration of isobutyraldehyde were made by injecting small amounts of the aldehyde into water and very quickly measuring the change in absorbance at 2700 Å. using a Cary spectrophotometer, Model 14.

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[14] All n.m.r. spectra were determined using a Varian-A-60 instrument.

Acetylation of Triptycene[1]

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Although many derivatives of triptycene (9,10-dihydro-9,10-*o*-benzenoanthracene) have become

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