THE HYDRATION OF ISO-BUTYLENE
TO
TERTIARY BUTYL ALCOHOL

Thesis submitted in partial fulfillment of the
requirements for the degree of Master of
Science in Chemical Engineering

California Institute of Technology

Pasadena, California

June, 1932 Henry Welge

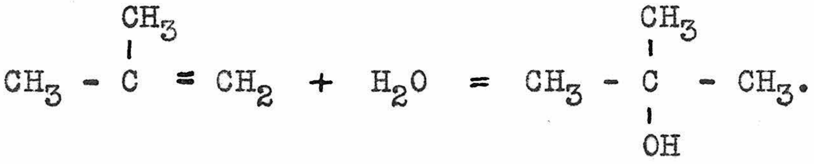
THE HYDRATION OF ISO-BUTYLENE
TO
TERTIARY BUTYL ALCOHOL

The hydration of unsaturated hydrocarbons to the corresponding alcohols is a process of both theoretical and practical interest. This process is already being practiced in several petroleum refineries in the United States, using cracked gases in the presence of sulphuric acid as a catalyst. It is of interest, therefore, to determine what, in the presence of certain necessary catalysts, the mechanism of the reaction is.

We decided to study first the hydration of iso-butylene, because that hydrocarbon is the most reactive olefin, and might be expected to react under conditions under which other unsaturated hydrocarbons would not. The reaction we have investigated may be written,

$$C_4H_8 + H_2O = C_4H_9OH,$$

or, writing it more specifically structurally,



$$CH_3 - \overset{\displaystyle CH_3}{\overset{|}{C}} = CH_2 + H_2O = CH_3 - \underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}} - CH_3.$$

It is necessary to catalyse this reaction; the catalysts investigated were acids and silver salts, generally together. In most of the experiments nitric acid and silver nitrate were used. It has been found that gaseous unsaturated hydrocarbons are much more soluble in aqueous solutions of silver salts than in water; consequently it might be expected that silver salts would catalyse the reaction of hydration.

The butylene was prepared by refluxing tertiary butyl alcohol with oxalic acid. The gas was passed through several efficient scrubbing bottles containing water to remove the alcohol, dried, and condensed in a tube surrounded by a freezing mixture of strong hydrochloric acid and ice; the tube in which it was thus collected was later sealed off. It is rather improbable that it contained more than very small amounts of impurities, such as other butylenes or polymers, but it was nevertheless redistilled from one such tube to another through several more scrubbing bottles, and was then considered sufficiently pure for use. The boiling point seemed to be quite constant at -6^{0}C.

Although butylene is much more soluble in aqueous solutions of silver salts than it is in water, as far as we were able to determine no hydration whatever takes place in such solutions until acid is added. Consequently the experiments were performed by passing iso-butylene almost to saturation into silver nitrate solutions of such strength that when diluted with standard acid in volumetric flasks, the concentrations of acid and of silver were very nearly those which it was desired to investigate. The exact concentrations of the two catalysts were determined at the conclusion of the experiments by titration.

The reaction was allowed to proceed in volumetric flasks placed in a thermostat at 25^{0}C. The reaction is slow at ordinary temperatures; the time of the determinations was of the order of several hours to several days. The molal concentration of the butylene in the solutions was determined as soon as possible after adding the acid and mixing; after the required length of time in the thermostat, the molal concentrations of both butylene and tertiary butyl alcohol were determined almost simultaneously, and all experiments in which the sum of the final butylene and alcohol molal concentrations did not equal, within a few percent at most, the initial concentration of the butylene were rejected.

The butylene was determined by a modification of Winkler's[1] method for iodine numbers, employing the special iodine flask illustrated in Figure 1, page 4. This flask consists merely of an ordinary iodine flask, B, into which has been ground a special stopper in which is sealed a glass tube, A, carrying a stopcock, C, a short distance above the stopper. In the flask is placed 10 cc. of carbon tetrachloride, previously purified of oxidizable impurities, according to the method of Griffin[2], by refluxing it for several hours with chromic acid and distilling from barium carbonate. The special stopper is set in position on the flask, water only being used as a lubricant for all ground glass surfaces in this work, and the flask is next partially evacuated by connecting for a moment a water pump to the upper end of the tube A. Then

---

[1] see <u>Allen</u>, Commercial Organic Analysis, p. 38, vol. II (V Ed.)

[2] see <u>Griffin</u>, Technical Methods of Analysis, p. 77 (1st Ed. 1921).

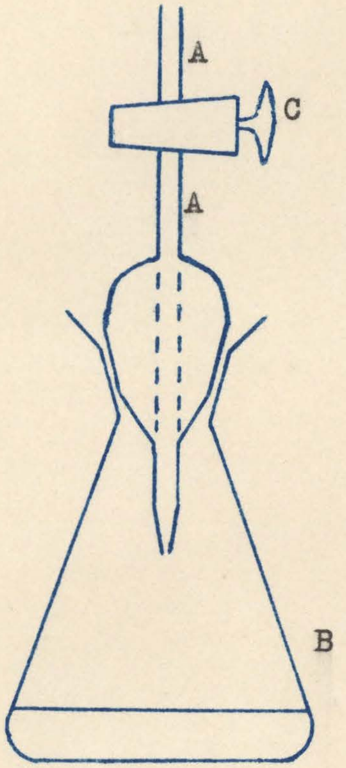


FIGURE 1

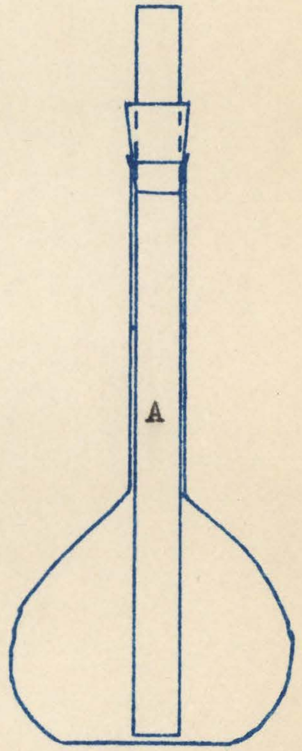


FIGURE 2

a sample of the solution containing the butylene to be determined is introduced into the flask from a pipette, the tip of which is inserted in a short length of rubber tubing attached to the upper end of the tube A. The pipette is removed, a small separatory funnel is inserted in its place, and that portion of the sample adhering to the walls of the glass tube A is washed down into the flask B with a little distilled water. It is to be noted that throughout the butylene determination, all the reagents used, as well as the sample itself, are introduced into the flask in which the determination is made under partial vacuum, so that nothing escapes from the flask when the reagents enter it. This is the chief idea of the flask.

Next a measured amount of standardized potassium bromate solution, containing also 40 g. of potassium bromide per liter, is pipetted into the separatory funnel, drawn down into the flask by means of the stopcock C, and washed down with water; and last 10 cc. of 10 per cent hydrochloric acid is similarly introduced and washed down. Bromine is liberated quantitatively in the flask, and part of it reacts with the butylene:

$$C_4H_8 + Br_2 = C_4H_8Br_2;$$

the remainder, after a few minutes' standing in the dark with occasional shaking, to insure complete reaction between the bromine and the butylene, is converted to iodine by the addition to the contents of the flask of 10 cc. of 10 per cent potassium iodide solution. The tip of the burette containing standard sodium thiosulphate solution is then connected, by means of a short piece of rubber tubing, to the upper end of the tube A. A partial vacuum still exists in the flask B, and the reagent is run slowly into the flask through the tube A, with shaking, until the color of iodine has well faded; then the burette is disconnected, the stopcock C is opened wide, and air enters the flask B. Finally the special stopper, having served its purpose, is removed, the sodium thiosulphate solution adhering to the walls of the tube A washed down into the flask, and the titration is completed in the usual way. The accuracy of butylene determinations carefully made in this way is probably better than .5 per cent.

The method of Ponndorf[3] used in the alcohol determinations is, to the knowledge of the author, the only satisfactory method available for determining tertiary butyl alcohol in small amounts, in dilute aqueous solution, and in the presence of other organic substances. When the sample of alcohol is shaken with an acidified solution of sodium nitrite, the following reaction is believed to occur:

$$ROH + HNO_2 = RNO_2 + H_2O,$$

apparently nothing but a simple esterification. What is remarkable about it is the fact that, in spite of the weakly acid properties of nitrous acid, no dehydrating agents need be used, the reaction on the contrary proceeding quantitatively in even the most dilute concentrations of alcohol.

The alkyl nitrite is extracted with several portions of carbon tetrachloride, previously purified as described on page 3, in a separatory funnel. The portions of carbon tetrachloride,

---

[3] Ponndorf, Zeit. Analyt. Chem. 80, 401-430 (1930).

containing the alkyl nitrite, are next shaken in another separatory funnel with a solution of sodium bicarbonate to remove excess nitrous acid. They are then drawn off into a glass stoppered flask containing a standard amount of manganese dioxide, which is obtained by previously pipetting a volume of standard potassium permanganate into the flask and adding an excess of manganese sulphate and a little sulphuric acid. The suspension of manganese dioxide is shaken vigorously with the solution of alkyl nitrite in carbon tetrachloride for 10 - 15 minutes, during which time the following reaction occurs:

$$MnO_2 + RNO_2 + H_2SO_4 = ROH + HNO_3 + MnSO_4.$$

What happens is that the equilibrium between the alkyl nitrite and the alcohol and nitrous acid is displaced by the oxidation of the nitrous acid to nitric acid. The excess manganese dioxide is then determined by adding potassium iodide solution to the contents of the flask and titrating the liberated iodine with thiosulphate.

Unfortunately, all of the alcohol is not recovered; consequently a correction has to be applied, which is carefully estimated by making similar determinations on a known amount of tertiary butyl alcohol obtained by dilution of pure tertiary butyl alcohol, and averaging the results of several such determinations, which agree to about 1 per cent. A further correction must be applied for slight interference by iso-butylene. This correction was estimated by making alcohol determinations as above described on samples of butylene dissolved in silver nitrate solutions. Since the alcohol determinations were less accurate than the butylene determinations, they were not used in calculating reaction rate constants, serving merely as checks on the butylene determinations.

At first it was simply attempted to put the acidified solutions of butylene and silver nitrate, contained in a volumetric flask, in a thermostat, leave them for awhile, and withdraw samples for analysis; but invariably this proceedure resulted in too low a combined molality of butylene and alcohol at the finish. The reason seemed to be that enough butylene would escape into the gas space above the liquid in the volumetric flask to cause the combined molalities at the end of an experiment to be quite appreciably low. Having assured ourselves on this point by a very simple gas law calculation, we got around the difficulty by decreasing the volume of the gas space by means of the simple device illustrated in Figure 2. Here we have merely a glass rod, A, chosen of such a diameter that it fits snugly inside the neck of the volumetric flask, and carried by a rubber stopper. The whole is inserted into the neck of the flask, and the glass rod lowered in its stopper until the level of the liquid rises by displacement well up into the neck. By means of this device the volume of the gas space in the flask after the insertion of the special stopper is made negligible.

The experiments, then, were finally carried out in the following way:

1. A volume of silver nitrate solution containing isobutylene was run into a volumetric flask from a pipette.

2. A volume of standard nitric acid was run into the flask, also from a pipette, and the flask was filled to the mark with distilled water.

3. An ordinary glass stopper was set on the volumetric

flask and the contents well mixed.

4. A sample was immediately withdrawn for butylene analysis, and the glass stopper was replaced by the special stopper described above and illustrated in Figure 2.

5. The time was noted, and the flask containing the reaction mixture was placed in a thermostat at 25° C.

6. After a sufficient length of time, the flask was removed from the thermostat, and samples were withdrawn almost simultaneously for butylene and tertiary butyl alcohol analyses.

7. The silver concentration in the reaction mixture was determined by titration with potassium sulphocyanate.

8. The nitric acid concentration in the reaction mixture was determined by titration with normal base after addition of an excess of sodium chloride solution to precipitate the silver; similar analyses of known acids proved the method sufficiently accurate.

The hydration of iso-butylene is a reversible reaction, the equilibrium being well displaced toward the alcohol side in aqueous solution at 25° C., but being nevertheless sufficiently finite to enable the concentration of the butylene at equilibrium to be roughly determined. The average value of the ratio,

$$\frac{\text{(tertiary butyl alcohol)}}{\text{(iso-butylene)}},$$

at 25° C., at equilibrium, as measured from both the alcohol and the butylene sides, is about 120; or, in other words, less than 1 per cent of the alcohol is dehydrated to isobutylene at equilibrium in aqueous solution at 25° C. It is apparent, however, that the equilibrium reverts toward the iso-butylene side on increasing the temperature, from the fact that the iso-butylene was originally made by heating tertiary butyl alcohol in the presence of a catalyst. Consequently heat must be evolved on hydration.

It is possible to verify these experimental findings approximately from thermodynamic considerations. Unfortunately, the absolute entropy of iso-butylene has not been measured; but Dr. H. M. Huffman, of the staff of the California Institute of Technology, has kindly supplied the author with an estimated value of this entropy, based on his experience with other unsaturated hydrocarbons, which he believed to be accurate to at least an entropy unit; this value is, at 25^0 C.,

$$C_4H_8\ (g,\ 1\ atm.);\quad S_{abs.} = 67.0\ cal./deg.\ K.$$

Using this value and other constants available in the literature, the author has calculated the thermodynamic constants of the reaction of the hydration of iso-butylene in the following way.

$$\begin{array}{lcccccccc} & C_4H_8\ (g) & + & 6\ O_2\ (g) & = & 4\ CO_2\ (g) & + & 4\ H_2O\ (l); \\ H & -8000 & & 0 & & 4x(-94240) & & 4x(-68310) \end{array}$$

$$\Delta H = -642{,}200\ cal.$$

From the heats of combustion of carbon, hydrogen, and iso-butylene the heat content of gaseous iso-butylene is found to be

$$C_4H_8\ (g);\quad H = -8000\ cal.$$

$$\begin{array}{lcccccc} & 4\ C & + & 4\ H_2 & = & C_4H_8(g,\ 1\ atm.); & \\ S & 4x1.3 & & 4x31.2 & & 67.0 & \Delta S = -63.0\ E.\ U. \\ H & 0 & & 0 & & -8000 & \Delta H = -8000\ cal. \end{array}$$

From these values the free energy of gaseous iso-butylene at 1 atmosphere is here found to be, since $\Delta F = \Delta H - T\Delta S$,

$$C_4H_8\ (g,\ 1\ atm.);\quad F = 10{,}774\ cal.$$

Similarly, for tertiary butyl alcohol the results are:

$$C_4H_9OH\ (l) + \frac{13}{2}\ O_2\ (g) = 4\ CO_2\ (g) + 5\ H_2O\ (l);$$

H	-89,410	0	4x(-94,240)	5x(-68,310)

$$\Delta H = -629{,}100 \text{ cal.}$$

From the heats of combustion of carbon, hydrogen, and tertiary butyl alcohol the heat content of liquid tertiary butyl alcohol is here found to be

$$C_4H_9OH\ (l); \quad H = -89{,}410 \text{ cal.}$$

$$4\ C\ (s) + 5\ H_2\ (g) + \frac{1}{2}\ O_2\ (g) = C_4H_9OH\ (l);$$

S	4x1.3	5x31.2	$\frac{1}{2}$x49.02	45.3
H	0	0	0	-89,410

$$\Delta S = -140.41 \text{ E. U.}$$

$$\Delta H = -89{,}410 \text{ cal.}$$

From these values the free energy of liquid tertiary butyl alcohol is found to be, by the relation $\Delta F = \Delta H - T\Delta S$,

$$C_4H_9OH\ (l); \quad F = -47{,}568 \text{ cal.}$$

Now, for the reaction in question,

$$C_4H_8(g, 1\text{ atm.}) + H_2O\ (l) = C_4H_9OH\ (l), \text{ at } 25^0\ C.;$$

F	10,774	-56,560	-47,568	$\Delta F = -\ 1{,}782$ cal.
H	-8,000	-68,310	-89,410	$\Delta H = -13{,}100$ cal.

These results show us, first, that the equilibrium is on the alcohol side, at 25^0 C., but is almost finite; and, second, that the equilibrium will revert toward the iso-butylene side as the temperature is raised.

The author has also calculated from the second law free energy equation,

$$d\left(\frac{-\Delta F}{T}\right) = \frac{\Delta H}{T^2}\, dT,$$

at what temperature the free energy change involved in the reaction of hydration would be zero, or, in other words, at which temperature gaseous iso-butylene at a pressure of 1 atmosphere can exist in equilibrium with liquid tertiary butyl alcohol and liquid water, assuming the heat effect attending the reaction constant over the small temperature range involved. The result of this calculation gives a temperature of 73° C., which again agrees very well qualitatively with observations, since we made iso-butylene by boiling tertiary butyl alcohol (82.5° C.) with oxalic acid. Therefore thermodynamic considerations bear out quite well, at least in a qualitative way, our experimental findings.

The reaction rate constants were calculated by the use of the integrated reaction rate expression for a first order reaction:

$$2.3026 \log \frac{C_0}{C_0 - C_a} = k\, t, \text{ where}$$

C_0 = molality of butylene at start of experiment,

C_a = molality of alcohol at finish of experiment,

k = reaction rate constant, and

t = elapsed time in hours.

The reaction rate constants obtained for various concentrations of nitric acid and of silver nitrate are given in Table 1, which summarizes the results obtained. Examination of Table 1 will reveal that, for any definite concentrations of the two catalysts, the reaction rate constant is, within the accuracy of the data, independent of the concentration of the butylene, indicating that the reaction is actually first order with respect to the butylene. Further examination of Table 1 will reveal the fact that the reaction rate constant, or, in other words, the rate of the reaction itself, increases with increasing acid concentration, but decreases with increasing silver concentra-

Table 1

Temperature = 25^0 C.

Normality of catalysts		Upper figure, per cent butylene reacted Lower figure, reaction rate constant in reciprocal hours					Average reaction rate constant
HNO_3	$AgNO_3$						
1.015	1.007	44.3	68.0				
		.077	.075				.076
.511	1.005	33.2	53.0	65.4			
		.0314	.0300	.0308			.0311
.254	1.004	25.8	34.0	46.6	64.2	75.0	
		.0135	.0142	.0155	.0149	.0135	.0143
.101	1.006	20.2	38.9	45.0	57.5		
		.0052	.0054	.0053	.0051		.00525
.982	.510	30.4	52.6	63.0			
		.1165	.1168	.1167			.1167
1.020	.258	29.5	49.1	78.8			
		.2053	.2032	.1995			.2042
.258	.518	30.5	44.5	64.1			
		.0208	.0217	.0207			.0211

tion; the silver is a negative catalyst.

It might be pointed out in passing that the equilibrium as measured is far enough displaced at 25^0 C. to make the correction, for the reverse reaction, which should be applied to the reaction rate expression, almost negligible within the limit of accuracy of the data. The correction in this work would be of approximately the order of .5 per cent in the reaction rate constant, and has therefore been neglected.

Apparently the reaction is first order with respect to the concentration of iso-butylene; but it may be a chain reaction. Consider, then, the effect of hydrogen ion. In Figure 3 the average values of the reaction rate constant, for stated values of silver nitrate concentration, are plotted against acid concentration. It will be noticed that the lines have little curvature; in other words, the reaction rate constant is almost proportional to the acid concentration. This fact suggests that if we had been able to measure the activity of the hydrogen ion, instead of the acid concentration, and had plotted the reaction rate constant against the activity of hydrogen ion, we might have obtained substantially straight lines; that is, the reaction may also be first order with respect to the hydrogen ion.

Since we do not know the hydrogen ion activities, we might use the acid concentrations as an approximation. If we assume that the reaction is first order with respect to the acid concentrations, as an approximation, we can derive the reaction rate expression,

$$2.3026 \log \frac{C_0}{C_0 - C_a} = k' (H^+) t,$$

where <u>k</u>' may be regarded as a universal constant applicable to

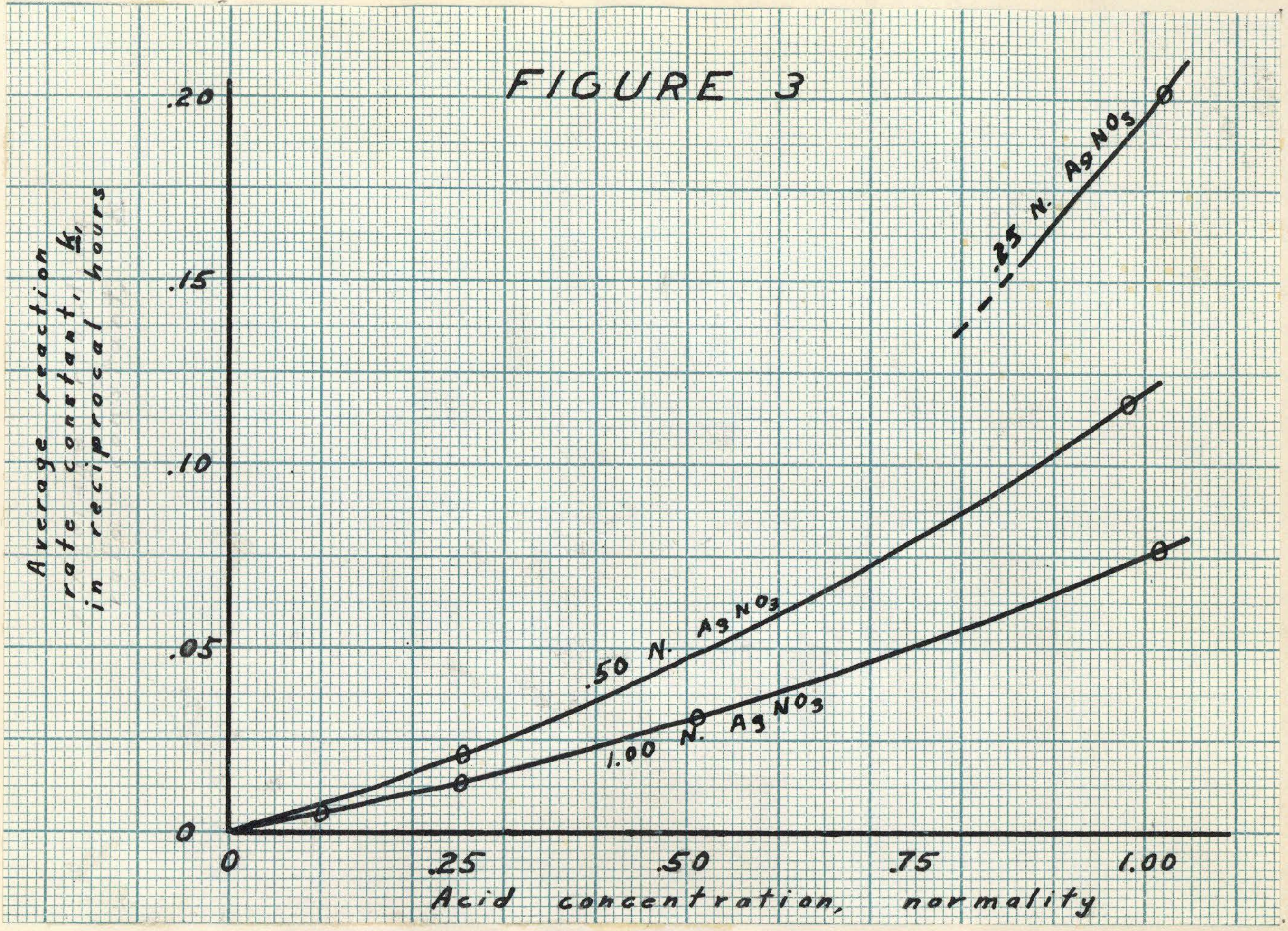


FIGURE 3

Average reaction rate constant, k_1 in reciprocal hours
.20
.15
.10
.05
0
0
.25
.50
.75
1.00
Acid concentration, normality
.25 N. AgNO3
.50 N. AgNO3
1.00 N. AgNO3

any definite silver ion concentration, (H^+) refers to the concentration of hydrogen ion, and the other symbols have the same meaning as before. The product $k' (H^+)$ is what we have up to this point called the reaction rate constant, so if we divide the average values of reaction rate constant in Table 1 by the acid concentrations we obtain, for the series in which the silver ion concentration was about 1 N., several values for the universal constant k' which should, but for our use of the acid concentrations as an approximation, be all the same. The values of k' obtained in this way for the series in which the silver ion concentration was about 1 N. are plotted against the acid concentrations in Figure 4. It will be noticed that k', the universal constant for 1 N. silver, does not remain constant, but on the other hand does not vary greatly.

Also on Figure 4, for comparison, is plotted similar data for the sugar hydrolysis, or inversion of cane sugar, in the presence of hydrochloric acid as a catalyst. The similarity in the two curves suggests that the two reactions may proceed along similar lines.

We can also account for the variation in the values of k' in the way indicated by Brönsted[4]. We can write the following possible mechanism for the hydration of iso-butylene:

(1) $H_2O + H^+ = H_3O^+$;

(2) $C_4H_8 + H_3O^+ = C_4H_8 \cdot H_3O^+$;

(3) $C_4H_8 \cdot H_3O^+ = C_4H_9OH + H^+$.

---

[4] see Contemporary Developements in Chemistry, Columbia University Press, 1927.

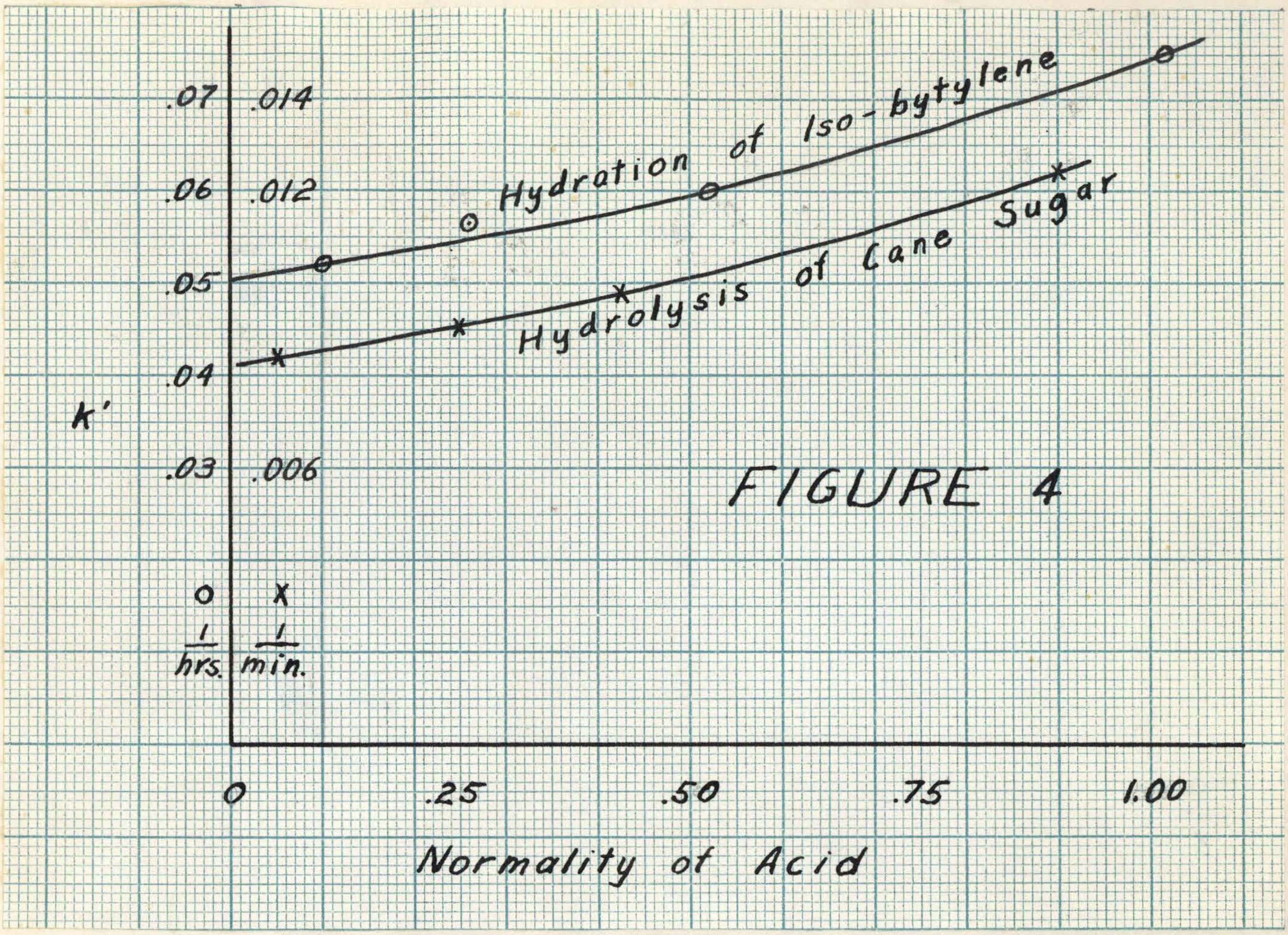


FIGURE 4

$$\underline{k}' = \frac{k}{(H^+)}$$

Now, assuming reactions (1) and (2) to be fast, and reaction (3) to be slow, the rate of alcohol formation will be proportional to the concentration of the critical complex $C_4H_8 \cdot H_3O^+$:

$$(4) \qquad \frac{dC_a}{dt} = k'' \cdot C_{C_4H_8 \cdot H_3O^+};$$

and from application of the law of mass action to reactions (1) and (2) we find

$$(5) \qquad \frac{C_{C_4H_8 \cdot H_3O^+}}{C_{H^+} \cdot C_{C_4H_8}} \cdot \frac{\gamma_{C_4H_8 \cdot H_3O^+}}{\gamma_{H^+} \cdot \gamma_{C_4H_8}} = \text{const.}$$

where <u>C</u> denotes concentration, and

<u>γ</u> denotes activity coefficient.

Substituting in equation (4) for the concentration of the critical complex its equivalent from equation (5),

$$(6) \qquad \frac{dC_a}{dt} = k'' \cdot C_{C_4H_8} \cdot C_{H^+} \cdot \frac{\gamma_{H^+} \cdot \gamma_{C_4H_8}}{\gamma_{C_4H_8 \cdot H_3O^+}} \cdot$$

Here <u>k"</u> is again a kind of universal constant which does not vary so long as the silver concentration is not changed.

Since, in equation (6), the activity coefficients of the two univalent ions can be considered equal, we can cancel them and write

$$(7) \qquad \frac{dC_a}{dt} = k'' \cdot C_{C_4H_8} \cdot C_{H^+} \cdot \gamma_{C_4H_8} \cdot$$

Substituting for the concentration of the butylene the value $(C_0 - C_a)$, the initial concentration of the butylene minus the concentration of the alcohol, and integrating, we obtain

$$(8) \qquad 2.3026 \log \frac{C_0}{C_0 - C_a} = k'' \cdot C_{H^+} \cdot \gamma_{C_4H_8} \cdot t,$$

in which the quantity $k'' \cdot C_{H^+} \cdot \gamma_{C_4H_8}$ has been called the reaction rate constant up to this point. Equation (8) indicates that if we were to divide the reaction rate constants in Table

1, for any given silver ion concentration, not, as before, by the acid concentration, but rather by the product of the acid concentration and the activity coefficient of the iso-butylene, we might obtain constant values of $\underline{k''}$. It is apparent also from equation (8) that if, instead, we divide the reaction rate constants by the acid concentration alone, what we obtain is the product of $\underline{k''}$ and $\gamma_{C_4H_8}$; and since activity coefficients of unionized molecules are often raised by increasing the ionic strength, due to the salting out effect, this product, as plotted in Figure 4, will increase with increasing acid concentration.

In any event, the reaction seems to be nearly first order with respect to the acid concentration, which indicates that the mechanism of acid catalysis is somewhat as indicated on page 16.

It is more difficult to explain the effect of silver ion on the reaction of hydration. It has been believed that the relatively large solubility of olefins in solutions of silver salts is due to the formation of a complex of the type

$$C_4H_8 + Ag^+ = C_4H_8.Ag^+.$$ [5]

---

[5] Lommel and Engelhardt, Ber. <u>57B</u>, 848 (1924).

In attempting to arrive at an explanation of the mechamism of catalysis by silver ion, it is important to first determine whether a complex is formed and what its nature is. For this purpose distribution experiments of iso-butylene between carbon tetrachloride and aqueous silver nitrate solutions were made. The experiments were performed by shaking, in a thermostat at 25° C., dilute solutions of iso-butylene in carbon tetrachloride with silver nitrate solutions. When equilibrium had been attained, the concentrations of iso-butylene in each phase was determined by the use of the special iodine flask described on page 3 of this paper; also the concentration of silver nitrate in the aqueous phase.

Carbon tetrachloride purified of oxidizable impurities according to the method described on page 3 was chosen as the solvent for the butylene in the distribution experiments, in order to permit the direct determination of the iso-butylene contained in solution by bromination in the way previously described, without any possibility of interference by bromination or oxidation of the solvent.

A consistent system of notation is adopted throughout this paper, and is summarized for purposes of reference in Table 3, page 31, at the end of this article.

Assuming Henry's Law to apply to dilute solutions of iso-butylene in carbon tetrachloride over the small concentration ranges involved,

$$(C_4H_8)\cdot\gamma_{C_4H_8} = a_{{C_4H_8}_{H_2O}} = a_{{C_4H_8}_{CCl_4}} = K\cdot c,$$

where a refers to activity,

γ refers to activity coefficient,

K is the distribution ratio of iso-butylene between carbon tetrachloride and water,

(C_4H_8) is the concentration of free iso-butylene in the aqueous phase, and

c is the concentration, expressed in molality, of butylene in the carbon tetrachloride phase.

$$\therefore (C_4H_8) = \frac{K \times e}{\gamma_{C_4H_8}}. \tag{9}$$

Now if we assume that one molecule of iso-butylene unites with one silver ion to form a complex ion,

$$C_4H_8 + Ag^+ = C_4H_8 \cdot Ag^+,$$

the following conditions must hold, in which for (C_4H_8) is substituted its equivalent from equation (9):

$$\kappa = \frac{(C_4H_8 \cdot Ag^+)}{\left(\frac{K \times e}{\gamma_{C_4H_8}}\right) \cdot (Ag^+)} \cdot \frac{\gamma_{C_4H_8 \cdot Ag^+}}{\gamma_{C_4H_8} \cdot \gamma_{Ag^+}}, \tag{10}$$

$$\frac{K \times e}{\gamma_{C_4H_8}} + (C_4H_8 \cdot Ag^+) = C, \tag{11}$$

$$(Ag^+) + (C_4H_8 \cdot Ag^+) = c, \tag{12}$$

where $\underline{\kappa}$ is the equilibrium constant of the reaction describing the formation of the complex,

$\underline{C}$ is the total (apparent) concentration of butylene in the aqueous phase, which is determined analytically, and

$\underline{c}$ is the total (apparent) concentration of silver in the aqueous phase, also determined analytically.

Cancelling the activity coefficients of the similar positive ions in equation (10) as an approximation, and combining equations (10), (11), and (12) with the elimination of the quantities (Ag^+) and $(C_4H_8 \cdot Ag^+)$, which we cannot measure, we derive the equation

$$\kappa = \frac{C - \left(\frac{K \times e}{\gamma_{C_4H_8}}\right)}{\left(\frac{K \times e}{\gamma_{C_4H_8}}\right)\left[c - C + \left(\frac{K \times e}{\gamma_{C_4H_8}}\right)\right]} \cdot \frac{1}{\gamma_{C_4H_8}}. \tag{13}$$

Making further cancellations of $\gamma_{C_4H_8}$, and neglecting the quantity $\frac{K \times e}{\gamma_{C_4H_8}}$, which is equal to (C_4H_8), the concentration of free butylene in the aqueous phase, in comparison with the concentration of complexed butylene, in the numerator, and in comparison with the silver ion concentration, in the denominator, silver being always present in large excess, equation (13) becomes

$$\kappa \cdot K = \frac{C}{e\,(c - C)} \cdot \tag{14}$$

Various values of the product $\underline{\kappa \cdot K}$ should be universally constant as long as the temperature is not varied, if our assumptions regarding the nature of the complex are correct. These values, calculated from the distribution data by means of equation (14), are given in Table 2, which summarizes the distribution data. It will be noted that constant values of the product $\underline{\kappa \cdot K}$ are actually obtained, within the error imposed by the simplifying assumptions made, by the application of Henry's law, and by unavoidable inaccuracies in the analytical data.

If we assume that any other complex is formed, such as, for example, $(C_4H_8)_2 \cdot Ag^+$ or $C_4H_8 \cdot Ag_2^{++}$, different equations are derived which lead to inconsistent results when applied to the analytical data. Consequently we can state with practical certainty that almost all of the butylene goes into the formation of a complex of the formula $C_4H_8 \cdot Ag^+$.

Now, in applying this information to the question of hydration, if we assume that only the free butylene takes part in the reaction, and that the only effect of silver ion on the reaction is the removal of butylene from solution by complex formation, we can derive the integrated reaction rate expression,

$$(1 + \kappa \cdot C_{Agt}) \ln \frac{C_o}{C_o - C_a} - \kappa \cdot C_a = kt,$$

where $\underline{C_{Agt}}$ is the total (apparent) concentration of silver in the

Table 2

Distribution experiments

Temperature = 25° C.

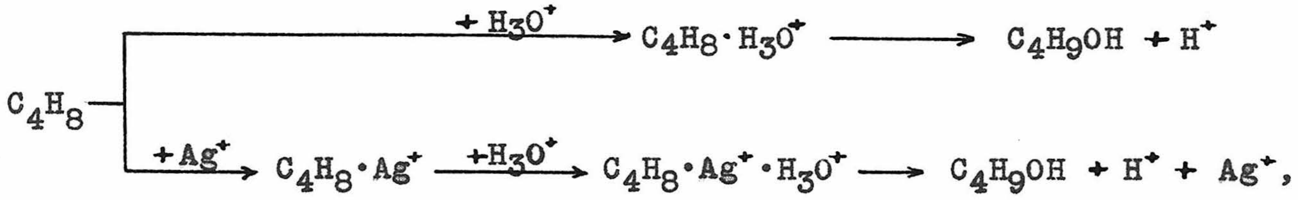
Normality Ag (c)	1.000	.4948	.7477	.2484	.965	.978
Molality of butylene in aqueous phase (C)	.01096	.00560	.00845	.00294	.005176	.005176
Molality of butylene in CCl_4 phase ($\mathcal{c}$)	.1460	.15415	.1492	.1555	.06938	.06898
$\kappa \cdot K$, assuming complex $C_4H_8 \cdot Ag^+$ formed	.0750	.0734	.0756	.0758	.0774	.0770

Note: The ionic strength in the aqueous phase was kept constant at unity throughout the distribution experiments by the addition of an inert solute (KNO_3).

solution, or the silver concentration which is determined analytically, and the other symbols have the usual significance. However, when this equation is applied to the reaction rate data, inconsistent results are obtained. This result is to be anticipated, for it will be noted from Table 1 that a reaction rate expression should be similar to the simple expression for a first order reaction in order to fit the data obtained.

If, on the other hand, we assume that it is only the complex which hydrates to the alcohol, it is difficult to explain why change in the silver ion concentration should have any marked effect on the rate of reaction; because silver ion is always present in large excess compared to butylene, and a further increase in the silver ion concentration can effect but slightly the concentration of the complex, and hance the rate of reaction.

However, if it is assumed that *both* the free and the complexed butylene take part in the reaction, according to the following scheme,



we can derive a reaction rate expression which satisfactorily fits the data obtained.

Let the concentration subscripts

a refer to tertiary butyl alcohol,

b refer to *free* iso-butylene,

bAg refer to silver-butylene complex,

bt refer to total (or apparent, sum of free and complexed) butylene, *Agt* refer to total (or apparent, sum of free and complexed) silver, and

o refer to total initial butylene. Then, neglecting activity coefficients as an approximation,

$$C_4H_8 + Ag^+ = C_4H_8 \cdot Ag^+,$$

$$\kappa = \frac{(C_4H_8 \cdot Ag^+)}{(C_4H_8) \cdot (Ag^+)} = \frac{C_{bAg}}{C_b \cdot (Ag^+)};$$

and from the conditions of the experiments,

$$C_{bAg} + C_b = C_{bt},$$

$$C_{bt} + C_a = C_o,$$

$$(15) \qquad C_{bAg} + (Ag^+) = C_{Agt}.$$

$$(16) \qquad \therefore C_b = \frac{C_{bt}}{1 + \kappa(Ag^+)}.$$

$$(17) \qquad C_{bAg} = C_{bt} - C_b = C_{bt} - \frac{C_{bt}}{1 + \kappa(Ag^+)}.$$

Now, if both complex and free butylene react in the process of hydration, we may write for our differential reaction rate expression,

$$(18) \qquad \frac{dC_a}{dt} = -\frac{dC_{bt}}{dt} = k_1 \cdot C_b + k_2 \cdot C_{bAg},$$

where k_1 and k_2 are reaction rate constants for the hydration of free and complexed iso-butylene, respectively. Substituting for C_b and C_{bAg} their equivalents in terms of C_{bt} from equations (16) and (17), and for (Ag^+) its equivalent in terms of C_{Agt} and C_{bt} from equation (15), we get as our final differential reaction rate equation,

$$(19) \qquad -\frac{dC_{bt}}{dt} = \frac{k_1 \cdot C_{bt} + k_2 \cdot C_{bt}[\kappa(C_{Agt} - C_{bt})]}{1 + \kappa(C_{Agt} - C_{bt})},$$

containing as variables only C_{bt} and *t*, the time. Integrating equation (19) between the concentration limits C_o and C_{bt} and the corresponding time limits 0 and t, we get for our final reaction rate expression,

$$\frac{1+\kappa\cdot C_{Agt}}{k_1+k_2\cdot\kappa\cdot C_{Agt}}\ln\frac{C_o}{C_{bt}} + \underbrace{\frac{(k_2-k_1)}{k_1+k_2\cdot\kappa\cdot C_{Agt}}\ln\frac{k_1+k_2\cdot\kappa(C_{Agt}-C_o)}{k_1+k_2\cdot\kappa(C_{Agt}-C_{bt})}} = t. \tag{20}$$

Equation (20) is difficult to manipulate, but fortunately the whole second term on the left hand side (indicated by a brace) can be safely disregarded in comparison with the first term with little error for the following reasons. C_{Agt}, the total silver concentration, is large in comparison with either C_o or C_{bt}, the initial and final butylene concentrations, because of the large excess of silver ion in the solutions. Therefore the numerator and the denominator of the fraction of which the logarithm is to be taken are very nearly equal, the fraction itself is very nearly unity, and its logarithm almost equal to zero. Cancelling this term, equation (20) becomes

$$\frac{1+\kappa\cdot C_{Agt}}{k_1+k_2\cdot\kappa\cdot C_{Agt}}\ln\frac{C_o}{C_{bt}} = t, \tag{21}$$

which is identical with the simple reaction rate expression for a first order reaction,

$$\ln\frac{C_o}{C_{bt}} = k\,t,$$

which has already been used in calculating the results of the experiments, except for the nature of the reaction rate constant. The fact that a first order reaction rate expression fits the data obtained is confirmatory evidence that our assumptions regarding the mechanism of the reaction are correct.

The quantity which we have called the reaction rate constant, k, and which we have calculated from our experimental data and tabulated in Table 1, is now seen from equation (21) to be equal to:

$$(22) \qquad k = \frac{\ln \frac{C_o}{C_{bt}}}{t} = \frac{k_1 + k_2 \cdot \kappa \cdot C_{Agt}}{1 + \kappa \cdot C_{Agt}},$$

where k_1 and k_2 are reaction rate constants independent of silver ion concentration but varying with acid concentration, and κ is the equilibrium constant for the reaction by which the silver ion-butylene complex is formed. Therefore if we have three values of k and C_{Agt} for the same acid concentration, we can calculate from equation (22) k_1 and k_2 for that acid concentration, and also κ. Three such values are given in lines 1, 5, and 6 of Table 1. Adjusting the three values of k by proportionality to the same acid concentration and substituting them, together with the corresponding total silver concentrations, into equation (22), we get,

$$(22a) \qquad \frac{k_1 + k_2 \cdot \kappa \cdot 1.007}{1 + \kappa \cdot 1.007} = .076,$$

$$(22b) \qquad \frac{k_1 + k_2 \cdot \kappa \cdot .510}{1 + \kappa \cdot .510} = .1206,$$

$$(22c) \qquad \frac{k_1 + k_2 \cdot \kappa \cdot .2594}{1 + \kappa \cdot .2594} = .2036;$$

and solving for the three constants,

$\kappa = 50,$

$k_1 = 2.47$ (for 1.015 N. HNO_3), and

$k_2 = .0284$ (for 1.015 N. HNO_3).

It will be noticed that k_1 is almost a hundred times k_2, indicating that the free iso-butylene hydrates almost a hundred times as rapidly as the butylene-silver ion complex. This result was to be anticipated, because hydrogen ion plays a very specific part in the reaction, and would be expected to react far less rapidly with the complex, which is another positive ion, than with the neutral molecules of free iso-butylene. On the other hand, the fact that κ is about 50 shows that when, for example, the silver ion concentration is 1 N., the concentration of the complex is about 50 times the concentration of the free butylene. Accordingly, since the complex reacts only a hundredth as fast as the free butylene, but is present in 50 times the concentration, under the above conditions about half as much alcohol is produced from the complex as from the free iso-butylene.

As a final check on the correctness of our mechanism for the reaction, and hence of our reaction rate expression, we apply the latter to one additional set of data we have obtained, that given in line 7 (the last line) of Table 1, page 13. The data in lines 1-4 of that table we cannot use for the purpose of explaining the effect of silver catalysis, because the total silver concentration was not varied; and the data in lines 5-6 we have already used above.

First, it is reasonable to assume that both the reaction rate constants k_1 and k_2 are affected nearly proportionately by change in the hydrogen ion concentration. This conclusion is indicated by the apparently first order nature of the reaction with respect to acid concentration. Assuming this to be the case, we can calculate the values for the constants k_1 and k_2 for .258 N. HNO_3, given their values for 1.015 N. HNO_3, by proportion as follows:

$$k_1 = 2.471 \times \frac{.0143}{.076} \times \frac{.258}{.254} = .4715;$$

$$k_2 = .0284 \times \frac{.0143}{.076} \times \frac{.258}{.254} = .00542;$$

In explanation of the preceding calculations, the quantities .0143 and .076 are the values for the reaction rate constant, $\underline{k}$, given in Table 1, for .254 N. and for 1.015 N. nitric acid, respectively. By multiplying the values of $\underline{k_1}$ and $\underline{k_2}$, for 1.015 N. acid, by the ratio .0143/.076, we obtain their values for .254 N. nitric acid; then by multiplying by the ratio .258/.254, we obtain their values for .258 N. acid, which is the concentration at which the data of line 7, Table 1, was obtained.

Now, inserting these values of $\underline{k_1}$ and $\underline{k_2}$, together with the other data for the run given in line 7, Table 1, into equation (22), we can solve for $\underline{\kappa}$, thus obtaining an additional value for that constant:

$$(22d) \qquad \frac{.4715 + .00542 \times \kappa \times .518}{1 + \kappa \times .518} = .0211,$$

$$\kappa = 55.5.$$

This value compares favorably with the previous one (50), bearing in mind the uncertainty of the data in line 3, Table 1, which it was necessary to use to obtain the result; and bearing in mind also the fact that the total ionic strength changed markedly throughout the reaction rate experiments, and still concentrations rather than activities had to be used in the calculations because of lack of knowledge of activity coefficients. The agreement between the values of $\underline{\kappa}$ obtained affords additional evidence that our final reaction rate expression is correct.

In conclusion, the experimental evidence indicates (1) that silver ion and iso-butylene form a mono-ionic, mono-molecular complex; (2) that <u>both</u> free and complexed iso-butylene hydrate to tertiary butyl alcohol in the presence of hydrogen ion; (3) that the free hydrocarbon reacts about a hundred times as rapidly as the complex; (4) that the reaction of hydration is first order with respect to the concentration of free butylene, of complexed butylene, and of hydrogen ion; and (5) that the only effect of silver ion on the reaction is the formation of the complex.

A mechanism for the reaction has been postulated, which leads to a reaction rate expression giving satisfactory results when applied to the experimental data. Tentative values for the constants which have been obtained, for a temperature of 25° C., are as follows:

$$\kappa = 50,$$

$$k_1 = 2.47 \text{ (for 1.015 N. } HNO_3\text{)},$$

$$k_2 = .0284 \text{ (for 1.015 N. } HNO_3\text{)};$$

and since $\kappa \cdot K = .075$,

$$K = \frac{.075}{50} = .0015.$$

It is expected that additional experimental evidence to be obtained will support the conclusions drawn. K, the distribution ratio of iso-butylene between water and carbon tetrachloride, is to be measured independently, enabling the calculation from the distribution data alone, by the use of equation (14), page 22, of a separate and more accurate value of κ to check the value obtained with the aid of the reaction rate data.

Table 3

Notation

k	reaction rate constant in first order reaction rate equation.
k'	special reaction rate constant, to be multiplied by acid concentration in first order reaction rate equation.
k''	special reaction rate constant, to be multiplied by acid concentration and activity coefficient of iso-butylene in first order eeaction rate equation.
k_1	reaction rate constant for hydration of free butylene.
k_2	reaction rate constant for hydration of complex $C_4H_8 \cdot Ag^+$.
K	distribution ratio of iso-butylene between carbon tetrachloride and water.
κ	equilibrium constant of the reaction $C_4H_8 + Ag^+ = C_4H_8 \cdot Ag^+$.
C_a	concentration of tertiary butyl alcohol.
C_b	concentration of free iso-butylene.
C_{bAg}	concentration of complexed iso-butylene.
C_{bt}	concentration of total (apparent) butylene.
C_{Agt}	concentration of total (apparent) silver.
C_o	initial concentration of butylene.
c	total silver concentration (distribution experiments).
C	total butylene concentration " "
$\mathscr{c}$	butylene concentration in CCl_4 " "
a	activity.
γ	activity coefficient.
t	time (hours).