part of the same temperature interval by both authors.

TABLE III

COMPARATIVE DATA ON TWO SUBSTITUTED ARSINES

°C.	Pressure in millimeters Dichloromethylarsine Baxter	 This Work	 Dichlorophenylarsine Baxter	 This Work
0	2.20	2.26	0.0037	0.0040
60	70.2	58.6	0.451	0.409
133[a]	1188	832	....	......
250[b]	.....	....	1259	855

[a] This is the value most frequently given in the literature as the boiling point at 760 mm. pressure for dichloromethylarsine. [b] This is an average value for the values quoted for the boiling point at 760 mm. of dichlorophenylarsine.

If we assume the two normal boiling points to be correct,[14] we then see that an error of about 10% is present in values calculated for the vapor pressure at temperatures considerably above the experimental range.

Summary

1. The volatility of nine substituted arsines has been measured between 0 and 60° by a transpiration method.

2. Vapor pressures have been calculated from the volatility measurements, and from these data logarithmic equations have been developed for both the volatility and the vapor pressure as a function of the temperature.

3. The mean molar latent heat of evaporation over the temperature range 0 to 60° has been computed from the vapor pressure equation for each compound.

4. The average precision of these measurements is better than ±2% over the specified temperature range. However, the equations may be used to extrapolate to other temperatures with somewhat less precision.

CHICAGO, ILLINOIS RECEIVED JULY 19, 1947

---

[14] This seems unlikely since normal boiling points are quoted for dichlorophenylarsine ranging from 247 to 257°, with the value 250° appearing most frequently.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

The Electrolyte Effects in the Hydration of Isobutene[1,2]

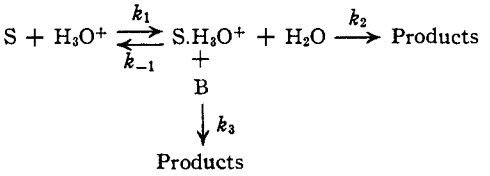
BY FRANK G. CIAPETTA[3] AND MARTIN KILPATRICK[4]

The problem of electrolyte effects of large magnitude in reactions involving an uncharged substrate and the hydrogen ion has been a subject of study in this Laboratory.[5,a,b,c,d] More recently Olson and Tong[6] have attempted to interpret these salt effects, and Sullivan and M. L. Kilpatrick,[7] and M. L. Kilpatrick[8] have advanced a different viewpoint which should be considered.

Whereas Leininger and Kilpatrick[5b] postulated the pre-equilibrium with k_2 the rate determining

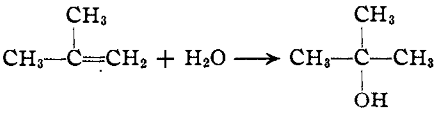
$$S + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \{S\cdot H_3O\}^+ \xrightarrow{k_2} \text{Products} \quad (1)$$

step, M. L. Kilpatrick[8] for the hydrolysis of cyanamide, where the cation is formed in appreciable concentration, found the rate determining step to be the reaction of the solvated cation with the base water (k_2), and if additional bases are present the rate is higher than that anticipated on the basis of a hydrogen ion catalysis. This is due to the concurrent reaction (k_3) of the base B with the solvated cation.

 (2)

$$S + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} S.H_3O^+ + H_2O \xrightarrow{k_2} \text{Products}; \quad S.H_3O^+ + B \xrightarrow{k_3} \text{Products}$$

The present investigation deals with the effect of electrolyte concentration on the rate of hydration of isobutene in aqueous solutions of strong acids and the weaker chloroacetic acids. The reaction in nitric acid solution has been shown to be

 (3)

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

first order with respect to isobutene and its rate proportional to the acid concentration at constant ionic strength,[9] and this conclusion has been verified by G. R. Lucas and Hammett.[10]

Lucas and Eberz followed the course of the reaction analytically but the dilatometric method

---

[1] Abstracted from the dissertation of Frank G. Ciapetta presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirement for the degree of Doctor of Philosophy, April, 1947.

[2] Presented before the Division of Physical and Inorganic Chemistry at the 112th meeting of the American Chemical Society at New York, N. Y., September, 1947.

[3] E. I. du Pont de Nemours and Company Fellow, 1946–1947. Present address: The Atlantic Refining Company, Philadelphia, Pa.

[4] Present address: Department of Chemistry, Illinois Institute of Technology, Chicago 16, Illinois.

[5] (a) L. C. Riesch and M. Kilpatrick, *J. Phys. Chem.*, **39**, 561 (1935); (b) P. M. Leininger and M. Kilpatrick, THIS JOURNAL, **60**, 2891 (1938); (c) P. M. Leininger and M. Kilpatrick, *ibid.*, **60**, 2510 (1938); (d) M. Kilpatrick, "Handbuch der Katalyse," Vol. II, Julius Springer, Wien, 1940, p. 258.

[6] A. R. Olson and L. K. J. Tong, THIS JOURNAL, **66**, 1555 (1944).

[7] M. J. Sullivan and M. L. Kilpatrick, *ibid.*, **67**, 1815 (1945).

[8] M. L. Kilpatrick, *ibid.*, **69**, 40 (1947).

[9] H. J. Lucas and W. F. Eberz, *ibid.*, **56**, 460 (1934).

[10] G. R. Lucas and L. P. Hammett, *ibid.*, **64**, 1928 (1942).

was employed in the present investigation. The hydration of isobutene proceeds with a contraction in volume, but due to the low solubility of isobutene (*ca.* 0.005 mole per liter at 25°) the experimental volume change is so small that it was necessary to employ dilatometers of larger volume than usual to obtain the desired accuracy. In considering the design of the dilatometer, the problem of obtaining rapid thermal equilibrium with the constant temperature bath becomes important. It is also necessary to control the bath temperature within narrow limits.

Experimental Part

Apparatus.—One of the dilatometers is shown in Fig. 1 where F_1, F_2, F_3 and F_4 are four interconnecting cylinders each of approximately 80-ml. capacity giving a total reaction vessel volume of 465 ml. The reaction vessel is connected through stopcock A to the mixing chamber G with side arm C, and through stopcock B to a small mercury reservoir fitted with a steel plunger operating on a screw (not shown). A fritted glass disc H was sealed in the bottom of the reservoir through which the isobutene was introduced to saturate the water. The calibrated capillary of 2.28×10^{-3} sq. cm. cross section gave a maximum linear change during an experiment of 8–9 cm. corresponding to a volume change of 0.017–0.020 ml. The other dilatometer was of similar dimensions. The dilatometers were mounted on brass racks in well-stirred insulated water-baths whose temperature was controlled by large-capacity mercury–alcohol thermoregulators and F. G. 57 thyratron tubes.[11] Every effort was made to minimize temperature fluctuations in the bath by vigorous stirring, careful regulation of heating and cooling periods and clean mercury surfaces. The temperature was determined by means of a certified platinum resistance thermometer in conjunction with a Mueller bridge. Tests with the resistance thermometer showed only slight variations ($< \pm 0.001°$) with time and only negligible stratification throughout the bath when the room temperature was quite constant ($\pm 1°$) and not more than 2–3° below the bath temperature. The importance of temperature control is emphasized by the fact that a change of $\pm$ 0.001° corresponds to a difference in reading of 0.07–0.08 cm. on the capillary of the dilatometer. Investigation of the time necessary for the dilatometer to come to thermal equilibrium using water revealed that the half-time was 2.6 minutes.

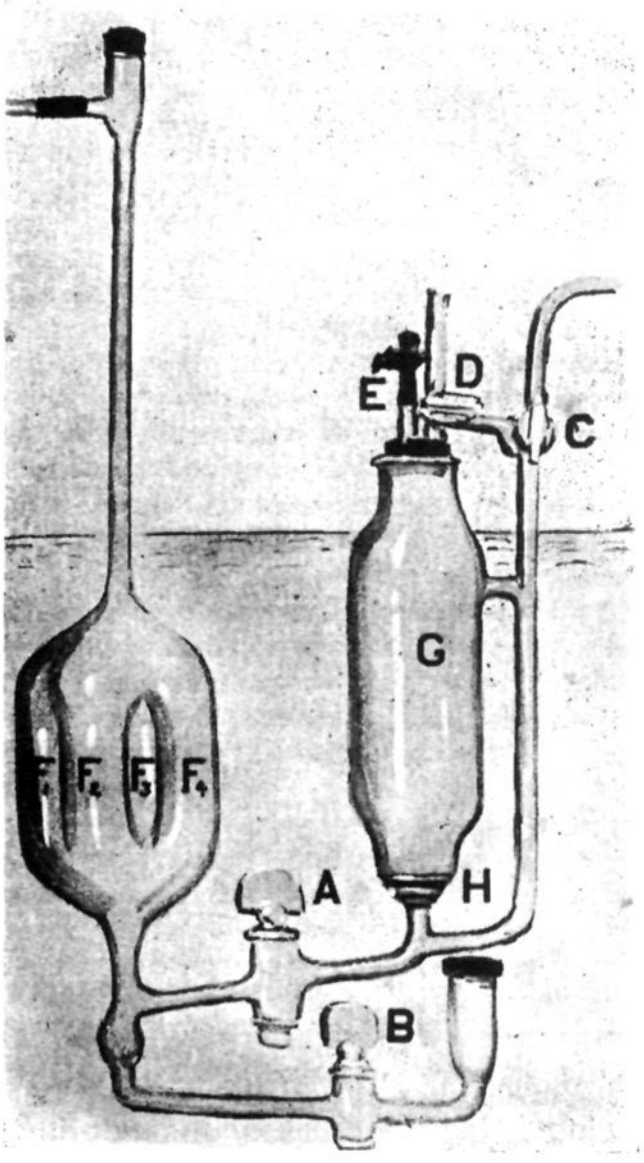


Fig. 1.—Dilatometer.

Determination of Rate.—The following procedure was adopted in the determination of the rate. With cocks D and B closed and tube E sealed off by means of a piece of rubber tubing with a screw clamp (Fig. 1), isobutene was introduced into the dilatometer through cocks C and A for fifteen minutes to purge the dilatometer of air. Cocks A and C were closed and 500 ml. of water placed in reservoir G. With cock D open, isobutene gas was introduced through cock C to the bottom of the reservoir where the gas was dispersed into small bubbles by the fritted disc before passing through the water. The isobutene was bubbled through the water for one and a half hours at a constant back pressure (*ca.* 5 cm.) of mercury. Cock C was closed and a 10-ml. pipet introduced below the surface of the solution through tube E and connected to it by a short piece of rubber tubing. By introducing isobutene gas through cock D a sample of the solution for the determination of the isobutene concentration could be obtained without loss of dissolved isobutene. The solution was stirred with a motor-driven glass stirrer for five minutes after which the required amount of acid was added and the stirring continued for five minutes longer. The solution was forced into the dilatometer by introducing isobutene through cock D (E closed) and opening cock A. Cock A was then sealed off with mercury using the procedure of Brönsted, Kilpatrick and Kilpatrick[12] and the readings started as soon as possible.

After the addition of the acid the time required to fill the dilatometer was approximately fifteen to twenty minutes. In experiments at temperatures of 30 and 35° the reaction mixture required ten to fifteen minutes after sealing in the dilatometer to come to thermal equilibrium. Hence no attempt was made to study reactions whose half-time was less than thirty to thirty-five minutes. No trouble was experienced from the formation of gas bubbles, except in the dichloroacetic acid–sodium dichloroacetate buffer experiment where the total electrolyte concentration was high. In this experiment small gas bubbles, probably isobutene, appeared during the filling of the dilatometer.

In all cases the progress of the reaction was followed by contraction of the solution as read from the graduated capillary of the dilatometer.

The observed velocity constants were evaluated by the method reported by Guggenheim.[13] In a few experiments the experimentally observed infinity reading was used for the second set of readings. In determining the best straight line through the experimental points observed values of ΔV which were less than one were not included since the errors due to temperature fluctuations were accentuated at these low values.

Isobutene.—Isobutene was prepared by the catalytic dehydration of tertiary butyl alcohol. Two different procedures were employed during the course of this investigation. In the first the alcohol was dehydrated over activated aluminum oxide pellets at a temperature of 370–

---

[11] A. W. Hull, *Gen. Elec. Rev.*, **32**, 213 (1929).

[12] J. N. Brönsted, M. L. Kilpatrick and M. Kilpatrick, THIS JOURNAL, **51**, 428 (1929).

[13] E. A. Guggenheim, *Phil. Mag.*, 538 (1926).

380°.[14] The catalyst was supported in a vertical reaction tube (2.8 cm. i.d. and 86 cm. in length) heated in an automatically controlled aluminum-bronze block furnace.[15] The alcohol was delivered at a constant rate of 3 ml. per minute to the top of the reaction chamber by a Tropsch-Mattox bellows pump.[16] After leaving the reaction chamber the products were cooled by a water condenser and the isobutene bubbled through two wash bottles in series containing water to remove entrained alcohol vapors. The scrubbed gas then passed through a drying tube and condensed in a high-pressure cylinder (200-ml. capacity) cooled in a Dry Ice-acetone-bath. Two samples of isobutene prepared by this procedure were analyzed by a Consolidated Mass Spectrometer.[16a] Both samples were found to contain 99.9% isobutene and 0.1% isobutane. The second procedure employed was similar to that described by Spence and Hurd.[17] The alcohol was dehydrated by refluxing with oxalic acid and the isobutene purified and collected in the same manner as described above. Consistent results were obtained using isobutene prepared by either procedure.

Determination of Concentrations.—The isobutene concentration was determined by a modification of the method employed by Lucas and Eberz.[9] The acid concentration was determined at the completion of an experiment by titration with carbonate-free sodium hydroxide standardized against benzoic acid. No change was found in the acid concentration, within the experimental error (0.10%) in those runs where both the initial and final acid concentrations were determined.

Experimental Results

Order of the Reaction.—Since Lucas and Liu[18] found some falling off in the velocity constant in the hydration of trimethylethylene, careful experiments were carried out to demonstrate that the reaction is first order. As the data cannot be shown graphically on a small scale the data and calculations for a typical run at 25° are tabulated in Table I. Column 2 gives the first set of readings taken over a period approximately two and a half times the half-time. Readings taken two and four hours later are given in columns 3 and 4. When the logarithms of ΔV, the differences between the readings in columns 2 and 3 and 2 and 4, are plotted against the time given in column 1 the slope of the best straight lines through the points is $-0.4343\ k_{\text{obs}}$. In this particular experiment the lines were exactly parallel. Columns 5 and 6 give $\Delta V_{\text{obs.}} - \Delta V_{\text{calcd.}}$, the deviations of any point from the line.

TABLE I

HYDRATION OF ISOBUTENE IN PERCHLORIC ACID SOLUTION AT 25.00°

$HClO_4$, 0.3974*M*; Isobutene, 0.00483*M*; $k_{\text{obs.}} = 13.22 \times 10^{-3}$; $t_{1/2} = 52$ min.

1	2	3	4	5	6
	Dilatometer reading			$\Delta V_{\text{obs.}} - \Delta V_{\text{calcd.}}$ from columns	
Time, min.	at t	After 2 hr.	After 4 hr.	(2), (3)	(2), (4)
0	18.84	13.50	12.43	+0.11	+0.11
5	18.34	13.42	12.41	+ .03	+ .04
10	17.91	13.35	12.40	− .01	.00
15	17.53	13.27	12.38	− .02	.00
20	17.19	13.19	12.36	.00	.00
25	16.86	13.12	12.35	− .01	− .01
30	16.56	13.05	12.35	.00	− .02
35	16.27	13.00	12.33	− .01	− .01
40	16.00	12.94	12.31	− .02	− .02
45	15.77	12.89	12.30	.00	.00
50	15.53	12.84	12.29	.00	.00
55	15.33	12.80	12.28	.00	+ .01
60	15.13	12.75	12.27	+ .01	+ .01
65	14.93	12.71	12.26	.00	.00
70	14.76	12.69	12.25	.00	+ .01
75	14.59	12.65	12.25	.00	.00
80	14.44	12.62	12.24	.00	+ .01
85	14.28	12.58	12.24	.00	.00
90	14.14	12.56	12.23	− .01	.00
97	13.97	12.51	12.23	+ .01	− .01
100	13.89	12.48	12.22	+ .01	− .01
105	13.79	12.47	12.21	+ .01	+ .01
110	13.68	12.46	12.21	.00	.00
115	13.58	12.44	12.20	.00	.00
120	13.50	12.43	12.20	.00	+ .01

The data shown in Table I are for the same experiment, the only difference being the time interval between the two sets of readings. The second set of readings was taken immediately after the completion of the first set, while the third set of readings was taken after an additional interval of two hours. By this procedure the reaction was followed to 99% completion. In both cases the deviations of the observed values of ΔV from those calculated, with the exception of the first value, are well within the experimental error. Thus the reaction is strictly first order with respect to the isobutene concentration over the entire range.

Results with Strong Acids.—The hydration of isobutene was studied in the presence of perchloric, hydrochloric, and *p*-toluenesulfonic acid to determine the electrolyte effect of these acids. The results are summarized in Tables II, III and IV. Column 1 gives the molarity of the acid, column 2 the observed velocity constant (in minutes) and column 3 the second order constant, $k_{H_3O^+}$, obtained by dividing the observed velocity constant by the acid concentration.

It is to be noted that at 25° the second order constant consistently increases with increasing electrolyte concentration. The results at 30 and 35° are somewhat erratic but show the same general increase in the second-order constant with increasing electrolyte concentration. The erraticalness is due to the fact that the isobutene is less soluble at higher temperatures and the smaller volume change combined with the poorer constancy of temperature (±0.003° compared to ±0.001°) means less accurate experiments. The initial concentration of isobutene ranged from 0.0052 to 0.0047 molar at 25°, 0.0046 to 0.0039 at 30° and 0.0037 to 0.0032 at 35°.

---

(14) V. N. Ipatieff and B. B. Corson, *Ind. Eng. Chem.*, **27**, 1069 (1935).

(15) A. V. Grosse, J. C. Morrell and W. J. Mattox, *ibid.*, **32**, 530 (1940).

(16) H. Tropsch and W. J. Mattox, *ibid.*, **26**, 1338 (1934).

(16a) These analyses were obtained through the courtesy of The Atlantic Refining Company.

(17) L. U. Spence and C. D. Hurd, THIS JOURNAL, **51**, 3561 (1929).

(18) H. J. Lucas and Y. P. Liu, *ibid.*, **56**, 2138 (1934).

TABLE II

THE EFFECT OF PERCHLORIC ACID ON THE RATE OF HYDRATION OF ISOBUTENE

Molarity of $HClO_4$	$10^3 k_{obs.}$	$10^2 k_{H_3O^+}$
	Temp., 25.00°	
0.0990	2.303	2.326
.1553	4.099	2.639
.2328	6.539[a]	2.809
.2784	8.566[b]	3.077
.3585	11.74	3.275
.3974	13.22	3.327
.4788	17.59	3.674
	Temp., 29.99°	
0.0563	2.671	4.748
.0757	3.730	4.927
.0771	3.638	4.717
.0969	4.513	4.657
.1221	5.802	4.752
.1283	6.631	5.168
.1520	7.552	4.968
.1739	8.658	4.977
.1810	9.671	5.343
.1987	9.855	4.960
.2019	10.22	5.062
.2174	10.87	5.000
.2390	13.17	5.511
.2420	13.17	5.442
.2799	15.93	5.691
	Temp., 35.00°	
0.0550	4.329	7.867
.0775	7.322	9.444
.0961	7.737	8.055
.1248	9.210[c]	7.380
.1463	13.54	9.255
.1957	19.02	9.719
.2009	23.07	11.48

[a] In presence of ultraviolet light. [b] Solution 0.1 M in *t*-butyl alcohol. [c] Solution 0.2 M in *t*-butyl alcohol.

TABLE III

THE EFFECT OF HYDROCHLORIC ACID ON THE RATE OF HYDRATION OF ISOBUTENE

Molarity of HCl	$10^3 k_{obs.}$	$10^2 k_{H_3O^+}$
	Temp., 25.00°	
0.1044	2.556	2.450
.2078	5.664	2.726
.3090	9.394	3.041
.3505	11.01	3.141
.3932	13.17	3.349
.4895	17.59	3.593
	Temp., 29.99°	
0.0563	2.487	4.421
.0763	4.052	5.314
.1034	4.974	4.810
.1284	6.355	4.949
.1517	7.460	4.918
.1835	9.487	5.170
.2085	10.68	5.122
.2451	13.49	5.504
.2511	13.54	5.392
.2673	14.83	5.548
.2947	16.86	5.721
	Temp., 35.00°	
0.05416	4.651	8.588
.07622	6.401	8.399
.1002	9.118	9.100
.1284	11.61	9.042
.1538	14.41	9.372
.1886	18.70	9.915

TABLE IV

THE EFFECT OF *p*-TOLUENESULFONIC ACID ON THE RATE OF HYDRATION OF ISOBUTENE

Molarity of *p*-$CH_3C_6H_4SO_3H$	$10^3 k_{obs.}$	$10^2 k_{H_3O^+}$
	Temp., 25.00°	
0.1062	2.533	2.385
.1857	4.743	2.554
.2517	6.631	2.635
.3193	8.842	2.769
3701	10.13	2.737
.4424	12.80	2.894
	Temp., 35.00°	
0.0544	4.743	8.727
.0794	6.401	8.058
.0959	8.289	8.640
.1127	9.993	8.867
.1593	14.18	8.901
.1907	17.41	9.130

Several experiments were carried out in perchloric acid solutions in the presence of *t*-butyl alcohol to determine the effect, if any, of the reaction product on the velocity constant. At 25° for a solution 0.1 molar in the alcohol the first and second order constants were consistent with those found in the absence of the alcohol. However, at 35° for a solution 0.2 molar in the alcohol, the values were lower than was expected for the acid concentration employed.

The effect of ultraviolet light on the reaction velocity was investigated at 25°; the results indicated that the radiation had no effect on the rate of the reaction.

In order to compare the magnitude of the electrolyte effects of the acids at 25° the second-order constants obtained at 30 and 35° were converted to 25° by means of the energy of activation for the reaction. The energy of activation was computed by the equation employing the average

$$E_A = \frac{2.303RT_1T_2}{T_1 - T_2} \log \frac{k_{T_1}}{k_{T_2}} \qquad (4)$$

values of the second-order constants at zero electrolyte concentration, $k^0_{H_3O^+}$, for 25 and 35°. The values of $k^0_{H_3O^+}$ for perchloric, hydrochloric, *p*-toluenesulfonic and nitric[9] acids at 25°, hydrochloric, *p*-toluenesulfonic and nitric[9] acids at 35°, and the average values of $k^0_{H_3O^+}$ at these temperatures are given in Table V.

With the exception of the value for nitric acid at 35°, the values of $k^0_{H_3O^+}$ were obtained by plot-

TABLE V

VALUES OF THE SECOND ORDER CONSTANT AT ZERO ELECTROLYTE CONCENTRATION

Acid	$10^2 k^0_{H_3O}$ 25°C.	35°C.
$HClO_4$	2.134	...
HCl	2.211	8.030
p-$CH_3C_6H_4SO_3H$	2.291	8.007
HNO_3	2.190	7.887
	Av. 2.207	7.975

ting the logarithm of the second order constant at a function of the acid concentration and taking the intercept at zero electrolyte concentration from the best straight line (as found by the method of averages) through the experimental points for each acid. The value of $k^0_{H_3O^+}$ for nitric acid at 35° was calculated from the value of $k^0_{H_3O^+}$ for this acid at 25° and the energy of activation found by Lucas and Eberz.[9] The energy of activation for the hydration of isobutene obtained from the data given in Table V is 23.46 kcal. per mole which is in agreement with the value 23.39 kcal. given by Lucas and Eberz.[9]

In Fig. 2 the logarithms of the second order constants obtained at 25° and those calculated to 25° by the above procedure for perchloric, hydrochloric and p-toluenesulfonic acids are shown plotted as a function of the acid concentration. Using the logarithm of the average value of $k^0_{H_3O^+}$ at 25° given in Table V as the intercept at zero electrolyte concentration the best straight line was drawn through the data for each of the acids. Also shown in Fig. 2 are the data of Lucas and Eberz[9] for nitric acid at 25°. Figure 2 shows that the logarithm of the second order constant for the acids investigated increases linearly with acid concentration over the range of acid concentration investigated and thus obeys an equation of the type where C is the concentration of the acid in

$$\log k_{H_3O} = \log k^0_{H_3O^+} + BC \qquad (5)$$

moles per liter and B is a constant depending on the acid employed. The following equations express the electrolyte effect of the various acids studied.

$$\log k_{H_3O^+} = \bar{2}.3433 + 0.47C_{HClO_4} \qquad (6)$$
$$\log k_{H_3O^+} = \bar{2}.3433 + 0.44C_{HCl} \qquad (7)$$
$$\log k_{H_3O^+} = \bar{2}.3433 + 0.30C_{p\text{-}CH_3C_6H_4SO_3H} \qquad (8)$$

The electrolyte effect of nitric acid on the second order constant at 25° calculated from the data of Lucas and Eberz[9] is given by the equation

$$\log k_{H_3O^+} = \bar{2}.3405 + 0.21C_{HNO_3} \qquad (9)$$

The values of the B term show that these acids have a large electrolyte effect on the rate of the reaction. The effect decreases in the order $HClO_4 > HCl > p\text{-}CH_3C_6H_4SO_3H > HNO_3$ which is different from that found by Lucas and Liu[18] for the hydration of trimethylethylene; their data indicate the order of decreasing electrolyte effect to be $HCl > HClO_4 > HNO_3 > p\text{-}CH_3C_6H_4SO_3H$.

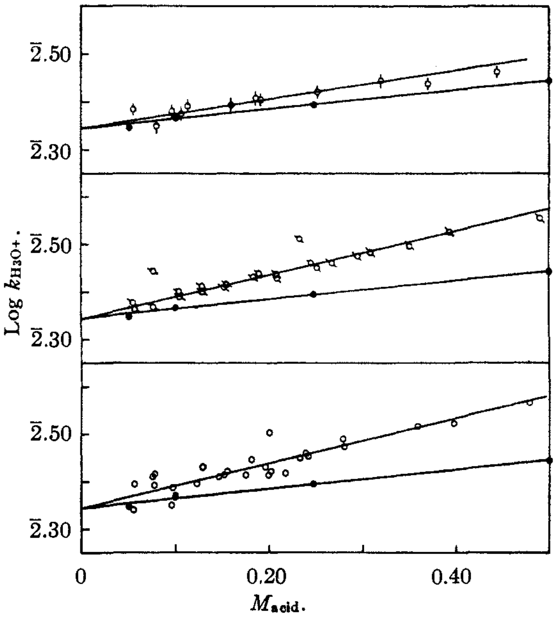


Fig. 2.—Hydration of isobutene: ○, $HClO_4$; ⌽, p-$CH_3C_6H_4SO_3H$; -○-, HCl; ●, HNO_3; temp. 25°.

However, with the exception of nitric acid this order of electrolyte effect on the rate of hydration of trimethylethylene is based on one experiment for each of the acids at a concentration of 0.1 M.

Hantzsch and Weissberger[19] studied the effect of strong monobasic acids on the rate of inversion of sucrose at 25°. Their data for perchloric, hydrochloric, hydrobromic, benzenesulfonic and nitric acids are shown in Fig. 3, where the logarithms of the second-order velocity constants are plotted as a function of the acid concentration. Over the range of acid concentrations investigated the second-order constants increase linearly with acid concentration. The electrolyte effects of these acids on the second-order constants are given by the equations

$$\log k_{H_3O^+} = \bar{3}.560 + 0.29C_{HClO_4} \qquad (10)$$
$$\log k_{H_3O^+} = \bar{3}.520 + 0.27C_{HBr} \qquad (11)$$
$$\log k_{H_3O^+} = \bar{3}.540 + 0.25C_{C_6H_5SO_3H} \qquad (12)$$
$$\log k_{H_3O^+} = \bar{3}.536 + 0.21C_{HCl} \qquad (13)$$
$$\log k_{H_3O^+} = \bar{3}.550 + 0.17C_{HNO_3} \qquad (14)$$

The values of the B term for the various acids indicate that for the inversion of sucrose, as for the hydration of isobutene, perchloric acid has the largest electrolyte effect on the velocity constant and nitric acid the lowest. However, for perchloric and hydrochloric acids the magnitudes of the B term are much greater for the hydration of isobutene than for the inversion of sucrose.

Riesch and Kilpatrick[5a] also observed that the perchlorate ion had the largest electrolyte effect on the rate of hydrolysis of diethyl acetal at 0°. For this reaction the order of decreasing electrolyte effect for the anion of the sodium salts in-

---

[19] A. Hantzsch and A. Weissberger, *Z. physik. Chem.*, **125**, 251 (1927).

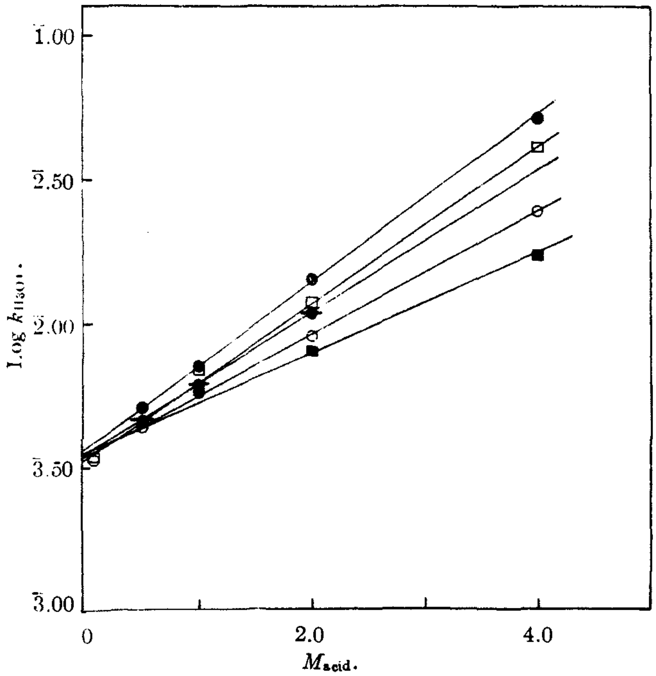


Fig. 3.—The inversion of sucrose at 25°: ●, $HClO_4$; -●-, $C_6H_5SO_3H$; ■, HNO_3; □, HBr; O, HCl.

vestigated was $ClO_4^- > Cl^- > NO_3^- > p\text{-}CH_3C_6H_4SO_3^- \approx C_6H_5SO_3^-$. The smaller electrolyte effect observed for the *p*-toluenesulfonate and benzenesulfonate ions than for the nitrate ion is not in agreement with the electrolyte effects of these ions on the rates of hydration of isobutene and the inversion of sucrose. The magnitudes of the *B* terms for sodium perchlorate and sodium chloride at a salt concentration of 0.5 *M* are similar to those found for perchloric and hydrochloric acids in the hydration of isobutene.

Results with chloro-substituted acetic acids.—In the hydrolysis of cyanamide[7] the observed velocity constant was in some cases found to be greater in solutions of trichloroacetic acid than in solutions of nitric acid of the same concentration. To compare the observed velocity constants for these two acids for the hydration of isobutene trichloroacetic acid was purified by recrystallization from benzene and hydration experiments carried out in the usual way. The reaction was first order and tests for chloride ion showed no decomposition of the acid during the reaction. The results are summarized in Table VI and the comparison of the observed velocity constants for the two acids presented graphically in Fig. 4. The data revealed that the observed velocity constants are higher for trichloroacetic acid below 0.4 *M* than for nitric acid, while the reverse is true at higher concentrations in spite of the fact that trichloroacetic acid is considered to be a weaker acid than nitric acid. The possibility that Scheme 2 is operative in the hydration of isobutene and we are not dealing with a specific hydrogen ion-catalyzed reaction was tested in the following way.

Dichloroacetic acid was purified by vacuum distillation and a middle fraction boiling from 95–96° (mainly at 95.5°) at 18 mm. mercury pressure was used to prepare a dichloroacetic acid–sodium dichloroacetate buffer solution with an acid to base ratio approximately unity. The observed velocity constant for the hydration was determined with a portion of this solution, and other portions of the original stock solution were diluted with water containing the required amount of sodium chloride to keep the ionic strength nearly constant and the velocity constant again determined. The last solution had approximately one fourth of the concentration of dichloroacetic acid and dichloroacetate of the first solution. The results are presented in Table VII.

The stoichiometric composition of the buffer solutions is given in columns 1 to 3, the observed velocity constant in column 4, the calculated hydrogen ion concentration based on a value of the dissociation constant of 7.05×10^{-2} calculated from the data of Harned and Hawkins[20] in column 5, and the value of the

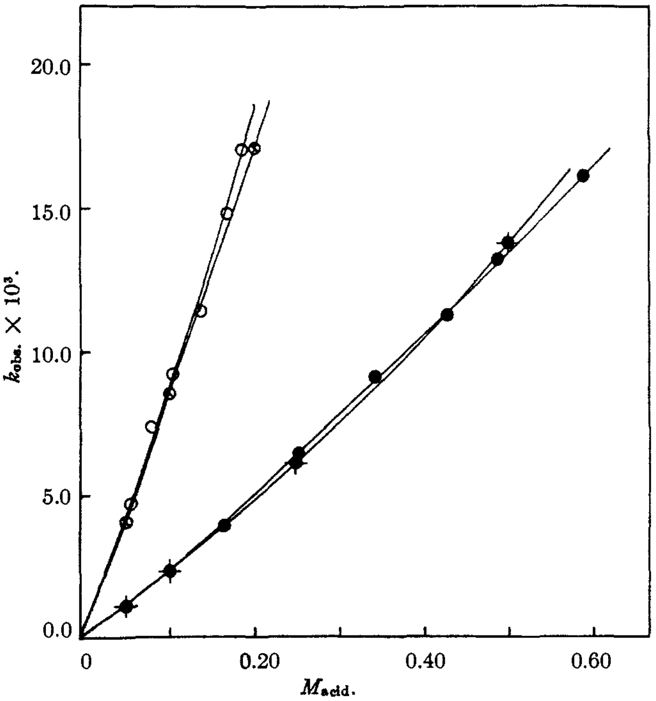


Fig. 4.—Hydration of isobutene at 25°: ●, CCl_3COOH: -●-, HNO_3 at 35°; O, CCl_3COOH; ⊘, HNO_3.

---

[20] H. S. Harned and J. E. Hawkins, This Journal, **50**, 85 (1928).

TABLE VI

EFFECT OF TRICHLOROACETIC ACID ON THE RATE OF HYDRATION OF ISOBUTENE

Molarity of CCl_3COOH	$10^3 k_{obs.}$	$10^2 k_{obs.}/M_{CCl_3COOH}$
	25.00°C.	
0.1637	3.914	2.391
.2523	6.447	2.555
.3432	9.118	2.657
.4275	11.28	2.639
.4881	13.22	2.709
5870	16.12	2.746
	35.00°C.	
0.0550	4.697	8.542
.07933	7.368	9.288
.1037	9.210	8.881
.1366	11.42	8.360
.1677	14.83	8.843
.1847	17.04	9.226

TABLE VII

HYDRATION OF ISOBUTENE IN DICHLOROACETATE BUFFER SOLUTIONS

Moles per liter					
Acid	Na salt	NaCl	$10^3 k_{obs.}$	$[H_3O^+]^a$	$10^2 k_{H_3O^+}$
0.5276	0.4623	....	2.533	0.0625	4.05
.3766	.3592	0.0862	2.349	.0547	4.30
.2506	.2395	.2114	2.187	.0491	4.45
.1285	.1126	.3732	1.681	.0405	4.15

[a] Calculated from $K_c = 7.05 \times 10^{-2}$.[20]

second order constant $k_{H_3O^+}$ obtained by dividing the observed velocity constant by the calculated hydrogen ion concentration in column 6. The first solution gave no test for chloride ion after the completion of the run so that there was no detectable decomposition of the acid or its anion. The constancy of $k_{H_3O^+}$ (last column) indicates there is no detectable effect of dichloroacetic acid or dichloroacetate on the velocity constant and one must conclude that the rate is proportional to the hydrogen ion concentration for these experiments.

A further test was carried out in monochloroacetic acid–monochloroacetate buffers at the same ionic strength and the results are reported in Table VIII. Here the hydrogen ion concentration remains constant as there is very little change in acid–base ratio on dilution. Unfortunately the chloroacetate ion loses chloride[21] and the contraction in volume is offset by an expansion due to this unavoidable side reaction. However, the half-times of the reaction in the two buffer solutions were approximately the same, indicating no difference in rate in spite of the fourfold difference in concentration of the buffer constituents, and scheme 2 does not appear to apply to this reaction.

TABLE VIII

HYDRATION OF ISOBUTENE IN MONOCHLOROACETATE BUFFER SOLUTIONS

Moles per liter				
Acid	Na salt	NaCl	$[H_3O^+]^a$	$(t^1/_2)_{obs.}$
0.5021	0.4979	....	0.00241	≈6 days
.1255	.1244	0.3750	.00250	≈6 days

[a] Calculated from $K_c = 2.51 \times 10^{-3}$.[22]

Discussion

If the reaction is an example of specific hydrogen ion catalysis with unusually large electrolyte effects it should be possible to calculate the dissociation constant of trichloroacetic and dichloroacetic acids and compare the results with values obtained by other methods. To make such a calculation a value for the electrolyte effect of the anion must be assumed. Since the observed velocity constants are in some cases lower for nitric acid the assumption that the primary kinetic electrolyte effect of trichloroacetate is equal to that of nitrate would lead to absurd answers. Hence, the assumption is made that the kinetic electrolyte effect of trichloroacetate is equal to that for perchlorate. If the electrolyte effect of the chloride ion were taken instead of perchlorate the calculated dissociation constant would be somewhat higher. The hydrogen ion concentration is determined by dividing the observed velocity constant for trichloroacetic acid by the second-order constant for the perchloric acid solution at the corresponding ionic strength, and the classical dissociation constant

$$K_c = [H_3O^+]^2/[CCl_3COOH] \qquad (15)$$

is computed and given in Table IX. Since these dissociation constants (column 5) are at different ionic strengths the activity coefficients are needed to obtain the thermodynamic dissociation constant, but as these are not known a fair approximation is to take those of acetic acid from the data of Harned and Hickey.[23] In other words, the K_c/K_a ratio for acetic acid is divided into the values of K_c in column 5 and the thermodynamic dissociation constant, K_a, obtained (column 6). The average value of K, 0.98, is in fair agreement with the value 1.2 reported by Ostwald[24] which was obtained from a value of the dissociation constant of dichloroacetic acid of 0.051 obtained from conductivity data and a determination of the ratio of the

TABLE IX

THE DISSOCIATION CONSTANT FOR TRICHLOROACETIC ACID AT 25°

Molarity CCl_3-COOH	$k_{obs.} \times 10^3$	$k_{H_3O^+} \times 10^2$	$[H_3O^+]$	Kc	Ka
0.1637	3.914	2.598	0.151	1.79	1.1
.2523	6.447	2.825	.228	2.15	1.2
.3432	9.118	3.048	.299	2.02	1.1
.4275	11.28	3.229	.349	1.55	0.8
.4881	13.22	3.369	.392	1.60	.9
.5870	16.12	3.577	.451	1.49	.8

---

(21) H. M. Dawson and E. R. Pycock, *J. Chem. Soc.*, 153 (1936).

(22) Saxton and Lange, THIS JOURNAL, **55**, 3638 (1933).

(23) H. S. Harned and F. C. Hickey, *ibid.*, **59**, 1284 (1937).

(24) W. Ostwald, *Z. physik. Chem.*, **3**, 369 (1889).

dissociation constant of tri- and di-chloroacetic acids by a comparison of the rates of inversion of sucrose for the two acids. A calculation neglecting the effect of ionic atmosphere on the mobilities of the ions using the conductance data of Ostwald[24] gives a value of the dissociation constant which is almost a power of ten lower after correction for activity coefficients. Hall[25] reports a value of 2×10^{-1} and Baughan[26] rightly claims there is no reliable value of the dissociation constant of trichloroacetic acid in water. The conductance data are not accurate enough to attempt a calculation using the procedure of Onsager.[27] A calculation of the dissociation constant from the data of Hantzsch and Weissberger[19] making the same assumptions as used in handling the kinetic data for the hydration of isobutene yields an average value of K_a, 0.478, which is not in agreement with the other kinetic data. A similar calculation using the data reported by Taylor[28] for the hydrolysis of ethyl acetate in trichloroacetic acid solutions with and without the addition of potassium trichloroacetate gives an average value 0.98 in agreement with that calculated from the kinetic data of the hydration of isobutene.

In Table X are given the calculated values of the dissociation constant for dichloroacetic acid based on the kinetic data of Table VII and calculated on the same assumptions used in obtaining the dissociation constant of trichloroacetic acid. The average value of $K_a = 0.043$ is higher than the value 0.0332 reported by Harned and Hawkins[20] from kinetic measurements on the rate of hydrolysis of ethyl acetate, but lower than the value 0.0514 reported by Ostwald[24] from conductance data. A recalculation of part of the conductance data taking into account the change in mobility and activity coefficients with ion concentration yields a value 0.046 for the thermodynamic dissociation constant at 25°, but too much reliance cannot be placed on this value as Ostwald himself pointed out that the experimental data in dilute solutions are not too reliable.

TABLE X

DISSOCIATION CONSTANT FOR DICHLOROACETIC ACID AT 25°

Moles per liter Acid	Na salt	NaCl	$[H_3O^+]$	K_c	K_a
0.1285	0.1126	0.3732	0.0429	0.078	0.0415
.2506	.2395	.2114	.0571	.088	.0468
.3766	.3592	.0862	.0613	.082	.0436
.5276	.4623		.0648	.074	.0394

With our present incomplete knowledge of the dissociation constant of trichloroacetic acid at infinite dilution and at any electrolyte concentration, no reliable calculation of the possibility of acid molecule catalysis can be made. The results with dichloroacetate and monochloroacetate buffer solutions do not indicate any detectable catalytic effect of the molecules of these acids. These experiments also indicate that the mechanism proposed in scheme 2 where the anion might have a catalytic effect is not applicable and one is forced to consider that the hydration of isobutene is another reaction catalyzed solely by hydrogen ion and exhibiting an unusually large electrolyte effect.

Summary

1. The rate of hydration of isobutene in aqueous solutions of perchloric, *p*-toluenesulfonic, hydrochloric and trichloroacetic acids has been investigated by the dilatometric method.

2. The electrolyte effects of the strong acids on the rate of the reaction are larger than predicted by the Brönsted theory of primary salt effects.

3. In trichloroacetic acid solutions the observed velocity constants appear to be larger than would be expected on the basis that the reaction is catalyzed solely by hydrogen ion. However, the results obtained in dichloroacetate and monochloroacetate buffer solutions do not indicate any basic catalysis of the cation of isobutene or catalysis by the molecular acid.

4. The dissociation constants of trichloro- and dichloroacetic acids have been calculated from the kinetic measurements.

PHILADELPHIA, PA. RECEIVED JULY 30, 1947

---

(25) N. F. Hall, *Chem. Rev.*, **8**, 191 (1931).

(26) E. C. Baughan, *Nature*, **146**, 461 (1940).

(27) L. Onsager, *Z. physik. Chem.*, **28**, 294 (1927).

(28) H. S. Taylor, *Meddel fran K. Vet-Akads Nobelinstitute*, **2**, no. 37 (1913).