

It appears that polybasic acids can be substituted for anhydrides in the polyester reaction to yield finally fairly equivalent polymerides.

Summary

The glyceryl phthalate reaction has been

investigated substituting phthalic acid for phthalic anhydride. Differences in the early stages of the reaction were observed but the later portions of the reaction to gelation are comparable.

BOUND BROOK, N. J.

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[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 ion² 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

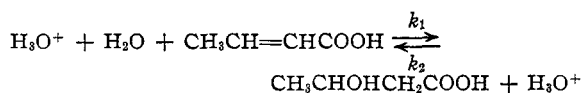
It was desirable to extend the study of the hydration on unsaturated compounds to an investigation of the kinetics of the hydration of crotonic acid, of the kinetics of dehydration of β -hydroxybutyric acid, and of the equilibrium between crotonic acid, β -hydroxybutyric acid, and water. Since it was 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 appreci-

able, 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



where k_1 is the specific reaction rate constant of

(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).

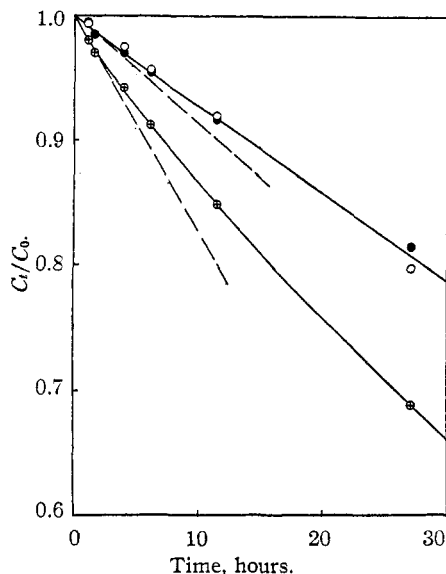


Fig. 1.—Hydration of crotonic acid showing the effect of hydrogen ion concentration and initial crotonic acid concentration on the initial slope of a plot of C_t/C_0 against time; T , 90.03°; μ , 2.06 molal.

	○	●	⊕
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

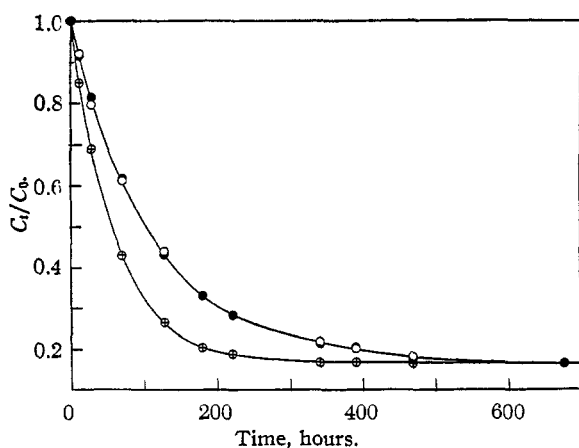


Fig. 2.—Hydration of crotonic acid showing the effect of hydrogen ion concentration and initial crotonic acid concentration on the equilibrium between crotonic acid and β -hydroxybutyric acid. Plot of C_t/C_0 against time. The last point is common to the three runs. T , 90.03°; μ , 2.06 molal.

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

both reactions to be monomolecular with respect to the organic reactant.

$$-d(\text{crotonic acid})/dt = k_1(\text{crotonic acid}) \quad (1)$$

$$-d(\text{hydroxybutyric acid})/dt = k_2(\text{hydroxybutyric acid}) \quad (2)$$

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

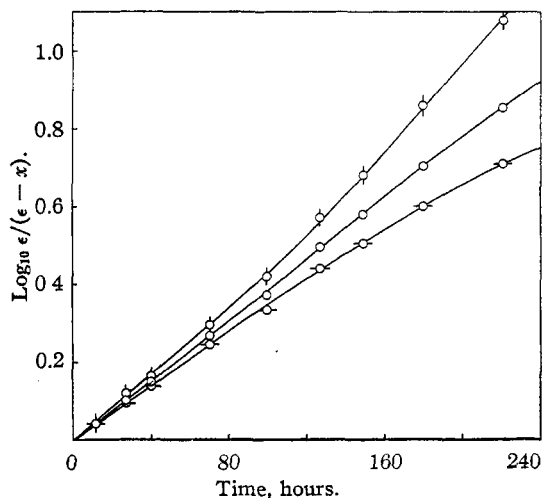


Fig. 3.—Effect of variation of ϵ on $\log_{10} \epsilon/(\epsilon - x)$ in the hydration of crotonic acid: initial crotonic acid, C_0 , 0.01282 molal; T , 90.03°; (H^+) , 1.060 molal; μ , 2.06 molal: ○, $\epsilon = 0.775$; ●, $\epsilon = 0.834$; ⊕, $\epsilon = 0.892$.

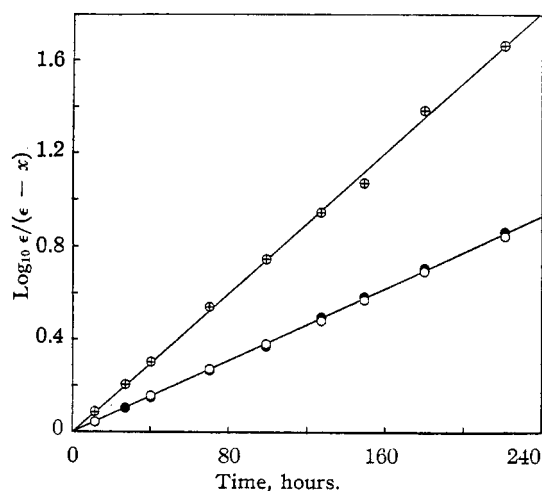
to show the effect of a variation of ϵ , the value was changed from the experimental value of 0.834 to 0.892 and 0.775. It can be seen that the experimental value produces a straight line but the variations induce marked curvature in the plots of $\log_{10} \epsilon/(\epsilon - x)$ against t . It will be noted that the values very close to equilibrium were discarded since very slight titration errors at these points in

TABLE I

EFFECT OF VARIATION OF ϵ ON $\log_{10} \epsilon/(\epsilon - x)$ IN THE HYDRATION OF CROTONIC ACID AT 90.03° $\text{HClO}_4 = 1.060$ molal; $\mu = 2.06$ molal; initial crotonic acid = 0.01282 molal.

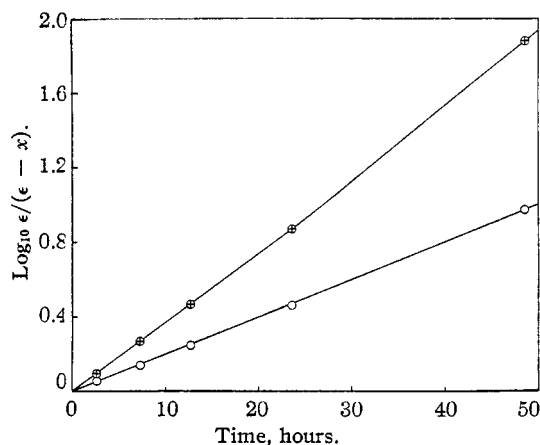
Time, hrs.	$1 - x$	$\epsilon = 0.834$ $\log \frac{\epsilon}{\epsilon - x}$	$\epsilon = 0.892$ $\log \frac{\epsilon}{\epsilon - x}$	$\epsilon = 0.775$ $\log \frac{\epsilon}{\epsilon - x}$
0	1.000			
0.5	1.000			
1.1	0.995	0.003	0.003	0.003
1.6	.985	.008	.008	.0085
4.0	.970	.0155	.0145	.017
6.1	.955	.024	.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 equilib-

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

rium 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. 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
	.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

 $T = 111.3^\circ$; $\mu = 2.06$ molal; $\text{HClO}_4 = 2.06$ 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

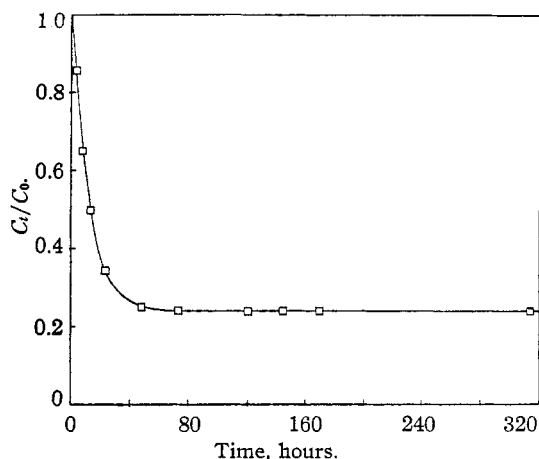


Fig. 6.—Stability of equilibrium between β -hydroxybutyric acid and crotonic acid when approached from crotonic acid. Plot of C_t/C_0 against time. Initial crotonic acid, C_0 , 0.0200 molal; T , 111.31°; (H^+) , 2.06 molal; μ , 2.06 molal.

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.

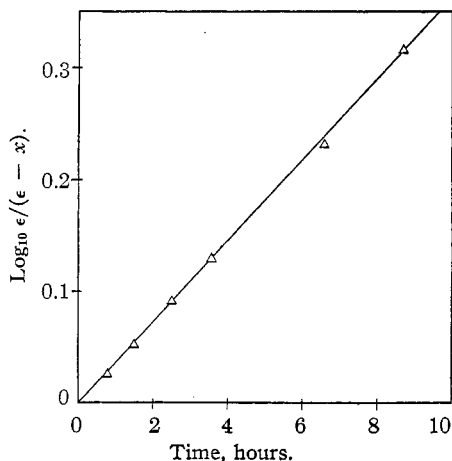


Fig. 7.—Dehydration of β -hydroxybutyric acid. Plot of $\log_{10} \epsilon/(\epsilon - x)$ against time. Initial β -hydroxybutyric acid, C_0 , 0.0225; ϵ , 0.228; T , 111.31°; (H^+) , 2.01 molal; μ , 2.01 molal.

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 (H^+) $T = 25^\circ$			Crotonic Acid (H^+) $T = 90^\circ$		
μ	K		μ	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	$T = 111.3^\circ$		
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 isobutene⁵; 21.04 kcal. for methylethylene⁶; 18.92 kcal. for trimethylethylene⁷; and 18.3 kcal. for crotonalde-

TABLE V

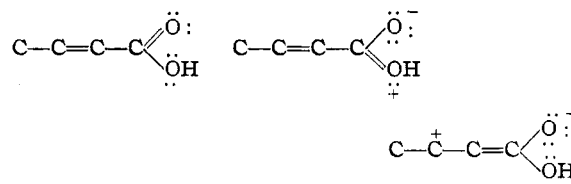
THERMAL DATA CONCERNING THE HYDRATION OF CROTONIC ACID

(H^+)	μ	Heats of activation		ΔH , kcal.	Temp. coefficient 90–100°	
		Q_1 , kcal.	Q_2 , 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

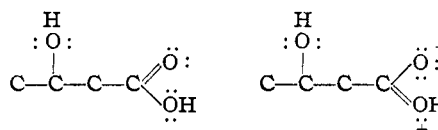
hyde.⁴ The heat of activation for the reverse reaction is 48.1 kcal. for crotonic acid as compared with 24.5 kcal. for crotonaldehyde.

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

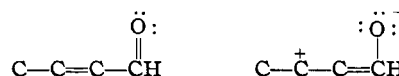
aqueous solution with respect to crotonic acid than aldol is with respect to crotonaldehyde. Resonance explains the relatively lower stability of the aldol. Crotonic acid in the acid solution can resonate between the unexcited forms



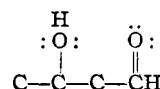
while β -hydroxybutyric acid resonates between the unexcited forms



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 Willrath⁸ 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-

(4) Eberz and Lucas, *THIS JOURNAL*, **56**, 1230 (1934).

(5) 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).

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 Basel¹ 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 \pm 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 \pm 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 ex-

plained by a lower loss of resonance energy in the hydration of crotonic acid.

PASADENA, CALIF.

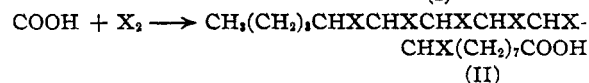
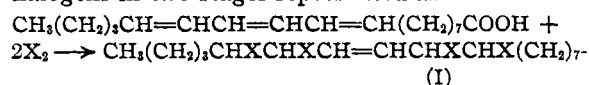
RECEIVED MAY 29, 1939

[A CONTRIBUTION FROM THE YALE-IN-CHINA SCHOOL OF SCIENCE, HUA CHUNG COLLEGE]

The Reaction of Wijs Solution with Tung Oil

By S. W. WAN AND D. B. HU

Tung oil contains mainly the glycerides of eleostearic acid and oleic acid and its drying power is due to the former unsaturated acid. In estimating the degree of unsaturation of tung oil with Wijs solution, the presence of eleostearic glyceride causes much uncertainty because the iodine value thus obtained varies with experimental conditions such as temperature, concentration and relative amount of reagent, and time of contact between reagent and oil.¹ Various methods have been tried for determining the percentage of eleostearic acid glyceride in tung oil, but have given no concordant results. Among the most recent methods may be mentioned the combined bromine vapor and Wijs method,² the differential halogen absorption method,³ the polymerization method,⁴ and the diene number method.⁵ The peculiar properties of eleostearic acid giving rise to analytical difficulties have been explained by Böeseken and co-workers by assigning to it the molecular constitution $\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CHCH}=\text{CHCH}=\text{CH}(\text{CH}_2)_7\text{COOH}$,⁶ which, in the light of Thiele's theory of partial valency, is expected to absorb halogens in two stages represented as



With Wijs solution, X_2 being a molecule of iodine monochloride, the first stage reaction is much faster and produces a chloro compound.⁶ On the other hand, compounds with non-conjugate double bonds take up the theoretical amount of iodine chloride in a short time, forming iodo-chloro compounds.

(1) Boughton, *Seventh Int. Congr. Appl. Chem.*, London (1909); Ho and co-workers, *Ind. Eng. Chem., Anal. Ed.*, **7**, 96 (1936).

(2) Toms, *Analyst*, **53**, 69 (1928).

(3) Croxford, *ibid.*, **54**, 445 (1929).

(4) Bolton and Williams, *ibid.*, **55**, 360 (1930).

(5) Kaufmann and Baltes, *Fette u. Seifen*, **43**, 93 (1936).

(6) Böeseken and Gelber, *Rec. trav. chim.*, **46**, 158 (1927); Böeseken, Hoogt, Broek and Smit, *ibid.*, **46**, 619 (1927).

This paper gives an account of the authors' attempt to apply the above-mentioned property of eleostearic acid to the determination of the concentration of its glyceride in tung oil, and an account of their investigation in the chemical kinetics of reaction (II).

Materials.—Glacial acetic acid, c. p., tested free from reducible substances. Iodine, c. p., twice resublimed. Sodium oxalate, c. p., giving an assay of 99.98%. Sodium thiosulfate, potassium iodide, carbon tetrachloride, oleic acid, potassium permanganate, all c. p. grade. Tung oil, supplied from the Chinese Vegetable Oil Corporation, Hankow. α -Eleostearic acid, prepared according to the method of Thomas and Thomson,⁷ m. p. 48.3°. Wijs solution, prepared according to the procedure given by Griffin⁸ with the important modification that the iodine and chlorine contents in the solution were adjusted to be exactly equivalent in amount.

The sodium thiosulfate solutions used in these experiments were standardized against potassium permanganate as a secondary standard and sodium oxalate as a primary standard.

Experimental

Part I.—Approximately equal weights of the carbon tetrachloride solution of a sample were placed in glass-stoppered conical flasks. To each was then added a weighed amount of Wijs solution and the mixture allowed to react for a definite length of time by shaking in a thermostat maintained at $25 \pm 0.1^\circ$. All reagents also had been allowed previously to reach temperature equilibrium in the same thermostat. The reaction in each mixture was stopped promptly by adding 20 cc. of 15% potassium iodide solution and the reaction mixture was immediately diluted with water and titrated with sodium thiosulfate solution from a weighing buret. A number of runs were made by following the above procedure and using samples of: (a) pure α -eleostearic acid with a reaction period of five minutes; (b) pure α -eleostearic acid with a reaction period of two minutes; (c) pure α -eleostearic acid with a reaction period of ten minutes; (d) pure oleic acid with a reaction period of ten minutes; (e) a known mixture of α -eleostearic and oleic acids with a reaction period of five minutes; (f) tung oil with a reaction period of five minutes.

Part II.— α -Eleostearic acid was weighed into a 100-cc. volumetric flask and carbon tetrachloride was added, mak-

(7) Thomas and Thomson, *THIS JOURNAL*, **56**, 898 (1934).

(8) Griffin, "Technical Methods of Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., p. 310.