THE HYDRATION OF CROTONIC ACID
AND β,β-DIMETHYLACRYLIC ACID

THESIS

by

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In Partial Fulfillment of the Requirement for the

Degree of Doctor of Philosophy

California Institute of Technology

Pasadena, California

1940

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Introduction

The correlation of structure with specific reaction rate constants is seldom of value since the relative order of the rate constants for a series of similar compounds undergoing the same reaction may change with temperature. It has been found empirically that when the logarithms of the specific reaction rate constants for a single reaction are plotted against the reciprocal of the absolute temperature, a straight line generally is obtained over a relatively wide range of temperatures. Thus a specific reaction rate constant, k, may be expressed in a form of the Arrhenius equation,

$$k = \nu e^{s/R} e^{-Q/RT} \tag{1}$$

where ν is a constant of unity with the dimensions of k, R is the gas constant, T is the absolute temperature, Q is the heat of activation with the dimensions of energy and s is an entropy quantity of activation with the dimensions of entropy.

Although it is quite probable that s and Q are temperature dependent, they usually may be assigned values independent of the temperature within experimental error. The effect of structure on s and Q then can be discussed much more clearly than the effect of structure on k, since the relative orders of s or Q for a series of similar compounds undergoing the same reaction will not change with temperature.

The values of s and Q are enhanced by the facts that, when the entropy quantities are taken as independent of the temperature, the heats of activation of the forward and reverse reactions are connected withe thermodynamic heat of the reaction by the relation,

$$-\Delta H = Q_r - Q_f \qquad (2)$$

and the entropy quantities of activation are connected with the thermodynamic entropy change in the reaction by the relation,

$$\Delta S = s_f - s_r \qquad (3)$$

These equations are derived at the end of the introduction.

The hydration of olefinic compounds in aqueous solution is catalyzed by hydronium ion and often is reversible according to the equation,

$$R_1R_2C{=}CR_3R_4 + H_2O \overset{(H_3O^+)}{\rightleftharpoons} R_1R_2COHCHR_3R_4$$

In many cases both the forward and reverse reactions proceed at measureable rates and the system comes to a measureable equilibrium. This is one of the few equilibrium systems in organic chemistry which lends itself readily to a thorough investigation.

It would be interesting to correlate, therefore, the effect of various substituents on the heats and entropy quantities of activation for the hydration and dehydration reactions and on the heat and entropy change in the hydraion reaction. A study of the hydration of substituted acrylic acids was undertaken. These compounds have the added feature that the double bond of the carbonyl group conjugates with the olefinic double bond.

This thesis presents the results of an investigation of the hydration of crotonic acid to β-hydroxybutyric acid and the hydration of β,β-dimethylacrylic acid to β-hydroxyisovaleric acid.

Derivation of equation 2.

When the difference of the logarithms of the Arrhenius equations for the forward and reverse reactions is taken, there results the equation,

$$\ln \frac{k_f}{k_r} = \frac{s_f - s_r}{R} - \frac{Q_f - Q_r}{RT} \tag{4}$$

Differentiation of this equation with respect to 1/T gives

$$\frac{d \ln k_f/k_r}{d\, 1/T} = - \frac{Q_f - Q_r}{R} \tag{5}$$

Since $K = k_f/k_r$, a comparison of equation 5 with the van't Hoff equation,

$$\frac{d \ln K}{d\, 1/T} = - \frac{\Delta H}{R} \tag{6}$$

gives equation 2,

$$-\Delta H = Q_r - Q_f \tag{2}$$

Derivation of equation 3.

When the thermodynamic equations,

$$-\frac{\Delta F}{RT} = \ln K = - \frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{7}$$

are incorporated with equation 2 and compared with equation 4, equation 3 results.

$$\Delta S = s_f - s_r \tag{3}$$

[Reprinted from the Journal of the American Chemical Society, 61, 2271 (1939).]

[Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 709]

The Hydration of Unsaturated Compounds. VII. The Rate of Hydration of Crotonic Acid; the Rate of Dehydration of β-Hydroxybutyric Acid; the Equilibrium between Crotonic Acid and β-Hydroxybutyric Acid in Dilute Aqueous Solution

By D. Pressman and H. J. Lucas

Introduction

Crotonic acid has been shown to hydrate slowly in the presence of boiling 20% sulfuric acid to form β-hydroxybutyric acid.[1] This reaction is unlike the hydration of acrylic acid, since the latter occurs in the presence of hydroxide ion[2] while crotonic acid is not affected under these conditions. Moreover, only about 80% of the crotonic acid hydrates, for it appears that at this point it is in equilibrium with the hydroxy acid. The fact that the hydroxyl group enters into the β-position during the hydration is shown by the identical properties of the acid obtained by this method and of β-hydroxybutyric acid obtained by other methods. Also the ethyl ester of the hydroxybutyric acid prepared by this method is identical with that from hydroxybutyric acid obtained by other syntheses.[3]

It was desirable to extend the study of the hydration on unsaturated compounds to an investigation of the kinetics of the hydration of crotonic acid, of the kinetics of dehydration of β-hydroxybutyric acid, and of the equilibrium between crotonic acid, β-hydroxybutyric acid, and water. Since it was known that crotonic acid is not hydrated at an appreciable rate at 25° in 1 normal nitric acid,[4] the reaction was carried out in 1.06 and 2.06 normal perchloric acid solutions at 90.03 and 111.31° in order to obtain a measurable rate. These solutions were of 2.06 molal ionic strength. Nitric acid could not be used since its oxidizing power at the elevated temperature was appreciable, as evidenced by the liberation of the oxides of nitrogen.

Data and Discussion

Kinetics of the Reaction.—The hydration was found to be first order with respect to crotonic acid since the plots against time of the fraction of crotonic acid unreacted, C_t/C_0, are practically identical for two runs at hydrogen ion concentration of 1.06 molal where the initial crotonic acid concentration has the values 0.0128 molal and 0.0249 molal. Here C_0 and C_t are the molar concentrations of crotonic acid at the respective times, zero and t (Fig. 1). That the reaction is first order with respect to hydrogen ion concentration is evidenced through a comparison of the initial slopes of the plots of C_t/C_0 against t when the hydrogen ion concentrations are 1.06 and 2.06 molal. The slope at the higher concentration corresponds to a rate constant of 0.014, which is twice that of the lower, approximately 0.007. However, hydrogen ion is not used up in the reaction and thus is constant during any one run.

The independence of the equilibrium value with respect to the hydrogen ion concentration, except for small second order differences, is clearly evident from Fig. 2, which shows the complete runs of which Fig. 1 contains only the first portions. The equilibrium value of the crotonic acid fraction remaining is practically identical for both acid concentrations. The reaction then may be considered to be

$$H_3O^+ + H_2O + CH_3CH{=}CHCOOH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CH_3CHOHCH_2COOH + H_3O^+$$

where k_1 is the specific reaction rate constant of

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(1) Kaufel and Basel, *Monatsh.*, **53**, 122 (1929).

(2) Linnemann, *Ber.*, **8**, 1095 (1875); Erlenmeyer, *Ann.*, **191**, 281 (1878).

(3) Dewael, *Bull. soc. chim. Belg.*, **34**, 341 (1925).

(4) Winstein and Lucas, This Journal, **59**, 1461 (1937).

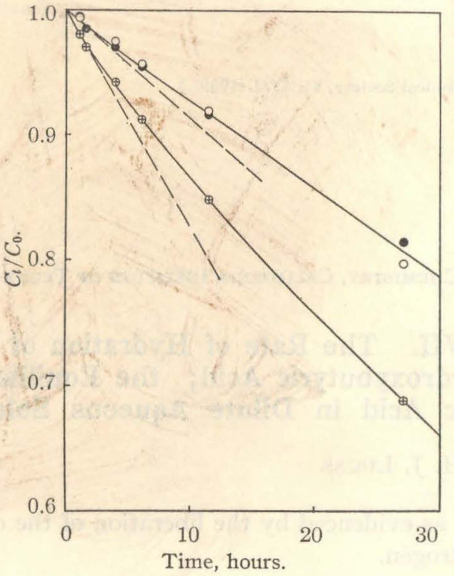


Fig. 1.—Hydration of crotonic acid showing the effect of hydrogen ion concentration and initial crotonic acid concentration on the initial slope of a plot of C_t/C_0 against time: T, 90.03°; μ, 2.06 molal.

	○	●	⊕
Crotonic acid, C_0 molal	0.02487	0.01282	0.01248
(H$^+$), molal	1.060	1.060	2.056

the forward reaction and k_2 is the specific reaction rate constant for the reverse reaction considering both reactions to be monomolecular with respect to the organic reactant.

$$-\mathrm{d(crotonic\ acid)}/\mathrm{d}t = k_1\mathrm{(crotonic\ acid)} \quad (1)$$

$$-\mathrm{d(hydroxybutyric\ acid)}/\mathrm{d}t = k_2\mathrm{(hydroxybutyric\ acid)} \quad (2)$$

Rather than calculate k_1 from the initial slope of the reaction rate curve, it was calculated by the analytical method which involves the integrated expression for a unimolecular reaction approaching equilibrium (equation 3) and the equilibrium constant (equation 4).

$$\log_{10} \frac{\epsilon}{\epsilon - x} = \frac{(k_1 + k_2)t}{2.303} \quad (3)$$

$$K = \frac{k_1}{k_2} = \frac{\epsilon}{1 - \epsilon} \quad (4)$$

Here ϵ is the fraction of the crotonic acid hydrated at equilibrium, x is the fraction hydrated at the time t, and K is the equilibrium constant. When the correct value of ϵ is chosen, a straight line results in a plot of $\log_{10} \epsilon/(\epsilon - x)$ against time. An example of this calculation is given in Table I, the data of which are plotted in Fig. 3. In order to show the effect of a variation of ϵ, the value was changed from the experimental value of 0.834 to 0.892 and 0.775. It can be seen that the experimental value produces a straight line but the variations induce marked curvature in the plots of $\log_{10} \epsilon/(\epsilon - x)$ against t. It will be noted that the values very close to equilibrium were discarded since very slight titration errors at these points in

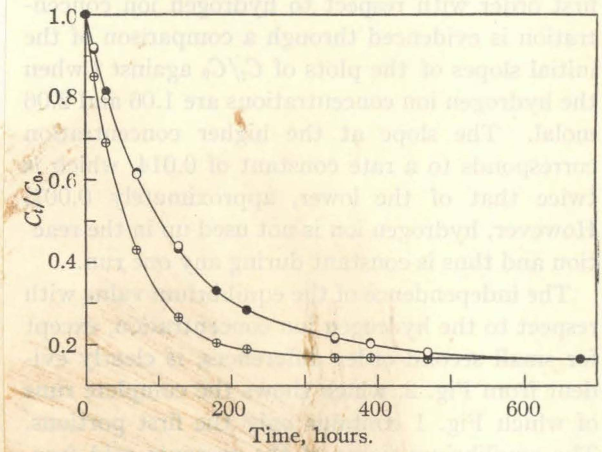


Fig. 2.—Hydration of crotonic acid showing the effect of hydrogen ion concentration and initial crotonic acid concentration on the equilibrium between crotonic acid and β-hydroxybutyric acid. Plot of C_t/C_0 against time. The last point is common to the three runs. T, 90.03°; μ, 2.06 molal.

	○	●	⊕
Crotonic acid, C_0, molal	0.02487	0.01282	0.01248
(H$^+$), molal	1.060	1.060	2.056

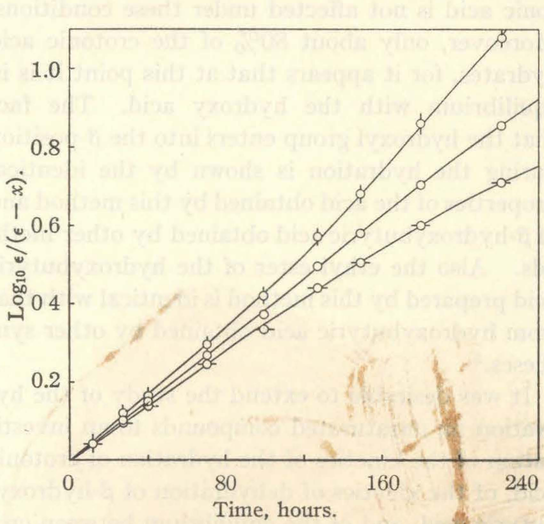


Fig. 3.—Effect of variation of ϵ on $\log_{10} \epsilon/(\epsilon - x)$ in the hydration of crotonic acid: initial crotonic acid, C_0, 0.01282 molal; T, 90.03°; (H$^+$), 1.060 molal; μ, 2.06 molal: ⦶, ϵ = 0.775; ○, ϵ = 0.834; -○-, ϵ = 0.892.

TABLE I

EFFECT OF VARIATION OF ϵ ON LOG$_{10}$ $\epsilon/(\epsilon - x)$ IN THE HYDRATION OF CROTONIC ACID AT 90.03°

$HClO_4$ = 1.060 molal; μ = 2.06 molal; initial crotonic acid = 0.01282 molal.

Time, hrs.	$1 - x$	ϵ = 0.834 $\log \frac{\epsilon}{\epsilon - x}$	ϵ = 0.892 $\log \frac{\epsilon}{\epsilon - x}$	ϵ = 0.775 $\log \frac{\epsilon}{\epsilon - x}$
0	1.000			
0.5	1.000			
1.1	0.995	0.003	0.003	0.003
1.6	.985	.008	.008	.0085
4.0	.970	.0155	.0145	.017
6.1	.955	.024	.022	.026
11.4	.917	.0445	.042	.048
27.1	.815	.1085	.101	.118
31.5	.795	.124	.115	.136
39.8	.756	.149	.138	.163
47.6	.714	.182	.168	.199
56.9	.665	.222	.204	.245
69.8	.616	.267	.244	.296
99.6	.520	.372	.335	.419
127.1	.482	.496	.439	.572
148.8	.385	.579	.506	.681
179.8	.331	.703	.601	.860
221	.282	.854	.708	1.079
340	.212			
389	.204			
468	.177			
677	.165			

the determination of the crotonic acid concentration would cause very appreciable errors in the value of $\log_{10} \epsilon/(\epsilon - x)$. In every case, the experimentally determined value for ϵ from the equilibrium constant gave an excellent straight line. The slope of this line is $(k_1 + k_2)/2.303$. The data of the several runs made are plotted in Figs. 4 and 5 as $\log_{10} \epsilon/(\epsilon - x)$ against time.

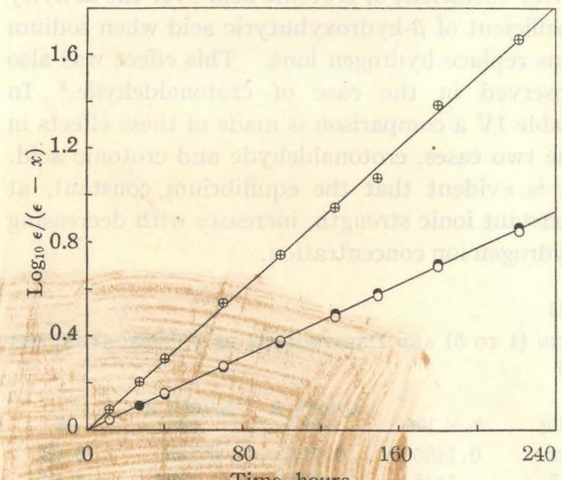


Fig. 4.—Hydration of crotonic acid at 90.03°. Plot of $\log_{10} \epsilon/(\epsilon - x)$ against time.

	●	○	⊕
μ, molal	2.06	2.06	2.06
(H^+), molal	1.060	1.060	2.056
C_0, molal	0.01282	0.02487	0.01248
	.835	.836	.829

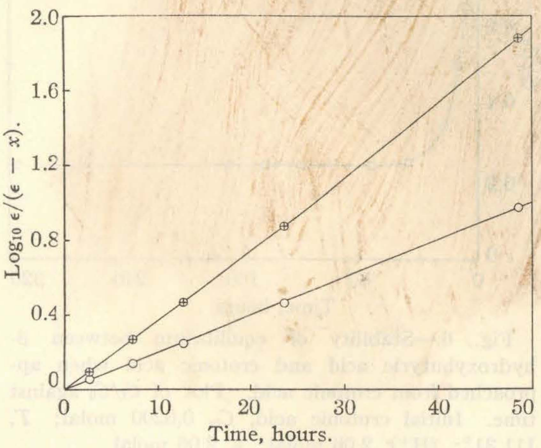


Fig. 5.—Hydration of crotonic acid at 111.31°. Plot of $\log_{10} \epsilon/(\epsilon - x)$ against time.

	○	⊕
μ, molal	2.06	2.06
(H^+), molal	1.060	2.056
C_0, molal	0.0186	0.0200
ϵ	.774	.760

As a test of the stability of the system at equilibrium one run was permitted to stand for three hundred and fourteen hours, whereas the system apparently had come to equilibrium after seventy-three hours. However, there was no observable shift in the equilibrium value of the system. These data are shown in Table II and plotted in Fig. 6.

TABLE II

STABILITY OF EQUILIBRIUM IN THE HYDRATION OF CROTONIC ACID

T = 111.3°; μ = 2.06 molal; $HClO_4$ = 2.06 molal; initial crotonic acid, C_0 = 0.0200 molal.

Time, hrs.	0	0.4	0.98	1.63	2.62	4.25
C_t/C_0	1	.983	.948	0.910	0.855	0.774
Time, hrs.		7.33	12.75	23.57	48.57	73.1
C_t/C_0		0.649	0.499	0.342	0.250	0.236
Time, hrs.		96.6	120.9	145.6	169.6	314.6
C_t/C_0		0.238	0.238	0.238	0.238	0.240

The calculation of the specific reaction rate constants for the dehydration of β-hydroxybutyric acid was carried out in a similar manner. In this case ϵ is the fraction of β-hydroxybutyric acid decomposed at equilibrium and x is the fraction decomposed at the time, t. A plot of $\log_{10} \epsilon/(\epsilon - x)$ against time for β-hydroxybutyric acid is found in Fig. 7. The specific reaction rate constants and

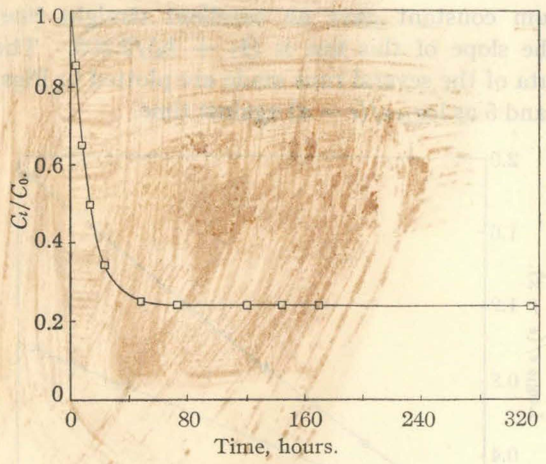


Fig. 6.—Stability of equilibrium between β-hydroxybutyric acid and crotonic acid when approached from crotonic acid. Plot of C_t/C_0 against time. Initial crotonic acid, C_0, 0.0200 molal; T, 111.31°; (H^+), 2.06 molal; μ, 2.06 molal.

the equilibrium constant determined in the dehydration run on β-hydroxybutyric acid are in excellent agreement with those obtained in the hydration of crotonic acid. This proves that a true equilibrium occurs since it can be approached from both sides.

The kinetic data obtained are listed in Table III. Experiments 1 to 5 deal with the hydration of crotonic acid while experiment 6 is concerned with the dehydration of β-hydroxybutyric acid. The specific reaction rate constants, k_1 and k_2, for the forward and reverse reactions are listed along with the constants which have been corrected for hydrogen ion concentration. The latter are listed as $k_1/(H^+)$ and $k_2(H^+)$. The constancy of these corrected values with acid concentration checks the observation that the reaction is first order with respect to hydrogen ion concentration.

The equilibrium constants, 5 at 90° and 3.4 at 111°, correspond to 84 and 78% hydration, respectively. These data substantiate the value of 80% hydration observed by Kaufel and Basel,[1] in boiling 20% sulfuric acid.

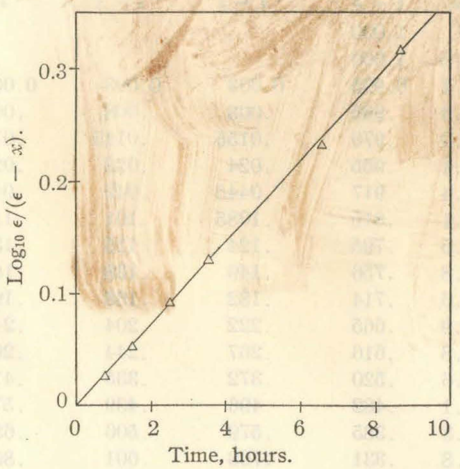


Fig. 7.—Dehydration of β-hydroxybutyric acid. Plot of $\log_{10} \epsilon/(\epsilon - x)$ against time. Initial β-hydroxybutyric acid, C_0, 0.0225; ϵ, 0.228; T, 111.31°; (H^+), 2.01 molal; μ, 2.01 molal.

Effect of Salt.—It is interesting to note that the equilibrium is shifted to the right when hydrogen ions are replaced by sodium ions. This shows that there is a relative increase in the activity coefficient of crotonic acid over the activity coefficient of β-hydroxybutyric acid when sodium ions replace hydrogen ions. This effect was also observed in the case of crotonaldehyde.[4] In Table IV a comparison is made of these effects in the two cases, crotonaldehyde and crotonic acid. It is evident that the equilibrium constant, at constant ionic strength, increases with decreasing hydrogen ion concentration.

Table III

Kinetic Data Concerning the Hydration of Crotonic Acid (1 to 5) and Dehydration of β-Hydroxybutyric Acid (6)

	Temp., °C.	(H^+)	(μ), M	Initial crotonic acid, M	$k_1 \times 10^2$	$k_2 \times 10^2$	$k_1/(H^+) \times 10^2$	$k_2/(H^+) \times 10^2$	K
1	90.03	1.06	2.06	0.01282	0.752	0.1485	0.710	0.140	5.05
2	90.03	1.06	2.06	.02487	.745	.1445	.703	.1365	5.14
3	90.03	2.06	2.06	.01248	1.43	.299	.696	.145	4.80
						Average	.703	.140	5.00
4	111.31	1.06	2.06	.01860	3.485	1.025	3.29	.97	3.41
5	111.31	2.06	2.06	.0200	6.765	2.135	3.28	1.03	3.16
						Average	3.29	1.00	3.28
6	111.31	2.01	2.01	.02249[a]	6.48	1.915	3.23	0.955	3.38

[a] Concentration of initial β-hydroxybutyric acid.

Table IV

Effect of Acid Concentration at Constant Ionic Strength on the Equilibrium Constants for the Hydration of Crotonaldehyde and Crotonic Acid

Crotonaldehyde			Crotonic Acid		
μ	(H^+) $T = 25°$	K	μ	(H^+) $T = 90°$	K
1.90	1.905	0.795	2.06	2.06	4.80
1.93	1.432	.816	2.06	1.06	5.10
1.96	0.956	.873		$T = 111.3°$	
1.98	.478	.930	2.06	2.06	3.16
			2.06	1.06	3.41

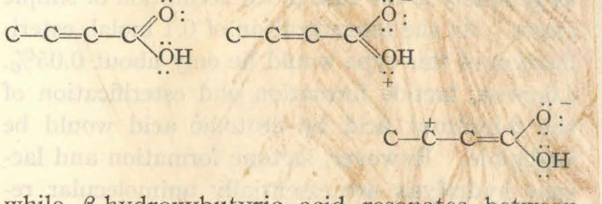
* **Thermochemistry of the Reaction.**—Table V contains the thermal data for the reactions involved. The heat of the reaction, ΔH, the heats of activation, Q_1 and Q_2 of the forward and reverse reactions, and the temperature coefficients are listed individually for the runs in the solvents of different acid concentration. The values of k_1, k_2 and K for the two runs at 90.03° in 1.06 N perchloric acid were averaged in this calculation. This averaging accounts for the discrepancy between the difference in the heats of activation and the heat of the reaction, since the latter was calculated from the temperature coefficient of the averaged equilibrium constants and the former from the averaged values of the rate constants. The heat of activation of the forward reaction is smaller than that of the reverse reaction. Thus, there results a ΔH of -10.1 kcal. for the reaction. However, the heat of activation of 38.0 kcal. for the forward reaction is larger than any of those observed previously for unsaturated compounds, which were 23.4 kcal. for isobutene[5]; 21.04 kcal. for methylethylethylene[6]; 18.92 kcal. for trimethylethylene[7]; and 18.3 kcal. for crotonaldehyde.[4] The heat of activation for the reverse reaction is 48.1 kcal. for crotonic acid as compared with 24.5 kcal. for crotonaldehyde.

Table V *

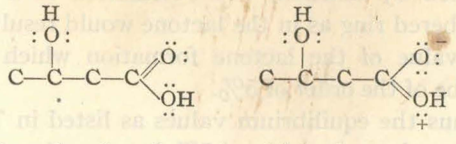
Thermal Data Concerning the Hydration of Crotonic Acid

		~~Heats of activation~~			~~Temp. coefficient~~ ~~90–100°~~	
~~(H+)~~	~~μ~~	~~Q_1, kcal.~~	~~Q_2,~~ kcal.	~~ΔH, kcal.~~	Hyd.	~~Dehyd.~~
~~1.06~~	~~2.06~~	~~37.85~~	~~47.85~~	~~−9.8~~	~~4.08~~	~~5.94~~
~~2.06~~	~~2.06~~	~~38.15~~	~~48.4~~	~~−10.3~~	~~4.14~~	~~6.05~~
	Average	~~38.00~~	~~48.1~~	~~−10.1~~	~~4.11~~	~~6.00~~

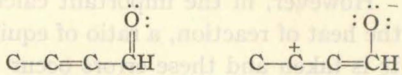
The fact that the hydration of crotonic acid liberates 10 kcal. while the hydration of crotonaldehyde liberates only 6 kcal. indicates that β-hydroxybutyric acid is relatively more stable in aqueous solution with respect to crotonic acid than aldol is with respect to crotonaldehyde. Resonance explains the relatively lower stability of the aldol. Crotonic acid in the acid solution can resonate between the unexcited forms



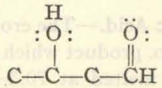
while β-hydroxybutyric acid resonates between the unexcited forms



On the other hand, crotonaldehyde can resonate between the unexcited forms



while the hydration product, aldol, can exist only in the single unexcited form



Thus, when crotonic acid hydrates it goes from a structure of principally three resonating forms to one of two, while crotonaldehyde loses nearly all of its resonance energy upon hydration. Hence, it would be expected that the evolution of energy during hydration would be less in the case of crotonaldehyde than in the case of crotonic acid, since each must retain energy equivalent to its loss of resonance energy and since the loss for the former is greater than for the latter. The difference in the heats of reaction, *viz.*, 4 kcal., is the difference in the resonance energy changes.

Ester Formation.—Gehrke and Willrath[8] have shown that β-hydroxybutyric acid loses water by itself to form a compound of lower free carboxyl content. This could be a linear ester, lactide or lactone since saponification of the compound of lower free carboxyl content liberates all these bound groups. In any case, it was stated that in a 0.1 molal solution of the hydroxy acid at 100° only 95.5% of the carboxyl groups are free. This would mean that 9% of the molecules are com-

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[5] Eberz and Lucas, This Journal, **56**, 1230 (1934).

[6] Lucas and Liu, *ibid.*, **56**, 2138 (1934).

[7] Liu and Wei, *J. Chinese Chem. Soc.*, **4**, 297 (1936).

[8] Gehrke and Willrath, *Z. physik. Chem.*, **A142**, 301 (1929).

* See page 36

bined as linear ester molecules or 4.5% are in the lactide or lactone form. Linear ester formation would be essentially negligible because of the high dilution, if it is assumed that in the pure acid, the extent of this reaction would be about 50%, as generally is the case in the formation of simple esters. At the concentration of 0.1 molal, esterification of this type would be only about 0.05%. Likewise, lactide formation and esterification of the β-hydroxy acid by crotonic acid would be negligible. However, lactone formation and lactone hydrolysis are essentially unimolecular reactions, and thus the equilibrium would not be affected by dilution. The formation of a four-membered ring as in the lactone would result in a low value of the lactone formation which may well be of the order of 5%.

Thus the equilibrium values as listed in Table III may be as much as 4.5% in error, due to the uncertainty of the β-hydroxybutyric acid concentration. However, in the important calculation, that of the heat of reaction, a ratio of equilibrium constants is taken and these errors occur then as second order corrections and are thus negligible.

Experimental

Materials. Crotonic Acid.—The crotonic acid used was the Eastman Kodak Co. product which had been recrystallized from water. It melted at 70.5–71.0° uncorr., and analysis for unsaturation showed 1.000 double bonds per mole.

β-Hydroxybutyric Acid.—This was prepared by the method of Kaufel and Basel[1] in which crotonic acid is hydrolyzed in the presence of boiling 20% sulfuric acid. The reaction mixture was neutralized to methyl orange with a freshly prepared paste of calcium hydroxide in order to remove sulfuric acid. The solution was filtered from the solid calcium sulfate and concentrated by vacuum distillation. This also removed most of the unconverted crotonic acid. A solid separated and was filtered. This was most likely a mixture of calcium sulfate and calcium β-hydroxybutyrate. The resulting sirup was extracted several times with ether to remove remaining crotonic acid. This was continued until the sirup indicated negligible unsaturation when analyzed by bromination. Upon standing in a vacuum desiccator over sulfuric acid, a precipitate of calcium hydroxybutyrate separated from the sirup. This was washed with alcohol and dried in a vacuum desiccator. An ash determination showed 15.9 and 16.0% calcium; calculated for calcium hydroxybutyrate 16.2% calcium. Since difficulties would occur in obtaining a known sample of the hydroxybutyric acid itself due to its self esterification and water loss, the calcium salt was used in its place since it could easily be weighed out quantitatively.

Perchloric Acid Solution of Constant Ionic Strength.—Equal portions of 60% perchloric acid were weighed out. To one was added enough sodium hydroxide to neutralize one-half of the acid. These portions were made up to equal volumes with distilled water. They were of equal ionic strength but unequal acidity.

Method of Analysis.—The solutions were analyzed by a quantitative bromination method. The solution to be analyzed was added to an excess of 0.05 normal bromate–bromide solution in an iodometric flask. If the solution to be analyzed did not contain a strong acid, 5 ml. of 6 N sulfuric acid was added at this time to liberate bromine. Potassium iodide solution was then added and the liberated iodine titrated with 0.02 N sodium thiosulfate solution. In the analysis of crotonic acid, it was found that a 50% excess of bromine gave theoretical bromination in five minutes while a 300% excess introduced an error of only 2% after one hour of standing. Experiments concerning the effect of bromine on hydroxybutyric acid showed that it substituted at the rate of 0.04%/minute when the mole ratio of bromine to β-hydroxybutyric acid was unity. Thus, the error incurred by the bromination of hydroxybutyric acid would be negligible under the conditions of analysis using a five-minute bromination period and a 50 or 100% excess of bromine.

Procedure of the Reaction.—Standard solutions of crotonic acid in perchloric acid were made up by roughly weighing the crotonic acid into an approximate volume of standard perchloric acid and then analyzing 20-ml. aliquots by bromination. The solutions of β-hydroxybutyric acid were made up gravimetrically by weighing out accurately a portion of calcium hydroxybutyrate and then making it up accurately to volume with perchloric acid solution. The runs were made by sealing off 20-ml. aliquots in test-tubes. These were placed in a thermostat at either 90.03° or 111.31 ± 0.05°. Tubes were withdrawn from time to time, quenched in water and the contents analyzed by bromination.

Summary

A study of the reversible hydration of crotonic acid to β-hydroxybutyric acid in 1.06 and 2.06 normal perchloric acid solutions of ionic strength 2.06 at temperatures of 90.03° and 111.31 ± 0.05° was made.

The hydration is first order with respect to crotonic acid and hydrogen ion. The dehydration is first order with respect to β-hydroxybutyric acid and hydrogen ion. The equilibrium is shown to be approachable from either the crotonic acid or the β-hydroxybutyric acid side. The equilibrium constant is 5.0 at 90° and 3.4 at 111°.

In solutions of constant ionic strength the equilibrium shifts toward crotonic acid with increasing acid concentration, thus showing that the replacement of sodium ion by hydrogen ion relatively increases the activity coefficient of β-hydroxybutyric acid over that of crotonic acid.

The energy of activation is 38.0 kcal. for the hydration and 48.1 kcal. for the dehydration.

The heat of the reaction is thus 10.1 kcal. The 4 kcal. greater heat of reaction than that which accompanies the hydration of crotonaldehyde is explained by a lower loss of resonance energy in the hydration of crotonic acid.

PASADENA, CALIF. RECEIVED MAY 29, 1939

[Contribution from the Gates and Crellin Laboratories of Chemistry,
California Institute of Technology, No. 758]

The Hydration of Unsaturated Compounds. VIII. The Rate of Hydration of β,β-Dimethylacrylic Acid; the Rates of Dehydration and Decarboxylation of β-Hydroxyisovaleric Acid; the Heat of Hydration of Dimethylacrylic Acid in Dilute Aqueous Solution

By David Pressman and H. J. Lucas

Introduction

In order to determine the effect of various substituents upon the heat of hydration of the ethylenic double bond, a number of compounds must be studied. It is reasonable to believe that the influence of the substituent may be exerted through two principal effects. One, which is the inductive effect, is shown by all substituents. The other, which affects the double bond character through resonance, is exhibited by only certain substituents. In addition there is bound to be a certain interaction between these two effects.

It is the purpose of the present hydration studies to evaluate the two principal effects and their interactions. The heats of hydration are determined from equilibria or kinetic data as in previous work.[1,2,3] A study is being made also of the kinetics and mechanism of the hydration and dehydration reactions and data are being obtained for a correlation of structural effects upon reaction velocities and heats of activation of the hydration and dehydration reactions. At the same time the influence of acid and base catalysts and of the ionic strength upon these two

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(1) W. F. Eberz and H. J. Lucas, THIS JOURNAL, 56, 1230 (1934).
(2) S. Winstein and H. J. Lucas, Ibid., 59, 1461 (1937).
(3) D. Pressman and H. J. Lucas, Ibid., 61, 2271 (1939).

reactions is being observed. Since the heat of hydration of crotonic acid has been determined already, it was desirable to extend the study of the hydration of unsaturated compounds to include that of $\underline{\beta}$,$\underline{\beta}$-dimethylacrylic acid and its equilibrium with $\underline{\beta}$-hydroxyisovaleric acid. No reference has been found concerning either the hydration of $\underline{\beta}$,$\underline{\beta}$-dimethylacrylic acid or the dehydration of $\underline{\beta}$-hydroxyisovaleric acid.

The plan of work was to obtain the heat of hydration from the kinetic constants of the hydration of the unsaturated acid and of the dehydration of the hydroxy acid and also from the equilibria between the two acids at two temperatures in dilute perchloric acid solution as in previous work. However, the decarboxylation of $\underline{\beta}$-hydroxyisovaleric acid to tertiary butyl alcohol under the conditions of the experiments is a complication which does not permit a direct measurement of the equilibria.

Decarboxylation in aqueous solution has not been reported for either $\underline{\beta}$-hydroxybutyric acid or $\underline{\beta}$-hydroxyisovaleric acid. Indeed, the great stability of the equilibrium between the former and crotonic acid is definite evidence that it could decarboxylate only at an infinitesimal rate in 2 $\underline{N}$ perchloric acid at a temperature of 100°. However, two homologs of the $\underline{\beta}$-hydroxyisovaleric acid, namely $\underline{\alpha}$-methyl-$\underline{\beta}$-hydroxyisovaleric acid[4] and $\underline{\alpha}$,$\underline{\alpha}$-dimethyl-$\underline{\beta}$-hydroxyisovaleric acid,[5] decarboxylate

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(4) Giljarow, <u>J. Russ. Phys. Chem. Gesell.</u>, <u>28</u>, 501 (1896).

(5) S. Reformatsky and B. Plesconossgoff, <u>Ber.</u>, <u>28</u>, 2839 (1895).

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in hot aqueous solution to yield dimethylethylcarbinol and dimethylisopropylcarbinol, respectively.

In spite of the decarboxylation reaction, the hydration and dehydration constants along with the decarboxylation constants could be determined from the kinetic data obtained in the hydration and dehydration experiments.

The hydration studies were carried out at hydrogen ion concentrations of approximately 0.3, 0.5, and 1.0 N at an ionic strength of 1.0 N, and at ionic strengths of 0.6, 1.0, and 2.06 N at a hydrogen ion concentration of approximately 0.5 N. The dehydration and acid catalyzed decarboxylation studies were carried out at ionic strengths of 1.0 and 2.0 N with a hydrogen ion concentration of approximately 0.5 N and at hydrogen ion concentrations of approximately 0.5 and 1.0 N at an ionic strength of 1.0 N.

Decarboxylation constants were also determined independently at ionic strengths 0.0, 1.0, and 2.0 N, but in the absence of added perchloric acid. These values were found to be quite different from those determined in the perchloric acid solutions indicating that there are two mechanisms of decarboxylation.

The hydration studies were carried out at 82.45°, 99.85°, and 111.85° while the dehydration and decarboxylation studies were carried out at the two higher temperatures only. Perchloric acid rather than nitric or a hydrohalic acid was used since nitric acid has a decided oxidizing action at the elevated temperatures and hydrogen halides might add to the ethylenic linkage.

Kinetics

Typical curves for the hydration of β,β-dimethylacrylic acid and for the dehydration of β-hydroxyisovaleric acid are shown in Figs. 1 and 2,

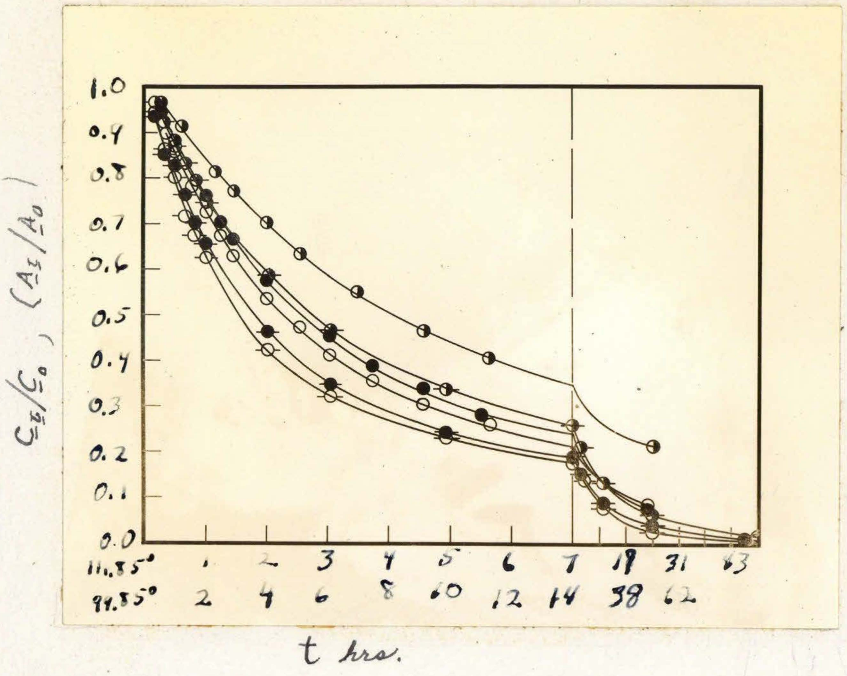
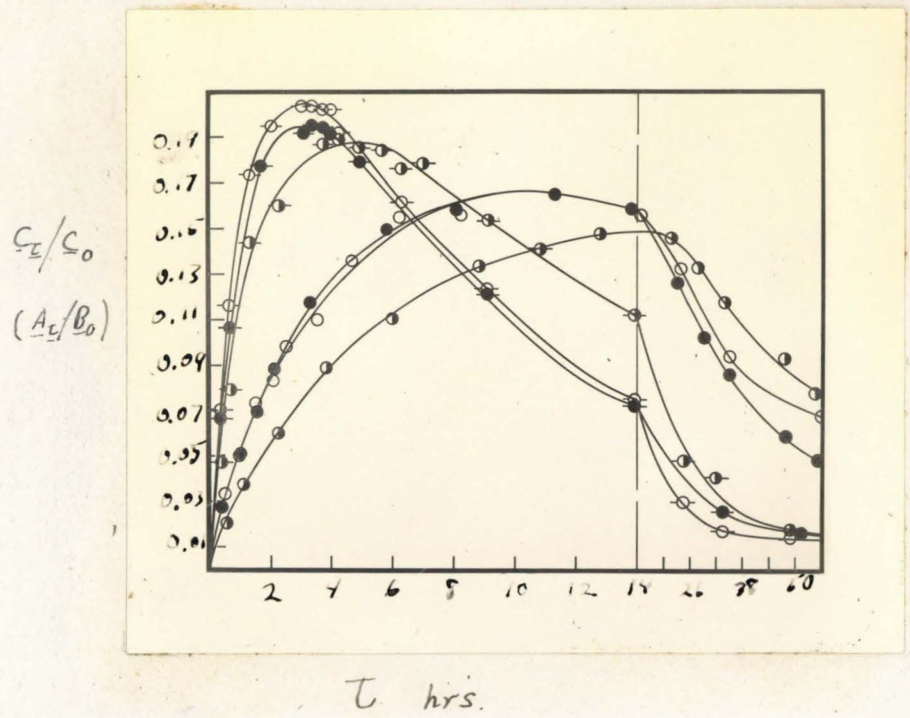


Figure 1

Plot against time of fraction of β,β-dimethylacrylic acid remaining, C_t/C_0, (A_t/A_0), in hydration experiments.

		(H^+) normal	μ normal	C_0 molar
99.85°				
	○	1.000	1.0	0.00828
	◑	0.544	1.0	0.00686
	●	0.480	2.1	0.00806
111.85°				
	-○-	1.000	1.0	0.00860
	-◑-	0.544	1.0	0.00690
	-●-	0.480	2.1	0.00749



<u>Figure 2</u>

Plot against time of fraction of initial β-hyroxyisovaleric acid present as dimethylacrylic acid, $\underline{C_t}/\underline{C_o}$, ($\underline{A_t}/\underline{B_0}$), in dehydration experiments.

	(H^+) normal	$\underline{\mu}$ normal	$\underline{C_0}$ molar
99.85°			
○	0.985	1.0	0.01520
◑	0.528	1.0	0.01590
●	0.466	2.1	0.01422
111.85°			
-○	0.984	1.0	0.01640
-◑	0.527	1.0	0.01705
-●	0.463	2.1	0.01691

respectively. Here $\underline{C}_t/C_0$, the fraction of the original acid either saturated or unsaturated, which is present as the unsaturated acid, is plotted against time. Since both hydration and dehydration curves approach the axis asymptotically, it is evident that eventually all of the dimethylacrylic acid and hence all of the hydroxyisovaleric acid disappears. In the curves for the dehydration (Fig. 2), the $\underline{\beta}$,$\underline{\beta}$-dimethylacrylic acid concentration passes through a maximum value and then decreases as the $\underline{\beta}$-hydroxyisovaleric acid is removed by irreversible decarboxylation. Typical decarboxylation curves for $\underline{\beta}$-hydroxyisovaleric acid in the absence of perchloric acid are shown in Fig. 3 where $\underline{C}_t/\underline{C}_0$, the fraction of the original $\underline{\beta}$-hydroxy acid present, is plotted against time. Since the fraction remaining approaches zero, all the acid decarboxylates eventually. The slow change in the value of $\underline{C}_t/\underline{C}_0$ for $\underline{\beta}$,$\underline{\beta}$-dimethylacrylic acid (Fig. 3) indicates that this decarboxylation reaction is negligible compared with the decarboxylation of the hydroxy acid.

The straight line character of the plot of $\log_{10} \underline{C}_0/\underline{C}_t$ indicates that the hydration of $\underline{\beta}$,$\underline{\beta}$-dimethylacrylic acid initially is first order with respect to the unsaturated acid (Fig. 4). Moreover, the equality in the slopes of these curves for runs at the same hydrogen ion concentration and ionic strength, but for different initial concentrations of $\underline{\beta}$,$\underline{\beta}$-dimethylacrylic acid indicates the same thing. The reaction therefore is pseudo-unimolecular. The increase in slopes of the plots with increasing hydrogen ion concentration and increasing ionic strengths shows the dependence of the rate constant upon these quantities. That the hydration is first order with respect to the hydrogen ion concentration can be seen from a comparison of the slopes of the curves for different hydrogen ion

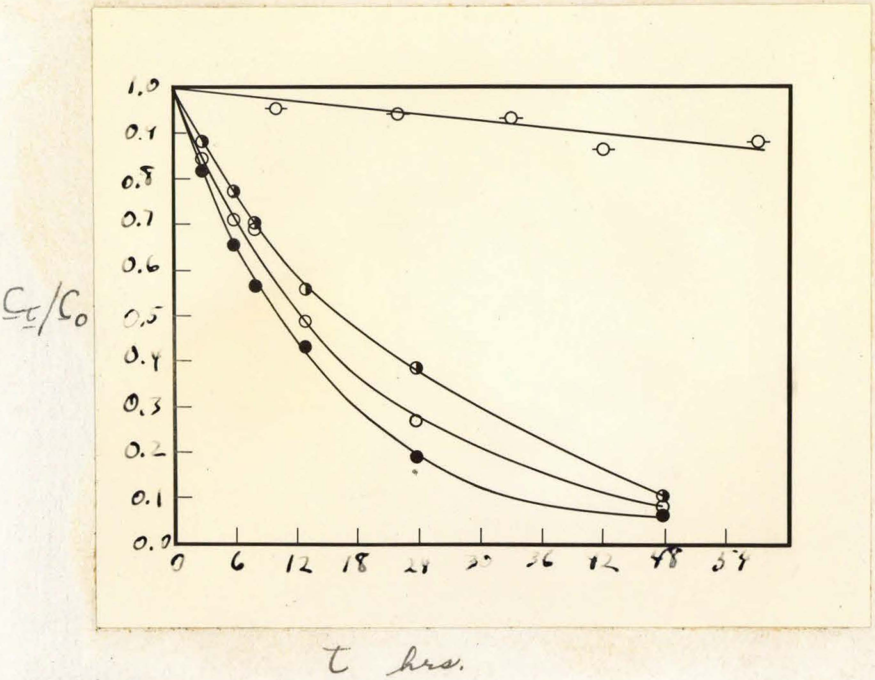


Figure 3

Decarboxylation of β,β-dimethylacrylic acid and of β-hydroxyisovaleric acid at 111.85° in absence of perchloric acid. Plot against time of the fraction of organic acid remaining, C_t/C_0.

	μ normal	C_0 molar
β,β-dimethylacrylic acid		
-○-	0.0	0.01158
β-hydroxyisovaleric acid		
◐	0.0	0.0202
○	1.0	0.0250
●	2.0	0.0237

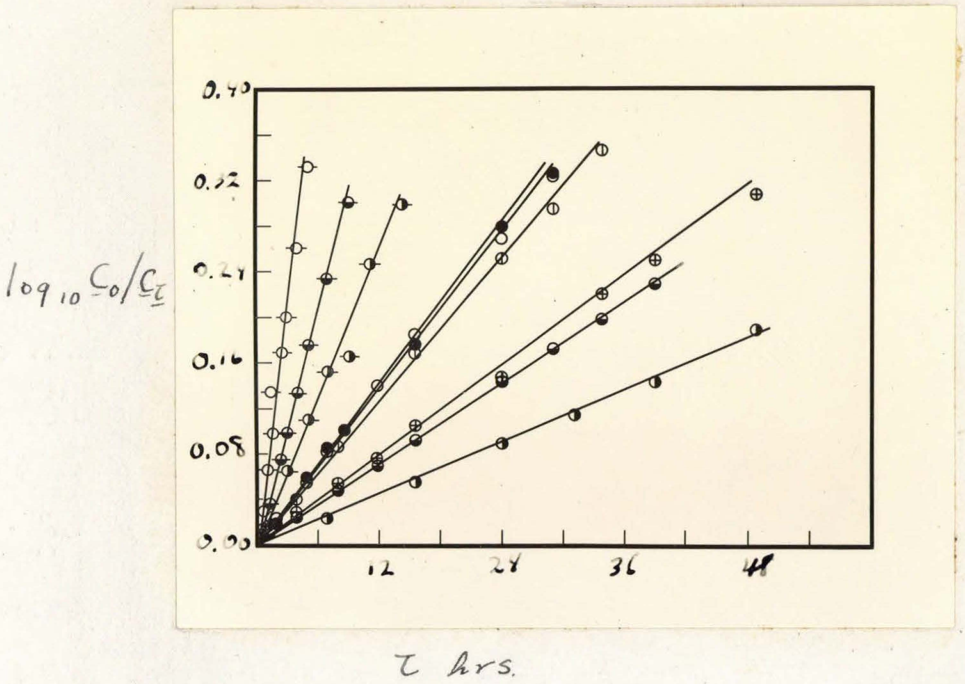


Figure 4

Plot against time of $\log_{10} C_0/C_t$ for the hydration of β,β-dimethylacrylic acid.

	(H) normal	μ normal	C_0 molar
82.45°			
○	1.000	1.0	0.00973
●	1.000	1.0	0.00414
⊕	0.544	1.0	0.00984
◐	0.302	1.0	0.01015
◒	0.610	0.6	0.00878
∅	0.480	2.1	0.00920
99.85°			
-○-	1.000	1.0	0.00516
-◐-	0.302	1.0	0.00883
-◒-	0.601	0.6	0.00875

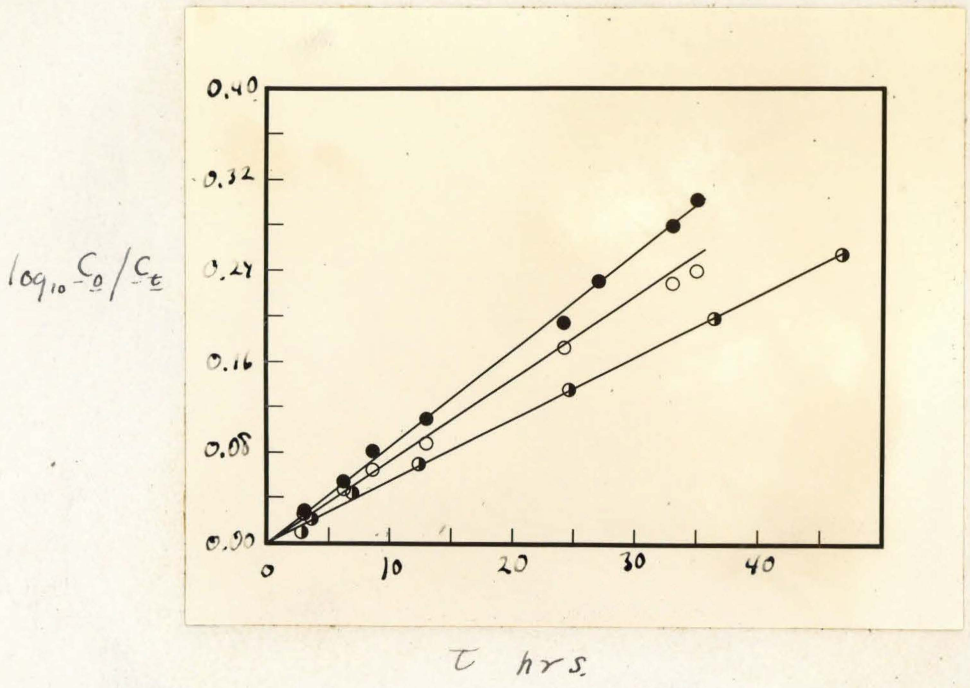


Figure 5

Plot against time of $\log_{10} \underline{C_0}/\underline{C_t}$ for the decarboxylation of β-hydroxyisovaleric acid at 99.85° in the absence of perchloric acid.

	$\underline{\mu}$ normal	$\underline{C_0}$ molar
◐	0.0	0.0187
○	1.0	0.0250
●	2.1	0.0237

decarboxylation constant, k_3, in the presence of acid is the sum of the acid catalyzed and uncatalyzed reactions, equation 2

$$k_3 = k_3^{O} + k_3^{H} \tag{2}$$

Using A to represent the concentration of β,β-dimethylacrylic acid, B of β-hydroxyisovaleric acid, and C of tertiary butyl alcohol, the time rate of change of these concentrations is given by equations 3, 4, and 5.

$$dA/dt = k_2B - k_1A \tag{3}$$

$$dB/dt = k_1A - (k_2 + k_3)B \tag{4}$$

$$dC/dt = k_3B \tag{5}$$

These equations integrate to give the following general expressions where the subscripts, 0, and t, indicate the concentrations at time initial and time t respectively.

$$A_t = \ell\, e^{\alpha(t - t_0)} + m\, e^{\beta(t - t_0)} \tag{6}$$

$$B_t = \ell \frac{k_1 + \alpha}{k_2} e^{\alpha(t - t_0)} + m \frac{k_1 + \beta}{k_2} e^{\beta(t - t_0)} \tag{7}$$

$$C_t = \ell \frac{(k_1 + \alpha)k_3}{k_2\alpha} e^{\alpha(t - t_0)} + m \frac{(k_1 + \beta)k_3}{k_2\beta} e^{\beta(t - t_0)} + \left\{ \left[A_0(k_1 + \beta) - k_2 B_0\right] \frac{k_1 + \alpha}{\alpha} + \left[k_2 B_0 - A_0(k_1 + \alpha)\right] \frac{k_1 + \beta}{\beta} \right\} \frac{k_3}{k_2(\alpha - \beta)} + C_0 \tag{8}$$

where

$$\ell = A_0 - \frac{k_2 B_0 - A_0(k_1 + \alpha)}{(\beta - \alpha)} \tag{9}$$

$$m = \frac{k_2 B_0 - A_0(k_1 + \alpha)}{(\beta - \alpha)} \tag{10}$$

$$\alpha = \frac{-(k_1 + k_2 + k_3) + \sqrt{(k_1 + k_2 + k_3)^2 - 4k_1 k_3}}{2} \tag{11}$$

$$\beta = \frac{-(k_1 + k_2 + k_3) - \sqrt{(k_1 + k_2 + k_3)^2 - 4k_1 k_3}}{2} \tag{12}$$

In the special case where $B_0 = 0$ and $C_0 = 0$ at $t_0 = 0$

$$A_t/A_0 = \frac{(k_1 + \beta)e^{\alpha t} - (k_1 + \alpha)e^{\beta t}}{(\beta - \alpha)} \qquad (13)$$

$$B_t/A_0 = \frac{(k_1 + \alpha)(k_1 + \beta)}{k_2(\beta - \alpha)} (e^{\alpha t} - e^{\beta t}) \qquad (14)$$

$$C_t/A_0 = \frac{(k_1 + \alpha)(k_1 + \beta)k_3}{k_2(\beta - \alpha)} \left[\frac{(e^{\alpha t} - 1)}{\alpha} - \frac{(e^{\beta t} - 1)}{\beta} \right] \qquad (15)$$

In the case where $A_0 = 0$ and $C_0 = 0$ at $t_0 = 0$

$$A_t/B_0 = \frac{k_2}{\alpha - \beta} \left(e^{\alpha t} - e^{\beta t} \right) \qquad (16)$$

$$B_t/B_0 = \frac{1}{\alpha - \beta} \left[(k_1 + \alpha)\, e^{\alpha t} - (k_1 + \beta)\, e^{\beta t} \right] \qquad (17)$$

$$C_t/B_0 = \frac{k_3}{\alpha - \beta} \left[\frac{k_1 + \alpha}{\alpha} (e^{\alpha t} - 1) - \frac{k_1 + \beta}{\beta} (e^{\beta t} - 1) \right] \qquad (18)$$

Since the hydration and dehydration reactions were followed by analysis for unsaturation, A_t, the concentration of the β,β-dimethylacrylic acid alone was determined. The value of A_t/A_0 or A_t/B_0 could be determined experimentally since known amounts of β,β-dimethylacrylic acid or β-hydroxyisovaleric acid were present initially. Hence equations 13 and 16, which determined values of A_t/A_0 and A_t/B_0 were those used in the evaluation of the constants, k_2 and k_3.

Evaluation of the Hydration Constant, k_1.-- Since k_1 happens to be larger than k_2, and k_3 is very close to k_2 in magnitude, the actual rate of dehydration of β-hydroxyisovaleric acid is always small compared to the actual rate of hydration of the β,β-dimethylacrylic acid in those experiments where dimethylacrylic acid is the starting material.

Therefore, it is possible to obtain the hydration constant, $\underline{k_1}$, from the initial slope of the plot of $\log_{10} \underline{A_0}/\underline{A_t}$ against $\underline{t}$ for the hydration of the unsaturated compound with an error of less than 1% due to the reverse reaction. These plots are straight lines at least up to 0.4 hydrated as shown in Fig. 4. It will be noticed that the intercept on the abscissa is positive. This is due to the time lag in reaching the thermostat temperature. The specific hydration constants, $\underline{k_1}$, for hydration experiments are tabulated in Table I.

Table I

Rate Constants for Hydration of $\underline{\beta}$,$\underline{\beta}$-Dimethylacrylic Acid

(H^+) Normal	μ Normal	$\underline{A_0}$ Molar	$\underline{k_1}$ hr^{-1}	$\frac{k_1}{(H_3O^+)}$	Relative V $\underline{k_1}$	$-\underline{\alpha}$	$-\underline{\beta}$
45°							
1.000	1.0	0.00973	0.0265	0.0265	1.000		
1.000	1.0	0.00414	0.0255	0.0255	0.963		
0.544	1.0	0.00984	0.01525	0.0280	1.059		
0.302	1.0	0.01015	0.00865	0.0287	1.082		
0.610	0.6	0.00878	0.0137	0.0224	0.845		
0.480	2.1	0.00920	0.0235	0.0490	1.85		
85°							
1.000	1.0	0.00828	0.165	0.165	1.000	0.0365	0.226
1.000	1.0	0.00516	0.165	0.165	1.000		
0.544	1.0	0.00686	0.0930	0.171	1.038	0.0268	0.131
0.302	1.0	0.00883	0.0530	0.176	1.068		
0.610	0.6	0.00875	0.0844	0.138	0.836		
0.480	2.1	0.00806	0.151	0.314	1.901	0.0392	0.214
85°							
1.010	1.0	0.00860	0.507	0.507	1.00	0.126	0.789
0.544	1.0	0.00690	0.300	0.552	1.09	0.0970	0.485
0.480	2.1	0.00749	0.449	0.935	1.84	0.145	0.705

<u>Calculation of the Dehydration and Decarboxylation Constants</u>, $\underline{k_2}$ <u>and</u> $\underline{k_3}$. <u>Evaluation of</u> $\underline{\alpha}$ <u>and</u> $\underline{\beta}$.--On the other hand, it is not practical to calculate the dehydration constant, $\underline{k_2}$, from the initial slope of the

dehydration curve since the decarboxylation is taking place at a comparable rate and the equilibrium lies well on the hydrated side. The most useful equation for the determination of both the dehydration constant, k_2, and the decarboxylation constant, k_3, is equation 16. A plot of A_t/B_0 against $(e^{\alpha t} - e^{\beta t})$ is a straight line with the slope $k_2(\alpha - \beta)$ when the correct values of α and β are used. Since A_t/B_0 passes through a maximum, the straight line plot reaches a maximum value of A_t/B_0 and of $(e^{\alpha t} - e^{\beta t})$ and then returns upon itself. Different values of α and β were substituted in the experimental data until a straight line was obtained. Fig. 6 demonstrates the effect of variations of α and β on a plot of A_t/B_0 against $(e^{\alpha t} - e^{\beta t})$. From the slope of this straight line k_2 can be calculated since

$$\text{slope} = k_2/(\alpha - \beta) \tag{19}$$

From α, β, k_1, and equation 20, k_3 can be calculated.

$$\alpha\beta = k_1 k_3 \tag{20}$$

Although many different straight lines are possible with the experimental data, only one line has the correct slope where the sum of the rate constants is equal to the negative of the sum of α and β, equation 21.

$$(k_1 + k_2 + k_3) = -(\alpha + \beta) \tag{21}$$

The constants obtained by this method are tabulated in Table II and it can be seen that the relation above for the sums of the constants checks quite well.

The hydroxy acid is added to the perchloric acid in the form of a silver salt, and since it is largely unionized in the strongly acid solution, a correction must be made in the hydrogen ion concentration to account for the hydrogen ion concentration decrease due to the formation of the unionized organic acid. The hydration constants, k_1, used in these

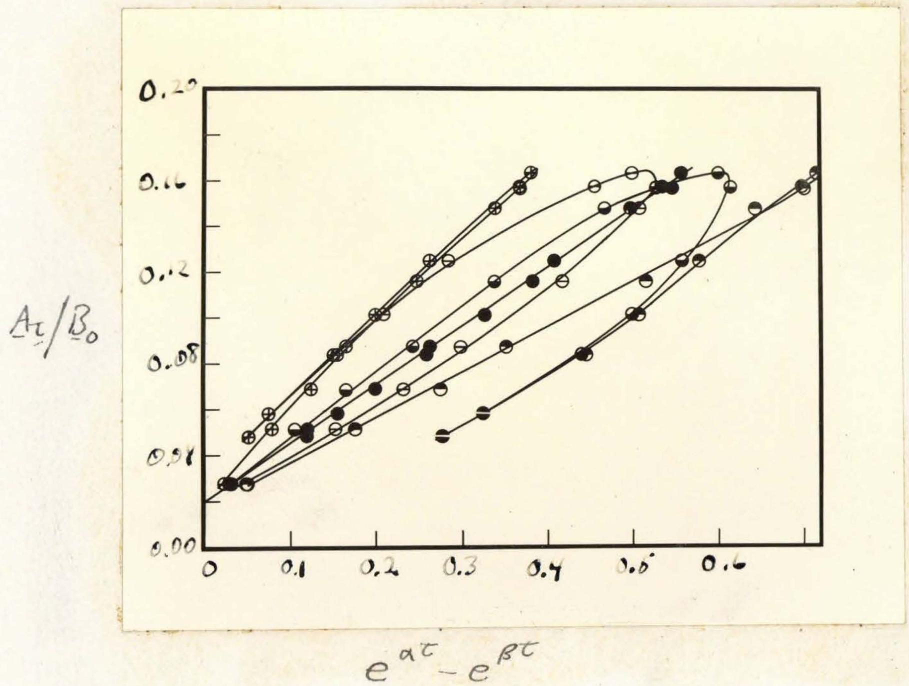


Figure 6

Effect of variation in α and β on a plot of A_τ/B_0 against $(e^{\alpha\tau} \quad e^{\beta\tau})$ for the dehydration experiments. (H) = 0.466 N, μ = 2.1 N, T = 99.85°.

	$-\alpha$	$-\beta$	
●	0.038	0.208	(chosen value)
◓	0.023	0.258	
◒	0.023	0.158	
⊖	0.053	0.258	
⊕	0.053	0.158	

Table II

Rate Constants for Dehydration of β-Hydroxyisovaleric Acid

(H^+) Normal	μ Normal	B_0 Molar	$-\alpha$	$-\beta$	Slope	k_1 hr^{-1}	k_2 hr^{-1}	k_3 hr^{-1}	Σk	$(-\alpha-\beta)$	$\frac{k_2}{(H_3O^+)}$
99.85°											
0.985	1.0	0.01520	0.036	0.223	0.256	0.1626	0.0480	0.0494	0.2600	0.259	0.0487
0.528	1.0	0.01590	0.026	0.127	0.257	0.0904	0.0260	0.0361	0.1536	0.153	0.0493
0.466	2.1	0.01422	0.038	0.208	0.259	0.1470	0.0442	0.0538	0.2450	0.246	0.0948
111.85°											
0.994	1.0	0.01640	0.125	0.780	0.314	0.499	0.2056	0.196	0.901	0.905	0.207
0.527	1.0	0.01705	0.094	0.470	0.320	0.291	0.1202	0.152	0.563	0.564	0.228
0.463	2.1	0.01691	0.140	0.680	0.325	0.454	0.1785	0.222	0.854	0.830	0.386

Relative γ_{k_2}	t maximum calc. hrs.	obs. hrs.	K
1.000	9.8	9-11	3.39
1.011	15.7	14-20	3.47
1.950	10.0	9-11	3.32
1.000	2.8	2.5-3.5	2.42
1.10	4.3	3-4	2.41
1.85	2.9	2.5-3.5	2.43

calculations were values determined from the initial slopes of the hydration experiments corrected for the new hydrogen ion concentration. The constant is proportional to the hydrogen ion concentration.

The time, t, is corrected in each case for the average time of warming to the thermostat temperature as determined by abscissa intercepts of the plot of $\log_{10} A_0/A_t$ against t for the hydration of the unsaturated acid. Although this is four minutes for the runs at 111.85° it comes out to be ten minutes at 99.85°. This can be accounted for easily by the fact that when the solutions were placed in the thermostat an extra heater was turned on to help provide the heat required to bring the cold solutions to temperature. Apparently, heat was supplied faster in the case of the runs at the higher temperatures. Since the runs at one temperature were all made at the same time, the same time lag would occur for all the rates at that temperature. The positive intercepts, 0.02, on the ordinates of the plots of A_t/B_0 against $(e^{\alpha t} - e^{\beta t})$ are nearly equal in the different runs. This is due to the fact that a little of the silver is reduced, since a slight amount of dark precipitate formed in the reaction tubes. This subsequently reacted during bromination to use bromine and thus a high value for the concentration of the unsaturated compound resulted. Of course, more silver is reduced in the tubes which are heated longer but uniform bromination of the same amount of the free silver takes place in each determination.

Evaluation of α and β by Other Methods.--The constants α and β can be obtained also from the plot of A_t/A_0 against $\left[(k_1 + \alpha)\, e^{\beta t} - (k_1 + \beta)\, e^{\alpha t}\right]$. This is a straight line with the slope $1/(\alpha - \beta)$. However, this is not as sensitive to variations in α and β as is the plot from equation 16 for it is sensitive only when the unsaturated acid has largely disappeared. However, these points are the least accurate. Fig. 7 shows the effect of variations of α and β on a plot of A_t/A_0 against $\left[(k_1 + \alpha)\,e^{\beta t} - (k_1 + \beta)\,e^{\alpha t}\right]$. The same corrections in time are made here as in the calculations concerning the dehydration experiments. Table I contains the values of α and β used in these calculations. The slopes and the calculated values of $1/(\alpha - \beta)$ are equal to each other from the nature of the point at zero time. Since the unsaturated acid is added to the aqueous perchloric acid solution as such, it does not remove any acid and hence the values of α and β are higher here than in the corresponding dehydration runs where a lower hydrogen ion concentration resulted from the addition of the silver salt of the organic acid to the same perchloric acid solution. For the small differences in the hydrogen ion concentrations in the hydration and dehydration runs the values of α and β are proportional to the hydrogen ion concentrations of the solutions.

Another check on the values of α and β can be obtained from the position of the maxima in the dehydration curves. The maximum lies at the point where the rate of change of the dimethylacrylic acid concentration is zero, equation 22.

$$d(A_t/B_0)/dt = 0 \tag{22}$$

At the maximum, the values of the time is given in equation 23.

$$t = 2.30 \log_{10} (\beta/\alpha) \;/(\beta - \alpha) \tag{23}$$

Table II contains the value of t, observed and calculated, for the maxima in the different runs. The satisfactory agreement here, as well as the fact that each set of values of α and β is satisfactory (Tables I and II) proves that the method of treatment is reliable.

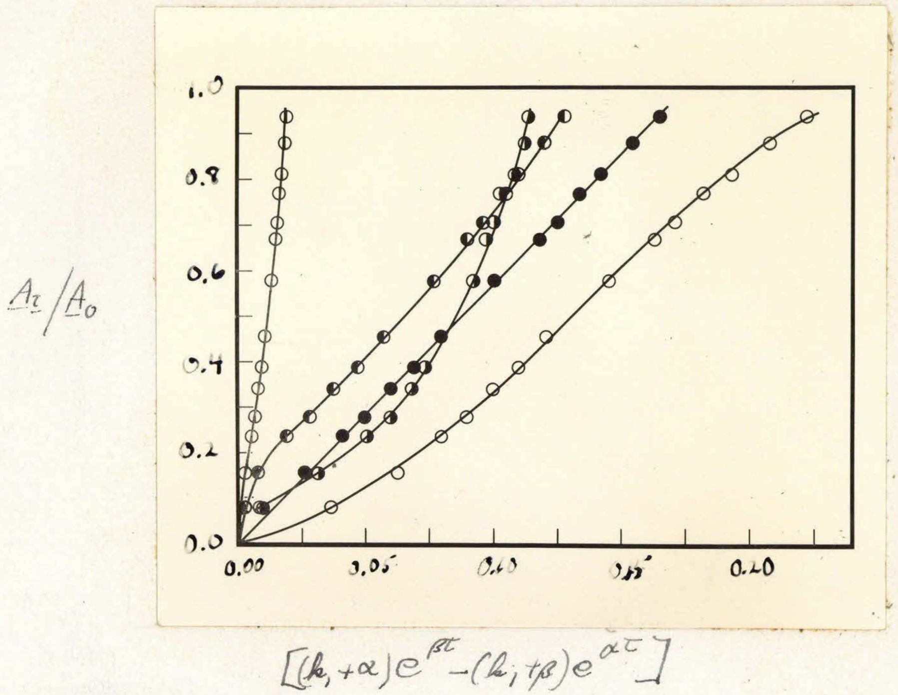


Figure 7

Effect of variation in α and β on a plot of A_τ/A_0 against $(k_1+\alpha)e^{\beta\tau} - (k_1+\beta)e^{\alpha\tau}$ for hydration experiments.

$(H^+) = 0.480$ N, $\mu = 2.1$ N, T= 99.85°.

	$-\alpha$	$-\beta$	
●	0.039	0.214	(chosen value)
○	0.023	0.258	
◐	0.023	0.158	
◑	0.053	0.258	
Φ	0.053	0.158	

Calculation of the Decarboxylation Constants, $\underline{k}_3^H$ and $\underline{k}_3^0$.--The decarboxylation constant obtained above is the apparent decarboxylation constant, $\underline{k}_3$. The value for the uncatalyzed reaction, $\underline{k}_3^0$, can be obtained from the slope of the plot of $\log_{10} \underline{C}_0/\underline{C}_t$ against time, Fig. 5, for the decarboxylation in a solution not containing perchloric acid.[6] The catalyzed decarboxylation constant, $\underline{k}_3^H$, is then the difference between the apparent constant and the uncatalyzed constant at the same ionic strength, equation 2. The values of the constants for the different decarboxylation runs are found in Tables III and IV.

Table III

Decarboxylation Rate Constants in the Absence of Perchloric Acid.

	μ Normal	$\underline{B}_0$ Molar	$\underline{k}_3^0$ / hr^{-1}	Relative $\underline{k}_3^0$
99.85°				
	0.0	0.0187	0.0122	0.775
	1.0	0.0250	0.0157	1.00
	2.1	0.0237	0.0195	1.24
111.85°				
	0.0	0.0202	0.0461	0.835
	1.0	0.0250	0.0555	1.000
	2.1	0.0237	0.0720	1.30
	0.0	0.012*	0.002	

* $\underline{\beta}$,$\underline{\beta}$-Dimethylacrylic acid

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(6) The first five figures have been so formed as to present all the experimental data available in an easily accessible form without an excessive number of plots and tables.

Effect of Hydrogen Ion Concentration and Ionic Strength on the Reaction Rate Constants

Hydration Rate Constant.--According to the Brönsted theory, the hydration rate is expressed by equation 24

$$\text{hydration rate} = \underline{k}_1''(H_2O)(H_3O^+)(C_5H_8O_2)\ f_{H_2O}\ f_{H_3O^+}\ f_{C_5H_8O_2} / f_{C_5H_8O_2.H_2O.H_3O^+} \quad (24)$$

Usually the assumption is made that the activity coefficients of the positive ions concel each other. However, since even the unionized β,β-dimethylacrylic acid activity is affected by ionic strength, it is quite likely that the large positive intermediate complex ion also should be similarly affected and thus its activity coefficient should be a function of the ionic strength different from that of the hydronium ion. Even the activity coefficient of water is calculated to decrease by about 8% when the solution is made 2 normal in sodium perchlorate. Hence the activity coefficients may all be grouped together in the term $f_{\underline{k}_1}$, since the individual activity coefficients are not known well enough to be discussed. The rate then can be expressed by equation 25.

$$\text{hydration rate} = \underline{k}_1'(H_3O^+)(C_5H_8O_2)\ f_{\underline{k}_1} \quad (25)$$

where $\underline{k}_1'$ contains the water concentration, which is practically the same for the different solutions, and the experimentally determined $\underline{k}_1$ is $\underline{k}_1'(H_3O^+)\ f_{\underline{k}_1}$. ~~xxxexperimentally determinedx~~ Indeed, $f_{\underline{k}_1}$ already has been shown to be different from the activity coefficient of the unsaturated compound, $f_{\underline{unsat}}$, in the case of the hydration of isobutene.[7] There, the $f_{\underline{k}_1}$ was compared with the activity coefficient of isobutene for different ionic strengths as determined by distribution experiments and found to differ by 10% and 40% ~~at~~

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(7) H. J. Lucas and W. F. Eberz, THIS JOURNAL, 56 , 460 (1934).

at ionic strengths of 1 and 2 N, respectively. This shows that γ_{k_1} for the hydration rate increases more rapidly with ionic strength than the activity of the butene. It can be seen therefore that the ratio $\gamma_{H_2O}\,\gamma_{H_3O^+}/\gamma_{C_4H_8.H_2O.H_3O^+}$ must increase with ionic strength. The activity of water acts in the opposite direction, however, decreasing with increasing ionic strength. Therefore, the ratio $\gamma_{H_3O^+}/\gamma_{C_4H_8.H_2O.H_3O^+}$ must increase with ionic strength. The same most likely holds true for dimethylacrylic acid.

The observed rate constant divided by the hydronium ion concentration, $k_1/(H_3O^+)$, should then be proportional to γ_{k_1}. The values of $k_1/(H_3O^+)$ for the various experiments are in Table I. The hydronium ion concentration, $(H_3O)^+$, is taken to be the same as the hydrogen ion concentration. As an aid in comparing the effect of the different ionic strengths and hydrogen ion concentrations on γ_{k_1} at different temperatures, there are also tabulated the ratios of γ_{k_1} to the γ_{k_1} at ionic strength of 1.0 N and hydrogen ion concentration of 1.0 N at the same temperature. This ratio determines the γ_{k_1} in various solutions relative to a standard γ_{k_1} in 1 N hydrogen ion concentration and 1 N ionic strength. This is termed the relative γ_{k_1} of the reaction rate constant. It is fairly constant for any one solution over the different temperatures. Fig. 8 shows that the relative γ_{k_1} values of the hydration constant for solutions of hydrogen ion concentration approximately 0.5 N, increase rapidly as the ionic strength increases. The relative γ_{k_1} is almost doubled by raising the ionic strength from 1 to 2 N. The increase of γ_{k_1} with ionic strength has also been observed in the hydration of other unsaturated compounds.[1,2,7,8]

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(8) H. J. Lucas and Y. Liu, THIS JOURNAL, 56, 2138 (1934).

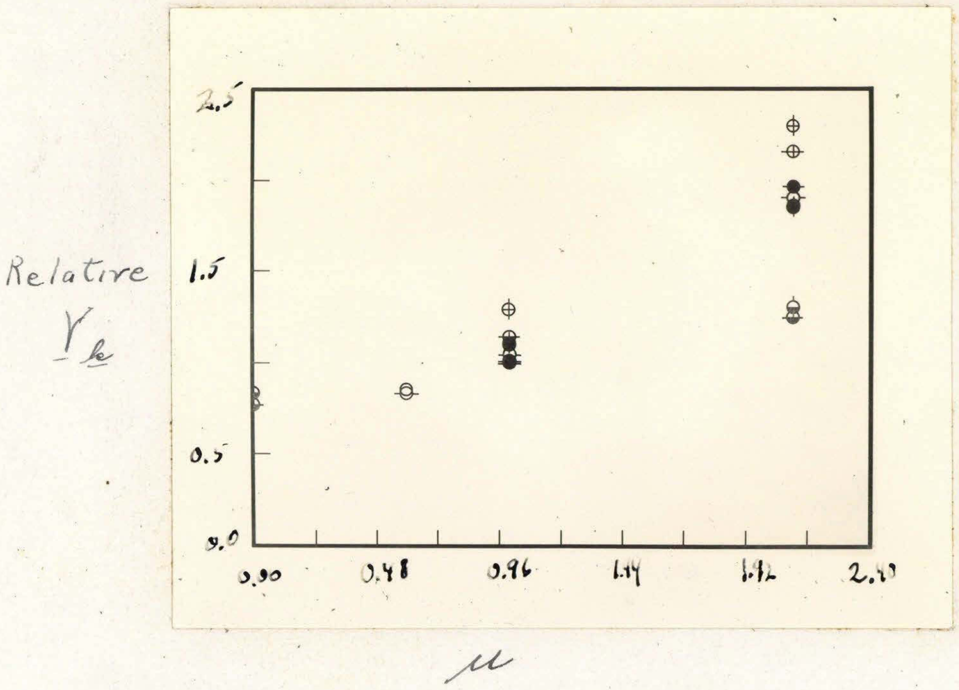

Figure 8

Plot of relative $\underline{\gamma_k}$ against ionic strength at approximately 0.5 $\underline{N}$ hydrogen ion concentration.

Relative $\underline{\gamma_k}$ for	82.45°	99.85°	111.85°
Hydration	○	⊖	⦶
Dehydration		●	●
Decarboxylation (acid catalyzed)		⊕	⊕
Decarboxylation (uncaltalyzed		◒	◒

In the reactions carried out at the same ionic strength but at different hydrogen ion concentrations, the replacement of hydrogen ion by sodium ion increases the values of the relative $\underline{\gamma}_{\underline{k}_1}$ of the reaction rate. This is due to the specific difference of the two ions in their effect on the activity of dimethylacrylic acid. This difference in action has been noticed chiefly in oxygenated compounds, crotonaldehyde, crotonic acid, and dimethylacrylic acid where the oxonium formation is appreciable. A more extended analysis of these effects in other systems is being made.

Dehydration Rate Constant.--The Brönsted expression for the dehydration rate constant is similar to that of the hydration rate except that water does not enter the expression, equation 26.

$$\text{dehydration rate} = \underline{k}_2''(H_3O^+)(C_5H_{10}O_3)\,\underline{\gamma}_{H_3O^+}\,\underline{\gamma}_{C_5H_{10}O_3} / \underline{\gamma}_{C_5H_{10}O_3.H_3O^+} \qquad (26)$$

From assumptions equivalent to those made for the hydration rate, this reduces to the expression

$$\text{dehydration rate} = \underline{k}_2'(H_3O^+)(C_5H_{10}O_3)\,\underline{\gamma}_{\underline{k}_2} \qquad (27)$$

where $\underline{k}_2'(H_3O^+)\,\underline{\gamma}_{\underline{k}_2} = \underline{k}_2$ as experimentally measured. The values of $\underline{k}_2/(H_3O^+)$, which are directly proportional to $\underline{\gamma}_{\underline{k}_2}$, are tabulated in Table II along with the relative $\underline{\gamma}_{\underline{k}_2}$ values for the different solutions. The latter values are plotted in Figure 8 to show the variation of the relative $\underline{\gamma}_{\underline{k}_2}$ with ionic strength at a hydrogen ion concentration of approximately 0.5 N. These variations are quite similar to those for the hydration experiments as are the variations occurring when hydrogen ion is replaced by sodium ion.

Decarboxylation Rate Constant.--The decarboxylation in the presence of perchloric acid must take place by two mechanisms, one acid catalyzed and the other not. The fact that this is a true hydrogen ion catalysis is indicated by the fact that the decarboxylation rate in 0.5 N perchloric acid is four times that in water, whereas the change in the concentration of the unionized acid ($K_A = 10^{-5}$) is only 2 percent.

The uncatalyzed decarboxylation rate, k_3^0, is itself a function of the ionic strength, Table III, and therefore the hydroxy-acid cannot decarboxylate by itself. Either the acid must react with water or the anion must decarboxylate. If the latter is the case the rate constant, k_3^0, would be a function of the ionic strength since dissociation and hence the anion concentration are also functions of that quantity. An experiment to test the decarboxylation of the anion was carried out by heating a concentrated solution of calcium β-hydroxyisovalerate at 100° for 3 days in a sealed tube. Since no tertiary butyl alcohol was formed, the anion cannot be the material which decarboxylates. Therefore, the uncatalyzed decarboxylation mechanism must be the reaction of the unionized acid with water.

Table IV

Decarboxylation Constants of β-Hydroxyisovaleric Acid in Perchloric Acid Solutions

(H^+) Normal	μ Normal	k_3 hr^{-1}	k_3^H $hr.^{-1}$	$\frac{k_3^H}{(H_3O^+)}$	Relative k_3^H
85°					
0.985	1.0	0.0494	0.0337	0.0342	1.00
0.528	1.0	0.0361	0.0204	0.0386	1.13
0.466	2.1	0.0538	0.0343	0.0735	2.15
85°					
0.994	1.0	0.196	0.140	0.141	1.00
0.527	1.0	0.152	0.096	0.182	1.29
0.463	2.1	0.222	0.150	0.324	2.30

The Brönsted expression for the reaction of $\underline{\beta}$-hydroxyisovaleric acid with water is given by equation 28:

$$\begin{aligned}\text{decarboxylation rate} &= \underline{k_3}^{0}\,(C_5H_{10}O_3)\\ &= \underline{k_3}'^{0}\,(H_2O)(C_5H_{10}O_3)\cdot \gamma_{H_2O}\,\gamma_{C_5H_{10}O_3}/\gamma_{C_5H_{10}O_3 \cdot H_2O} \qquad (28)\end{aligned}$$

The activity coefficients and hence the observed rate constant, $\underline{k_3}^{0}$, are functions of the ionic strength.

In Table IV are shown the decarboxylation constants, observed at different ionic strengths, hydrogen ion concentrations and temperatures. The decarboxylation constant for the acid catalyzed reaction, $\underline{k_3}^{H}$, is actually the difference between the observed constant, $\underline{k_3}$, and the constant at zero hydrogen ion concentration, $\underline{k_3}^{0}$, but at the same ionic strength, neglecting the difference in the effect of a hydrogen and sodium ion on $\gamma_{\underline{k_3}^{0}}$ of the uncatalyzed reaction. The Brönsted equation for the acid catalyzed decarboxylation is similar to equation 26, the expression for the dehydration reaction. The values of $\underline{k_3}^{H}$ corrected for the hydrogen ion concentration and also the values of the relative $\gamma_{\underline{k_3}^{H}}$ for the different solvents are in Table IV and Fig. 8. It can be seen that these values are somewhat greater than those for the hydration and dehydration reactions.

The relatively low effect of ionic strength on the unionized decarboxylation reaction is due to the fact that the other cases deal with positive ions and it would be reasonable to expect a larger effect of ionic strength on ions than on electrically neutral substances.

Equilibrium Constants.--The theoretical equilibrium constants which would determine the final concentrations of the two organic acids if decarboxylation were not taking place can be calculated as the quotient of the hydration and dehydration rate constants. These values are in

Table II. The effects of both hydrogen ion concentration and ionic strength on the dehydration and hydration rate constants are essentially the same within experimental error. Thus there is no definite shift in the observed equilibria with salt as was observed in the aldol-crotonaldehyde and the β-hydroxybutyric acid-crotonic acid equilibria. The effect of salt can be seen to be practically the same at the different temperatures.

Thermochemistry

In Table V are the heats of activation for the hydration, dehydration, non-catalyzed decarboxylation, and the acid catalyzed decarboxylation. Most of the hydration runs were made at three temperatures. The values for the heat of activation were obtained from the slopes of the plots of the $\log_{10} k_1$ against the reciprocal of the absolute temperature (Fig. 9). The activation energy is independent of ionic strength and hydrogen ion concentration since the straight line curves are parallel. The dehydration and decarboxylation runs were made at only two temperatures. The heats of activation were calculated from the rate constants by the Arrhenius equation.

In Table V also are the values of the heat of hydration calculated as the difference between the activation energies of the hydration and dehydration reactions. The average is 8.1 kcal. An analysis of the effect of structure on the heat of hydration will be made in a future communication.[9]

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(9) Table V of hydration paper number VII of the thermal data concerning the heat of hydration of crotonic acid should read

		Heats of activation		$-\Delta H$	Temp. coefficient	
(H^+)	μ	Q_1	Q_2	kcal.	90-100°	
					Hyd.	Dehyd.
1.06	2.06	20.1	25.4	5.3	2.11	2.57
2.06	2.06	20.2	25.6	5.4	2.12	2.60

Thus the heat of hydration of crotonic acid is 5.4 kcal. instead of 10.1 kcal. as previously stated. This is 0.6 kcal. lower than the heat of hydration of crotonaldehyde rather than 4 kcal. higher. Since it has been shown that one would expect crotonaldehyde to lose more resonance energy than crotonic acid in the hydration reaction the small difference in the heats of hydration of the aldehyde and acid must be due to another property of the carboxyl and aldehyde groups which would decrease relatively the heat of hydration of the acid. This may be due to the different inductive effects of the carboxyl and carbonyl group. This problem is being investigated further with respect to various other hydration reactions.

Table V

Thermal Constants of the Hydration, Dehydration

and Decarboxylation Reactions

(H^+) Normal	$\underline{\mu}$ Normal	$\underline{Q_1}$ Fig.9 kcal.	$\underline{Q_1}$ kcal. 82.45-99.85°	$\underline{Q_1}$ kcal.	$\underline{Q_2}$ kcal. 99.85-111.85°	$\underline{Q_3}^O$ kcal.	$\underline{Q_3}^H$ kcal.	ΔH of hydration kcal.
1.0	1.0	27.3	28.1	26.8	34.7	30.2*	33.8	-7.9
0.5	1.0	27.4	27.4	28.0	36.6		37.0	-8.6
0.3	1.0		27.5					
0.5	2.1	27.6	28.2	26.0	33.6	31.2*	35.3	-7.6
0.6	0.6		27.5					
0.0	0.0					31.8*		
	Average		27.7	26.9	35.0	31.1*	35.4	-8.1
				Temperature Coefficient for 100-110°				
				2.58	3.42	2.98	3.47	

$*(H^+) = 0.0$

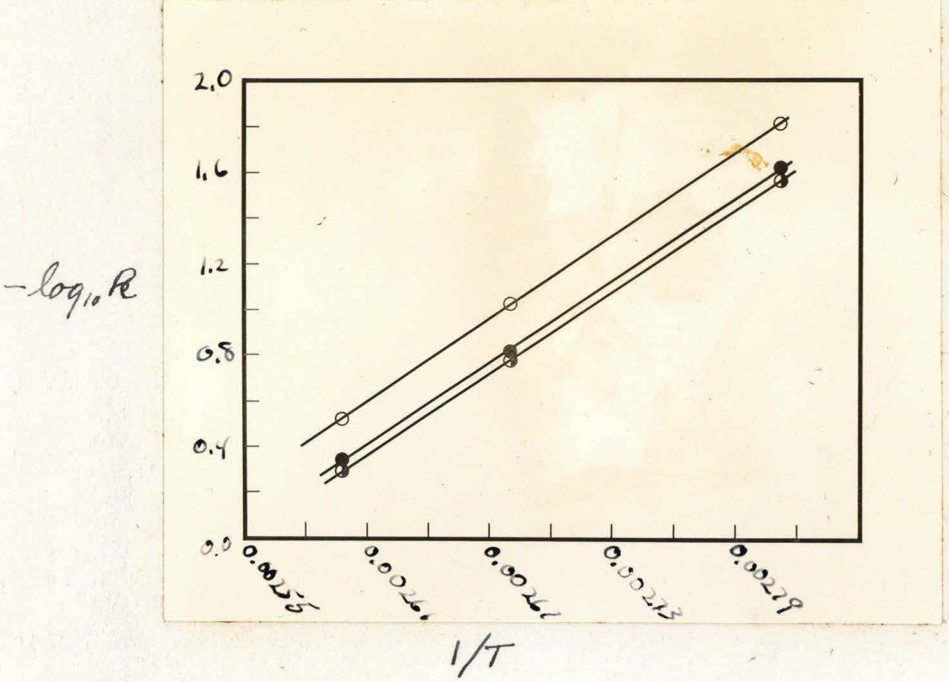

Figure 9

Plot of $\log_{10} k$ against $1/T$ for the hydration of β,β-dimethylacrylic acid.

	(H^+) normal	μ normal
○	1.000	1.0
◐	0.544	1.0
●	0.480	2.1

Interfering Reactions

Dehydration of Tertiary Butyl Alcohol.--The dehydration of tertiary butyl alcohol with the formation of isobutene is inappreciable even at 111.85° since at equilibrium the concentration of the alcohol is 100 times that of butene if the heat of hydration in aqueous solution remains constant at 11.6 kcal. since the equilibrium constant of $(C_4H_9OH)/(C_4H_8)$ is 4000 at 35°.[1] The presence of butene in the vapor is evidenced by its odor. The butene concentration in the vapor when the tube is opened is very low and is calculated to be of the order of 0.2 mm., for most of the butene in the vapor at the high temperature would hydrate at room temperature before the tube was opened since it has been shown[7] that in 1 *N* nitric acid butene hydrates 90% in one-half hour at a temperature of 25°. A calculation cannot be made as to the fraction of the system in the vapor phase since it would be proportional to the volume of the space above the solution which varied from 1 to 15 ml. In any case the analyses of the last tubes of a run for unsaturation showed negligible bromine absorption indicating that the butene either hydrated on cooling or was lost in the pouring of the solution and the butyl alcohol present did not brominate.

Lactone Formation.--According to Gerhke and Willrath,[10] *β*-hydroxybutyric acid loses water to form a compound of lower free carboxyl content, a 0.1 molal solution at 100° having 4.5% of the carboxyl groups bound. It has been shown that if the formation of a lactone is the cause, dilution would have no effect on this value.[3] From the stabilizing effect of methyl groups on small rings[11] one would

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(10) M. Gerhke and H. H. Willrath, *Z. physik. Chem.*, *A* *142*, 301 (1929).

(11) C. K. Ingold, *Ann. Report of Chem. Soc.*, *22*, 127 (1925).

expect β-lactone formation to be favored in β-hydroxyisovaleric acid over β-hydroxybutyric acid. The formation of the lactone would increase the values k_2 and k_3 for dehydration and decarboxylation. Since the small change would roughly be the same for the two temperatures it cancels out in the important calculation of the heat of hydration. Any bimolecular esterification would be negligible at the high dilutions prevailing.

Experimental

β,β-Dimethylacrylic Acid.--β,β-dimethylacrylic acid was prepared according to a modification of the method of Barbier and Leser[12] from the chloroform reaction of mesityl oxide. Into a liter of 1.5 N sodium hydroxide solution was passed in 185 g. (2.6 mole) of chlorine with cooling, and to this 75 g. (0.77 mole) of mesityl oxide (Eastman Kodak Company product redistilled through Vigreaux column and boiling at 126-128° uncorr.) was added with vigorous mechanical stirring, at first in a steady stream until about 25% was added which brought the reaction mixture to the boiling point under a reflux. The rest was added dropwise to maintain the temperature about 60°. There was no residual hypochlorite. The aqueous solution was neutralized with 300 ml. 6 N sulfuric acid and then acidified with 200 ml. more. At first a large amount of carbon dioxide was evolved. A white oil separated and crystallized on cooling. The mother liquor was extracted with four 200-ml. portions of ether. The residue on evaporation was combined with the original crystals and the mixture recrystallized from hot water yielding large individual needle-like crystals. Yield was 30 g. (0.34 mole), 44%. The crystals

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(12) P. Barbier and G. Leser, *Bull. Soc. Chim.*, (3), **33**, 815 (1905).

were recrystallized again from hot water. M.P. = 66.5-67.5° corr. Analysis for unsaturation by bromination showed 1.02 double bonds per mole.

Silver β-Hydroxyisovalerate.--β-Hydroxyisovaleric acid was prepared from diacetone alcohol by the chloroform reaction. To a solution of 320 g. (8 moles) of sodium hydroxide in 1.5 liters of water was added with cooling, 230 g. (3.1 moles) of chlorine, and then 100 g. (0.85 mole) of diacetone alcohol with vigorous stirring. The reaction mixture became hot and the chloroform distilled out as it was formed. The slight excess of chlorine was removed by sodium bisulfite and the solution was decomposed with 1250 ml. of 6 N sulfuric acid. The solution was extracted with eight 1-liter portions of ether which were subsequently extracted with a thin paste of 20 g. calcium hydroxide in 200 ml. water. The lime extract was diluted to 400 ml., filtered, and carbonated until the solution was just neutral to phenolphthalein. A clear solution was obtained by filtering hot with the aid of "hyflow" diatomaceous earth. Crystals of calcium β-hydroxyisovalerate separated after concentration to 250 ml. These weighed 9 g. (.03 mole) when dried in vacuum over phosphoric anhydride at 70° but were contaminated with chloride. On adding the calcium salt to a solution of 34 grams of silver nitrate in 500 ml. of boiling water, silver β-hydroxyisovalerate precipitated immediately. To the mixture 3 g. of "hyflow" was added, and the mixture filtered hot. The light grey crystals which separated on cooling were filtered off and the original precipitate of the silver salt was extracted twice more with the mother liquor. The combined crystals of three such extractions (only a little precipitated the third time) were recrystallized out of 800 ml. boiling water. The solid was a very light grey. The crystals were quite stable and were dried at 78° over phosphorus pentoxide. Yield, 8.5 g. (.04 mole).

~~The silver β-hydroxyisovalerate was analyzed for silver by the Volhard method~~ Anal. Calculated for $C_5H_9O_3$ Ag, Ag, 48.1%; Found (by Volhard method), 48.0%.

Perchloric Acid Solutions of Constant Ionic Strength.--The solutions of different acidity were made merely by adding different amounts of solid sodium hydroxide to portions of a perchloric acid solution of known concentration. The change in volume caused by this addition was neglected. No correction was applied for the effect of temperature on the volume since the change in volume from 82 to 110° is only 2%. The equilibrium constant is not affected by the volume change. These solutions then had the same ionic strength (within 2%) but different acid concentrations.

Method of Performing Hydrations and Dehydrations.--Dimethylacrylic acid solutions were made up to approximate concentration with standard perchloric acid and analyzed volumetrically by bromination. β-Hydroxyisovaleric acid solutions were made up to exact volume with the perchloric acid solution from a known weight of silver β-hydroxyisovalerate. 15.00 ml. aliquots of these solutions were pipetted into test tubes with constricted necks and sealed off. They were then placed in an oil thermostat at temperatures of 82.45 ± .05°, 99.85 ± .05°, or 111.85 ± .05°. Tubes were removed at different time intervals and quenched in ice water. The tip of the tube was broken and the contents washed into the flask used for analysis. The tubes in the latter part of any one run showed an appreciable pressure of carbon dioxide and evolved a very slight odor of isobutene on opening.

Method of Analysis.--This was essentially the same as that described previously.[3] The bromination of the β,β-dimethylacrylic acid took place as rapidly as bromine was liberated with the result that bromination was complete as soon as the bromine color appeared. That the brominated product is stable is shown by the fact that the analysis does not change when 125% excess bromine is present for 5 minutes after the first appearance of the bromine color. The β-hydroxyisovaleric acid seemed to substitute about 0.5% when brominated under the conditions of the experiment.

Method of Performing Decarboxylations.--The solution of β,β-dimethylacrylic acid was made up by dissolving an approximate amount of the solid in pure water and standardizing the solution volumetrically. Solutions of the β-hydroxyisovaleric acid were made by adding a known amount of the silver salt to an exactly equivalent amount of perchloric acid solution. The reaction was carried out in sealed tubes similar to that of the dehydration. The solutions were analyzed by titration with a standard sodium hydroxide solution to the phenolphthalein end point with boiling to remove carbon dioxide as the end point was approached. The silver ion was first precipitated by the addition of 5 ml. of one-half saturated sodium chloride since otherwise silver hydroxide would form before the phenolphthalein end point was reached.

Isolation of Tertiary Butyl Alcohol as the Decarboxylation Product.--Five grams of β,β-dimethylacrylic acid and 20 ml. of 2 *N* perchloric acid were sealed in a tube and heated at 100° for 20 hours. The pressure was released from time to time. At the end of that period some light oil seemed to be separating. The aqueous phase was separated, neutralized to phenolphthalein with sodium hydroxide and then distilled. The first portion of the distillate was saturated with potassium carbonate and the 1 ml. of oil which separated was dried with the carbonate. The boiling point was 80.0° uncorr. When 0.25 ml. of this substance was mixed with $1^1/_2$ ml. $HCl-ZnCl_2$ reagent,[13] 0.25 ml. of a second oil which boiled at 50.5° uncorr.

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(13) H. J. Lucas, *THIS JOURNAL*, *52*, 802 (1930).

was obtained. The constants in the literature for tertiary butyl alcohol and chloride are 82.9° and 51°, respectively.

The oil which separated in the original reaction mixture probably was polymerized isobutene for a similar oil was observed to separate when 5 ml. of tertiary butyl alcohol and 20 ml. of 2 N perchloric acid were heated under similar conditions.

Attempted Decarboxylation of Calcium β-Hydroxyisovalerate.--Twenty ml. of an aqueous solution containing about 10 grams of calcium β-hydroxyisovalerate were heated at 100° in a sealed tube for 60 hours. The mixture was distilled through a 2 ft. Vigreaux column with a reflux condenser. Only enough alcohol was present to give the first few drops a faint odor of tertiary butyl alcohol but no alcohol separated on saturating these drops with potassium carbonate. If the ion decarboxylates, one would expect essentially complete decomposition, even under milder conditions.

Summary

The acid catalyzed hydration of β,β-dimethylacrylic acid to β-hydroxyisovaleric acid was investigated in aqueous perchloric acid and sodium perchlorate solutions of hydrogen ion concentrations varying from 0.3 to 1.0 N and ionic strengths varying from 0.3 to 2.0 N at temperatures of 82.45, 99.85 and 111.85°.

The acid catalyzed dehydration of β-hydroxyisovaleric acid to β,β-dimethylacrylic acid was investigated in various perchloric acid and sodium perchlorate solutions at 99.85 and 111.85°.

The interpretation of the data of the hydration and dehydration reactions was complicated by the simultaneous decarboxylation of the β-hydroxyisovaleric acid to form tertiary butyl alcohol. The acid

catalyzed decarboxylation was investigated under the same conditions as the acid catalyzed dehydration.

A mathematical treatment was developed to handle a system of reactions of the type $A \rightleftharpoons B \rightarrow C$, where the reaction rate constants are comparable.

The acid catalyzed hydration, dehydration and decarboxylation reactions are first order with respect to the organic acid concentration and first order with respect to the hydrogen ion concentration.

The reaction rate constants of these three reactions increase rapidly with ionic strength and slowly when sodium ion replaces hydrogen ion at constant ionic strength.

The uncatalyzed decarboxylation of β-hydroxyisovaleric acid in distilled water and in aqueous sodium perchlorate solutions was investigated at 99.85 and 111.85°. The reaction is first order with respect to the organic acid. The constant is somewhat smaller than the constant for the acid catalyzed decarboxylation, and increases ~~rapidly~~ moderately with ionic strength. Decarboxylation involves the free acid and not the anion.

The rate of decarboxylation of β,β-dimethylacrylic acid in pure water is negligible compared to that of β-hydroxyisovaleric acid.

The heat of activation of the hydration of β,β-dimethylacrylic acid essentially is not a function of ionic strength or hydrogen ion concentration.

For the hydration of dimethylacrylic acid, ΔH is -8.1 kcal. The correct value for crotonic acid is -5.4 kcal.

Additional Discussion

The compounds and data which are available from this thesis and the work of previous investigators for a discussion of the effect of structure on the heat and the entropy quantity of activation for the hydration and dehydration reactions and on the heat and entropy change in the hydration reactions are in Table I.

β,β-dimethylacrylic acid differs from crotonic acid by having a second methyl group in the beta position. Its heat of hydration is 2.6 kcal. greater than that of crotonic acid. This may be the result of three effects: (a) A methyl group is electropositive with respect to hydrogen and hence its presence on the beta carbon atom would relatively stabilize a positive charge on that atom. This would increase the conjugation energy of the double bond with the carboxyl group and would tend to decrease the heat of hydration of the dimethylacrylic acid. (b) Alcohols are stable according to the order tertiary > secondary > primary. Since the product of hydration of dimethylacrylic acid is a tertiary alcohol while that of crotonic acid is a secondary alcohol, the former should tend to evolve more heat on hydration than the latter. (c) The steric effect of a methyl group cis to the carboxyl group may also contribute to the greater heat of hydration of dimethylacrylic acid. Cis crotonic acid is less stable than the trans acid and, since it yields the same product on hydration, its heat of hydration would be greater. Since dimethylacrylic acid is similar to cis crotonic acid with respect to having a methyl group and a carboxyl group on the same side of the double bond, it is quite probable that this contributes to the difference in the heats of hydration. The

Table I

Unsaturate	Hydrate	$-\Delta H$ kcal.	Q_f kcal.	Q_r kcal.	$-\Delta S$ kcal/°	$\Delta S_f/2.3R$	$\Delta S_r/2.3R$	K	k_f hr^{-1}	k_r $hr.^{-1}$	T °C
Crotonic acid	β-hydroxybutyric acid	5.5	20.1	25.6	11.9	9.9	12.5	4.07	0.0148	0.00364)	100°
Dimethylacrylic acid	β-hydroxyisovaleric acid	8.1	26.9	35.0	19.7	14.9	19.9	3.39	0.165	0.0487)	
Isobutene[1]	Tert. butyl alcohol	11.6	23.3	34.8	21.4	17.2	21.8	7400	1.43	0.000193)	25°
Crotonaldehyde[2]	Aldol	6.3	18.2	24.5	21.5	11.6	16.3	0.88	0.0022	0.025)	

1. W. F. Eberz and H. J. Lucas, J.A.C.S., 56, 1230 (1934)
2. S. Winstein and H. J. Lucas, Ibid., 59, 1461 (1937)

differences in the other thermodynamic quantities for this pair may be due to similar considerations.

Dimethylacrylic acid is similar structurally to isobutene in that both have branched chains at one end of the molecule and both hydrate to give tertiary alcohols. However, the former has a carboxyl group in place of a hydrogen atom and the difference between the two groups may exert its effect in three ways: (a) The electromeric effects on the olefinic double bonds are different. (b) The electromeric effects on the hydrated molecules are different, (c) The carboxyl group can resonate with the double bond. The combined effects, a and b must be less than or in the same direction as the resonance effect, for the latter alone would make the heat of hydration of the acid less than that of isobutene and this is what is actually observed.

Crotonaldehyde is similar in structure to crotonic acid except for the formyl group in place of the carboxyl group. The difference in the effects of these two groups may exert itself in three ways, which are similar to those listed above. However, both of these groups can resonate with the olefinic double bond, but the resonance energies are probably different and would thus cause a difference in the heats of hydration. As has already been pointed out (pg. 7), the difference in the electronegativity effects for the two must be greater than the difference in resonance effects.

It is interesting to note that for the heats of activation of the dehydration reactions the value of 25 kcal. holds for the compounds with a secondary alcohol group but a value of 35 kcal. holds if the alcohol group is tertiary.

There are not enough data available at the present time to permit a more extensive discussion of the effect of structure on the terms concerned in the kinetics and thermodynamics of the hydration and dehydration reactions.

Summary

A study was made of the kinetics and thermodynamics of the reversible hydration of crotonic acid to β-hydroxybutyric acid and of β,β-dimethylacrylic acid to β-hydroxyisovaleric acid in dilute aqueous perchloric acid solutions of various ionic strengths and hydrogen ion concentrations.

Both the hydration and dehydration reactions are first order with respect to the organic acid concentration and the hydrogen ion concentration. The first order reaction rate constants for the organic acids increase with ionic strength and with the replacement of hydrogen ion with sodium ion. The crotonic acid reaches a stable equilibrium but the hydration of dimethylacrylic acid is complicated by the decarboxylation of the β-hydroxyisovaleric acid.

The equilibrium constant for crotonic acid is 5.00 at 90.0° and 3.28 at 111.3°. That calculated for dimethylacrylic acid if decarboxylation were not taking place is 3.4 at 99.9° and 2.4 at 111.8°. The heats of hydration of crotonic acid and dimethylacrylic acid are 5.5 and 8.1 kcal. respectively.

The decarboxylation of β-hydroxyisovaleric acid was investigated in water and dilute sodium perchlorate solutions with and without added perchloric acid. The reaction was found to proceed by two mechanisms, one was acid catalyzed and the other was not. The rate of the acid catalyzed decarboxylation increased much more rapidly with ionic strength than did the uncatalyzed reaction.

Propositions

1. Although optically active 2-bromo-3-hydroxy butane racemizes upon conversion to the 2,3-dibromobutane with HBr, it is probable that optically active 2-bromo-3-hydroxy pentane or 2-hydroxy-3-bromo pentane would not racemize upon conversion to the 2,3-dibromopentane.

   S. Winstein and H. J. Lucas, J. Am. Chem. Soc. 61, 2845 (1939).

2. The apparent heat of activation of the reaction of unsymmetrical ethylene dibromide derivatives with potassium iodide in methanol solution should be a function of the temperature.

3. Contrary to the statement of J. B. Conant and G. B. Kistiakowsky that "the effect (on the heat of hydrogenation of ethylene) of progressively substituting the four hydrogen atoms by methyl groups is not additive" the effect can be shown to be additive when consistent correction terms are included.

   J. B. Conant and G. B. Kistiakowsky, Chem. Rev. 20, 181 (1937).

   G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, W. E. Vaughn, J. Am. Chem. Soc. 58, 137 (1936).

4. The heat of activation of the dehydration of tertiary amyl alcohol is probably less when trimethylethylene is the product than when methyl ethyl ethylene is the product.

   H. J. Lucas and Y. Liu, J. Am. Chem. Soc. 56, 2138 (1934).

   Y. Lui and Wei, J. Chinese Chem. Soc. 4, 297 (1936).

   F. D. Rossini and J. W. Knowlton, Nat. Bur. of Stand. J. of Res. 19, 249 (1937).

   F. D. Rossini, ibid. 13, 21 (1934).

Propositions (continued)

5. The relative electronegativity order of a series of organic radicals according to bond moments as tabulated by H. C. Brown is not valid.

   H. C. Brown, J. Am. Chem. Soc. 61, 1483 (1939).

6. It should be possible to determine the relative acidities of various organic compounds such as alcohols, malonic esters, and acetoacetic esters from kinetic data concerning the reaction rate of the sodium salts of the above with an alkyl halide.

7. The low heat of dimerization of benzoic acid relative to that of formic and acetic acids is reasonable from a resonance point of view.

   L. Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press, Ithaca, N. Y., 1939, p. 187.

   A. S. Coolidge, J. Am. Chem. Soc. 50, 2166 (1928).

   F. H. MacDougall, ibid. 58, 2585 (1936).

8. The heats of combustion of various isomeric aldohexoses may be correlated with their structures.

   H. M. Huffman and S. W. Fox, J. Am. Chem. Soc. 60, 1400 (1938).

   T. H. Clarke and G. S. Stegeman, ibid. 61, 1726 (1939).

   G. S. Parks and S. B. Thomas, ibid., 56, 1423 (1934).

   A. Weissberger, J. Org. Chem. 2, 245 (1937).

9. The explanation by Buswell, Dunlop, Rodebush and Swartz of the ultraviolet absorption spectrum of aged aqueous acrolein solutions is not valid.

   A. M. Buswell, E. C. Dunlop, W. H. Rodebush, J. B. Swartz, J. Am. Chem. Soc. 62, 325 (1940).

   E. E. Gilbert and J. J. Donleavy, ibid. 60, 1911 (1938).

   J. V. Nef, Ann. 335, 219 (1904).

Propositions (continued)

10. When lethal substances are compared by tests on living cells, the relative concentrations which kill the same fraction of the cells in a standard time is often taken as the inverse ratios of their potencies. This measure is not valid when a substance being tested is unstable. The true relative lethality may be calculated by the application of a factor containing the decomposition constant of the unstable poison.

    Kronig and Paul, A. f. Hygiene, 25, 1 (1897)

    O. Gross, Biochem. Zeit. 29, 350 (1910).

    R. Weindling, Phytopathology 24, 1153 (1934).

11. The fact that the observed lethal activity of gliocladium fimbriatum toxin toward rhizoctonia solani is a constant when tested at a pH range of 3.5 to 5.0 but decreases with increasing pH at other values of pH may be explained from the known properties of the toxin and the growth of fungi.

    R. Weindling, Phytopathology, 24, 1153 (1934).

12. Definite courses should be devoted to the humanitarian side of chemistry.

ACKNOWLEDGMENT

I wish to make known my appreciation
of the aid and encouragement
Professor H. J. Lucas
provided in the pursuit of this research