min). Since the alcohol mixture consisted of 31.1% XII-OH plus XIII-OH, there must have been 2.0% VIII ketone in the ketone mixture and thus 2.0% VIII-OH in the alcohol mixture.

Combination of the data from the three gc analyses gave the composition of the XIII-OBs acetolysis product mixture: 6.6% V-OAc, 49.9% VI-OAc, 6.1% VII-OAc, 1.9% VIII-OAc, 6.5% XII-OAc, 22.5% XIII-OAc, 5.1% bird-cage hydrocarbon, and 1.4% twisted monoene.

Registry No.—VI-OH, 40577-16-0; XII-OH, 40577-17-1; XII-OBs, 40577-18-2; XII ketone, 40577-19-3; XIII-OH, 40577-20-6; XIII-OBs, 40577-21-7; endo,endo diene 1076-13-7; brosyl chloride, 98-58-8.

Isobutyraldehyde. The Kinetics of Acid- and Base-Catalyzed Equilibrations in Water[1]

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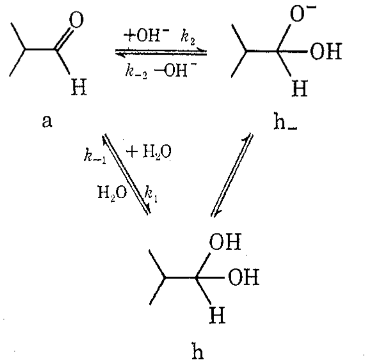
The rates and equilibrium constants for the reversible acid- and base-catalyzed hydration of isobutyraldehyde in water have been determined by temperature jump and nmr spectrometry. The standard enthalpy and entropy changes for isobutyraldehyde hydration are −5.6 kcal/mol and −19.9 eu. The standard enthalpy and entropy for the reaction of isobutyraldehyde hydrate with hydroxide ion is 0.6 kcal/mol and −1.9 eu. The activation enthalpies for the hydrogen ion and hydroxide ion catalyzed hydration of isobutyraldehyde are 7.8 and 11.7 kcal/mol, respectively.

Among the many studies on the hydration of aldehydes and ketones[2] are reports concerning isobutyraldehyde.[3-7] A solution of isobutyraldehyde in water equilibrates rapidly to a mixture of hydrate (h), hydrate anion (h−) and isobutyraldehyde (a) (Scheme I).

SCHEME I



$$K_h = \frac{[h]}{[a]} \quad (1)$$

$$K_{h_-} = \frac{[h_-]}{[h][OH^-]} \quad (2)$$

$$K_{ao^-} = \frac{[h_-]}{[a][OH^-]} \quad (3)$$

In connection with various studies on isobutyraldehyde we needed reliable values of these rate and equilibrium constants over a wide range of temperatures. Recently Pocker and Dickerson reported on the rates of hydration of isobutyraldehyde.[6b] By extrapolation to a time immediately following the mixing of reactants, and assuming the extinction coefficient of the free aldehyde to be temperature independent, they were able to obtain values of K_h at several temperatures. A plot of log K_h *vs.* $1/T$ gave values of K_h at 25 and 35° in good agreement with the earlier values[4b] obtained by nmr experiments. However, the nmr data were not corrected for possible saturation effects, and the hydration above 25° is so fast as to make extrapolation to zero time much less reliable than at 0°. Furthermore, a precise relationship between ln K_h and reciprocal temperature, especially around 25–35°, is necessary for a study by temperature jump spectrometry. A rapid kinetic technique was necessary to study hydroxide ion catalysis under conditions where the hydroxide ion concentration was known accurately.

Experimental Section

Isobutyraldehyde (bp 63.5–64.0°) was freshly distilled before preparing solutions. No impurities were detected by glpc analysis. Oxidation of isobutyraldehyde to isobutyric acid was negligible under the conditions used. Doubly distilled dust-free degassed water (boiled) was used for the preparation of all solutions. Standard solutions of perchloric acid and sodium hydroxide were periodically checked by use of primary standard (potassium hydrogen phthalate) by titration to a phenolphthalein end point. Carbonate-free sodium hydroxide solutions were prepared by filtration of saturated sodium hydroxide solutions.

T-Jump and combined T-jump stopped-flow experiments were conducted on a Durrum-Gibbson stopped-flow spectrometer equipped with a D-150 modular control unit. A permanent record of the photomultiplier signal was obtained by photographing the image on a Tektronix 564 storage oscilloscope.

A standard solution of about 0.08 *M* isobutyraldehyde was placed in one of two storage reservoirs. Acid catalysis was studied by placing 0.02–0.18 *M* perchloric acid in the second reservoir. The ionic strength of the acid solution was adjusted to 0.2 by adding sodium chloride. Equal volumes of the two solutions were mixed by actuating the stopped-flow apparatus, and T-jump experiments were conducted on the resultant mixture (ionic strength 0.1). The effect of base on the rate of equilibration was studied by placing in the second reservoir solutions 0.02–0.1 *M* in sodium hydroxide with enough sodium chloride to give an ionic strength of 0.2. Since isobutyraldehyde and base react to form aldol condensation products, it was neces-

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[1] This investigation was supported in part by Grants GP-14697 and GP-32461X from the National Science Foundation.

[2] R. P. Bell, *Advan. Phys. Org. Chem.*, **4**, 1 (1966).

[3] L. C. Gruen and P. T. McTigue, *J. Chem. Soc.*, 5217, 5224 (1963).

[4] (a) J. Hine, J. G. Houston, and J. H. Jensen, *J. Org. Chem.*, **30**, 1184 (1965); (b) J. Hine and J. G. Houston, *ibid.*, **30**, 1328 (1965).

[5] (a) P. Greenzaid, Z. Luz, and D. Samuel, *J. Amer. Chem. Soc.*, **89**, 749 (1967); (b) P. Greenzaid, Z. Rappoport, and D. Samuel, *Trans. Faraday Soc.*, **63**, 2131 (1967).

[6] (a) Y. Pocker and J. E. Meany, *J. Phys. Chem.*, **71**, 3113 (1967); **72**, 655 (1968); **73**, 1857 (1969); (b) Y. Pocker and D. G. Dickerson, *ibid.*, **73**, 4005 (1969).

[7] M. G. Champetier and P. Le Henaff, *C. R. Acad. Sci., Ser. C*, **265**, 175 (1967).

sary that the two substrates remain apart until immediately prior to discharge of the heating cell capacitor. The rate of aldolization is sufficiently slow that no appreciable fraction of the aldehyde is lost due to aldol condensation in the first several seconds if concentrations of aldehyde and base are small.[4] Experiments were conducted in such a manner that the T-jump occurred precisely 2 sec after the mixing of reactants. No correction was made for the amount of hydroxide ion used up in conversion of aldehyde hydrate to hydrate anion, since the concentration of hydroxide ion is in all cases several times that of the hydrate.

A heating pulse of 250 μsec and oscilloscope delay of 400 μsec proved to be sufficient to ensure that perturbations attributable to the heating pulse were absent. The rate of isobutyraldehyde equilibration was determined at the carbonyl absorption maximum (285 nm) spectrometrically.

All nmr experiments were made using a Varian Model A-60A spectrometer equipped with a temperature controller Model V6040. The probe temperature was determined by the methanol resonance technique.[8] The ratio of the area of the methyl doublet of the hydrate to that of the free aldehyde was determined by use of a polar planimeter, Keuffel and Esser Model 62-0015, and found to be highly reproducible. The average of three integrations was in all cases well within 0.5% of any individual integration. No appreciable variation in the relative areas could be detected for solutions 0.1–0.3 *M* in aldehyde.

All ultraviolet measurements were made using a Cary Model 16 spectrometer and 10-cm thermostated cells. Solutions and pipettes were precooled prior to measurements in a bath adjusted to the same temperature as that of the cell. Since isobutyraldehyde reacts in basic solution to yield aldol condensation products, it was necessary to determine the absorbance (at 285 nm) immediately after mixing the aldehyde and base solutions. Several solutions of varying concentrations of sodium hydroxide were adjusted so that the total volume was 45 ml and then immersed in a thermostated bath. Another solution of isobutyraldehyde in doubly distilled water was also brought to thermal equilibrium and 5-ml aliquots were added to each base solution just before the uv determination. The amount of time (approximately 50 sec) necessary to mix solutions and place them in the cell was taken into account and the actual absorbance reading was determined by extrapolation to the time of mixing. Although the extrapolation never gave a very large difference in absorbance value, it was felt to be a more accurate measure of the true value immediately after the equilibration of free aldehyde, hydrate, and hydrate anion. The absorbance of the aldehyde in the absence of base was determined similarly, using a sample containing doubly distilled water rather than sodium hydroxide.

Results

The nmr spectrum of an aqueous solution of isobutyraldehyde shows two methyl doublets, one of which is at a higher field than the other. The area ratios of the two doublets are dependent on the temperature. Contamination of the sample with a trace amount of isobutyric acid shows that the methyl doublet of isobutyric acid is easily discernible in the mixture of hydrate, aldehyde, and acid. The low-field methyl doublet was attributed to isobutyraldehyde, and the higher field methyl doublet was attributed to isobutyraldehyde hydrate. The equilibrium constant for hydration was calculated as the ratio of integrated areas of the two doublets.

The calculated equilibrium constants at a particular value of the oscillator field strength are found to correlate precisely (linear least-squares analysis) with the equation

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{4}$$

where ΔH° is the standard enthalpy change (assumed to vary negligibly over the temperature range studied), ΔS° is the standard entropy change, R is the gas constant (cal/deg mol), and T is the temperature (degrees Kelvin). The value of K_h calculated is found to depend greatly on the field strength at which the experiment is conducted. For example, at 286.55°K, the values of K_h calculated are 0.884 (0.005 mG), 0.896 (0.0075 mG), 0.911 (0.010 mG), and 1.120 (0.020 mG). The results of a number of experiments are summarized in Tables I and II. Values of K_h at 0 mG field strength are obtained as follows. Values of K_h at 0.02, 0.01, 0.0075, and 0.0050 mG are calculated for a particular temperature. The results of these calculations are then placed on a graph correlating K_h and field strength, and a smooth curve is drawn to enable extrapolation to zero field strength (Figure 1).

TABLE I

DEPENDENCE OF K_h ON TEMPERATURE AND FIELD STRENGTH

	K_h		
Temp, °K	0.0050 mG	0.0075 mG	0.0100 mG
320.42		0.334	0.353
317.52			0.412
316.55		0.356	0.348
303.49	0.580	0.528	
301.07	0.615	0.598	0.608
297.20	0.612	0.639	0.640
295.75	0.667	0.640	0.686
292.84	0.678	0.723	0.769
290.91	0.788	0.805	0.805
286.55	0.884	0.896	0.911
283.65	0.931	1.051	1.035
277.84	1.219	1.133	1.137
276.39	1.285	1.250	1.277
272.52	1.585	1.620	1.712

TABLE II

SLOPES AND INTERCEPTS OF EQUATION 4 AS A FUNCTION OF APPLIED OSCILLATOR FIELD STRENGTH

Field, mG	No. of expts	ΔH°, kcal/mol	ΔS°, eu
0.0200	22	−5.01	−17.2
0.0100	14	−5.36	−18.9
0.0075	13	−5.44	−19.2
0.0050	10	−5.59	−19.7
0.0000		−5.64	−19.9

The ultraviolet spectral results are in accord with these nmr results, as evidenced by the temperature dependence of the optical density at 285 nm. A dilute solution of isobutyraldehyde in water obeys the Beer–Lambert law. The apparent extinction coefficient is given by the equation

$$\epsilon_{\mathrm{app}} = \frac{\epsilon_{\mathrm{C-O}}}{1 + K_h} \tag{5}$$

The equilibrium constant for the hydrate–hydrate anion equilibrium was determined by the equation

$$K_{h^-} = \frac{\Delta D(K_h + 1)}{DK_h[\mathrm{OH}^-]_e} \tag{6}$$

where D, ΔD, and $[\mathrm{OH}^-]_e$ are defined as the optical density of a solution in the absence of base, the difference in optical density between that of such a solution and that of a solution of identical isobutyraldehyde concentration in the presence of base, and the equilibrium concentration of base, respectively. For example, at 34.0° a solution calculated to be 1.548 *M*

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[8] A. L. Van Geet, *Anal. Chem.*, **40**, 2227 (1968); **42**, 679 (1970).

sodium hydroxide before the addition of isobutyraldehyde had an absorption of 0.7664, whereas a solution of identical isobutyraldehode concentation in water alone had an absorption of 1.1195.[9] From these data a value of 0.956 for K_{h-} may be calculated ($K_h = 0.337$). The average of six values determined at 34.0° is 0.93 with an average deviation of ± 0.09. A summary of results appears in Table III.

TABLE III

EFFECT OF TEMPERATURE ON THE ISOBUTYRALDEHYDE HYDRATE-HYDRATE ANION EQUILIBRIUM CONSTANT

Temp, °C	K_{h-}, N^{-1}	No. of expt
34.0	0.932 ± 0.09[a]	6
29.0	0.968 ± 0.05	5
28.8	1.170 ± 0.04	8
21.0	1.045 ± 0.09	8
15.0	1.031 ± 0.17	9

[a] Average deviation from the average.

The value of k_{obsd} was determined by a linear least-squares analysis of the integrated first-order equation

$$\ln \log \frac{P}{P_e} = -k_{obsd}t + \ln \log \frac{P_0}{P_e} \tag{7}$$

where P is the amplitude of the recorded photomultiplier signal and the subscripts 0 and e refer to the initial and equilibrium values. In general the data gave excellent linear correlations for time periods in excess of 3 half-lives. The temperature at which the reaction occurred was determined by the equation

$$\ln\left(\frac{a_T}{a_0 + \frac{1}{\epsilon_l}\log\frac{P_0}{P_e} - 1}\right) - \ln\{K_h(1 + K_{h-}[OH^-])\} = 0 \tag{8}$$

where a is the amount of aldehyde present and the subscripts T and 0 refer to the total amount of aldehyde and the initial amount of aldehyde present in the free form. The left side of eq 8 will at some temperature (from which are calculated the values of K_h and K_{h-}) satisfy the equality expressed by eq 8. That temperature is the temperature at which the reaction occurred.

Variations in the magnitude of the temperature jump were observed even though the ionic strength remained constant (0.1). These variations are attributable to the different ions present in the various solutions employed. A summary of results for the sodium hydroxide and perchloric acid catalyzed equilibrations of isobutyraldehyde appears in Tables IV and V.

Discussion

A number of investigators have reported on the common features a solution containing both the free carbonyl and its hydrate shows in its nmr spectrum.[2-5] The nmr spectrum at several different oscillator field strengths reveals the degree to which the applied field has affected the calculated equilibrium constant. This behavior is most reasonably attributable to the effects of selective saturation. Anderson has reported that saturation effects generally increase with decreasing half-width.[10] The experimental findings reveal that the half-width of the aldehyde band is less than that of the hydrate band. These results, coupled with the generality of Anderson, lead to the expectation that the methyl protons of the aldehyde are saturated to a greater degree than those of the hydrate, in accordance with the results of Table I.

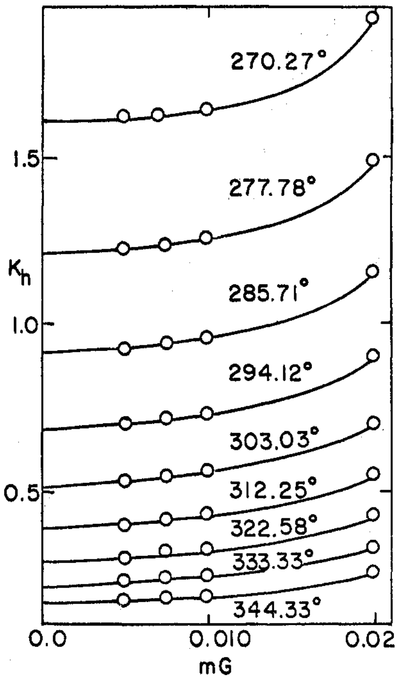

Figure 1.—Variations in apparent values of K_h as a function of R_f field at several temperatures.

The correlation of the logarithm of the equilibrium constant with $1/T$ tacitly assumes that $\Delta H°$, the standard enthalpy change, is nearly temperature independent. This is known to be true for the hydration of acetaldehyde, for which $\Delta C_p°$ is reported to be only -10 ± 5 cal/deg mol,[11] and appears to be true in the present case, where there is no obvious curvature in the plot of ln K_h *vs.* $1/T$. A summary of thermodynamic parameters and the results of other investigators appears in Table VI.

The results of this study are in excellent agreement with those of Pocker and Dickerson. Other results[3,4] appear to be in error by slightly overestimating the magnitude of both $\Delta H°$ and $\Delta S°$.

We observed no variation in the extinction coefficient other than that attributable to experimental difficulties over a wide range of temperatures. The calculated value, 22.13 ± 0.52, is within the experimental uncertainty of Pocker and Dickerson's value of 22.3 determined at 0° by extrapolation to a time where the initially added isobutyraldehyde was completely unhydrated. One may conclude that the extinction coefficient does not vary appreciably as a function of temperature. This result is reasonably strong evidence in support of the hypothesis that only the aldehyde and hydrate species are present in aqueous solution over the range of temperatures herein employed. If a significant fraction of enol is present, the equilibrium between the aldehyde and its enol is surprisingly temperature independent (over the temperature range 0–35°). Furthermore, no enol absorption signals were detectable in the nmr spectra.

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[9] The absorptivity of all solutions has been corrected for the small but nonnegligible absorption of the sodium hydroxide solutions at 285 nm.

[10] W. A. Anderson, *Phys. Rev.*, **104**, 850 (1965).

[11] J. L. Kurz, *J. Amer. Chem. Soc.*, **89**, 3524 (1967).

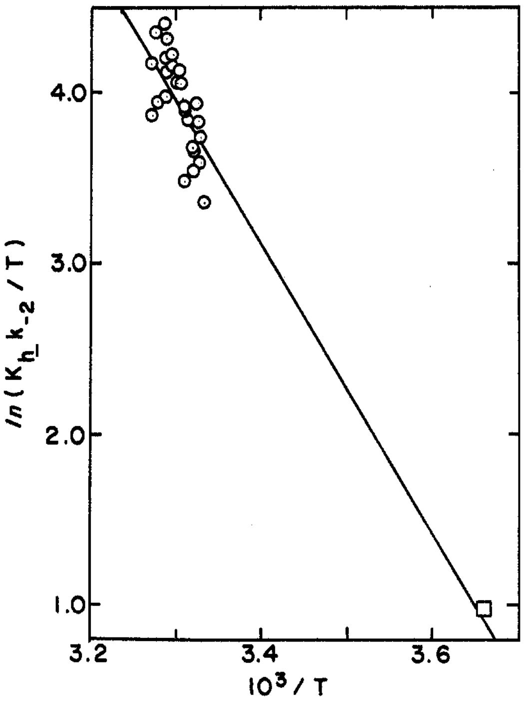

Figure 2.—Correlation (least squares) of ln (K_hk_{-2}/T) *vs.* $1/T$ (standard deviation, 0.18).

The only previous report on the acidity of isobutyraldehyde hydrate gave a $K_{h\_}$ value of 1.68 at 25°.[4a] The results of the present study indicate that the true value is considerably smaller ($K_{h\_}$ 1.03 at 25°). Although the temperature dependence of this equilibrium is very slight, it does appear that the hydrate is less acidic at high temperatures than at low temperatures. On the basis of the five values at 15–34°, the calculated standard enthalpy change and entropy change for the reaction of the hydrate with hydroxide ion is −0.6 kcal/mol and −1.9 eu, respectively. The acidity constant of isobutyraldehyde hydrate at 25° is 1.03×10^{-14}, which may be compared with the values of acetaldehyde (2.7×10^{-14}) and formaldehyde (5.4×10^{-14}) hydrates determined by Bell and Onwood.[12]

The rate of appearance of isobutyraldehyde, following thermal equilibration of the reaction cell, is given by the equation

$$\frac{d[a]}{dt} = (k_{-1}[h] + k_{-2}K_{h-}[h][OH^-]) - (k_1[a] + k_2[a][OH^-]) \tag{9}$$

As shown in Scheme I, the rate constants k_1 and k_{-1} are specifically associated with the reaction of isobutyraldehyde and water, and the rate constants k_2 and k_{-2} are to be associated with the reaction of isobutyraldehyde and hydroxide ion. The assumption is that the equilibration of isobutyraldehyde hydrate with the hydrate anion ($h \rightleftharpoons h_-$) is much faster than any of the other reactions.[13]

TABLE IV
EXPERIMENTAL RESULTS OF BASE-CATALYZED EQUILIBRATION OF ISOBUTYRALDEHYDE

NaOH, *M*	*KV*	P_e[a]	Temp,[b] °K	k_{obsd}, sec^{-1}
0.05[c]	4.0	81.75	304.79	1460
	3.75	83.25	304.16	1167
	3.5	92.00	300.84	1174
	3.0	94.75	299.76	1348
0.045[d]	5.0	80.00	305.64	1276
	4.75	81.00	305.16	1256
	4.5	83.50	304.10	1365
	4.25	87.00	302.70	1091
	4.0	86.50	302.88	1172, 817
	3.75	88.75	302.02	1092, 893
	3.5	90.00	301.54	1050, 1124
	3.25	91.50	301.01	904
	3.0	92.38	300.72	980
0.040[d]	5.0	80.75	305.30	844
	4.5	84.75	303.58	1038
	4.25	86.50	302.88	1213
	4.0	87.50	302.51	907
	3.5	90.13	301.54	984
	3.25	92.50	300.66	1099
	3.0	93.25	300.38	852
0.035[d]	5.0	81.25	305.10	806
	4.75	83.75	304.03	961
	4.5	84.75	303.58	1087
	4.25	87.75	302.39	983
	4.0	87.00	302.70	845, 1017
	3.75	90.00	301.54	373
	3.5	91.00	301.19	548
	3.25	91.63	300.95	614
	2.5	95.00	299.76	459
0.030[d]	5.0	81.00	305.16	1220
	4.75	83.13	304.29	1094
	4.5	86.00	303.07	898
	4.25	87.00	302.70	950
	4.0	86.50	302.88	660
	3.75	88.50	302.14	441
	3.5	90.63	301.30	541
	3.25	92.25	300.72	426, 627
	3.0	93.00	300.49	407, 504
0.020[d]	5.0	83.50	304.10	713
	4.75	86.50	302.88	648
	4.5	85.00	303.51	613
	4.0	88.25	302.20	458
	3.0	93.25	300.38	351, 390
0.010[c]	3.5	91.25	301.07	166
	3.25	91.25	301.07	170
	3.0	92.00	300.84	234
	2.5	93.00	300.49	128

[a] Photomultiplier signal at equilibrium relative to the initial value (at $t = 0$) of 800 mV in per cent. [b] Temperature (°K) calculated. Initial temperature 298.15°K. [c] Isobutyraldehyde $0.5 \times 8.339 \times 10^{-2}$ *M*, μ 0.1. [d] Isobutyraldehyde $0.5 \times 8.278 \times 10^{-2}$ *M*, μ 0.1.

The pseudo-first-order rate constant k_{obsd} is given by the equation

$$k_{obsd} = (k_2[OH] + k_1)\left(1 + \frac{1}{K_h(1 + K_{h-}[OH^-])}\right) \tag{10}$$

from which are obtained the catalytic constants for acid and base catalysis. The results of our study are found in Table VII along with those results obtained by other investigators.[4,6,14]

Pocker and Dickerson have reported that the acid-catalyzed hydration of isobutyraldehyde is characterized by a catalytic constant ($k_{h+} + k_{-h+}$) of 97.5 M^{-1} sec^{-1} at 0°. Their results, based on a series of successive approximations, were under the constraints of the best fitting to a linear polynomial in hydronium ion, hydroxide ion, water, acetate ion, and acetic acid, from which were derived the catalytic coefficients of

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(12) R. P. Bell and D. P. Onwood, *Trans. Faraday Soc.*, **58**, 1557 (1962).
(13) M. Eigen, *Discuss. Faraday Soc.*, **39**, 7 (1965).
(14) J. Hine and F. A. Via, *J. Amer. Chem. Soc.*, **94**, 190 (1972).

TABLE V

EXPERIMENTAL RESULTS FQR ACID-CATALYZED EQUILIBRATION OF ISOBUTYRALDEHYDE

$HClO_4$, M	KV	P_e[a]	Temp,[b] °K	k_{obsd}, sec^{-1}
0.090	5.0	75.00^c	312.2	146
	4.25	89.87^d	311.0	134
	4.0	84.50^c	305.9	121
		91.25^d	309.0	130
	3.5	93.00	306.6	104
	3.25	93.75	305.6	98.4
	3.0	94.63	304.4	99.6
		91.25^c	302.3	71.2
	2.5	93.25	301.2	81.7
		96.38^d	302.3	92.1
0.0878	4.0	93.50	305.9	108
	3.5	95.13	303.8	113
	3.25	95.63	303.2	102
	3.0	96.25	302.4	96.1
	2.5	97.38	301.1	99.7
0.080	4.25	92.25	307.7	126
	3.5	94.25	305.0	99.8
	3.25	95.44	303.5	102
	2.5	97.44	301.0	82.0
0.075	5.0	73.43^c	313.4	83.2
	4.25	89.15^e	305.6	130
	4.0	84.00^c	306.3	90.3
		90.13^e	305.4	95.4
	3.5	86.00^c	305.0	83.1
		92.13^e	303.8	80.4
	3.25	92.81	303.2	71.4
	3.0	90.50^c	302.6	86.4
		94.50^e	302.0	76.8
0.060	4.25	88.50	306.7	104
		91.75^d	308.3	102
	4.0	90.13^e	305.4	88.1
		92.88^d	306.8	99.2
	3.5	92.13^e	303.8	63.0
	3.25	92.75	303.3	55.6
		95.13^d	303.8	79.6
	3.0	93.75^e	302.5	56.3
		95.88^d	302.9	89.6
	2.5	95.69^e	301.1	45.9
		97.31^d	301.2	51.0
0.050	5.0	76.88^c	310.9	86.5
	4.25	81.50	307.7	73.6
	4.0	83.50	306.6	71.8
	3.5	87.50	304.2	71.8
	3.0	90.00	302.9	52.3
0.040	4.25	87.50^e	307.6	41.0
		91.88^d	308.1	68.8
	4.0	92.50	307.3	63.6
	3.5	90.63^e	305.0	31.2
		94.00^d	305.3	51.7
	3.25	91.88^e	304.0	28.6
		94.88^d	304.2	53.5
	3.0	93.50^e	302.7	30.3
		95.63^d	303.2	36.8
	2.5	95.06^e	301.5	23.7
0.025	4.25	79.00^c	309.3	29.4
		90.63^d	309.9	30.3
	4.0	81.50^c	307.7	28.5
		91.50^d	308.6	29.5
	3.5	85.00^c	305.5	27.8
		93.00^d	306.6	24.1
	3.25	86.50^c	304.8	22.9
		93.75^d	305.6	23.4
	3.0	89.00^c	303.5	22.6
		94.50^d	304.6	20.8
	2.5	96.25	302.4	23.3
0.01	4.25	77.50^c	310.4	12.2
		90.00^d	311.0	11.5
	4.0	90.63	309.9	13.2
	3.75	82.50^c	307.2	11.8
	3.5	85.75	305.2	11.3
		91.50^d	308.6	9.28
	3.25	93.25	306.3	9.14
	3.0	89.75^c	303.1	10.5
		94.00^d	305.3	8.32
	2.5	95.94	302.8	7.96

[a] Photomultiplier signal at equilibrium relative to the initial value (at $t = 0$) of 800 mV in per cent. [b] Temperature calculated. Initial temperature 298.15°K. [c] Isobutyraldehyde 0.030 M, μ 0.1. [d] Isobutyraldehyde 0.012 M, μ 0.1. [e] Isobutyraldehyde 0.020 M, μ 0.1.

TABLE VI

SUMMARY OF THERMODYNAMIC PARAMETERS

Reaction	ΔH[a]	ΔS[b]	$\epsilon_{C=O}$[c]	K_X 0°	K_X 25°	K_X 35°	Ref
X = h	−6.5	−26.9			0.61	0.428	5
	−7.3	−26	17.7		0.44		4
	−5.8	−20.4	22.3	1.58	0.66	0.43	8b
	−5.6	−19.9	22.1	1.43	0.600	0.440	This work
	−5.4				0.615		11
					0.43		7a
X = h₋	−0.6	−1.9		1.13	1.03	1.00	This work
					1.68		5
X = ao⁻	−6.2	−21.8		1.62	0.620	0.441	This work

[a] kcal/mol. [b] cal./mol deg. [c] l./mol cm.

each substrate. They have also reported on the base-catalyzed hydration of isobutyraldehyde, where it was found that a linear polynomial was best fit by use of the parameter k_{OH-} equal to 1.77×10^3 M^{-1} sec^{-1} at 0°. At the small concentration of hydroxide ion present, k_{OH-} is essentially identical with what we define as $(k_2 + K_{h-}k_{-2})$.

TABLE VII

SUMMARY OF RATE CONSTANTS FOR THE ACID- AND BASE-CATALYZED HYDRATION OF ISOBUTYRALDEHYDE

Rate constant	K_X 0°	K_X 25°	K_X 35°	Ref
$(k_{H_2O} + k_{-H_2O})^a$	0.000515			8d
			0.00769	31
$(k_{h+} + k_{-h+})^b$	97.5			8d
	122	693	1340	This work
			1470	5b
k_{h+}	71.5	260	411	This work
k_{-h+}	50.0	433	933	This work
$(k_2 + K_{h-}k_{-2})^b$	1770			8d
	1660	1590	37,000	This work
			32,000	31
k_2	987	5980	11,400	This work
$K_{h-}k_{-2}$	688	10,000	26,000	This work
k_{-2}	610	9690	26,000	This work

[a] Dimensions, sec^{-1}; water included in the rate constant. [b] Dimensions, M^{-1}, sec^{-1}.

The results of Pocker and Dickerson and those of Hine and Houston have been used in determining the most reasonable slope and intercept associated with the equation correlating $\ln k/T$ with reciprocal temperature. Those values of K_hk_{-2} and $(k_{h+} + k_{-h+})$ determined at 0°, where the rate of reaction is considerably slower, should serve to estimate the true rate constant better than values that we would obtain by extrapolation. The enthalpy and entropy of activation were calculated from the plot of ln $(K_h k_{-2}/T)$ *vs.* $1/T$ shown in Figure 2.[15]

The hydrogen ion and hydroxide ion catalyzed hydration of isobutyraldehyde is characterized by enthalpies of activation of 7.8 and 11.7 kcal/mol, respectively. Enthalpies of activation for dehydration of isobutyraldehyde hydrate are 13.4 kcal/mol for the acid catalysis and 17.3 kcal/mol for hydroxide ion catalysis. Calculated entropies of activation for hydration are 26 and 45 eu for hydrogen ion and hydroxide ion, respectively. Entropies of activation for the acid- and base-catalyzed dehydration of isobutyraldehyde hydrate are 46 and 65 eu, respectively.

The magnitudes of our rate constants are similar to those recently obtained by Ahrens and Maass for the acid-catalyzed hydration of 2-methylbutyraldehyde.[16] These authors apparently assumed that the extinction coefficient of their aldehyde was the same in water as in tetrahydrofuran. Because of the uncertainties arising from this approach,[2] it is probably not worthwhile to make a detailed comparison of data.

The hydration and dehydration of isobutyraldehyde has previously been reported to be subject to both general acid and general base catalysis.[4a,6,16b] In an attempt to measure the rate of carbinolamine formation through the use of dimethylamine and isobutyraldehyde, we observed on several occasions the marked acceleration of the overall rate of hydration, apparently attributable to the action of dimethylamine as a general base. Unfortunately, we have not been successful in our attempts to determine the rates of carbinolamine formation, which appears to proceed at a pace beyond the capabilities of our present instrumentation.

Registry No.—Isobutyraldehyde, 78-84-2.

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[15] Values of k_{h+} were determined by the equation $k_{h+} = k_{obsd}[HClO_4]^{-1} \cdot K_h/(1 + K_h)$. A weighting factor of 7 was used and the value of k_{h+} taken from the work of Hine and Houston entered into the correlation. Values of k_{h+} and K_h–k_{-2} (*ca.* 728 M^{-1} sec^{-1} at 0°) taken from the work of Pocker and Dickerson were each weighted as one.

[16] M. Ahrens and G. Maass, *Angew. Chem., Int. Ed. Engl.*, **10**, 80 (1971)

Reaction of Sulfonium Ylides with Diene Esters

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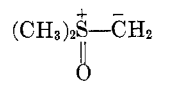
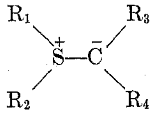
The reaction between diphenylsulfonium isopropylide and the diene esters, ethyl 1,3-cyclohexadienecarboxylate and methyl *trans*-2,4-hexadienoate, has been examined in dimethoxyethane, tetrahydrofuran, and tetrahydropyran. Both gave mixtures of isomeric cyclopropane products resulting from ylide addition across the α,β and γ,δ double bonds. The isomer distribution in the case of the cyclic diene ester was found to be solvent dependent, whereas the acyclic system showed preferential addition to the γ,δ double bond irrespective of solvent. The widely used method of preparing *n*-alkyldiphenylsulfonium salts by reaction between diphenyl sulfide, *n*-alkyl halide, and silver tetrafluoroborate was found to give mixtures of primary and secondary sulfonium salts. However, pure primary alkyldiphenylsulfonium salts can be prepared, although in low yield, by the reaction of diphenyl sulfide with *n*-alkyl trifluoromethanesulfonates.

Since the isolation of the first sulfur ylide[1] other more reactive and less stable sulfur ylides such as **1** and **2** have been prepared.[2] These ylides have found much use in organic syntheses, especially for the formation of epoxides and cyclopropanes. Both dimethylsulfoxonium methylide (**1**) and sulfonium alkylides **2** add to aromatic and unconjugated aldehydes and ketones to give epoxides. However, the sulfoxonium ylide **1** adds to α,β-unsaturated ketones to give cyclopropanes, while the sulfonium ylides **2** add to the same unsaturated systems to give oxiranes exclusively.[2,3] Further studies showed that, under certain circumstances, **2** also will add to an olefin conjugated to an ester.[2c,3,4]



$$(CH_3)_2\overset{+}{S}(=O)\text{—}\overset{-}{C}H_2$$

1



2a, $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$
2b, $R_1 = CH_3$; $R_2 = C_6H_5$; $R_3 = R_4 = H$
2c, $R_1 = R_2 = C_6H_5$; $R_3, R_4 = H$ or alkyl
1d, $R_1 = R_2 = C_6H_5$; $R_3 = R_4 = CH_3$

Much less is known about the action of sulfur ylides on substrates containing extended conjugation, *viz.*, an $\alpha,\beta,\gamma,\delta$-unsaturated carbonyl. The ylide **1** in DMSO (dimethyl sulfoxide) has been shown to add to eucarvone to give the α,β-cyclopropyl ketone **3**, while **2a** in DMSO–THF (tetrahydrofuran) added exclusively at the carbonyl of eucarvone to give the oxirane **4**.[2b] Only two other examples of sulfur ylide addition to an $\alpha,\beta,\gamma,\delta$-unsaturated carbonyl system have been reported. The dicyclopropylamide **5** was obtained when 2 mol of ylide **1** in DMSO or DMF (dimethylformamide) were allowed to react with sorbic acid anilide.[5] The other example is the addition of diphenylsulfonium isopropylide (**2d**) in DME (dimethoxyethane) to methyl 5-methyl-*trans*-2,4-hexadienoate to give methyl *trans*-chrysanthemate (**6**).[6]

We now wish to report our findings on the reaction of diphenylsulfonium isopropylide **2d** with a cyclic diene ester, ethyl 1,3-cyclohexadienecarboxylate (**7**), and an acyclic diene ester, methyl *trans*-2,4-hexadienoate (**10**, methyl *trans,trans*-sorbate).

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[2] (a) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **84**, 867 (1962); (b) **84**, 3782 (1962). (c) V. Franzen and H. E. Driessen, *Chem. Ber.*, **96**, 1881 (1963). (d) A. W. Johnson, V. J. Hruby, and J. L. Williams, *J. Amer. Chem. Soc.*, **86**, 918 (1964).

[3] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965), and references therein.

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