

showed no loss in activity. A large fraction of the surface must have been permanently covered with hydrogen except in the last few experiments in which a carefully cleaned surface was used.

It would be interesting to try experiments with acetylene, to see whether it decomposed more readily than ethylene. It may well be that the breaking of the C-C bond would proceed through adsorbed ethylene rather than adsorbed acetylene. For, unless the latter was attached to four nickel atoms simultaneously there would be some double bond character in the C-C bond which should make it more difficult to break.

Acknowledgment.—One of us (C. K.) wishes to express his thanks to the Commonwealth Fund for the generous Fellowship which made this work possible.

Summary

1. The mass spectrometer can be used to follow the reaction of ethane and hydrogen producing methane using the ratio of the "16 peak" to the "30 peak."

2. The ethane-hydrogen decomposition on a supported nickel catalyst obeys the expression

Rate = $k p_{\text{C}_2\text{H}_6}^{0.7} p_{\text{H}_2}^{-1.2}$ over a wide range of composition with an energy of activation of 52 kcal./mole.

3. At low ratios of hydrogen/ethane, abnormal kinetics, depending on a high inverse power of the hydrogen pressure, set in. This is ascribed to heterogeneity of the surface.

4. Ethane will decompose quantitatively over this catalyst to methane and carbon with a rate dependent on $p_{\text{C}_2\text{H}_6}^{0.7}$ and an energy of activation of 40 kcal./mole.

5. The carbon is reversibly deposited and can be converted to methane by hydrogen.

6. The rate-determining step of methane formation must be the breaking of the carbon-carbon bond. Both the ethane-hydrogen and the ethane decompositions can be interpreted by a mechanism involving the presence on the surface of adsorbed ethylene, in equilibrium with adsorbed ethyl radicals and hydrogen. This mechanism was supported directly by showing that the initial rate of production of methane is greater from ethylene than from ethane.

PRINCETON, NEW JERSEY

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF SARAH LAWRENCE COLLEGE]

Vapor Pressure of Isobutene over Dioxane as Basis of Manometric Kinetic Studies. The Dissociation of *t*-Butyl Benzoate

BY ROLF ALTSCHUL AND JOANNE HERBERT

This paper has as its primary objective the presentation of an improved method for kinetic measurements of liquid-phase reactions involving isobutene. Such an investigation was relevant to our present effort to expand a previous preliminary study of acid-catalyzed dissociations of tertiary esters.¹ In order to expedite this general project we tested a different analytical procedure, which, with equal accuracy, was to afford identical results with greater facility.

Vapor pressure measurements by a static method served as a basis for this alternate analysis. Two separate problems were involved to adapt this generally useful method to our particular needs: (a) A calibration to establish the vapor pressure of dioxane solutions as a function of their isobutene content. A constant and small amount of sulfuric acid (0.835 mole/liter), necessary to catalyze the subsequent kinetic runs, was included with these standardizations. (b) Application of these data to the reversible dissociation of *t*-butyl benzoate into benzoic acid and isobutene.¹ These manometric rate constants were then matched against parallel experiments resorting to acidimetric analysis by the orthodox procedure.

Since strong mechanical agitation was a prerequisite, a thermostated Van Slyke instrument appeared most opportune for this study.

(1) Altschul, *THIS JOURNAL*, **68**, 2605 (1946).

Experimental

Materials.—Benzoic acid, *t*-butyl benzoate, isobutene, dioxane,² and 100% sulfuric acid were prepared, purified, and stored as before.¹ All gave the previous physical constants.

Manometric Determinations.—A Van Slyke instrument was equipped with a thermostated chamber which was maintained at $25 \pm 0.05^\circ$ by means of rapid circulation of water from a constant temperature bath. The detailed directions for this instrument were adapted from manometric analysis of insoluble gases³ to our problem of measuring saturation pressures of soluble vapor. The optimum procedure described below was checked against pure dioxane, for which the vapor pressure at 25° has been accurately determined.⁴ For our description we have adopted the terminology used by Peters and Van Slyke in their detailed outline.⁵

(a) Calibration.—Five cc. of 1.670 molar anhydrous sulfuric acid in dioxane is placed in the cup above the chamber, and, with the 3-way cock open and the mercury in the leveling bulb at slight negative pressure, the solution is drawn slowly into the chamber by careful opening and closing of the 4-mm. connecting stopcock. This is followed by the introduction of 5 cc. of an isobutene solu-

(2) The solvent was purified by Mr. Jon J. Sugrue.

(3) Peters and Van Slyke, "Quantitative Clinical Chemistry," Volume II, The Williams and Wilkins Company, Baltimore, Md., 1932, Chapters 1, 3, 7.

(4) $p_d = 3.55$ cm.: Teague and Felsing, *THIS JOURNAL*, **65**, 485 (1943).

(5) See ref. 3, pp. 267-280. Figure 37 on p. 272 will be especially relevant to the following discussion. Descriptions of the manometric Van Slyke instrument have also been published in the literature: Van Slyke and co-workers, *J. Biol. Chem.*, **61**, 523 (1924); **73**, 121 (1927).

tion of indeterminate concentration in an identical manner. The 4-mm. cock is closed when the solution has been drained from the cup into the chamber except for a negligible residue remaining in the capillary of the cup. Degassing: after closing of the 3-way cock, the contents of the chamber is evacuated by lowering of the leveling bulb, with the 4-mm. cock open, until the mercury is about 2 cm. below the 50-cc. mark in the chamber. The 4-mm. cock is now closed and the solution is freed of air and some isobutene by rapid shaking for two to three minutes. Mercury is then slowly introduced from the raised leveling bulb by means of partial opening of the 4-mm. cock until the chamber is under very slight excess pressure. The extracted air is immediately expelled through the opened 3-way cock, with the liquid now again filling the capillary of the cup. Vapor pressure determination: the 4-mm. cock is closed, the leveling bulb lowered to slight negative pressure, and a drop of mercury placed into the cup of the chamber. This is slowly drawn into the capillary and into the bore of the 3-way cock by careful opening of the 4-mm. cock, to be turned off instantly when the desired adjustment is attained. With the 3-way cock closed and effectively sealed by means of the mercury, the chamber is evacuated as before, by means of the lowered leveling bulb with the 4-mm. cock temporarily open, until the mercury is again slightly below the 50-cc. mark in the chamber. After a brief period of shaking, the mercury is brought exactly to the 50-cc. mark from below by means of careful opening and closing of the 4-mm. cock, to be followed by a manometer reading. Shaking is resumed and the latter procedure repeated in order to assure equilibration of the system.

All our data seemed easily reproducible. The pressures are corrected for the weight of the liquid resting on the mercury in the chamber. The same total volume (10 cc.) was employed for all measurements.

Before the bromometric assay for isobutene,¹ the solution is forced back into the chamber by means of the raised leveling bulb with the 4-mm. cock open, until complete re-absorption has occurred. Aliquot samples are then withdrawn and titrated with thiosulfate as described before.¹ The concentrations in Table II are corrected for the constant and small fractions of isobutene present in the vapor phase by simple application of the ideal gas law.

To measure the vapor pressure of dioxane solutions containing varying quantities of sulfuric acid, a similar procedure is followed with these simplifications: Ten cc. of an acid solution is introduced into the chamber. After initial brief degassing shaking becomes superfluous for the measurement of the saturation pressure. Final re-absorption can of course be dispensed with. These preliminary studies are summarized in Table I.

(b) **Kinetic Studies.**—Five cc. of a 1.670 molar solution of anhydrous sulfuric acid in dioxane is introduced into the chamber, to be followed by 5 cc. of an ester solution of known molarity. The subsequent manipulations leading to expulsion of air follow the previous procedure exactly. This short degassing effects an inconsequential shift from the calculated zero point. With the dissolved air extracted and eliminated, the 3-way cock is sealed with mercury as above, and, with the 4-mm. cock temporarily open and the leveling bulb lowered, the mercury in the chamber is adjusted to the 50-cc. mark, or slightly below. Constant shaking is advisable, with brief interruptions for pressure recordings. These are taken on the manometer, at timed intervals, until equilibrium is attained, by careful and slow raising of the mercury to the 50-cc. mark, with the leveling bulb raised and the 4-mm. cock carefully opened until the desired point is reached.

At equilibrium, samples were withdrawn to be analyzed for benzoic acid by titration. They were always in good agreement with the values calculated from the manometric data and also with the known dissociation equilibrium constant.⁶

(6) Blank tests established that comparable quantities of ester and benzoic acid had no effect on the vapor pressure of isobutene.

Acidimetric Runs.—To the reversible runs the previous sealed-ampoule technique was applied.¹

Anhydrous nitrogen was saturated with dioxane vapor by bubbling through 0.83 molar sulfuric acid at 25° and was then passed through the reaction mixture contained in a loosely plugged vessel for the irreversible determinations. The stream was regulated to 1 to 2 bubbles per second. One cc. samples of the solutions were withdrawn at timed intervals and analyzed acidimetrically as usual. A blank run, containing 0.202 mole/liter of benzoic acid and no ester, established that the gas stream caused no concentration drifts for at least 2.5 hours, since the acid molarity remained unaltered within the experimental error over this period.

Results and Discussion

Preliminary measurements of the vapor pressure of dioxane, P_d , containing varying amounts of sulfuric acid, are presented in Table I. The values

TABLE I
VAPOR PRESSURE OF SOLUTIONS OF SULFURIC ACID IN
DIOXANE AT 25 ± 0.05°

(H ₂ SO ₄), m./l.	N_d	Density	p_d , cm.	$N_d \times p_d$, ^a cm.
0	1.000	1.03	3.56 ^a	3.56
0.835	0.932	1.08	3.18	3.32
1.670	.866	1.12	2.98	3.18
1.941	.845	1.12	2.82	3.01

^a See ref. 4.

in the last column were computed for an ideal system (Raoult's law); N_d stands for the mole fraction of dioxane. The trend shows a deviation from ideality in the expected direction, emphasizing the formation of oxonium salt.

In Table II there are contained the data for solutions of isobutene in 0.835 molar sulfuric acid. The partial pressures of the solute, P_i , were calculated by means of the equation

$$p_i = p_{\text{total}} - p_d \quad (1)$$

assuming for p_d a constant value over the measured range (3.18 cm.). A simple check shows the error introduced through this approximation to be negative and to remain always below 0.5%. The values of the constant α in the last column illustrate how closely the data adhere to the ideal law

$$p_i = M_i \times \alpha \quad (2)$$

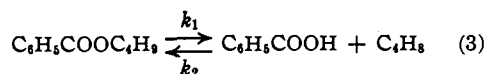
into which the molarity of isobutene, M_i , rather

TABLE II
VAPOR PRESSURE OF ISOBUTENE OVER DIOXANE SOLUTIONS CONTAINING 0.835 MOLE/LITER OF H₂SO₄ AT
25 ± 0.05°

M_i	p_{total} , cm.	p_i , cm.	α cm. × liters/ mole
0	3.18	0	..
0.043	5.35	2.17	50.5
.113	9.5	6.3	55.7
.234	16.8	13.6	56.9
.245	17.2	14.0	57.1
.382	25.4	22.2	58.6
.493	32.0	28.8	58.3
.606	37.4	34.2	56.5

than its mole fraction, was substituted as is customary for dilute solutions.

The information above should clearly facilitate the manometric investigation of reactions in which isobutene is a participant, provided the other products and reactants are non-volatile. This surmise was put to the test of a kinetic inquiry. It was applied to the reversible dissociation of *t*-butyl benzoate in anhydrous dioxane solution with 100% sulfuric acid as a catalyst, a system which has been characterized before.^{1,7}



The previously derived mathematical function for the dissociation rate constant k_1 can be adapted to the manometric process as follows

$$C + k_1 t = \frac{K_d}{(2p_0/\alpha) + K_d} \ln Q \quad (4)$$

where

$$Q = \frac{(K_d\alpha) + p_0 + p_1}{p_0 - p_1} \quad (5)$$

C is the usual integration constant, K_d is the known dissociation equilibrium constant ($K_d = 0.68$), and p_0 stands for the equilibrium pressure of isobutene. The constant α serves to translate pressure, from cm., into concentration, moles/liter ($\alpha = 57.5$).⁸

Table III contains the data for two representative manometric runs, while Fig. 1 emphasizes that the linear relationship postulated by Equation (4) is observed over their entire course.

TABLE III
MANOMETRIC RATES OF DISSOCIATION OF *t*-BUTYL BENZOATE IN DIOXANE CONTAINING 0.835 M./L. OF SULFURIC ACID AS A CATALYST, AT 25 ± 0.05°

Hr.	p_1 , cm.	Q	Hr.	p_1 , cm.	Q
	Run no. 2A			Run no. 7	
0.12	0	2.31	0.28	0.82	2.93
.32	2.62	2.66	0.45	2.15	3.23
.56	6.27	3.32	0.64	4.42	3.85
.93	10.79	4.56	1.12	8.89	5.87
1.25	14.3	5.95	1.55	11.07	7.62
1.55	16.8	7.98	2.03	13.16	10.40
2.60	22.5	20.5	2.84	16.29	20.93
3.1	24.1	34.1	3.17	17.00	26.7
5.0	26.6	...	3.43	17.5	33.1
5.6	26.6	...	3.90	18.29	52.6
			6.16	19.67	...
			7.50	19.67	...

(7) Additional instances of the breakage of the alkyl oxygen-bond in esters have recently been reported: Balfe, Downer, Evans, Kenyon, Poppett, Searle and Tarnoky, *J. Chem. Soc.*, 797 (1946); Balfe, Evans, Kenyon and Nandi, *ibid.*, 803 (1946); Balfe, Kenyon and Wicks, *ibid.*, 807 (1946).

(8) With a small and constant fraction of isobutene present in the vapor phase, its molarity in the dioxane solution is somewhat smaller than that of benzoic acid. This required an adjustment of the rate equation. Such a correction is embodied in the factor α , which, as indicated by Equation (2), is based on the concentration of *i*-butene in the liquid phase only. See the Experimental Part also.

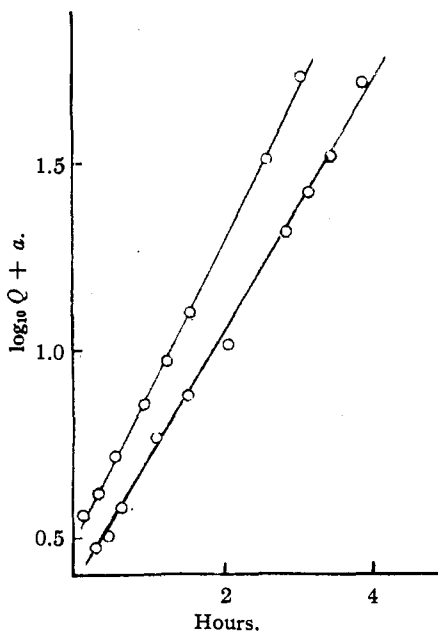


Fig. 1.—Manometric rates of sulfuric acid-catalyzed dissociations of *t*-butyl benzoate in dioxane at 25°: from left to right, no. 2A ($\alpha = 0.2$) and no. 7 ($\alpha = 0$).

Three separate approaches substantiated the measurements of the rate constant k_1 , and, by implication, justified the manometric procedure. Thus, the ester decompositions were followed either manometrically in a reversible setting, as presented in Table III; or acidimetrically under reversible and under irreversible conditions. The latter was achieved by entraining the volatile olefin in a rapid stream of dry nitrogen, previously saturated with dioxane. The kinetic results obtained with these last experiments were interpreted by plotting the logarithm of ester concentration against the time, as is customary for first-order irreversible reactions. The results are summarized in Table IV. All runs were followed

TABLE IV
RATE CONSTANTS FOR THE DISSOCIATION OF *t*-BUTYL BENZOATE IN DIOXANE CONTAINING 0.835 M./L. OF SULFURIC ACID AS A CATALYST AT 25 ± 0.05°

Run	(Ester), m./l.	Method	k_1 , (hr. ⁻¹)
2A	1.112	Manometric	0.35
3A	0.552	Manometric	.33
7	0.787	Manometric	.34
1	1.112	Acidim., rev.	.33
3	1.112	Acidim., irrev.	.34
4	1.112	Acidim., irrev.	.33

to completion with the exception of no. 4, for which only the initial 20% of its course was measured. Agreement among the diverse methods is obviously satisfactory. The manometric approach is clearly superior, since, with equal accuracy and reproducibility, it is more economic with respect to time and materials, dispensing as

it does with manipulations of aliquot portions and titrations.

Combined with the previous data at 35°, the new rate constant permits an estimate of the activation energy for the dissociation in 0.835 molar sulfuric acid, $\Delta E = 17$ kcal./mole at 30°.

Summary

The partial pressure of isobutene over dilute solutions in dioxane containing 0.835 molar sulfuric acid was measured by a static method in a Van Slyke instrument at 25°. In its dependence on the concentration, the pressure adheres closely to the ideal law.

The data, applied to the acid-catalyzed reversible dissociation of *t*-butyl benzoate into benzoic acid and isobutene in dioxane solution, provide a basis for manometric kinetic studies and give a first-order rate constant for this reaction. This is in good agreement with the values obtained acidimetrically under reversible and under irreversible conditions.

The activation energy for this reaction is approximately 17 kcal./mole at 30°.

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[CONTRIBUTION NO. 50 FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF TENNESSEE]

The Salts of Perrhenic Acid. I. The Alkali Metals and Ammonium¹

BY WM. T. SMITH, JR., AND SELMA HARMON LONG

Although the perrhenates of many of the metals have been prepared, in most cases the physical properties of these salts have been determined only approximately if at all. Of the perrhenates of the alkali metals and ammonium the potassium salt has been most thoroughly characterized, apparently due to the fact that this salt is precipitated in a common method for the recovery of rhenium² and that it is easily purified by recrystallization from water. The melting point,^{3,4,5,6} boiling point,⁶ solubility,^{6,7,8,9} heat of solution^{9,10} and crystal structure¹¹ have been reported. The density of the potassium salt was calculated from X-ray measurements of the crystal structure.¹¹ The density of no other perrhenate of this family has been reported. The only other melting point reported is for sodium perrhenate.³ The solubilities at room temperature have been reported for all of these salts except lithium perrhenate.⁷ The crystal structures of all of the salts except lithium perrhenate have been reported.^{11,12,13,14}

Preparation of the Salts.—Rhenium was burned in a stream of oxygen at atmospheric pressure. The finely divided metal ignites under these conditions at approximately 300°. The heptoxide formed was dissolved in water to form perrhenic acid. The acid solution was then neutralized with the C. p. carbonate or hydroxide of the

metal.³ Litmus paper was used as an indicator. The salts so obtained were purified by several recrystallizations from water. They are all white in appearance. Evaporation of water from lithium perrhenate solutions was carried out at room temperature. The vapor from heated solutions of this salt was acidic and contained rhenium which indicated hydrolysis of the salt at elevated temperatures.

After each recrystallization the freezing point of the salt was determined. This was repeated until the same freezing point was observed after successive recrystallizations. The freezing points so obtained are listed in Table I.

The freezing points were obtained by cooling molten samples of 20 to 40 g. at a rate of approximately 2° per minute. The temperatures for the cooling curve for the dihydrate of lithium perrhenate were read on a mercury in glass thermometer while all others were read to 0.2° (0.01 millivolt) on a Brown Portable Potentiometer, Model 1117, using a Chromel-Alumel thermocouple which had been calibrated by direct comparison with a calibrated Iron-Constantan couple furnished by the Brown Instrument Company and guaranteed to give standard voltages corresponding to within 3°F. over the range 0–1200°F. Distinct "arrests" in the cooling curves were noted for each salt which could be melted at atmospheric pressure. The dihydrate of lithium perrhenate does not completely melt at 87.5° but undergoes a transition in which the hydrate decomposes to form a liquid and a white solid which will not completely dissolve in the liquid at 100°. Some of this white solid was separated from the liquid by decantation. The loss in weight of this wet solid on complete dehydration was not so great as the theoretical loss for the monohydrate to anhydrous salt. Apparently the equilibrium is $\text{LiReO}_4 \cdot 2\text{H}_2\text{O}(s) \rightleftharpoons \text{saturated solution}(l) + \text{LiReO}_4(s)$.

The purified salts were analyzed gravimetrically for rhenium as a check on the formula for the salt and its purity. The procedure outlined by Willard and Smith¹⁵ was followed in general. It was found in washing the precipitate of tetraphenylarsonium perrhenate with ice water that precipitation occurred when the wash water was allowed to mix with the original filtrate. Whether this was due to the solubility of the precipitate in the wash water or to the decrease in solubility of the rhenium compound as the salt water filtrate was diluted was not definitely established. The procedure was modified by preparing the reagent, tetraphenylarsonium chloride, already mixed with the specified concentration of sodium

(1) This paper is based on a thesis presented by Selma Harmon Long to the Graduate School of the University of Tennessee in partial fulfillment of the requirements for the M.S. degree, May 26, 1947.

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(3) I. and W. Noddack, *Z. anorg. allgem. Chem.*, **181**, 1–37 (1929).

(4) Biltz, *Z. angew. Chem.*, **46**, 271 (1933).

(5) Vorlander and Dalichau, *Ber.*, **66B**, 1534 (1933).

(6) Holemann and Klesse, *Z. anorg. allgem. Chem.*, **237**, 172 (1938).

(7) I. and W. Noddack, *Z. angew. Chem.*, **44**, 215 (1931).

(8) Puschin and Kovac, *Z. anorg. allgem. Chem.*, **199**, 369 (1931).

(9) Smith, *THIS JOURNAL*, **68**, 394 (1946).

(10) Roth and Becker, *Z. physik. Chem.*, **A159**, 27–39 (1932).

(11) Broch, *Z. physik. Chem.*, **6B**, 22–26 (1929).

(12) Beintema, *Z. Krist.*, **97**, 300–322 (1937).

(13) Jaeger and Bientema, *Proc. Acad. Sci. Amsterdam*, **36**, 523 (1933).

(14) Machatschki, *Z. Krist.*, **72**, 541 (1930).

(15) Willard and Smith, *Ind. Eng. Chem., Anal. Ed.*, **11**, 305 (1939).