The Hydration of Isobutene.

I The Hydration Rate of Isobutene in Dilute Nitric Acid.

II The Free Energy of Hydration of Isobutene.

III The Hydration of Isobutene in the Presence of Silver Nitrate.

Thesis by

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Contents of this Thesis

The three articles contained in this thesis describe the investigation of the hydration of isobutene.

In the first paper the rates of hydration of isobutene were measured in dilute nitric acid solutions both with and without other ions present to observe possible catalytic effects.

In the second paper the equilibrium of the hydration reaction in aqueous solution was determined and, by means of additional data, the standard free energy change and change in heat content of the reaction were calculated.

In the third part the hydration in the presence of silver ion was investigated and the role of this metal in the reaction was elucidated.

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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.

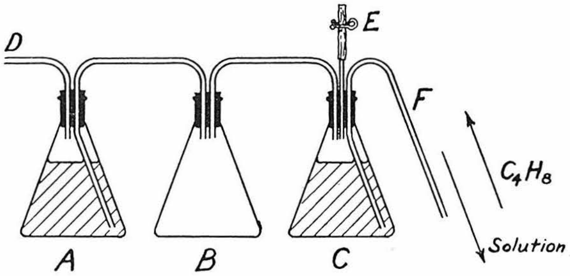

Fig. 1.—Apparatus for preparing aqueous butene solutions.

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.

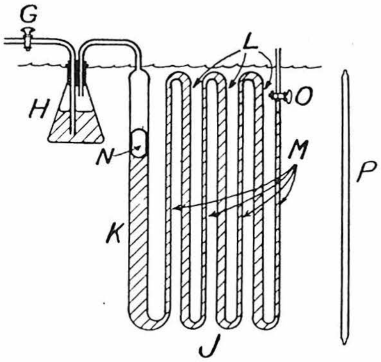

Fig. 2.—Apparatus in which the hydration of butene was carried out.

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

Reaction time, hrs.	Bromate used by 9.35 ml. as 0.02 *N* $Na_2S_2O_3$ $Na_2S_2O_3$, 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.

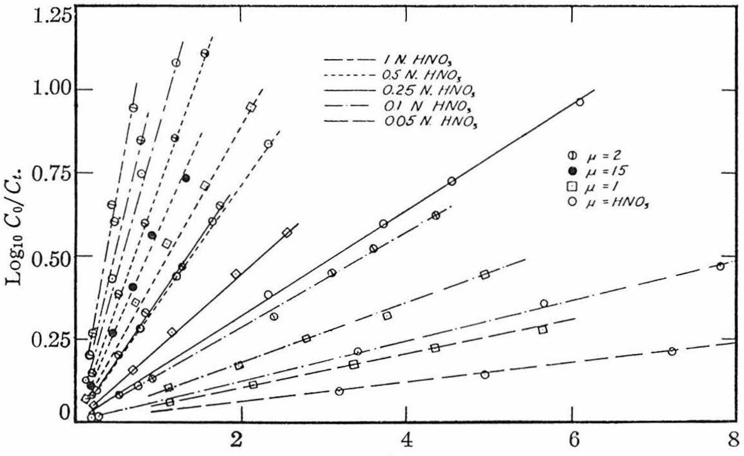

Fig. 3.—Plot of $\log_{10} C_0/C_t$ against t for the hydration of isobutene at 25°.

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)

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

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

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

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)

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

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

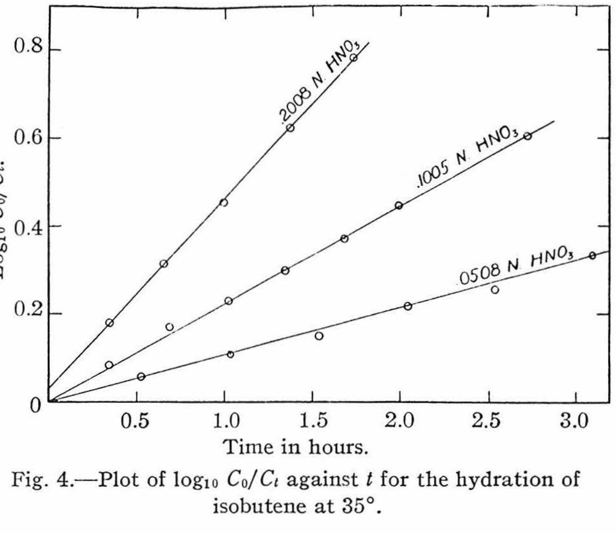

Fig. 4.—Plot of $\log_{10} C_0/C_t$ against t for the hydration of isobutene at 35°.

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,

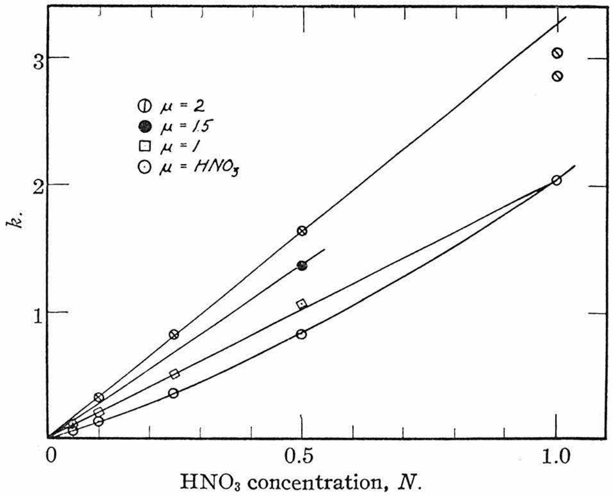

Fig. 5.—Plot of hydration constant, k, at 25° against the nitric acid concentration.

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.

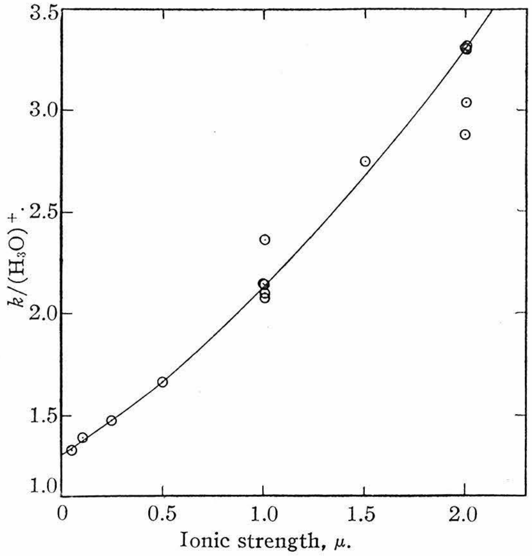

Fig. 6.—Plot of adjusted hydration constant $k/(H_3O^+)$ against the ionic strength.

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.

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

PASADENA, CAL. RECEIVED OCTOBER 24, 1933

THE HYDRATION OF ISOBUTENE

Part III

The Hydration of Isobutene in the Presence of Silver Nitrate.

Introduction.

Various metallic ions have at times been described as catalytic in the hydration of olefins. Swann, Snow, and Keyes studied the hydration of ethylene and propylene in aqueous solutions of hydrohalogen acids containing $AlCl_3$, $BiCl_2$, Cu_2Cl_2, and $HgCl_2$. Also in nitric acid solution with silver nitrate present. These experiments were carried out, using what was essentially preparation technique. They concluded as a result of their experiments that the acids and salts used were actually catalytic. However, an inspection of their data would lead one to the conclusion that the salts were better described as anticatalytic, since their presence in many cases actually decreased the yield. Particularly surprising in view of the present work is a comparison of two runs ($P = 800\#/sq.\ in.$, $T = 150^{\circ}C$) in which 10% hydrochloric acid gave a final concentration of .0867% alcohol, whereas 20% nitric acid containing 1% silver nitrate gave only .0043%.

Two I. G. Farbenindustrie[2,3] patents claim the hydration of olefins above ethylene by dilute acids in the presence of salts of silver, copper, or bismuth at high temperatures and pressure.

Smith and Bridges[4] claim the process of hydrating ethylene to ethanol at 200-300°C and high pressures in the presence of aqueous solutions or suspensions of salts having an affinity for ethylene, such as $AgNO_3$, Cu_2Cl_2, or $HgCl_2$.

It has also been reported that certain addition compounds between olefins and zinc chloride yield alcohols upon treatment with water.

In another type of experiment, the absorbtion of olefins in strong acid for the purpose of producing alcohols, complex forming ions have often been recommended as assisting in the process. Brooks[5] found that in the absorbtion of olefins higher than propylene in 70% sulfuric acid the presence of cuprous, mercurous, and silver sulfates exerted a catalytic effect in that the rate of absorbtion was markedly increased.

A British patent[6] claims that the presence of cyanic acids or salts of the cyanic acids of ferrous, or ferric ions, and of cobalt, platinum, and chromium is advantageous when absorbing olefins in solutions of sulfuric, phosphoric, or sulfonic acids.

It is probable that this second type of process differs from the first in that the catalysis is actually exerted upon the reaction to form addition products between the olefin and concentrated acid, rather than upon direct hydration, although both types of reaction may well proceed simultaneously.

While the most commonly specified catalysts are usually capable of forming complex ions there is no definite connection between this power and catalytic activity. For example, mercuric ion is often described as catalytic. In the first paper of this series it was shown that isobutene in aqueous solutions of mercuric nitrate hydrates at the normal rate until the quantity of olefin remaining is just sufficient for the complex formation. This does not hydrate. Moreover, if isobutene be passed into a solution containing a fair concentration of mercuric nitrate a solid addition product is precipitated. On treatment with hydrochloric acid this is separated into its components, without hydration of the isobutene.

In view of this collection of poorly connecting qualitative information a quantitative study of such a catalytic hydration would seem to be of value. Such a study is presented in this paper, using isobutene hydration in the presence of nitric acid, silver nitrate, and potassium nitrate.

Bibliography.

(1) Ind. Eng. Chem. 22, 1048-51 (1930)

(2) British patent 324,897 (1928) C.A. 24,3802.

(3) " " 325,192 (1928)

(4) " " 308,468 (1928)

(5) Chem. Reviews 2, 369-94 (1926)

(6) N.V. de Bataafsche Petroleum Maatschappij
Brit. 323,748 (1928) C.A. 24, 3247.

Plan of Investigation.

The plan of this study of the hydration of isobutene in the presence of silver ion consists in allowing the reaction to proceed in solutions of definite acidity, silver content, and ionic strength, so that by reference to certain other data it is possible to separate the components of the total hydration.

This auxiliary data consists, firstly , of an establishment of the nature of the complex ion formed between isobutene and silver ion, and, secondly of the determination of the numerical value of the mass action constant for this reaction, since it is incomplete. The former was carried out by Mr. H. Welge of this laboratory by determining a series of distribution ratios for isobutene between carbontetrachloride and aqueous silver nitrate solutions. These determinations show that one isobutene molecule and one silver ion unite to form the complex ion, and the data gives no suggestion of the formation of other complexes. The results of these measurements combined with the value of the distribution ratio of isobutene between carbontetrachloride and water containing potassium nitrate at 1n. ionic strength (which is the value of the ionic strength in the distribution ratios with silver present) enable the above mass action constant to be evaluated.

Knowing the value of the mass action constant for this reaction it is possible, when the total isobutene content and total silver concentration are known, to calculate the amounts of free and of complexed isobutene in the solution. If the rate of hydration of free isobutene be known, the rate of hydration of complexed isobutene may be calculated by equating it to the difference between the total hydration and that due to the free isobutene. The rate of hydration of free isobutene under a variety of conditions was determined in the first paper of this series.

A general expression for this hydration reaction has been derived using this plan of analysis, and is given upon the following pages.

In this derivation it is assumed that all solutions are at 1n ionic strength so that activities may be replaced by concentrations. This is not an entirely valid procedure at this high ionic strength, but it is apparently unavoidable, since the instability of the complex ion and its much lower rate of reaction compared to uncomplexed isobutene make it necessary to use large concentrations of silver ion in order to obtain an appreciable amount of this component of the hydration.

Derivation of Rate Expression.

Let; (Bt) = Total isobutene concentration at time t.
(B) = Free " " " " "
(BAg) = Complexed " " " " "
$(\overset{+}{Ag})$ = Free silver ion " " " "
(Agt) = Total " " " any time.

For the reaction: $C_4H_8 + Ag^+ = C_4H_8Ag^+$

Set up: (1)

$$K = \frac{(BAg)}{(B)(\overset{+}{Ag})}$$

Assuming both free and complexed isobutene are hydrated:

$$(2) \quad -\frac{d(Bt)}{dt} = k_1(B) + k_2(BAg)$$

$$(3) \quad (B) = (Bt) - (BAg)$$

From (1)

$$(BAg) = K(B)(\overset{+}{Ag})$$

$$\therefore \quad (4) \quad (B) = (Bt) - K(B)(\overset{+}{Ag})$$

$$\text{or} \quad (B) = \frac{(Bt)}{(1 + K(\overset{+}{Ag}))}$$

From (3) and (4):

$$(5) \quad (BAg) = (Bt) - \frac{(Bt)}{(1 + K(\overset{+}{Ag}))}$$

From (2), (4), and (5):

$$(6) \quad -\frac{d(Bt)}{dt} = k_1 \frac{(Bt)}{(1 + K(\overset{+}{Ag}))} + k_2(Bt)\frac{K(\overset{+}{Ag})}{(1 + K(\overset{+}{Ag}))}$$

Since $(\overset{+}{Ag}) = (Agt) - (BAg)$

Then (approx.) $(\overset{+}{Ag}) = (Agt) - (Bt)$ This is very nearly rigorous since (B) is quite small compared to (Agt)

$$\therefore \quad (7) \; -\frac{d(Bt)}{dt} = \frac{(Bt)\left[k_1 + k_2K\left\{(Agt) - (Bt)\right\}\right]}{1 + K\left\{(Agt) - (Bt)\right\}}$$

or

$$-\frac{d\ \ln(Bt)}{dt} = \frac{k_1 + k_2K\left\{(Agt) - (Bt)\right\}}{1 + K\left\{(Agt) - (Bt)\right\}}$$

Since a substitution of the magnitudes involved shows that the right hand side of this equation varies only slowly with (Bt), it follows that a plot of ln (Bt) against t should be nearly a straight line and have a slope equal to the value of this expression.

Near the end of a run, when (Bt) has become quite small, this equation simplifies to

$$(8) \; -\frac{d\ \ln(Bt)}{dt} = \frac{k_1 + k_2K(Agt)}{1 + K(Agt)} = k$$

and the reaction is accurately first order.

Determination of Nature of Complex Ion

To determine the nature of this complex ion a series of distribution ratios of isobutene between carbon tetrachloride and aqueous solutions of silver nitrate and potassium chloride were determined. The purpose of the potassium nitrate was to maintain the ionic strength constant while allowing the silver content to be varied. These experiments were carried out in separatory funnels. They were performed by Mr. H. Welge of this laboratory.

Results of Distribution Ratio Measurements (Welge).

(Agt)	$(B)_{H_2O}$	$(B)_{CCl_4}$		$\frac{(B)_{H_2O}}{(B)_{CCl_4}\left\{(Agt) - (B)_{H_2O}\right\}}$
1.000	.01906	.1460		.0750
.4948	.00560	.1542		.0734
.7477	.00845	.1492		.0756
.2488	.00294	.1555		.0758
.965	.005176	.06938		.0774
.978	.005176	.06898		.0770
			mean	.0757

From a consideration of the law of mass action it may readily be shown that the function tabulated in the last column should be constant if the complex formed consists of the product of the union of one isobutene molecule and one silver ion. Since this function is constant within the limits of experimental error the correct formula for the complex ion has been chosen.

It may further be shown that if this function be multiplied by the distribution ratio of isobutene between carbontetrachloride and water the product is the value of the mass action constant, K, for the formation of the complex ion. This distribution ratio was determined by the author, the results being given below. The value to be used in this connection is that for 1n ionic strength, since that is the ionic strength maintained in the measurements by **Welge.** The other values are those determined for use in part **I.**

Distribution Ratios of Isobutene CCl_4/H_2O

$(B)_{H_2O}$	$(B)_{CCl_4}$	Ratio.
.002055	1.238	602
.001623	.989	609
.000632	.378	598
.001268	.782	616
.000802	.4845	604
.000702	.428	609
.0005565	.3378	606 mean 606
	CCl_4/KNO_3 1n	
.000812	.667	822
.001287	1.0775	838 mean 830
	CCl_4/KNO_3 2n	
.000611	.666	1090
.000850	.910	1070 mean1080

Therefore $K = 830 \times .0757 = 62.8$

DATA

Run #1

$AgNO_3$ = .2431m
HNO_3 = .2427m
KNO_3 = .25m

time hrs.	(Bt)m.	log (Bt)+2
0.0	.04259	.6293
2.73	.03722	.5708
3.49	.03623	.5591
6.48	.03094	.4906
17.79	.01884	.2751
22.48	.01545	.1890
27.57	.01302	.1147

Run #2

$AgNO_3$ = .3639m
HNO_3 = .2428m
KNO_3 = .375m

time hrs.	(Bt)m	log (Bt)+2
o.o	.06162	.7897
2.10	.05752	.7598
4.33	.05344	.7279
6.32	.05030	.7016
8.33	.04657	.6681
16.00	.03662	.5637
223.21	.02943	.4688

Run #3

$AgNO_3$ = .4900m
HNO_3 = .2427m
KNO_3 = .25

time hrs.	(Bt)m.	log (Bt)+2
0.0	.08503	.9295
2.92	.08092	.9080
4.75	.07788	.8914
19.62	.05289	.7234
24.03	.04795	.6808
27.58	.04531	.6562
44.07	.03028	.4801
48.28	.02788	.4454

Run #4

$AgNO_3$ = .6157m
HNO_3 = .2433m
KNO_3 = .125m

time hrs.	(Bt)m	log (Bt)+2
0.0	.1268	1.1032
3.44	.1187	1.0745
20.90	.0827	.9174
24.33	.0783	.8940
29.12	.0716	.8546
45.88	.0510	.7077
51.24	.0476	.6779
70.90	.0320	.5048

Run #5

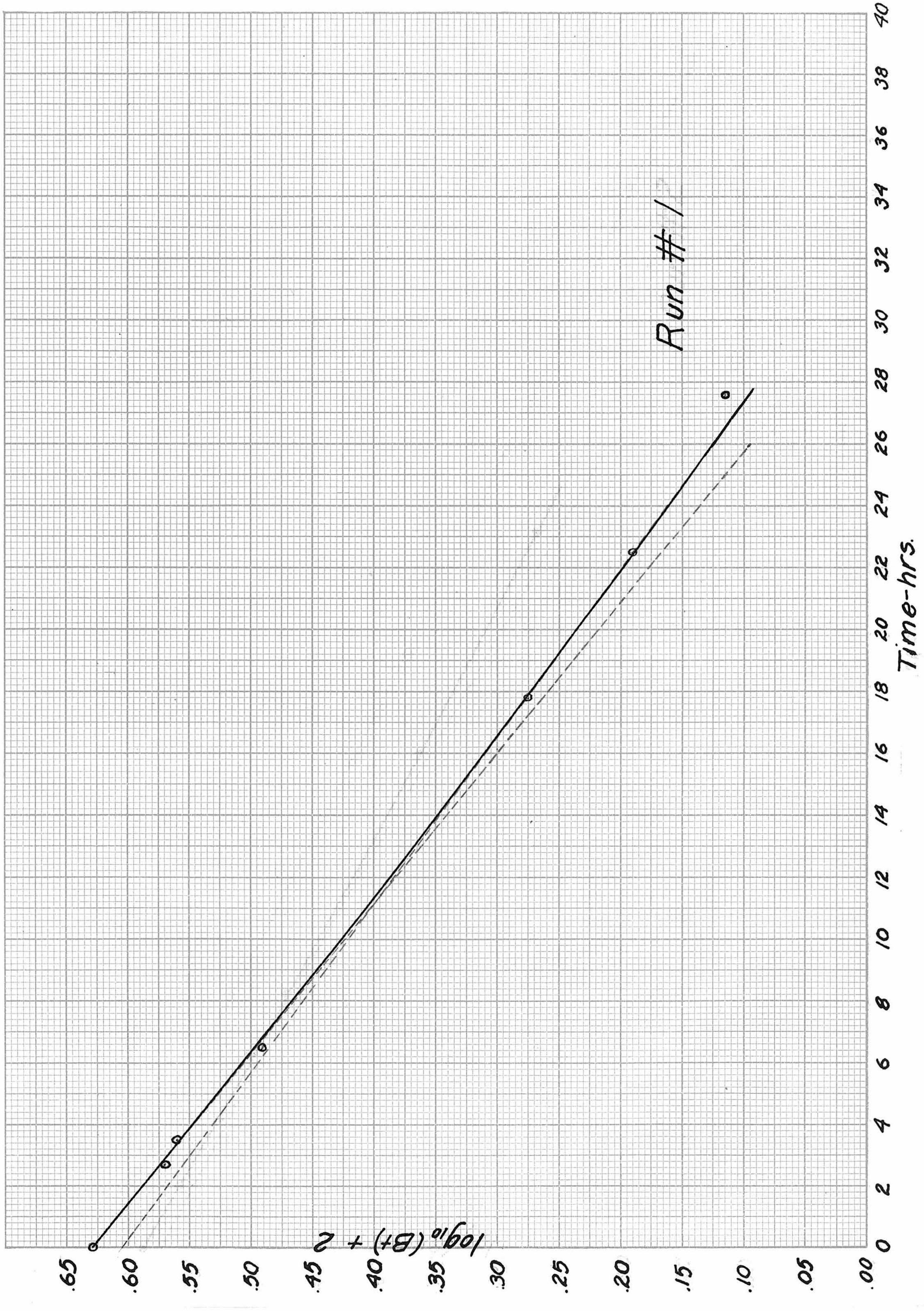
$AgNO_3$ = .7346m
HNO_3 = .2417m
KNO_3 = .000

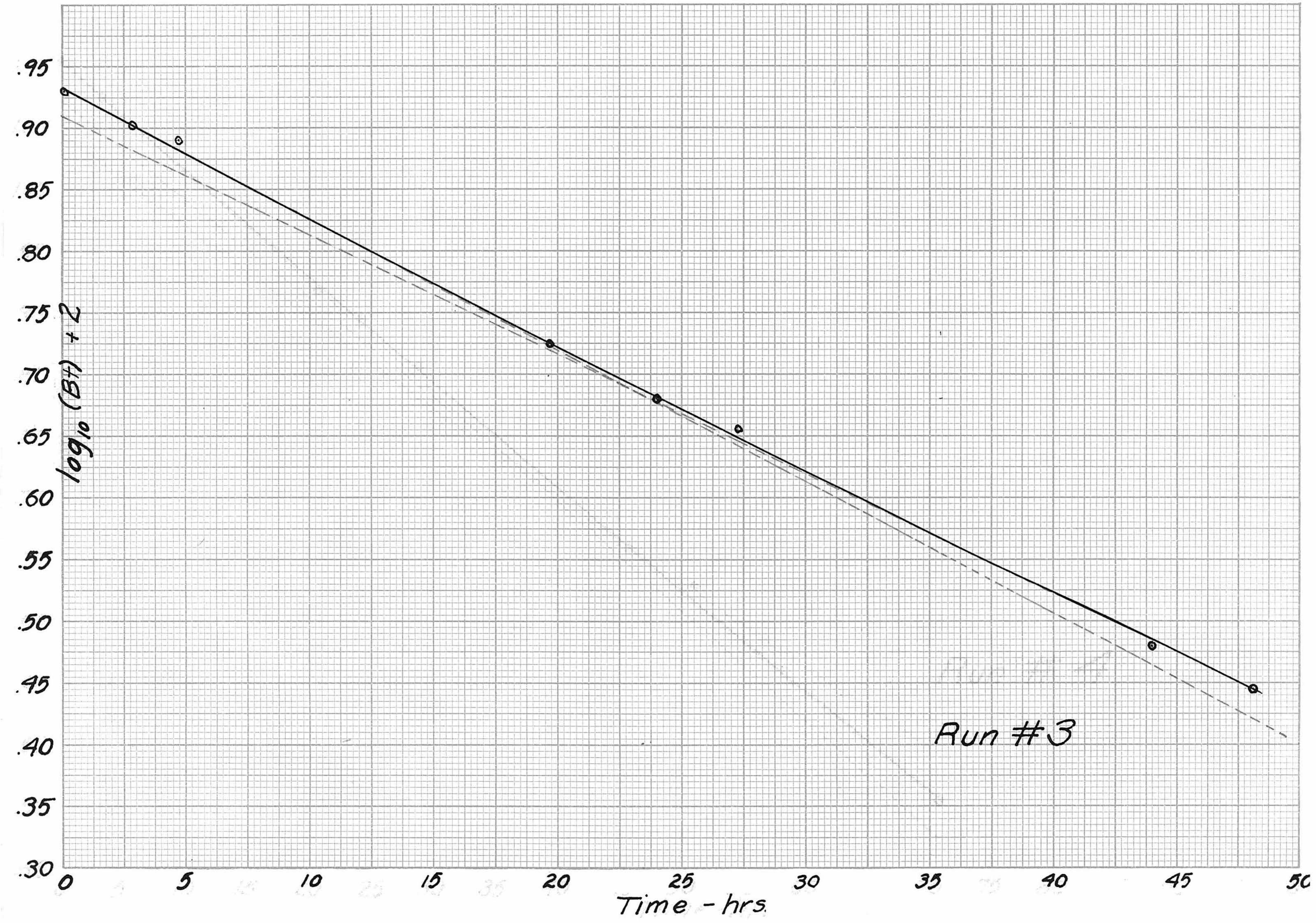
time hrs.	(Bt)m	log (Bt)+ 2
0.0	.1551	1.1905
5.66	.1427	1.1543
23.57	.1009	1.0038
32.83	.0893	.9510
46.58	.0716	.8549
56.88	.0612	.7871
70.1	.0504	.7024

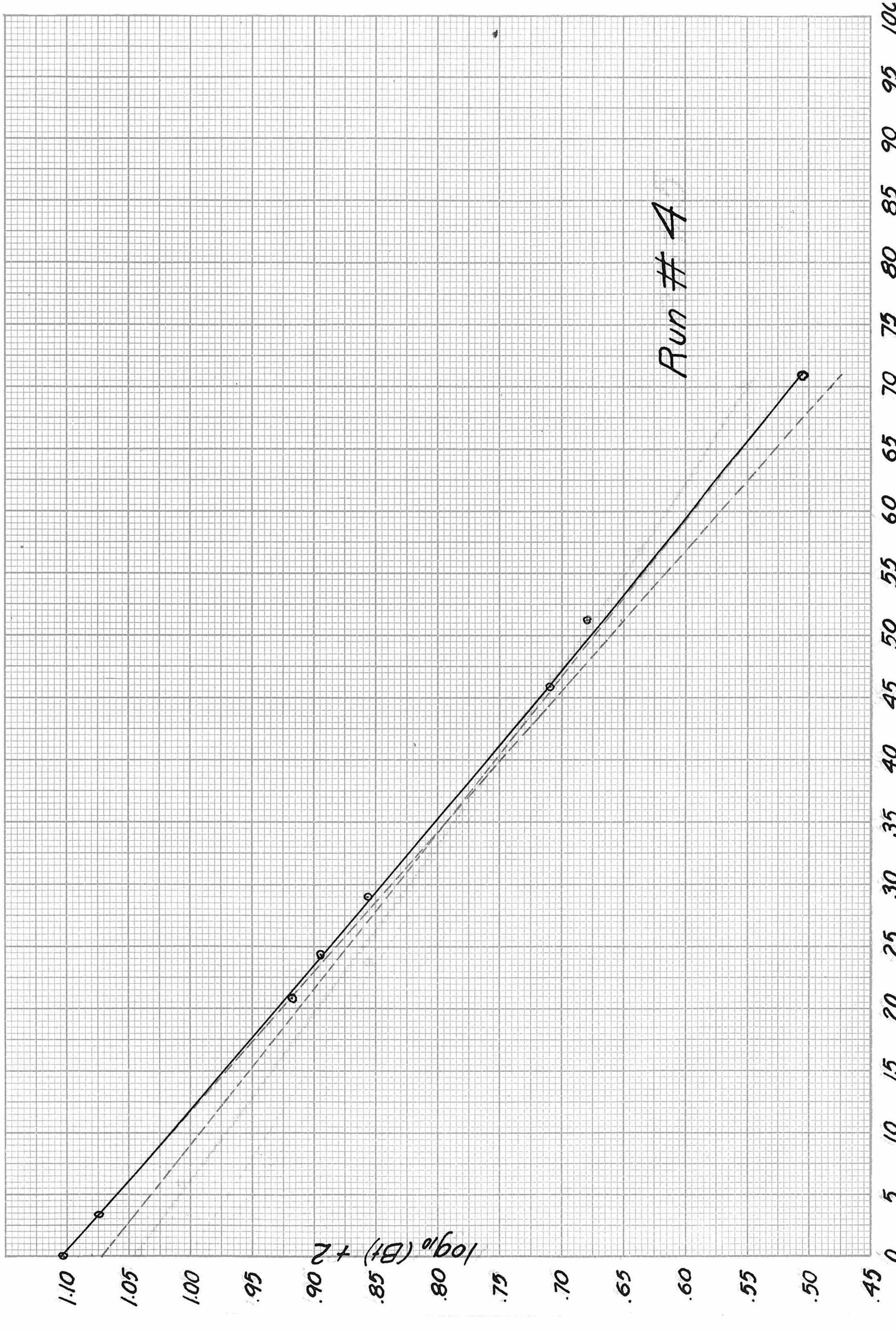
Run #6

$AgNO_3$ = .0125m
HNO_3 = .100m
KNO_3 = .0125m

time hrs.	(Bt)m	log (Bt)+ 3
0.0	.00933	.9698
1.473	.00831	.9197
3.240	.00702	.8461
4.645	.00625	.7961
6.345	.00544	.7356


Run # 1
Time-hrs.
log10 (B+) + 2
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
.65
.60
.55
.50
.45
.40
.35
.30
.25
.20
.15
.10
.05
.00


Run #3
log₁₀ (B+) + 2
.95
.90
.85
.80
.75
.70
.65
.60
.55
.50
.45
.40
.35
.30
0
5
10
15
20
25
30
35
40
45
50
Time - hrs.


Run # 4
Time-hrs.
$\log_{10}(B_t) + 2$
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
1.10
1.05
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.95
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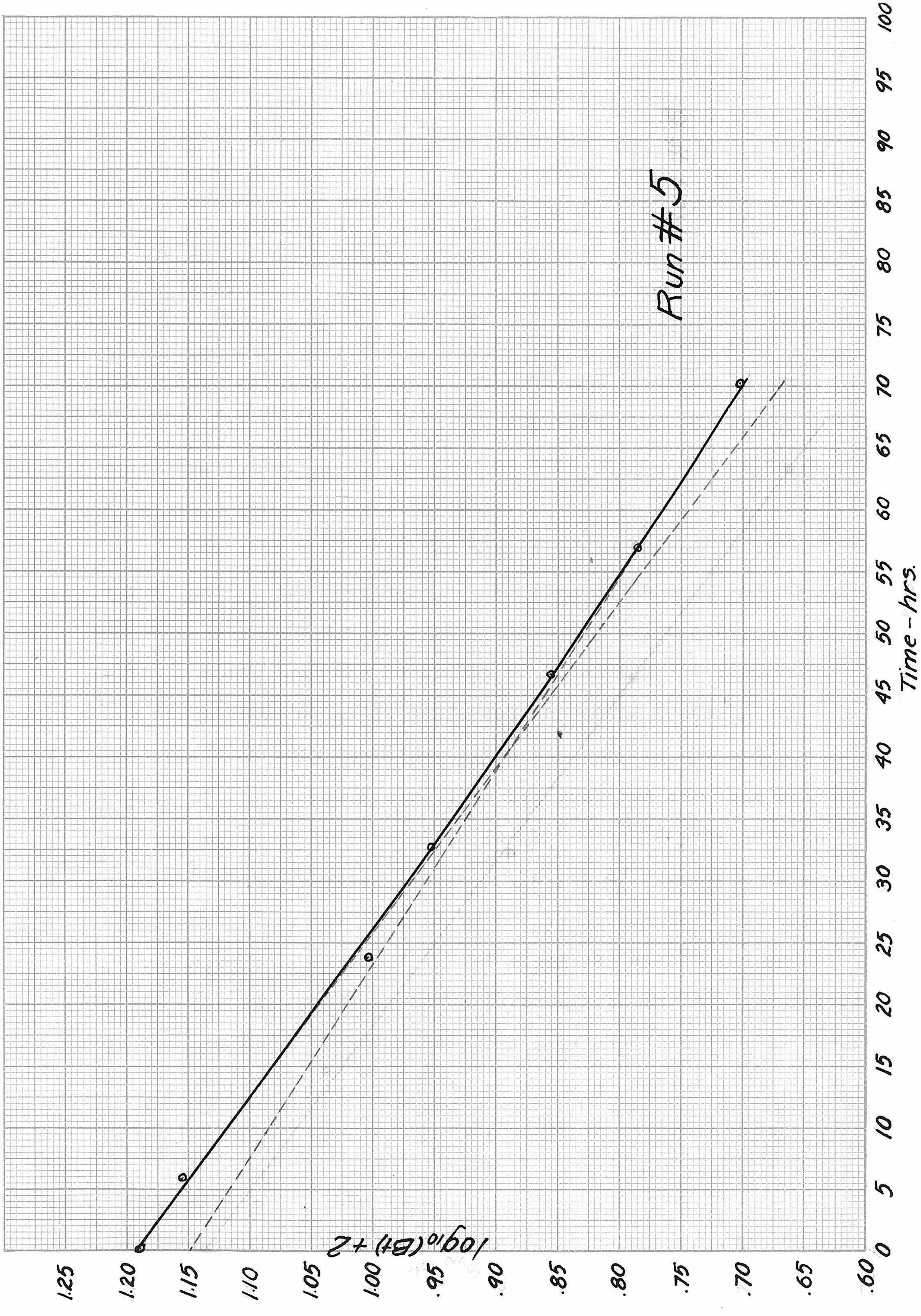
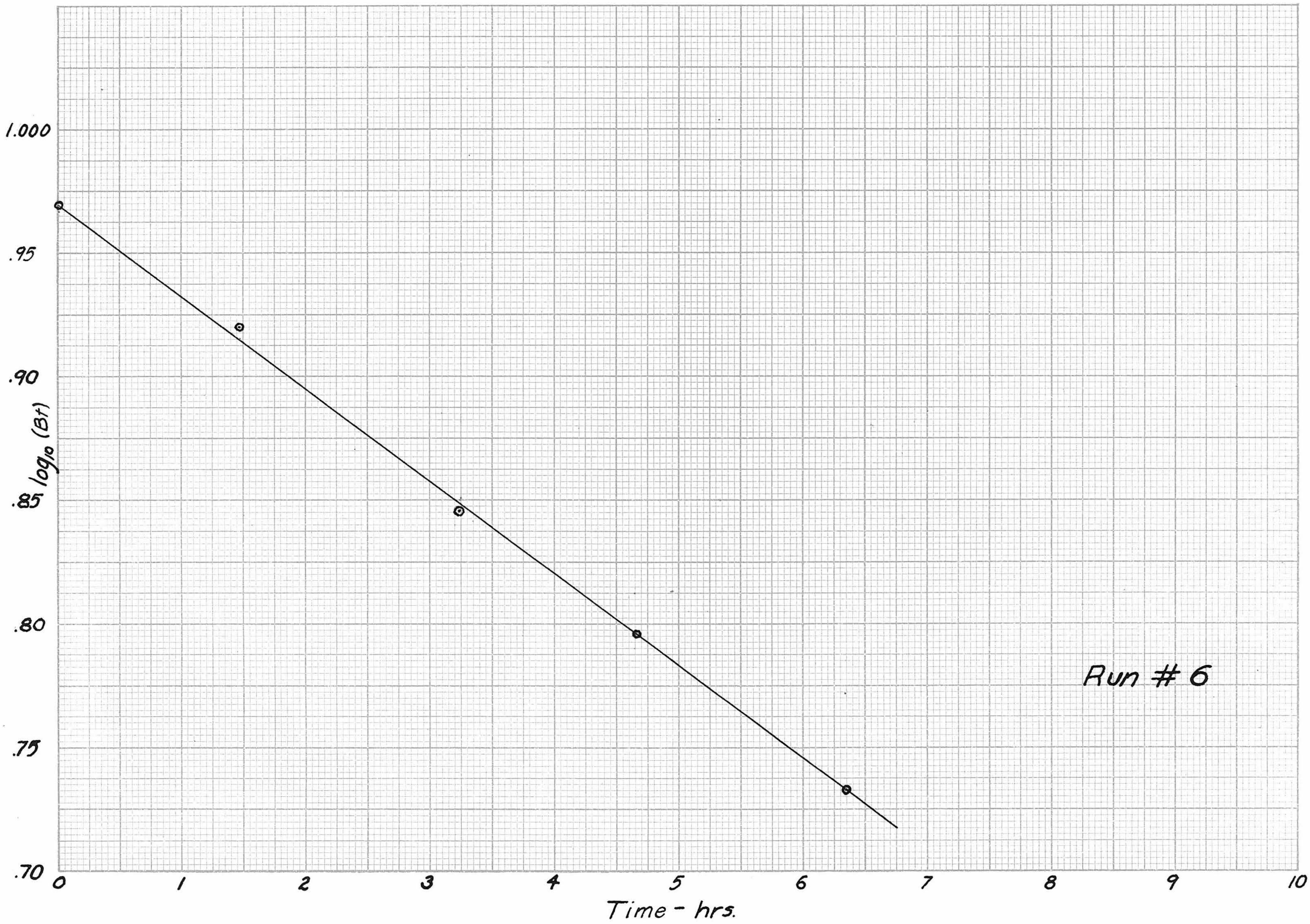
.65
.60
.55
.50
.45


Run #5
Time - hrs.
$\log_{10}(B_t)+2$
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
1.25
1.20
1.15
1.10
1.05
1.00
.95
.90
.85
.80
.75
.70
.65
.60


Run # 6
1.000
.95
.90
.85
.80
.75
.70
$\log_{10}$ (Bt)
0
1
2
3
4
5
6
7
8
9
10
Time - hrs.

Calculation of k_2.

Since by equ'n (7)

$$-\frac{d \ln(Bt)}{dt} = \frac{k_1 + k_2K\{(Agt) - (Bt)\}}{1 + K\{(Agt) - (Bt)\}} = S$$

If the value of k_1 be taken from the first paper for the proper acidity and ionic strength and inserted in the above equation together with the observed slope S, and concentration of isobutene (Bt) at that point, the value of k_2 will be immediately obtainable.

In this treatment two slopes are measured on each curve, one at the beginning of the run, and one at the end; and the values of k_2 for both of them are calculated. This gives a check upon the constancy of k2 within the run.

Another slightly different method of treatment is possible from this equation. This consists in setting up a pair of simultaneous equations for each run and then solving for the value of k1 as well as for k_2. Such a procedure is unsatisfactory, however, because the use of simultaneous equations causes the results to be highly sensitive to errors in the slope. A 1% error in the slope can easily become a 20% error in the value of k_2 (although k_1 is less sensitive). In the preceding method, under the same conditions, a 1% error in the slope produces an error of about 4% in the value of k_2. The first method is used in the following calculations.

Results of Calculation of k_2

(Agt) n.	S (curve)	(Bt) m.	k_2 hrs.$^{-1}$
.2431	.0472	.0426	.01000
.2431	.0425	.0130	.00960
.3639	.0335	.0616	.00806
.3639	.03065	.0294	.00757
.490	.02435	.0850	.00500
.490	.02215	.0350	.00523
.6157	.02045	.1268	.00426
.6157	.01845	.0480	.00444
.7346	.01733	.1550	.00365
.7346	.01480	.0504	.00314

Discussion of results.

It is seen that, within any given run, the calculated value of k_2 is essentially constant. The discrepancies observed are well within the limits of error since the calculation of k_2 represents the determination of a small difference between two considerably larger quantities. Moreover, one of these quantities depends upon the accurate determination of a slope, a difficult operation.

The comparison of values of k2 for the various runs is not as favorable. A large trend is apparent, with k_2 decreasing as the silver content increases.

Since this might well be considered as overthrowing the assumptions upon which the calculations are based, it is well to consider the effect of altering these assumptions.

The first possibility is that the complex reacting has some other formula than the 1:1 complex. Since the distribution ratio work gave no sign of such a complex, if it be present it must be in small quantity; and, therefore highly reactive, if it is to be an important contributor to the reaction. If it contain a relatively larger amount of silver, say two silver ions, this would lead to the incorrect prediction that the value of k_2 calculated on the 1:1 assumption should rise with silver content. One silver ion to two isobutene molecules would make the apparent k_2 increase rapidly with isobutene concentration. Actually it does not vary with isobutene beyond the extent of experimental error. Therefore the presence of more complicated complexes seems improbable.

It might be suspected that the value of K is in error. The values of k_2 within any run are sensitive to variations in K, but a trial calculation shows that it would require a very great change in K to remove the trend, and even then there are unsatisfactory results. That there cannot be a large error in K is shown by the following calculation based on run #6. Since the silver content in this run was quite low, the hydration due to the complex is practically negligible when compared to that due to the free isobutene. Consequently it is possible to predict the rate of this reaction, knowing the value of K, and of k_1 from the measurements in nitric acid solution.

This calculation results:

$$k_{calc} = .0874$$

$$k_{obs} = .0853$$

For the determination of k_{obs} the best straight line that could be fitted to the data was used. It is thus established that K cannot be greatly in error.

The only apparent conclusion is that the constants as calculated are correct, and the trend observed is due to the changing nature of the solution in spite of the ionic strength being constant. The change in nature of the solution actually is considerable.

Further support of the theory as presented is that the values of k_1 calculated by the method of simultaneous equations previously described do not show much greater variation from run to run as silver is varied than could be ascribed to experimental error; and, moreover, are in rather good agreement with k_1 as determined in dilute nitric acid alone.

That the value of k_2 varies with the ionic content of the solution, while k_1 does not, probably is related to the fact that the former represents the rate of reaction of an ion while the latter is for a neutral substance.

The curvature of the plots of log(Bt) against time is in good agreement with the analysis given.

Summary.

The rate of hydration of isobutene in aqueous solutions of nitric acid and silver nitrate has been investigated.

The nature of the complex ion formed has been established and its mass action constant of formation has been determined.

The hydration due to the complex ion alone has been determined.

Acknowledgment.

The author wishes to thank Professor Howard J. Lucas for suggesting this investigation, and for his frequent assistance during its accomplishment.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 399]

The Hydration of Unsaturated Compounds. II. The Equilibrium between *i*-Butene and *t*-Butanol and the Free Energy of Hydration of *i*-Butene[1]

BY W. FERDINAND EBERZ AND HOWARD J. LUCAS

Parks and Huffman[2] deplore the fact that the free energies of unsaturated hydrocarbons are in an unsatisfactory state, especially since these hydrocarbons are becoming increasingly important from an industrial standpoint. The accurate determination of the free energy change of hydration of such a hydrocarbon is of value, even though it does not in itself give the free energy of the hydrocarbon.

The attainment of satisfactory conditions for measuring the hydration equilibria of olefins has, in general, not been realized. Marek and Flege,[3] in their study of the hydration of 1-butene at elevated temperatures, found that polymerization was an interfering factor.

During an investigation of the rate of hydration of isobutene in a solution containing nitric acid and silver nitrate,[4] it was noted that the reaction is reversible, although only to a small extent. It is the purpose of this paper to describe the measurement of the equilibrium constant of the reaction between isobutene, water and tertiary butanol and the calculation of thermodynamic constants of the reaction.

Francis[5] has measured the gas phase hydration of isobutene and from his results Parks and Huffman have calculated the following

$$(CH_3)_2C{=}CH_2(g) + H_2O(l) = (CH_3)_3COH(l); \quad \Delta F^\circ_{298} = -1890 \text{ cal.}$$

The maximum error is one or two thousand calories. The data (preliminary) of Francis indicate that the third law calculation of the free energy of this change is, as Parks and Huffman have pointed out, considerably in error. Our value for ΔF°_{298} is -1330 ± 20 cal., with which the value of Francis is in substantial agreement. The method employed, *i. e.*, the hydration at 25° in aqueous solution, has advantages over the gas phase equilibrium in that the butene, although present in very small amounts, can be determined accurately and extrapolation is avoided.

Experimental

The equilibrium was established at 25 or at 35° in a one-liter glass-stoppered bottle of known capacity containing the alcohol, water, nitric acid at either 0.2 or 0.1 *N*, and sufficient potassium nitrate to give an ionic strength of 0.2 *N*. Because of the necessity of making several minor corrections, it is desirable to describe the procedure employed in considerable detail.

Materials.—Eastman tertiary butyl alcohol, m. p. 22°, was purified by repeated crystallizations until the melting point was 25.10°, when approximately 95% was solid. Since roughly 1% of water lowers the melting point by 5°, the depression of 0.43° indicated a purity of 99.8–99.9% on the assumption that the impurity was water. This product was regarded as sufficiently pure to determine the concentration of the alcohol by weighing it.

Procedure.—About 500 ml. of water was placed in the one-liter bottle, the desired amount of alcohol was weighed in, and the contents thoroughly mixed. Since the alcohol is contaminated by a very small amount of unsaturated material, the mixture was completely purified from this by two extractions with carbon tetrachloride in the following way. Twenty ml. of the solvent was added, the bottle was filled to the stopper with water, except for a quite small bubble, and then rotated end over end at 70 r. p. m. for one hour. The carbon tetrachloride was removed, another 20 ml. added, and the extraction repeated. The carbon tetrachloride was removed quantitatively through a capillary tube drawn down to a fine point and attached to an evacuated iodine flask through a stopcock. Since the moderate agitation did not produce an emulsion, the carbon tetrachloride fortunately could be collected at the bottom of the bottle and removed completely. Its removal must be complete, otherwise a serious error would arise later in the analysis of the butene contained in the equilibrium mixture. During this operation a small amount of the aqueous phase was also drawn over. This was measured.

The solution was brought to the desired acidity by adding the calculated amount of standardized nitric acid from a buret. Sufficient water was then added to fill the bottle, leaving only a minute air space when the glass stopper was inserted tightly. The bottle was rotated for fifteen minutes, then immersed up to the neck in water at 25.00 ± 0.02° and left for a period varying from two to eight days.

At the desired time the bottle was removed from the thermostat and the equilibrium was "frozen" by adding a 5% excess of anhydrous sodium tetraborate after having quickly pipetted out a suitable quantity of the solution (usually 35 ml.) and having added 20 ml. of purified carbon tetrachloride. The bottle was then filled as before and placed on the rotating machine for one hour. If these operations, which could be performed in sixty seconds or less, were not performed quickly the equilibrium

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[1] For the previous publication in this series see Lucas and Eberz, THIS JOURNAL, **56**, 460 (1934).

[2] Parks and Huffman, "Free Energies of Some Organic Compounds," The Chemical Catalog Co., New York, 1932.

[3] Marek and Flege, *Ind. Eng. Chem.*, **24**, 1428 (1932).

[4] By H. Welge, in this Laboratory.

[5] Ref. 2, p. 124; private communication to P. and H.

would shift, due to extraction of butene before the acid was neutralized. Sodium borate was ideal for the latter purpose because no gas was evolved and the heat effect was small; thus no butene was lost and the bottle did not break. When sodium hydroxide was used, carbon dioxide was evolved and several bottles broke. At the acidities of 0.1 and 0.2 *N* the boric acid which separated out gave no trouble.

The carbon tetrachloride layer was drawn off into the evacuated iodine flask containing 10.00 ml. of 0.05 *N* potassium bromate–potassium bromide. Extraction of the equilibrium mixture was repeated with three 10-ml. portions of the purified carbon tetrachloride with the bottle completely filled but rotating for one-half hour instead of one hour. The extent to which the butene was removed by the individual extractions was found to agree well with an assumed distribution ratio of 300, rather than with a more probable value of 550,[6] as shown in Table I, which gives the volumes of standard sodium thiosulfate solution used by the different carbon tetrachloride extractions.

TABLE I

BUTENE REMOVED BY SUCCESSIVE EXTRACTIONS

CCl_4 extract	0.02 *N* $Na_2S_2O_3$, ml. Calcd.	Found
First, 20 ml.	3.01	3.00
Second, 10 ml.	0.38	0.38
Third, 10 ml.	.09	.10
Fourth, 10 ml.	.03	.03

Thus four extractions were found to be sufficient for the quantitative removal.

The titration of the combined carbon tetrachloride extracts in the evacuated iodine flask was made in the usual way,[1] except that the bromination time was five minutes, instead of ten. From this result the concentration of butene in the equilibrium mixture could be calculated. The concentration of alcohol remaining was known.

Before the equilibrium constant could be calculated it was necessary to correct for (a) the loss of alcohol during the first extraction with carbon tetrachloride through extraction by this solvent; (b) the loss of alcohol during this extraction through the removal of some of the aqueous phase; (c) the loss of both alcohol and butene through removal of a part of the equilibrium mixture before "freezing" the equilibrium; (d) the effect of alcohol, dissolved out by the carbon tetrachloride during the analytical extraction, upon the bromine titration. Of these, (a), which can be calculated from the known distribution[7] of tertiary butanol between water and carbon tetrachloride, was usually about 0.65%; (b) and (c) were obtained from the measured volumes. The effect of (d) was noted by adding 10 ml. of tertiary butyl alcohol to the usual amount of standard bromate–bromide solution in the absence of carbon tetrachloride and noting the amount of bromine consumed after the alcohol and the liberated bromine stood for different periods of time. It is to be noted from the data in Table II that there is an impurity in the alcohol which reacts in five minutes with an amount of bromine equivalent to 0.17 ml. of 0.02 *N* thiosulfate and that thereafter bromine disappears at a slow uniform rate equivalent to 0.04 ml. every five minutes.

TABLE II

BROMINE USED BY TERTIARY BUTYL ALCOHOL

Time, minutes	5	10	60
0.02 *N* $Na_2S_2O_3$, ml.	0.17	0.21	0.63

Since the quantity of alcohol in this test is approximately seven-fold that present during an actual titration, it is evident that the small amount of alcohol present can have no appreciable effect upon a butene analysis.

Before the free energy values could be calculated from the equilibrium data it was necessary to determine the vapor pressure of tertiary butyl alcohol from the equilibrium mixtures, 0.20 *M* in potassium nitrate instead of nitric acid, and to determine also the solubility of isobutene in these same mixtures. Instead of directly determining the vapor pressure of the alcohol, the ratio of the partial pressure of alcohol to that of water was determined and the partial pressure of the alcohol was calculated from that of the water on the assumption that the latter was proportional to its mole fraction, which was either 0.992 or 0.987. The ratio of the partial pressures was calculated from the composition of the condensate obtained by cooling, with a bath of solid carbon dioxide and isopropyl ether, the air which had been passed through the equilibrium mixture.

A comparatively simple modification of Dobson's apparatus[8] for vapor pressure determinations consisted of three spiral wash-bottles in series containing the equilibrium mixture and completely immersed in the thermostat at 25°, a heating coil on the exit tube leading from the last wash-bottle to the collecting tube and a Dewar flask containing "dry ice" and isopropyl ether to cool the latter. A plug of cotton was placed in the exit tube to catch any spray. This plug was never observed to have accumulated any liquid at the end of any run. The efficiency of the apparatus for saturating the air stream was demonstrated by noting that the change in density of the third bottle (see Table III) was negligible after a volume of air had been passed through which carried over 6 ml. of liquid aqueous alcohol, an amount about twice that usually obtained.

TABLE III

EFFICIENCY OF SATURATORS

	Density	Change in density
Original solution	1.00706	.....
Third bottle	1.00712	0.00006
Second bottle	1.00740	.00034
First bottle	1.00890	.00184

Even if saturation were slightly incomplete, no error would arise in determining the partial pressure of butanol in the equilibrium mixtures, since this was calculated from the mole fractions of the distillate. The composition of

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[6] The distribution ratio of isobutene between carbon tetrachloride and water at 25°, to be reported in more detail later, is 606.

[7] This constant is 6.15 ± 0.2, when the concentration of the alcohol in the aqueous phase is 9%, as determined by H. Welge in this Laboratory.

[8] Dobson, *J. Chem. Soc.*, **127**, 2866 (1925).

the distillate was obtained by density measurements.[9] The vapor pressure results are shown in Table IV.

TABLE IV

VAPOR PRESSURE OF TERTIARY BUTANOL FROM AQUEOUS SOLUTIONS, 0.200 M IN KNO_3

Temperature, °C.	25	25	35
Molality of alcohol	0.25	0.50	0.25
Vapor pressure of alcohol, mm.	2.39	4.80	5.27

The solubility of isobutene in the equilibrium mixture (0.2 M in potassium nitrate) was determined by passing gaseous isobutene, at one atmosphere pressure, first through two spiral wash-bottles containing the equilibrium mixture in order to saturate the gas with water and with the butanol, then into a 500-ml. conical flask containing 400 ml. of the equilibrium mixture and finally into a cold trap for recovery of the butene. The wash bottles and flask were immersed in a thermostat, the latter not completely, since the neck by which it was clamped was exposed. The flask was closed by a stopper carrying the inlet and outlet tubes and a third short glass tube to which a short piece of rubber closed by a clamp was attached. The inlet tube did not dip beneath the surface of the liquid. Saturation of the liquid was obtained by closing off first the inlet and then the outlet tubes and shaking vigorously for a short time.

A sample was pipetted out by inserting the special pipet (see Fig. 1) of 10 ml. capacity through the third tube but not below the surface, closing the exit tube, increasing the flow of butene until the pipet was filled with it, then dipping the lower end below the surface. The liquid was forced into the pipet and up into arm A. Then the stopcock was closed, the tip of the pipet was attached to the evacuated iodine flask, the funnel B was filled with water, and the stopcock opened to admit air through B, thus washing the contents into the titration flask. The pipet was rinsed out with water into the latter and the butene determined in the usual way. By the above procedure none of the volatile butene was lost. The procedure was repeated until successive determinations of the butene content checked.

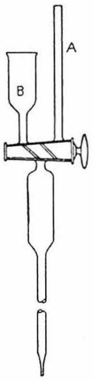

Fig. 1.

The solubilities of butene in the equilibrium mixtures, corrected to 760 mm. of butene, are shown in Table V.

TABLE V

SOLUBILITY OF ISOBUTENE IN AQUEOUS TERTIARY BUTYL ALCOHOL

$P_{C_4H_8} = 760$ mm. $KNO_3 = 0.200\ M$

Temperature, °C.	25	25	35
Tertiary butanol, M	0.25	0.50	0.25
Isobutene, M	.00543	.00566	.00454

Discussion

In Table VI are shown the final, corrected molalities, the partial pressures of the alcohol, the calculated partial pressures of the hydrocarbon, the mole fractions of water, the calculated equilibrium constants, $K_c = (C_4H_9OH)/(C_4H_8)N_{H_2O}$, $K = R_{C_4H_9OH}/P_{C_4H_8}N_{H_2O}$ and the free energy changes. In the expressions for K_c and K, molality is represented by brackets, mole fraction by N, and partial pressure in atmospheres by P. $R_{C_4H_9OH}$ signifies the ratio of the partial pressure of the alcohol to the vapor pressure of the pure liquid at the same temperature. The latter was taken as 42 mm. at 25° and as 76.3 mm. at 35°.[10]

The conditions of the experiments were varied. The trebling of the time in runs 5 and 6 as compared with runs 1, 2, 3 and 4 (these were practically identical) produced no substantial change in the constant, a result which indicated that polymerization was a negligible factor. The similarity of results when the acid is halved, as in runs 7 and 8, indicated that complex formation also is negligible.[11] A doubling of the alcohol concentration and an increase in the time (runs 9 and 10) did not change the constant, nor did a doubling of the alcohol and a decrease in the time (runs 11 and 12). At 25° the constant is smaller, showing that the equilibrium in equation 1 is shifted toward the left (runs 13, 14 and 15).

$$C_4H_8 + H_2O + H_3O^+ = C_4H_9OH + H_3O^+ \qquad (1)$$

In treating the kinetics of this reaction at some definite ionic strength, in this case 0.2 N, activities can be neglected. Therefore the rate of disappearance of isobutene is given by equation 2

$$-\mathrm{d}c_{C_4H_8}/dt = k_{01}(C_4H_8)(N_{H_2O})(H_3O)^+ \qquad (2)$$

and its rate of formation by equation 3, on the assumption that the rate is first order with respect to the alcohol:

$$\mathrm{d}c_{C_4H_8}/dt = k_{02}(C_4H_9OH)(H_3O^+) \qquad (3)$$

Here k_{01} and k_{02} are the specific reaction rates of the disappearance and the formation of isobutene, respectively. Since the measured rate of disappearance (Ref. 1) is $k_1 = k_{01}\ (H_3O^+)$ and a measurable rate of formation would similarly be $k_2 = k_{02}\ (H_3O^+)$, these measurable rates at equilibrium are related to each other as shown in equation 4.

$$\frac{k_1}{k_2} = \frac{(C_4H_9OH)}{(C_4H_8)N_{H_2O}} = K_c \qquad (4)$$

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[9] "International Critical Tables," McGraw-Hill Book Co., New York, 1926, Vol. 3, p. 112.

[10] Parks and Barton, THIS JOURNAL, 50, 25 (1928).

[11] In this case the ionic strength was kept at 0.2 N by the addition of potassium nitrate. It has been shown (Ref. 1) that nitric acid and potassium nitrate have an equal salt effect on the hydration reaction, and hence are probably of equal effect on the equilibrium.

TABLE VI

EXPERIMENTAL DATA, EQUILIBRIUM CONSTANTS AND FREE ENERGY OF THE REACTION

$i\text{-}C_4H_8 + H_2O = t\text{-}C_4H_9OH$ AT 25°

			Molality		Mole fract.	Partial Press.		Equilibrium consts.		
No.	HNO_3 N	Time, hrs.	$C_4H_{10}O$ M	C_4H_8 $M \times 10^5$	H_2O N_{H_2O}	$P_{C_4H_{10}O}$ mm.	$P_{C_4H_8}$ mm.	$K_c \times 10^{-3}$	K	$-\Delta F$ cal.
1	0.200	24	0.2465	3.273	0.992	2.357	4.581	7.59	9.385	1326
2	.200	24	.2496	3.393	.992	2.386	4.749	7.42	9.165	1312
3	.200	24	.2457	3.390	.992	2.349	4.745	7.31	9.027	1303
4	.200	25	.2432	3.186	.992	2.325	4.459	7.69	9.562	1334
5	.200	70	.2462	3.314	.992	2.354	4.638	7.49	9.260	1318
6	.200	71	.2508	3.473	.992	2.398	4.861	7.28	8.997	1301
7	.100[a]	70	.2449	3.313	.992	2.341	4.637	7.45	9.212	1315
8	.100[a]	68	.2394	3.259	.992	2.289	4.561	7.41	9.165	1312
							Mean	7.46	9.222	1315
9	.200	92	.4861	6.616	.987	4.667	8.884	7.44	9.642	1342
10	.200	93	.4755	6.455	.987	4.565	8.667	7.46	9.658	1343
11	.200	22	.4773	6.408	.987	4.582	8.604	7.55	9.773	1350
12	.200	23	.4762	6.395	.987	4.572	8.587	7.54	9.756	1349
							Mean	7.50	9.707	1346
					At 35°					
13	.200	40	.2425	6.190	.992	5.112	10.362	3.949	4.706	948
14	.200	44	.2376	6.021	.992	5.009	10.079	3.978	4.737	952
15	.200	45	.2470	6.408	.992	5.207	10.727	3.885	4.630	938
							Mean	3.937	4.691	946

[a] Contained KNO_3, 0.100 N.

Calculation of $\Delta F°$.—The standard free energy change, $-\Delta F°$, for the reaction shown in equation 5

$$C_4H_8(1\text{ atm.}) + H_2O(l) = C_4H_9OH(l) \qquad (5)$$

is given by equation 6, in which R was taken as 1.9869

$$-\Delta F° = RT \ln K \qquad (6)$$

It is to be observed that, whereas the average equilibrium constant K_c of the runs at 25° is 7.46×10^3 when the alcohol concentration is 0.25 M and 7.50×10^3 when it is 0.5 M, the agreement in the corresponding free energy values, *viz.*, $-\Delta F°_{298} = 1315$ cal. and 1346 cal., is not quite as satisfactory. This is due to the fact that although isobutene is somewhat more soluble in the solution which is 0.5 M in alcohol, the amount of isobutene at equilibrium in this solution is practically twice as great, instead of somewhat more than twice as great as in the solution 0.25 M in tertiary butyl alcohol. This effect, however, is not very large and leads to a deviation of only about 25 cal. We shall take the mean of the two values, namely, $\Delta F°_{298} = -1330 \pm 20$ cal.

Calculation of ΔH.—On combining the average free energy values of the first twelve runs at 25° and the average of the last three at 35° by means of equation 7, and assuming that ΔH is constant over this small interval

$$\Delta H = \frac{d(\Delta F/T)}{d(1/T)} = \frac{-(946/308.1) + (1330/298.1)}{(1/308.1) - (1/298.1)} = -12{,}775 \text{ cal.} \qquad (7)$$

It is possible to calculate the ΔH value also by combining the observed entropy of tertiary butyl alcohol and the estimated entropy of isobutene as given by Parks and Huffman[12] with the new ΔF value, as follows

$$\begin{array}{lllll} & C_4H_8(1\text{ atm.}) + & H_2O(l) & = C_4H_9OH(l) & \\ S_{298.1} & 67.3 & 16.9^{13} & 45.3 & \Delta S = -38.9\text{ E. U.} \end{array}$$

$$\Delta H = \Delta F + T\Delta S = -1330 - 298.1 \times 38.9 = -12{,}900\text{ cal.} \qquad (8)$$

The satisfactory agreement of these two values, in spite of the fact that the temperature interval is not very large, confirms the entropy approximation.

The Dehydration of Tertiary Butyl Alcohol.—From the equilibrium constant K_c and the previously determined rate of hydration of isobutene, it is possible to calculate the dehydration of the alcohol at an ionic strength of 0.2 N, on the assumption that the rate is first order with respect to the alcohol. From equation 4 it is evident that the rate of dehydration of tertiary butyl alcohol, k_2 is

$$k_2 = k_1/K_c \qquad (9)$$

Since the equilibrium is not shifted by a change in the acidity, it is evident that the dehydration rate must be first order with respect to the acidity. This is illustrated in Table VII, in which are shown the calculated values of k_2. The values

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(12) Reference 2, pp. 108 and 81, respectively.

(13) Giauque and Ashley, *Phys. Rev.*, **43**, 81 (1933).

of k_1 have been interpolated from data previously given (Ref. 1).

TABLE VII

RATE OF DEHYDRATION OF TERTIARY BUTYL ALCOHOL k_2, AT 0.2 *N*

Run No.	*T.* °C.	HNO_3 *M*	KNO_3 *M*	k_1 hrs.$^{-1}$	K_c $\times 10^{-3}$	k_2 hrs.$^{-1} \times 10^5$
2	25	0.200	...	0.286	7.42	3.85
8	25	.100	0.100	.143	7.41	1.93
10	25	.200	...	.286	7.46	3.835
13	35	.200	...	1.022	3.949	25.88

The temperature coefficient and the heat of activation are shown in Table VIII in which, for comparison, are given also similar data for the hydration reaction. The temperature coefficient of the dehydration rate has the exceedingly high value of 6.73.

TABLE VIII

TEMPERATURE COEFFICIENT AND HEAT OF ACTIVATION

	Temp. coeff., k_{35}/k_{25}	Heat of activation kg. cal./mole
Dehydration of $(CH_3)_3COH$	6.73	34.82
Hydration of $(CH_3)_2C{=}CH_2$	3.57	23.26
ΔH in aqueous solution .		11.56

Summary

The equilibrium between isobutene, water and tertiary butyl alcohol has been measured in dilute aqueous solution in the presence of 0.1 and 0.2 *N* nitric acid, starting from the alcohol side. The equilibrium constant at an ionic strength of 0.2 *N* has a value of 7.48×10^3 at 25° and 3.94×10^3 at 35°.

The free energy change has been calculated and found to be:

$$C_4H_8(g) + H_2O(l) = C_4H_9OH(l)$$
$$\Delta F^\circ_{298 \cdot 1} = -1330 \text{ cal}; \quad \Delta F_{308 \cdot 1} = -946 \text{ cal.}$$

When ΔH is calculated by two different methods, *viz.*, from the change in ΔF with temperature and from the relation $\Delta H = \Delta F + T\Delta S$, two values are obtained, *viz.*, $-12{,}800$ cal. and $-12{,}900$ cal., respectively.

On the assumption that the reverse reaction of dehydration of tertiary butyl alcohol is first order with respect to the alcohol, the dehydration rate was calculated by combining the equilibrium constant with the known rate of hydration of isobutene. It was found that (a) the dehydration rate at an ionic strength of 0.2 *N* is proportional to the acid concentration, (b) the temperature coefficient of this reaction for the ten-degree interval between 25 and 35° is 6.73, an unusually high value, and (c) the heat of activation is 34.82 kg. cal. per mole.

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