TABLE I

| | Neutral equiv. | | M. p., °C. | B. p., °C. | *m*-Toluidine salts M. p., °C. | %, S | |
|---|---|---|---|---|---|---|---|
| | Calcd. | Found | | | | Calcd. | Found |
| $HO_3S(CH_2)_2SO_3H$ | 95 | 98 | 97 | ... | 230 | 33.68 | 32.62[a] |
| $HO_3S(CH_2)_3SO_3H$ | 102 | 103 | .. | 157 (1.4 mm.) | 222 | 31.35 | 30.91 |
| $HO_3S(CH_2)_4SO_3H$ | 109 | 111 | 84 | ... | 214 | 29.34 | 28.80 |
| $HO_3S(CH_2)_5SO_3H$ | 116 | 120 | .. | 198 (1.7 mm.) | 187 | 27.57 | 26.62[a] |
| $HO_3S(CH_2)_6SO_3H$ | 123 | 125 | 78 | ... | 158 | 26.01 | 25.61 |
| $HO_3S(CH_2)_{10}SO_3H$ | 151 | 152 | 76 | ... | 178 | 21.19 | 20.32 |

[a] Analysis indicates lack of purity.

**Preparation of the *m*-Toluidine Salts.**—A half gram of the acid was dissolved in a few cubic centimeters of ethyl alcohol and a slight excess of *m*-toluidine added. If precipitation of the salt occurred, more alcohol was added to redissolve it at this point. Slow addition of ether caused the precipitation of the salts which were then purified several times by repeating the above process of precipitation. In this manner it is possible to obtain the pure salt free of excess *m*-toluidine.

## Discussion

The α,ω-disulfonic acids of the alkane series resemble the dicarboxylic acids in respect to melting points. The two, four, six, and ten carbon chain acids are white crystalline solids, while the three and five carbon chain members could not be crystallized but remained as clear slightly-colored liquids. These acids are soluble in water and alcohol but are insoluble in ether, carbon tetrachloride, benzene, and acetone. They are slightly hygroscopic, melt sharply, and then decompose. Distillation can be accomplished only under a pressure of below 2 mm.

## Summary

1. The α,ω-disulfonic acids of ethane, propane, butane, pentane, hexane, and decane have been prepared in the anhydrous state.

2. The boiling points, melting points and *m*-toluidine salts have been used to characterize the above acids.

BOSTON, MASSACHUSETTS RECEIVED JUNE 14, 1941

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

# The Hydration of the Ethylenic Linkage.[1] I. The Equilibrium between Isobutene, *t*-Butyl Alcohol and Water[2]

BY CHARLES W. SMART,[3] HERBERT BURROWS,[3] KATHERINE OWEN AND OSBORNE R. QUAYLE

Very few exact data are available on the equilibria between alcohols, olefins and water. Tertiary alcohols with three identical alkyl groups were chosen to be studied as only one olefin results upon dehydration. Ebertz and Lucas[4] have made the only equilibrium study upon the dehydration of isobutene. Since in their work the equilibrium was approached only from the alcohol side of the reaction and with highly disproportionate concentrations of the components (almost 1000 to 1), the equilibrium was investigated using sealed reaction tubes at 100° and was approached from both sides.

## Experimental

**Procedure.**—The reaction tubes were of soft glass, 1 × 7 cm., and contained approximately 5 ml. of the reaction mixture. Those from the alcohol side were made up from a reaction mixture containing known quantities of water, alcohol, the solvent dioxane and the catalyst mercuric chloride. From the olefin side each constituent was weighed separately into the tube. The gaseous isobutene was condensed into the tube by immersion in an acetone–dry-ice bath. The tubes were sealed immediately after filling. After heating for twenty-one days at 100° each tube was broken under carbon tetrachloride, washed with water and analyzed. The unsaturate was determined by quantitative bromination and the alcohol and water calculated by the change in the amount of unsaturate present.

**Preparation of Materials.**—(1) Water—distilled three times over potassium permanganate and calcium hydroxide. (2) Dioxane—repeatedly frozen to constant freezing

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[1] The authors wish to express their appreciation to Dr. E. Emmet Reid, Research Consultant to the Department, and to Dr. G. B. Taylor, E. I. du Pont de Nemours and Company, for their interest and suggestions in the course of this research.

[2] Abstracted from material presented by Charles W. Smart to the Graduate Faculty of Emory University in partial fulfillment of the requirements for the degree of Master of Science.

[3] Now, respectively, at the University of Texas, Austin, Texas; and the Georgia School of Technology, Atlanta, Ga.

[4] Ebertz and Lucas, THIS JOURNAL, **56**, 1230 (1934).

TABLE I

THE HYDRATION OF ISOBUTENE

Reactions at 100° for 21 days. The equilibrium constants marked + are omitted from the average. Average equilibrium constant from alcohol side = 3.7 × 10. Average equilibrium constant from isobutene side = 4.0 × 10.

| | Original moles | | | | Final moles | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Tube | Water × $10^2$ | Dioxane × $10^2$ | Isobutene × $10^3$ | Alcohol × $10^3$ | Isobutene × $10^4$ | Alcohol × $10^3$ | Water × $10^2$ | $K$ × $10^{-1}$ | % hydration |
| 13 | 1.987 | 1.869 | | 5.570 | 2.760 | 5.294 | 2.015 | 4.3 | 95 |
| 14 | 2.177 | 2.047 | | 6.104 | 2.777 | 5.826 | 2.205 | 4.6 | 95 |
| 15 | 1.809 | 1.701 | | 5.072 | 2.634 | 4.809 | 1.835 | 4.1 | 94 |
| 102 | 3.287 | 0.732 | | 6.139 | 3.303 | 5.809 | 3.320 | 2.5+ | 94 |
| 105 | 3.382 | .753 | | 6.309 | 2.666 | 6.042 | 3.409 | 3.2 | 96 |
| 106 | 3.411 | .761 | | 6.378 | 2.779 | 6.100 | 3.439 | 3.1 | 95 |
| 107 | 3.524 | .785 | | 6.580 | 2.077 | 6.372 | 3.545 | 4.3 | 97 |
| 109 | 3.448 | .768 | | 6.440 | 2.465 | 6.194 | 3.472 | 3.5 | 96 |
| 111 | 3.564 | .795 | | 6.667 | 2.759 | 6.381 | 3.592 | 3.3 | 96 |
| 112 | 3.563 | .794 | | 6.654 | 1.938 | 6.460 | 3.583 | 4.7 | 99 |
| 113 | 3.326 | .741 | | 6.209 | 2.232 | 5.986 | 3.348 | 3.8 | 96 |
| 115 | 3.062 | .682 | | 5.718 | 2.418 | 5.476 | 3.086 | 3.1 | 95 |
| 116 | 3.228 | .719 | | 6.029 | 3.303 | 5.699 | 3.261 | 2.4+ | 94 |
| 117 | 3.090 | .688 | | 5.770 | 1.969 | 5.573 | 3.110 | 4.0 | 96 |
| 118 | 3.556 | .792 | | 6.641 | 2.387 | 6.402 | 3.580 | 3.8 | 96 |
| 119 | 5.255 | 1.170 | | 9.813 | 3.519 | 9.461 | 5.290 | 3.8 | 96 |
| 204 | 4.755 | 1.051 | 1.655 | | 0.884 | 1.567 | 0.895 | 5.5 | 95 |
| 134 | 3.809 | 1.602 | 5.024 | | 2.866 | 4.737 | 3.335 | 2.7+ | 94 |
| 209 | 5.505 | 0.928 | 2.497 | | 0.760 | 2.421 | 0.686 | 8.7+ | 97 |
| 212 | 5.380 | .895 | 1.374 | | 0.831 | 1.290 | 0.766 | 3.6 | 94 |
| 215 | 5.248 | .828 | 1.938 | | 1.116 | 1.826 | 0.645 | 4.2 | 94 |
| 220 | 7.824 | 1.619 | 3.487 | | 1.690 | 3.318 | 1.287 | 5.0 | 95 |

fraction, 11°. (3) Isobutene—generated by dehydration of *t*-butyl alcohol, washed with water and dried over calcium chloride. (4) Trimethylcarbinol—frozen to constant freezing fraction, 25°. (5) Mercuric chloride—commercial C. P. product was recrystallized from distilled water. (6) Carbon tetrachloride—commercial C. P. grade was used.

**Analysis.**—The tubes were held tip down in carbon tetrachloride and the tip broken off, the contents flowing out under the surface of the solvent. The catalyst was removed by washing with water and the remaining material made up to 250 ml. with carbon tetrachloride. Twenty-five milliliter aliquot portions were placed in glass-stoppered bottles and were brominated in the dark for ten minutes by a measured excess of a bromine solution (approximately 0.05 *N* in carbon tetrachloride). After bromination, to each bottle was added 10 ml. (an excess) of a saturated solution of potassium iodide. After shaking, the liberated iodine was titrated at once with sodium thiosulfate (approximately 0.05 *N* previously standardized with weighed samples of the olefin) until colorless with starch indicator. The difference between the thiosulfate for the bromine blank (without olefin) and that for the sample multiplied by the thiosulfate–olefin factor gave the amount of unsaturated material present.

## Discussion of Results

In the table are listed the initial and final values for the number of moles of the various components and also the values of $K$, the equilibrium constant for the hydration of isobutene to trimethylcarbinol, calculated from the mole fractions of olefin, alcohol, water and dioxane.

At 100° the average equilibrium constant from the alcohol side is 3.7 × 10 (omitting tubes 102 and 116), and from the isobutene side is 4.0 × 10 (omitting tubes 134 and 209). Not only are these results in close agreement, but the fact that the values approach and pass each other is valid evidence that equilibrium was reached. The results are also expressed in terms of per cent. hydration of the olefin. An attempt was made to study the reaction at a higher temperature. This was abandoned as polymerization was indicated by discoloration in the tubes and as the values obtained were widely variant.

Several possibilities of error in the measurements at 100° were considered to account for the apparently large experimental error. The possibility of the formation of isobutyl alcohol by the addition of water to the olefin in a reversal of Markownikoff's rule was considered. Esterification experiments to show the presence of a primary alcohol gave no indication of its formation. Errors due to substitution were proved to be negligible by experiments in which isobutene solutions were allowed to stand in contact with the bromine solutions for varying lengths of time. Errors due to polymerization, reaction with the solvent, or other side reactions were discounted for if any such reactions had occurred they would hardly have taken place to the same extent in the tubes starting from the opposite sides of the reaction. The same constant could hardly have been obtained from both sides of the reaction. The difficulty of preparing the tubes containing isobutene as a starting material is an unavoidable contributing factor. Less agreement was obtained in the values approaching the equilibrium from this direction. The largest factor in experimental error is attributed to the free space in the reaction tubes. Unsuccessful attempts were made to determine the amount of unsaturate in this space. The space was kept as small as possible and still prevent explosions. The method of analysis determines the entire unsaturated material in the tube and not in the liquid phase only. The results reported by this method have this inherent small error.

Additional work upon triethylcarbinol and tripropylcarbinol, as yet incomplete, indicates that the constant for trimethylcarbinol is approximately one hundred times as large as that for triethylcarbinol, while the constant for tripropylcarbinol is approximately three times that of the triethylcarbinol.

## Summary

1. The equilibrium constant for the hydration of isobutene at 100° is $3.8 \times 10$.

2. While the constants were obtained, by both hydration and dehydration measurements, in good agreement, the method is subject to an experimental error which cannot be minimized.

3. Preliminary measurements have been made upon triethyl and tripropyl carbinols. The percentage dehydration of tripropylcarbinol is between that of trimethyl- and triethylcarbinols.

EMORY UNIVERSITY, GEORGIA RECEIVED MAY 12, 1941

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

# Association of Benzoic Acid in Benzene

BY F. T. WALL AND P. E. ROUSE, JR.[1]

Several different methods have been used to study association in solution.[2] Among them is the investigation of the distribution of a solute between immiscible solvents. For example, the distribution of benzoic acid between water and benzene is found to be in agreement with the idea that benzoic acid is dimerized in benzene and exists as a monomer in water.[3] From a measurement of the dependence of such a distribution coefficient on temperature, Hendrixson[4] obtained a measure of the heat of dissociation of the benzoic acid dimer. This method, however, was subject to some uncertainties due to the mutual solubilities of the solvents.

Another method, which was employed by Lassettre and Dickinson,[5] involved the distribution of a volatile solvent between two solutions of (practically) non-volatile solutes. In the investigation here reported, a method similar to that of Lassettre and Dickinson was used to study the association of benzoic acid in benzene. The chemical reaction involved is

$$(C_6H_5COOH)_2 \leftrightarrows 2C_6H_5COOH \qquad (1)$$

**Apparatus.**—The isopiestic apparatus used was similar in design to that of Lassettre and Dickinson.[5] Two solution bulbs were joined by an inverted U-tube and each was provided with a calibrated side arm for volume measurements. When the apparatus was in a horizontal position, the solutions rested in the bulbs mentioned, but when the apparatus was rotated through ninety degrees, the solutions drained into their respective side arms.

To speed up the rate of distillation it was necessary, as far as possible, to remove all air from the system. The apparatus was evacuated by pumping through a tube attached to the U-tube, the gases passing through a mercury trap before entering the vacuum line. The mercury trap was present to make visible the rate of evacuation and to prevent too rapid ebullition of solvent with consequent danger of mixing the solutions.

The system was attached to the vacuum line by neoprene tubing which was closed by a heavy brass clamp that also served to regulate the rate of evacuation. Neoprene tubing and a brass clamp were used in place of a glass stopcock because solvent vapor was found to attack the stopcock grease.

Calibration of the graduated side-arms was carried out by weighing the apparatus alone and then with varying amounts of mercury in one arm or the other. In order that the volume readings could be applied to benzene solutions,

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[1] Du Pont fellow in Chemistry, 1940–1941.

[2] See E. N. Lassettre, *Chem. Rev.*, **20**, 259 (1937), for a discussion.

[3] Creighton, *J. Franklin Inst.*, **180**, 63 (1915); Nernst, *Z. physik. Chem.*, **8**, 110 (1891).

[4] W. S. Hendrixson, *Z. anorg. Chem.*, **13**, 73 (1897).

[5] E. N. Lassettre and R. G. Dickinson, THIS JOURNAL, **61**, 54 (1939).