saturated solution of dimedone and left for twenty-four hours. The formaldehyde dimedone derivative was filtered and dried to constant weight (10 mg.). This was equivalent to 26 mg. of formaldehyde in the total solution. The total formaldehyde, if one mole had been split off, should be 59 mg.

The rest of the solution was extracted with ether and the ether extract was dried over anhydrous sodium sulfate. On filtration and removal of the ether, 200 mg. of a colorless oil was obtained. This darkened progressively on keeping. Attempts to characterize the oil, by preparation of crystalline derivatives, were unsuccessful.

Reduction of Methyl Dihydroanhydromonocrotalate with Lithium Aluminum Hydride.—By following the procedure previously described for methyl monocrotalate, 3.2 g. of the ester gave 2.6 g. (93%) of the reduction product as an extremely viscous colorless sirup. A small portion of the product was distilled at 0.05 mm.

Rotation. 0.1259 g. made up to 1 ml. with absolute ethanol at 32° gave α_D +0.44°; *l*, 1; $[\alpha]^{32}_D$ +3.49°.

Anal. Calcd. for $C_8H_{18}O_3$: C, 59.24; H, 11.19. Found: C, 59.10; H, 11.15.

Di-*p*-nitrobenzoate of the Above Compound.—This was prepared by the usual procedure and purified by three recrystallizations from benzene. It formed colorless crystals, m. p. 174° (cor.).

Anal. Calcd. for $C_{22}H_{24}O_9N_2$: C, 57.38; H, 5.25; N, 6.09. Found: C, 57.67; H, 5.36; N, 5.96.

Action of Sodium Metaperiodate on the Lithium Aluminum Hydride Reduction Product from Methyl Dihydroanhydromonocrotalate.—A solution of 506 mg. of the sirup in 5 ml. of water was treated with 14.2 ml. of 0.196 *M* sodium metaperiodate solution and made up to 25 ml. with water. The mixture was shaken vigorously and left for twenty-four hours.

One ml. of the solution was then withdrawn and the excess periodate was estimated by the standard procedure. The amount of periodate consumed was 13.95 ml. (approximately one mole).

One ml. of the solution was employed for estimating the formaldehyde content of the solution. The total formaldehyde in solution was found to be 78 mg. and on the basis of the periodate consumed 82 mg. should be present.

The rest of the solution was added to 0.9 g. of dimedone in 50 ml. of hot water, shaken vigorously and left for twenty-four hours. The yield of dimedone derivative was 736 mg., m. p. 188–189°.

The filtrate was basified with sodium hydroxide solution to phenolphthalein end-point, saturated with sodium sulfate and repeatedly extracted with ether. The ether extract was dried over anhydrous sodium sulfate. After filtration, most of the ether was distilled off. The final portions of the ether were removed by slow evaporation at room temperature. The residue was a colorless oil with a pronounced camphoraceous odor. Attempts to characterize it through preparation of a crystalline derivative were unsuccessfull.

Summary

A study of the reduction of methyl monocrotalate, methyl anhydromonocrotalate and methyl dihydroanhydromonocrotalate with lithium aluminum hydride and the behavior of the reduction products toward sodium metaperiodate, suggests a new structural formula for monocrotalic acid.

Methyl monocrotalate yielded a tetrahydroxy compound, $C_8H_{18}O_4$, whose structure was proved to be 1,2,3,5-tetrahydroxy-2,3,4-trimethylpentane by its cleavage with two moles of sodium metaperiodate to a mixture of formaldehyde, acetic acid and β-methyl-γ-ketobutanol.

The dibenzoate of the tetrahydroxy compound reacted with one mole of lead tetraacetate to yield a mixture of carbonyl compounds which were converted to the 2,4-dinitrophenylhydrazones and separated by chromatography. The derivatives were identified as those of methyl isopropenyl ketone (formed by the elimination of benzoic acid from β-methyl-γ-ketobutanol benzoate) and of acetol benzoate, by comparison with authentic specimens, confirming the structure proposed for the tetrahydroxy compound. Monocrotalic acid is therefore deduced to be α,β,γ-trimethyl-β-hydroxy-γ-carboxy-γ-valerolactone.

Reduction of methyl anhydromonocrotalate and methyl dihydroanhydromonocrotalate gave the trihydroxy compounds $C_8H_{16}O_3$ and $C_8H_{18}O_3$, respectively, both of which reacted with sodium metaperiodate yielding formaldehyde as products of cleavage. Although the other fragments obtained in the cleavage process could not be properly characterized, these observations lend additional support to the newly proposed structural formula for monocrotalic acid.

URBANA, ILLINOIS RECEIVED JULY 25, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Cryoscopic Studies in Methanesulfonic Acid[1]

BY RAYMOND A. CRAIG,[2] A. B. GARRETT AND MELVIN S. NEWMAN*

Cryoscopic investigation of the behavior of oxygenated organic compounds in sulfuric acid has provided useful information.[3,4] In some respects, however, this information is limited because the high acidity of the solvent leads to a leveling effect. Thus compounds differing in intrinsic basicity, such as ether, acetic acid, benzoic acid and methyl benzoate, all yield *i*-factors of two.[3,4]

In order to find out more about the relative basicities of such compounds and many others by cryoscopic measurements, a solvent of lower acid strength is required. A number of such acids have been studied, *e. g.*, acetic,[5] formic,[5] cinnamic,[6]

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* Harvard University Postdoctoral Fellow, 1934–1936.

(1) The material herein presented is taken from the Ph.D. thesis of R. A. C. presented to the Ohio State University, March, 1948.

(2) Standard Oil Company of Indiana Fellow, 1946–1947. Present address: du Pont Experimental Station, Wilmington, Delaware.

(3) See Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 45–48, 53–56 and 277–285.

(4) Newman, Craig and Garrett, THIS JOURNAL, **71**, 869 (1949).

(5) Raoult, *Ann. chim. phys.*, [6] **2**, 66 (1884).

(6) Falciola, *Gazz. chim. ital.*, **52**, I 175 (1922).

mono-,[7] di-[8] and trichloroacetic[9] acids, but all are unsatisfactory to use in studies by the cryoscopic method because of their low dielectric constants. The availability of methanesulfonic and its reported relatively strong acidity prompted us to study its behavior as a cryoscopic solvent.[10] During the course of this work we learned that methanesulfonic acid has a high dielectric constant,[11] a fact that appeared probable at the outset.

Experimental

Procedure.—In general, the apparatus and procedure were the same as have been previously described.[12] The freezing point equipment was modified to provide improved insulation around the acid reservoir so that slower cooling would be effected.

Methanesulfonic Acid.—Methanesulfonic acid received through the courtesy of the Standard Oil Company (Indiana) was purified by distillation and fractional crystallization. The highest freezing point observed was 19.66°.

Solutes.—All solutes were carefully purified and dried prior to use. Physical constants compared favorably with literature values in all cases.

Solute additions were of such magnitude as to raise the molality 0.02–0.05 per addition. From two to four individual additions of solute were made in each run (except triphenylcarbinol with which only one addition was made) leading to final solute concentrations of 0.08–0.15 molal. The maximum deviation of *i* was in most cases within 0.10 of the average value. When greater deviations occurred, sufficient additional determinations were made to establish a reliable *i*-value. In cases where only two solute additions were made the maximum deviation of *i* from the average was less than 0.05.

TYPICAL RUN: PIPERIDINE (MOL. WT. = 85.1), WT. CH_3SO_3H = 56.22 G.

No.	Solute, g.	Δ Molality	F. p., °C.	ΔT	i
1	....	.....	19.658	...	..
2	0.0759	0.01586	19.486	0.172	1.91
3	After two hours		19.484	.174	1.93
4	0.1600	.03344	19.113	.371	1.95
5	.1968	.04113	18.620	.493	2.11
	0.4327	0.09043		1.036	2.01

Data

A. Determination of the Cryoscopic Constant, K_f, of Methanesulfonic Acid.—Nitromethane, picric acid and 1,3,5-trinitrobenzene were used as solutes in the determination of the cryoscopic constant of methanesulfonic acid. All of these have an *i*-factor of one in sulfuric acid. They gave K_f values of 5.69 ± 0.05, 5.66 ± 0.26 and 5.56 ± 0.50, respectively.

The spread in the K_f values obtained using picric acid and 1,3,5-trinitrobenzene was caused by the difficulty with which these high molecular weight materials dissolve in methanesulfonic acid. For this reason the value K_f = 5.69, found in determinations with readily soluble nitromethane, was taken as the best value for the cryoscopic constant.

B. Determination of *i*-Factors in Methanesulfonic Acid.—In the absence of data concerning deviations in cryoscopic constant of methanesulfonic acid with change in freezing point, a simple equation was used

$$i = \Delta T / mK_f$$

TABLE I

i-FACTORS IN METHANESULFONIC ACID

Solute	i	Calculated per cent. ionization
Water	1.60	60
Benzoic acid	1.31	31
2,4,6-Trimethylbenzoic acid	1.50	50
Piperidine	2.01	100
Triethylamine	1.99	99
Propyl alcohol	1.77	77
Trimethylcarbinol	1.72	72
Triphenylcarbinol	3.8	
Tetrahydrofuran	1.73	73
Tetrahydropyran	1.67	67
Methyl ethyl ketone	1.75	75
Cyclohexanone	1.77	77
Cyclopentanone	1.59	59
Dibenzalacetone	1.94	94
Ethyl acetate	1.72	72

Discussion

Before discussing the *i*-factor data, it should be pointed out that *i*-factors intermediate between one and two may be the result of either one or both of two properties: the incomplete proton transfer from the solvent to the solute; or the incomplete dissociation of the ions formed by such proton transfer. The fact that triethylamine and piperidine exhibit *i*-factors of two indicates that methanesulfonic acid is capable of causing complete dissociation of ion pairs. In this paper we assume that complete dissociation of ion pairs occurs.

Inspection of the *i*-factor data reveals that oxygenated organic compounds ionize in methanesulfonic acid. Many compounds that ionize completely in sulfuric acid are only partially ionized in the weaker proton donor methanesulfonic acid, the degree of ionization showing a dependence on basic strength of the solute as would be expected when the ionization is of the acid–base type

$$B + HA \rightleftharpoons BH^+ + A^- \qquad (1)$$

The strong organic bases triethylamine and piperidine exhibit *i*-factors of two, signifying complete proton transfer. Therefore their measured completeness of ionization is a check on the cryoscopic constant and provides evidence that solvent autoionization is insufficient in the range of concentrations studied to cause apparent diminished ionization of the solute.

Nearly the same degree of ionization is observed with all the remaining compounds except dibenzalacetone and the carboxylic acids, implying that the basicities of a wide variety of organic compounds are too nearly alike to allow effective

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(7) Nameli, *Gazz. chim. ital.*, **39**, II, 579 (1909).

(8) Craig, Ph.D. Thesis, The Ohio State University, 1948.

(9) Walden, *Rec. trav. chim.*, **48**, 880 (1929).

(10) We are indebted to Dr. B. Shoemaker, Standard Oil Co. of Indiana, and Professor H. C. Brown, Purdue University, for suggesting methanesulfonic acid.

(11) Private communication from William Heston concerning work done at Princeton University by John D. Hoffman.

(12) Newman, Kuivila and Garrett, THIS JOURNAL, **67**, 704 (1945).

differentiation by the freezing point method. This is unexpected in view of results of several other investigations. According to Hammett's equation[13] two bases which are 60 and 80% ionized in

$$H_0 = pK_a + \log [B]/[BH^+] \qquad (2)$$

the same solvent have pK_a values which differ by only 0.4.

Since compounds as nearly similar as *n*-butyrophenone and isobutyrophenone have pK_a values differing by 0.5 unit in a sulfuric acid–water mixture,[14] it was to be expected that many of the solutes used in our experiments in methanesulfonic acid would show greater differences in *i*-factors than was the case. Nine compounds showed *i*-factors between 1.6 and 1.8, indicating a maximum difference in pK_a of only 0.4 unit. It thus appears that a sort of "leveling effect" is operating in these solutions but more work would be required to elucidate its nature. For this reason methanesulfonic acid proved not to be an ideal solvent for distinguishing between the basicities of organic solutes by cryoscopic measurements. However, one may conclude from our results that organic acids are more weakly basic than ethers, alcohols, ketones and esters, a result which although not surprising could not have been verified by similar studies in sulfuric acid.

The *i*-factors of 2,4,6-trimethylbenzoic acid, dibenzalacetone and propyl alcohol all lie between one and two in contrast to values of four,[15] four[15] and three,[16] respectively, exhibited by these compounds in sulfuric acid. The absence of complex ionization in methanesulfonic acid with compounds which undergo this reaction in sulfuric acid proves that such ionization is not due solely to inherent properties of the conjugate acid of the molecule involved. Triphenylcarbinol has an *i*-factor of approximately four in both solvents.[17]

The *i*-factor of 2,4,6-trimethylbenzoic acid appears to be a function of concentration and temperature. At low concentrations it is about 1.5, well above that of benzoic acid, but decreases to a value of around 1.35 at 0.06 molal concentration and was observed to be as low as 1.10 at a concentration of 0.1 molal. When a 0.04 molal solution was heated to 70° for twenty minutes, the *i*-factor dropped from 1.40 to 1.01. When this solution was heated an additional thirty minutes at 85° the *i*-factor was 0.99. This decrease in *i*-factor was not the result of time effects since solutions with *i*-values of 1.5 were essentially unchanged after standing two hours at room temperature. The *i*-factor of benzoic acid decreased about 0.2 upon standing twelve hours at room temperature; such decreases were observed with no other compounds. We have no explanation for these phenomena.

Dibenzalacetone was included in this study because of its *i*-factor of four in sulfuric acid.[15] It seems noteworthy that its *i*-factor (1.94) is appreciably higher (0.2) than that of the other ketones studied.

The *i*-factor of 1.72 obtained for *t*-butyl alcohol was originally thought to be the result of a 72% ionization into an oxonium salt. Recently, however, Dr. Norman Deno[18] has observed a colorless layer of hydrocarbon polymer on the surface of the acid shortly after adding the alcohol. Accordingly we now interpret the *i*-factor as indicating immediate dehydration of the *t*-butyl alcohol, followed by rapid polymerization of the four-carbon fragment. In a recent paper[4] we discussed the behavior of *t*-alcohols in sulfuric acid in terms of a dissociation of the *t*-alkyl oxonium salts. This explanation is no longer tenable. The facts that *i*-factors of slightly over two are found at first and that the *i*-factors then continue to rise with time to values over five (with *t*-butyl alcohol and triethylcarbinol) are now reasonably explained as follows: the alcohols are immediately dehydrated on adding to sulfuric acid; the water yields an immediate *i*-factor of two and the hydrocarbon fragment polymerizes to an insoluble polymer so rapidly that it adds little to the *i*-factor; oxidation of the polymer layer then causes the slow rise in *i*-factor noted. The picture is essentially the same with methanesulfonic acid, except that no oxidation of the polymer layer occurs.

In our work with sulfuric and methanesulfonic acids two differences in properties have been found which help in explaining the divergent solution properties cited in the paragraphs below:

(1) Sulfuric acid is a much stronger desiccant than methane–sulfonic acid. The initial step in many complex ionizations involves splitting water from the conjugate acid of the solute, suggesting that a solvent's affinity for water is a factor in this reaction.

(2) Sulfuric acid is a stronger acid than methanesulfonic acid. Calculation of H_0 from equation (2) utilizing literature values[14,19] of pK_a and experimental values of $[B]/[BH^+]$ obtained from *i*-factors gives a value for the acidity function of about -6.0 indicating that the acidity of methanesulfonic acid corresponds to that of a solution which is 75% sulfuric acid and 25% water.[20]

Summary

Cryoscopic studies have shown that representa-

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[13] (a) Hammett and Deyrup, THIS JOURNAL, **54**, 2721 (1932); (b) Hammett and Paul, *ibid.*, **56**, 827 (1934).

[14] Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, p. 271.

[15] Treffers and Hammett, THIS JOURNAL, **59,** 1708 (1933).

[16] Oddo and Scandola, *Gazz. chim. ital.*, **39**, II, 1 (1909).

[17] Value in sulfuric acid reported by Hammett and Deyrup, THIS JOURNAL, **55**, 1900 (1933).

[18] Office of Naval Research post-doctoral fellow, 1948–1949. The hydrocarbon layer formed from *t*-butyl alcohol and methanesulfonic acid contains about 60–65% of triisobutylene; that formed from *t*-amyl alcohol about 50% of dimeric olefin; that from methyldiethylcarbinol about 75% dimeric olefin; and that from triethylcarbinol is mainly monomeric olefin.

[19] Gordy and Stanford, *J. Chem. Phys.*, **9**, 204 (1940).

[20] Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, p. 268.

tive ketones, esters, alcohols, ethers, amines and carboxylic acids ionize when dissolved in methanesulfonic acid. Many of these compounds are completely ionized, the degree of ionization being a function of their respective basic strengths. Several compounds which display complex ionization in sulfuric acid have normal *i*-factors in methanesulfonic acid. The *i*-factor of triphenylcarbinol is four in both solvents. Methanesulfonic acid has a cryoscopic constant of 5.69 and an acidity function, H_0, of about -6.0.

COLUMBUS 10, OHIO RECEIVED MAY 31, 1949

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XLV. Conductance of Some Salts in Benzene at Higher Concentrations[1]

BY LAURENCE E. STRONG[2] AND CHARLES A. KRAUS*

I. Introduction

In solvents of high dielectric constant, such as water, the equivalent conductance of normal salts decreases continuously with increasing concentration. In solvents of low dielectric constant, the conductance initially decreases, passes through a minimum and thereafter passes through a maximum. The maximum is due to the rapidly increasing viscosity of the solution. In solvents of intermediate dielectric constant, having values in the neighborhood of 15 or 20, the conductance passes through a minimum for some salts and levels off and then decreases rapidly for others.

The conductance of a number of salts in benzene has been measured by several investigators in this Laboratory.[3,4,5] They found the conductances of different salts to vary over a rather wide range, depending on the constitution of their ions. However, measurements were not carried to high concentrations. It seemed worthwhile, therefore, to measure a number of salts at higher concentrations in order to determine how their conductance is related to various constitutional factors. Accordingly, eight salts were measured up to the limit of their solubility. Two of these, tetraisoamylammonium thiocyanate[3] and triisoamylammonium picrate[4] had been measured earlier at lower concentrations. Tetra-*n*-butylammonium thiocyanate and bromide were measured to compare with tetraisoamylammonium thiocyanate, as was also amyltributylammonium iodide. Dioctadecyldimethyl- and methyltributylammonium thiocyanate were measured for comparison with dioctadecyldibutylammonium thiocyanate. The solubility of the last named salt is rather low; measurements were therefore carried out at 35° as well as at 25° in order to extend these measurements to somewhat higher concentrations. Dioctadecyldimethylammonium thiocyanate was measured at 35° for the same reason.

The densities of solutions of the five most soluble salts were determined in order to be able to express conductances on a volume basis. The viscosity of solutions of tetraisoamylammonium thiocyanate was measured. The dielectric constant of solutions of several salts was measured for the purpose of comparison of molecular polarization values with earlier results.

II. Experimental

1. **Materials.**—Salts were prepared by conventional methods and purified by recrystallization from suitable solvents. The dioctadecyl salts were prepared according to the method of Evers[6] by treating the iodide with the dialkylamine. Octadecyl iodide was heated with dibutylamine at 70° in a sealed tube for a week. The iodide was converted to nitrate with silver nitrate and the nitrate was converted to the thiocyanate by metathesis with potassium thiocyanate in absolute ethanol. The following salts were prepared: tetraisoamylammonium thiocyanate (m. p. 104°); tetra-*n*-butylammonium thiocyanate (m. p. 124°); di-*n*-butyldi-*n*-octadecylammonium thiocyanate (m. p. 83-5°); tri-*n*-butylmethylammonium thiocyanate (m. p. 101°); *n*-amyltri-*n*-butylammonium iodide (m. p. 107°); tetra-*n*-butylammonium bromide (m. p. 118°); triisoamylammonium picrate (m. p. 127°). The sample of dimethyldi-*n*-octadecylammonium thiocyanate was prepared by Dr. E. C. Evers[6] by a method similar to that used for the corresponding butyl derivative.

In computations, the density of benzene was taken to be 0.8737 at 25° and 0.8627 at 35°. The dielectric constant of benzene was taken to be 2.268 at 25°.

2. **Apparatus and Procedure.**—Conductances in the lower resistance range were measured by means of a Jones bridge; high resistances were measured by means of a specially designed, shielded parallel arm bridge constructed by the Leeds and Northrup Company. This bridge was also used in measuring the dielectric constant of several solutions.

Seven different cells were employed varying in design and free volume as well as cell constant. The constants ranged from 0.3 to 0.003. For the more dilute solutions the usual dilution procedure was employed[6a]; for some of the more concentrated solutions the salt was weighed directly into the cell.

Densities of solutions of the more soluble salts were determined with a Westphal balance.

Viscosities of solutions of tetraisoamylammonium thiocyanate were measured with a modified Ostwald viscometer. The solutions were made up in the viscometer.

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* Harvard University Faculty, 1928–1929.

[1] This paper is based on a portion of a thesis presented by Laurence E. Strong in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1940.

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[3] Kraus and Fuoss, THIS JOURNAL, **55**, 21 (1933).

[4] Fuoss and Kraus, *ibid.*, **55**, 3614 (1933).

[5] Luder, Kraus, Kraus and Fuoss, *ibid.*, **58**, 255 (1936).

[6] E. Charles Evers, Thesis, Brown University, May, 1941.

[6a] Mead, Fuoss and Kraus, *Trans. Faraday Soc.*, **32**, 594 (1936).