constants determined. These derivatives were obtained from the alcoholysis of trimethyl citrate in the presence of the corresponding alcohol and a catalyst (*p*-toluenesulfonic acid). Some new constants are given for trimethyl citrate.

LAFAYETTE, IND. RECEIVED OCTOBER 23, 1933

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 384]

The Hydration of Unsaturated Compounds. I. The Hydration Rate of Isobutene in Dilute Nitric Acid

BY HOWARD J. LUCAS AND W. FERDINAND EBERZ

Introduction

The hydration of isobutene has been observed by others. Butlerow[1] found that dilute nitric acid (10%?) or very dilute sulfuric acid brings about the change at the ordinary temperature and Miklaschewsky[2] found that a 5–10% solution of formic, acetic or oxalic acid brings about the hydration, not only of isobutene but also of some pentenes and hexenes. Michael and Brunel[3] obtained tertiary butyl alcohol as well as the iodide in the reaction between isobutene and aqueous hydriodic acid.

Experimental

In this investigation the rate of disappearance of isobutene has been measured at 25° in aqueous solutions containing variable amounts of nitric acid and of potassium nitrate.

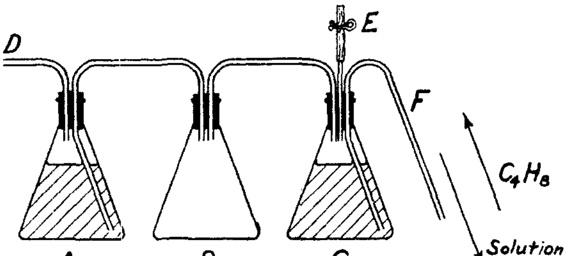

Fig. 1.—Apparatus for preparing aqueous butene solutions.

Materials.—The isobutene was prepared by refluxing tertiary butyl alcohol (Eastman's Pract.) with crystallized oxalic acid[4] and the evolved butene was passed through three spiral wash bottles each containing water in order to remove the alcohol, next through a tower containing soda lime and calcium chloride and then into a tube where it was condensed and sealed off until wanted. When needed the tube was opened and the evolved gas was passed directly into the water to be saturated.

Apparatus and Solutions.—The solution of butene in water of known acidity was prepared by passing butene through the flasks (500 ml.) shown in Fig. 1. The flask C contained a known volume of water at 25° and this was saturated, or nearly saturated, by passing in butene for one-half hour, shaking occasionally. The unabsorbed butene passed first into the empty flask B and then bubbled through the water in the flask A and finally through apparatus J (Fig. 2), filling it with butene. The butene solution was brought to the desired acidity by pipetting through E a known amount of standardized nitric acid. In those experiments in which the solution was brought to the desired ionic strength, a known amount of potassium nitrate was previously placed in the flask. After a thorough mixing the solution was forced, by blowing into the tube D, through F into the apparatus shown in Fig. 2. As the liquid was removed from C the butene in B took its place, so that there was always a butene atmosphere above the solution.

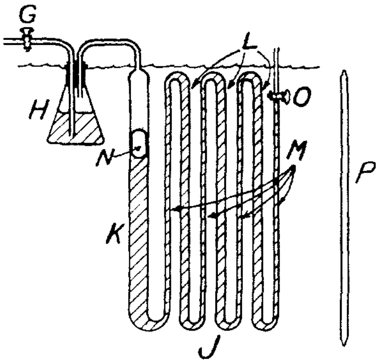

Fig. 2.—Apparatus in which the hydration of butene was carried out.

The liquid entered the apparatus J (capacity 240 ml., Fig. 2) at O, flowed down the four small vertical tubes M (30 cm. × 5 mm. bore) and up the three large vertical tubes L (30 cm. × 10 mm. bore) and finally filled the large vertical tube K (30 cm. × 20 mm. bore) in which the float N fitted snugly. About 150 ml. of solution was forced into the flask H (250-ml.) in order to wash out any liquid which had lost butene to the air. By this means H and J were filled with the solution to be examined. The apparatus was designed to allow withdrawals of samples of the solution without appreciable changes in composition. The float minimized the diffusion of butene into the air

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[1] Butlerow, *Ann.*, **180**, 245 (1876).

[2] Miklaschewsky, *Ber.*, **24**, ref. 26a (1891).

[3] Michael and Brunel, *Am. Chem. J.*, **48**, 267 (1912).

[4] Hurd and Spence, THIS JOURNAL, **51**, 2561 (1929).

space above it and the long, narrow tubes minimized diffusion of butene into the less concentrated solution under the float. H and J were kept at 25 ± 0.05° for most of the measurements and at 35 ± 0.05° for some others.

Sampling.—This was accomplished by means of the pipet P (Fig. 2) which was constricted at both ends and contained 9.35 ml. of water at 25°. This was connected by a short length of rubber tubing to the stopcock O which was kept closed while air was blown in at G. The pressure in J, conserved by closing G, served to force liquid into P as soon as O was opened. A quantity of liquid was allowed to overflow in order to discard any of the solution which might have lost butene through contact with air in the pipet P. The top of the pipet was closed with the finger, the pipet was connected with the evacuated iodine flask used in the analysis and the contents of P were washed into the flask. The error in measuring with this pipet was negligible in comparison with the titration errors.

Analysis.—The butene was determined essentially according to the method of Davis, Crandall and Higbee[5] as follows: 10.00 ml. of 0.05 *N* bromide–bromate solution was pipetted into the flask, which was then evacuated by means of a water aspirator. Following the addition of 5 ml. of 6 *N* sulfuric acid, the sample was then introduced from the pipet, which was rinsed thoroughly. Still under partial vacuum, the flask was shaken frequently for ten minutes in the dark, then a freshly made solution of 1 g. of potassium iodide in a small amount of water was run in and titration was made with 0.02 *N* thiosulfate. A blank was run at the same time and the amount of butene was calculated from the difference in the two values. Since practically identical results were obtained when the bromine and butene stood for different lengths of time, even up to one hour, the amount of substitution taking place was negligible. The bromine liberated by the sulfuric acid was never less than approximately five times the theoretical amount.

The nitric acid was determined by titration of a sample with 0.1 *N* sodium hydroxide, after the hydration rate was over. The values obtained were close to the normalities desired.

Reaction Product.—The reaction taking place is given in equation 1.

$$(CH_3)_2C{=}CH_2 + H_2O = (CH_3)_3COH \qquad (1)$$

The product of the reaction was shown to be tertiary butyl alcohol as follows. Butene was passed for one hour into approximately 1 liter of 1.0 *N* nitric acid and the solution was allowed to stand for a week. The acid was neutralized with sodium hydroxide and the neutral solution was distilled through a 25-cm. column of glass rings. The first 4 ml. distilling over was saturated with anhydrous potassium carbonate, and this gave a non-aqueous phase of 0.3 ml., the micro-boiling point of which was 79.5°. On the addition of 1.5 ml. of hydrochloric acid–zinc chloride reagent[6] a second phase of approximately 0.3 ml. separated. The micro-boiling point of this was 50.0°. These constants check the respective boiling points of tertiary butanol and its chloride.

Data and Discussion

The integrated first order reaction rate expression for the hydration of isobutene in dilute aqueous solution according to equation (1) is shown in equation (2)

$$2.3026 \log_{10} C_0/C_t = kt \qquad (2)$$

where C_0 is initial molality of butene, C_t is the molality of butene at the time t (expressed in hours) and k is the specific reaction rate constant.

The experimental data of a typical run and the specific first order rate constants calculated as above are shown in Table I.

TABLE I

HYDRATION OF ISOBUTENE AT 25° IN 0.498 *N* NITRIC ACID

Bromate used by 9.35 ml. as 0.02 *N* $Na_2S_2O_3$

Reaction time, hrs.	$Na_2S_2O_3$, ml.	Butene molality	C_0/C_t	k hrs.$^{-1}$
0.0	3.35	0.00358	1.000	
.266	2.70	.00288	1.241	0.807
.775	1.75	.00187	1.914	.838
1.233	1.22	.00130	2.75	.819
1.750	0.75	.00080	4.47	.855
2.333	.49	.00052	6.84	.824
			Mean	.828

The values obtained for k show that the reaction is first order with respect to the butene concentration.

An easier and more accurate evaluation of k is the slope of the curve obtained by plotting log C_0/C_t against t (Figs. 3 and 4). Since in all cases except one these straight line curves passed through the origin, the constants obtained in this way proved to be as accurate as those obtained by plotting log C against t. The advantage of plotting log C_0/C_t against t lies in the fact that the different families of curves can be more conveniently compared.

Figure 3 contains the plots of log C_0/C_t against t for the hydration reaction at 25°. The concentrations of nitric acid varied from 1.0 *N* to 0.05 *N* and the ionic strengths from 2 *N* to 0.05 *N*. It is to be observed that in all cases straight lines are obtained and this shows that the rate in all cases is first order with respect to the butene concentration.

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(5) Davis, Crandall and Higbee, *Ind. Eng. Chem., Anal. Ed.*, **3**, 108 (1931).

(6) Lucas, THIS JOURNAL, **52**, 802 (1930).

Table II

Hydration Constants of Isobutene at 25 ± 0.05°

HNO_3 N	KNO_3 N	μ N	k hrs.$^{-1}$	HNO_3 N	KNO_3 N	μ N	k hrs.$^{-1}$	HNO_3 N	KNO_3 N	μ N	k hrs.$^{-1}$
0.0500	0	0.0500	0.0667	0.0500	0.950	1.000	0.118				
.1005	0	.1005	.140	.100	.900	1.000	.210	0.0992	1.900	1.992	0.327
.2475	0	.2475	.368	.250	.750	1.000	.520	.249	1.750	1.999	.827
.498	0	.498	.828	.498	.500	0.998	1.070	.497	1.500	1.997	1.64
				.498	1.00	1.498	1.367				
1.000	0	1.000	2.143					1.000	1.000	2.000	3.04[a]
								0.994	1.000	1.994	2.86[a]

[a] Rate too great for accurate measurements.

The constants calculated from the curves in Fig. 3 are listed in Table II. It is worthy of note that at any given concentration of nitric acid an increase in the ionic strength of the solution causes an increase in the rate.

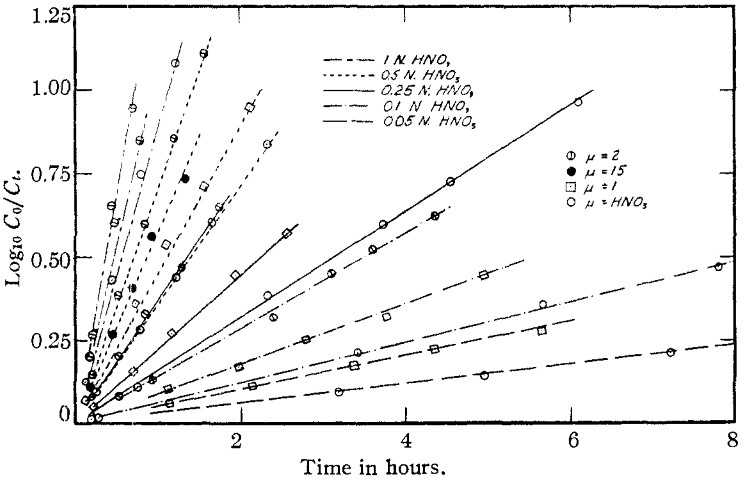

Fig. 3.—Plot of $\log_{10} C_0/C_t$ against t for the hydration of isobutene at 25°.

In Fig. 4 are plotted the data obtained at 35°. In Table III are presented the constants obtained from these curves, together with the temperature coefficients for three different concentrations of nitric acid, and the heats of activation. The values of the temperature coefficient are identical within the limits of experimental error.

In Fig. 5 the rate constants at 25° are plotted against the concentration of nitric acid. Four curves are obtained, one at the variable ionic strengths corresponding to the nitric acid concentrations and three at ionic strengths of 1, 1.5 and 2 N. The straight-line character of the curves at 1 and 2 N indicates that the reaction at constant ionic strength is directly proportional to the nitric acid concentration and therefore is first order with respect to it. It is evident, also, that nitric acid and potassium nitrate are equivalent in their salt effect upon the hydration rate of isobutene.

Since the hydration rate is proportional to the concentration of nitric acid, equation (1) should be replaced by equation (3)

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

On the basis of the Brönsted theory, the rate is represented by equation (4)

$$\text{Rate} = k_0(C_4H_8)(H_3O^+)\gamma_B\gamma_{Hy^+}/\gamma_{x^+} \quad (4)$$

in which γ_B, γ_{Hy^+} and γ_{x^+} are the respective activity coefficients of butene, B, hydronium ion, Hy^+, and the butene-hydronium ion complex, x^+. The expression is simplified by the cancellation of the activity coefficients of the two positively charged ions, Hy^+ and x^+ as shown by equation (5)

$$r = k_0(C_4H_8)(H_3O^+)\ \gamma_B \quad (5)$$

According to this the rate is proportional to the concentrations of butene and hydronium ion and also to the activity coefficient of butene.

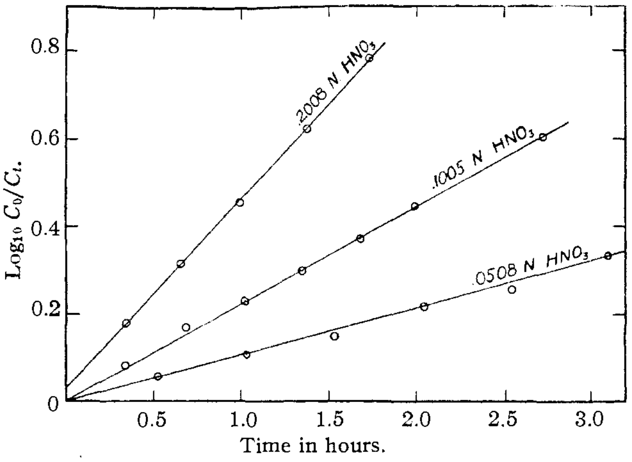

Fig. 4.—Plot of $\log_{10} C_0/C_t$ against t for the hydration of isobutene at 35°.

TABLE III

HYDRATION CONSTANTS OF ISOBUTENE AT 35 ± 0.05°

HNO_3 N	k_{35} hours^{-1}	$k_{35°}/k_{25°}$	Heat of activation, kg. cal.
0.0508	0.244	3.60	23.37
.1005	.511	3.64	23.57
.2008	1.026	3.57	23.22
			Mean 23.39

The rate constants, k, at 25° were adjusted to an acidity of 1 N when divided by the normality of nitric acid. Plotting these adjusted constants, $k/(H_3O^+) = k_0\gamma_B = k_\mu$, against the ionic strength gave the curve shown in Fig. 6. From this it is evident that the specific reaction rate progressively increases with increase in ionic strength. The curve was drawn so as to pass through points of greatest accuracy since it was realized that the constants obtained at fairly high acidities involved considerable error.

An ionic strength coefficient of the reaction rate may be obtained by dividing the rate at zero ionic strength into the rate at any given ionic strength. This coefficient should be identical with the activity coefficient of isobutene at the same ionic strength. The activity of isobutene has been determined in another manner, *i. e.*, by means of its distribution between carbon tetrachloride and aqueous solutions containing potassium nitrate, as shown in Table IV.[7] Here K, the distribution constant, is the ratio of the isobutene concentration in the carbon tetrachloride phase to its concentration in the water phase; γ'/γ is the ratio of the butene activity in salt solution to its activity in water, or the activity coefficient; k'_μ/k_μ is the ratio of the hydration rate in salt solution to the hydration rate in water, or the ionic strength coefficient of the hydration rate. Although these two coefficients increase with the ionic strength, the coefficient of the rate increases the more rapidly, and also apparently at an accelerating rate.

TABLE IV

ACTIVITY COEFFICIENT OF ISOBUTENE AND THE IONIC STRENGTH COEFFICIENT OF THE HYDRATION RATE

Normality of KNO_3	K	γ'/γ	k'_μ/k_μ
0.00	606	1.00	1.00
1.00	830	1.37	1.55
2.00	1080	1.78	2.44

The helpful criticism of Professor Don M. Yost, especially in connection with the discussion above, is gratefully acknowledged.

Miscellaneous Experiments

Effect of Metallic Salts upon the Hydration Rate.—Since it has been claimed that many metal salts catalyze the hydration of alkenes under different conditions[8] a series of experiments were carried out in which metallic salts[9] were added to dilute nitric acid solutions of isobutene at ionic strength of 0.25 N. The data are given in Table V. For purposes of comparison, the rate constants have been adjusted to an acidity of 0.2 N nitric acid. It is evident that none of the various salts have any substantial effect upon the rate. In the presence of mercuric nitrate the increase in the solubility of isobutene indicated the formation of the complex $Hg(NO_3)_2 \cdot C_4H_8$. The free butene,

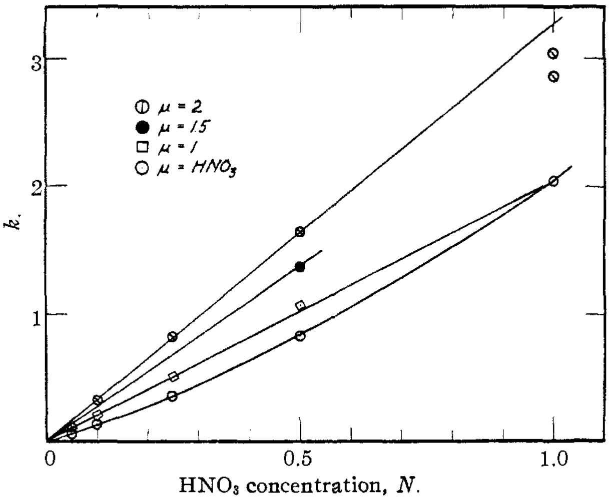

Fig. 5.—Plot of hydration constant, k, at 25° against the nitric acid concentration.

TABLE V

EFFECT OF ADDED SALTS ON THE HYDRATION CONSTANT OF ISOBUTENE AT 25° ± 0.05 AT IONIC STRENGTH OF 0.25 N

HNO_3 N	Salt added	Concn. of added salt M	k hrs.$^{-1}$	k adjusted to 0.2 N HNO_3
0.204	$CuSO_4$	0.0125	0.299	0.293
.199	$NiSO_4$	.0125	.304	.305
.199	$Pb(NO_3)_2$	.01667	.290	.291
.200	$MnCl_2$	.01667	.306	.306
.202	$Cd(NO_3)_2$	.01667	.294	.291
.200	$Hg(NO_3)_2$	.01667	.318	.318
.198	$Zn(NO_3)_2$	.01667	.292	.295
.203	$Th(NO_3)_4$	.0050	.313	.308
.248	H_3BO_3	.100	.384	.310
.248	....	.....	.368	.297
0	NaOH	.200	.000	....

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[7] These results will appear in detail in a subsequent publication.

[8] Smith and Bridges, British Patent 308,468 (1928); Swan, Snow and Keyes, *Ind. Eng. Chem.*, **22**, 1048 (1930); I. G. Farb., French Patent 662,968 (1928); Carpmeal, British Patent 324,897 (1928); Marek and Flege, *Ind. Eng. Chem.*, **24**, 1428 (1932).

[9] An investigation of the effect of silver ion upon the hydration rate is now being made.

in excess of the complex, hydrated at a rate slightly greater than that for butene in pure nitric acid. After about eighteen hours the total butene concentration reached a constant value which was equal to that of the mercuric nitrate. Except in the case of the mercuric nitrate, the metallic salt concentration was a few times that of the initial butene, which was close to 0.005 molal, the approximate saturation value of butene in water.

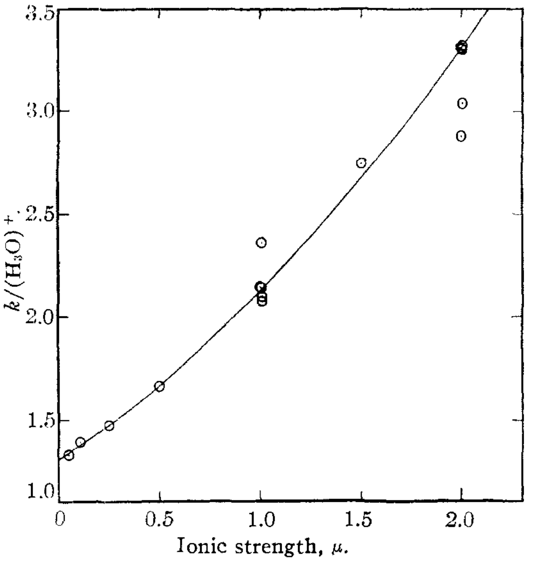

Fig. 6.—Plot of adjusted hydration constant $k/(H_3O^+)$ against the ionic strength.

Hydration of Mixtures of Normal Butenes.—The mixture of *cis*- and *trans*-2-butene obtained by the decomposition of 1-butanol with sulfuric acid and the mixture of approximately 70% 1-butene and 30% 2-butene obtained by the decomposition of 1-butanol over alumina[10] were substituted for isobutene in the hydration apparatus. There was no observable decrease in butene concentration at 1 N nitric acid in either case, even after several days of standing.

Summary

The hydration of isobutene is catalyzed by nitric acid and at constant ionic strength the rate is first order with respect to both the butene concentration and the nitric acid concentration. The rate at a given acid concentration is increased on the addition of potassium nitrate. This increase in rate is greater than the increase in the activity of isobutene when determined by means of distribution experiments in carbon tetrachloride.

In the presence of certain metallic ions, some of which have been stated to be catalysts for the hydration of alkenes in more concentrated acids, the specific reaction rate for the hydration of isobutene in 0.20 normal nitric acid is substantially unchanged.

Mixtures of the normal butenes are not hydrated at 25° in 1.0 N nitric acid.

[10] Young and Lucas, THIS JOURNAL, **32**, 1964 (1930).

PASADENA, CAL. RECEIVED OCTOBER 24, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Super-Aromatic Properties of Furan. III. Nitration

BY HENRY GILMAN AND R. V. YOUNG

Introduction

Nitration is one of the few substitution reactions essentially characteristic of aromatic compounds. It is not, however, a reaction peculiar to aromatic compounds inasmuch as it is observed also with cycloparaffins[1a] and with saturated[1b] and unsaturated hydrocarbons.[1c] Of more pertinent interest is the fact that compounds like alkylbenzenes[1d] and styrene[1e] can undergo lateral nitration. Rigorous comparisons of these several types and aromatic nuclei may be inadmissible because of differences in experimental conditions. For example, dilute nitric acid and elevated temperatures are generally used in aliphatic nitrations.

If correlations be restricted to benzene as a typical aromatic nucleus, there is no doubt of the more ready nitration of furan. There are several ways for determining relative reaction velocities of nitration. One of these, now reported, involves the nitration of a symmetrical compound containing both the furyl and the phenyl radicals. 2-Furyl phenyl ketone was selected for this purpose, and it has been found that the nitro group replaces a hydrogen of the furan nucleus.

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(1) (a) Markownikoff, *Ann.*, **302**, 15 (1898); (b) Worstall, *Am. Chem. J.*, **20**, 202 (1898); Markownikoff, *Ber.*, **33**, 1907 (1900); (c) Wieland and Sakellarios, *ibid.*, **53**, 201 (1920), as well as other citations contained in this paper; (d) Konowalow, *ibid.*, **28**, 1858 (1895); (e) Wieland and Rahn, *ibid.*, **54**, 1770 (1921).