A mixture of this picrate with that of 6-ethylquinoline melted at 147–150°.

CENTRAL RESEARCH DEPT.
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Metathetical Reactions of Silver Salts in Solution. II. The Synthesis of Alkyl Sulfonates[1]

BY WILLIAM D. EMMONS AND ARTHUR F. FERRIS

RECEIVED JANUARY 2, 1953

Alkyl sulfonates have normally been prepared by the base-catalyzed action of a sulfonyl chloride upon an alcohol.[2] This method is dependent on the availability of the appropriate alcohol and is limited to the preparation of those esters which are not sensitive to base. A less useful method has been the heating of a silver sulfonate with an alkyl iodide.[2] This procedure is severely limited by the

$$RSO_3Ag + R'I \longrightarrow RSO_3R' + AgI$$

heterogeneous reaction conditions employed and the relatively high temperatures frequently necessary to effect complete reaction.

We have been able to make a significant improvement in the preparation of alkyl sulfonates by the silver salt method using acetonitrile as a solvent for the reaction. The silver salts of methanesulfonic acid, *p*-toluenesulfonic acid and benzenesulfonic acid are all extremely soluble in acetonitrile at room temperature. Accordingly, the metathetical reaction between these silver salts and primary alkyl halides may be carried out smoothly under mild conditions and with nearly quantitative yields of esters. The following mesylates were all prepared from silver methanesulfonate and the corresponding alkyl iodides except where noted: methyl mesylate (97% yield), ethyl mesylate (94% yield), butyl mesylate (97% yield), allyl mesylate (96% yield from allyl bromide), methallyl mesylate (81% yield from methallyl chloride), methylene bismesylate (72% yield from methylene iodide) and benzyl mesylate (92% yield from benzyl bromide). Tosylates were prepared by essentially the same procedure: methyl tosylate (77% yield), ethyl tosylate (76% yield), ethylene bis-tosylate (65% yield from ethylene bromide), methylene bistosylate (88% yield from methylene iodide) and benzyl tosylate (52% yield from benzyl chloride). Methyl benzenesulfonate was also prepared in 69% yield from methyl iodide and silver benzenesulfonate.

The reaction of silver sulfonates in solution with secondary and tertiary halides was, as might be expected, of no synthetic value for the preparation of sulfonates. Under these conditions dehydrohalogenation takes place; indeed, from *t*-butyl bromide and silver tosylate the only product isolated was *p*-toluenesulfonic acid.

Experimental[3]

The procedures described herein for allyl mesylate and methylene bis-mesylate are typical of those used for preparation of all the other esters. Physical constants and analytical data are given for those esters which have not been described previously in the literature. The yields reported in the discussion refer in most cases to the distilled product. The silver salts were conveniently prepared by addition of a slight excess of silver oxide to an acetonitrile solution of the sulfonic acid. Evaporation of the solvent gave the silver salts in excellent yield and purity. All melting points and boiling points are uncorrected.

Allyl Mesylate.—To a solution of 10.2 g. (0.05 mole) of silver methanesulfonate in 50 ml. of dry acetonitrile was added 7.3 g. (0.06 mole) of allyl bromide. The mixture was allowed to stand one hour and was then filtered. The solvent was removed at reduced pressure and the liquid residue distilled. There was obtained 6.5 g. (96%) of colorless allyl mesylate, b.p. 45–47° (0.05 mm.), $n^{20}\mathrm{D}$ 1.4435.

Anal. Calcd. for $C_4H_8O_3S$: C, 35.28; H, 5.92; sapn. equiv., 136.2. Found: C, 35.04; H, 5.66; sapn. equiv., 133.0.

Methylene Bis-mesylate.—To a hot solution of 22.3 g. (0.11 mole) of silver methanesulfonate in 100 ml. of acetonitrile was added 26.8 (0.1 mole) of methylene iodide. The solution was stirred at reflux for 20 hours. It was then filtered and the volatile solvent removed at reduced pressure. The solid product was dissolved in 150 ml. of warm ethylene dichloride and then filtered to remove the excess silver methanesulfonate. The solvent was removed by distillation yielding the crystalline product which was recrystallized from ethanol; yield 7.4 g. (72%), m.p. 75–76°.

Anal. Calcd. for $C_3H_8S_2O_6$: C, 17.64; H, 3.95; sapn. equiv., 102.1. Found: C, 17.83; H, 3.87; sapn. equiv., 103.6.

Methallyl Mesylate.—This compound was prepared by heating 10.2 g. (0.05 mole) of silver methanesulfonate and 6.4 g. (0.07 mole) of methallyl chloride in 50 ml. of acetonitrile for one hour; yield 6.1 g. (81%), $n^{20}\mathrm{D}$ 1.4468, b.p. 54–56° (0.02 mm.).

Anal. Calcd. for $C_5H_{10}O_3S$: C, 39.98; H, 6.71; S, 21.35; sapn. equiv., 150.2. Found: C, 40.39; H, 6.60; S, 20.95; sapn. equiv., 151.5.

Benzyl Mesylate.—This ester was prepared from 11.2 g. (0.055 mole) of silver methanesulfonate and 8.5 g. (0.05 mole) of benzyl bromide. The product decomposed on attempted distillation, and the data reported here were obtained from the crude sample; yield 8.6 g. (92%), $n^{20}\mathrm{D}$ 1.5199.

Anal. Calcd. for $C_8H_{10}O_3S$: C, 51.59; H, 5.41; S, 17.22; sapn. equiv., 186.2. Found: C, 52.42; H, 5.51; S, 17.32; sapn. equiv., 183.9.

Methylene Bis-tosylate.—A solution of 14.0 g. (0.05 mole) of silver *p*-toluenesulfonate and 6.0 g. (0.023 mole) of methylene iodide in 50 ml. of acetonitrile was heated under reflux for 24 hours. The product was worked up in the same manner as methylene bis-mesylate. The crystalline solid was recrystallized from absolute ethanol, yield 7.0 g. (87%), m.p. 116–117°.

Anal. Calcd. for $C_{15}H_{16}O_6S_2$: C, 50.55; H, 4.53; S, 17.99; sapn. equiv., 178.2. Found: C, 50.27; H, 4.44; S, 17.61; sapn. equiv., 182.1.

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Estimation of Entropy

BY GEORGE HOOD

RECEIVED SEPTEMBER 30, 1952

Various methods furnish estimates of the standard entropy of a compound with an uncertainty of a few entropy units. A better estimate can be obtained for the members of a substitution series such as CH_4, CH_3Cl, . . . , CCl_4 if the standard entropies of two members are known.

Figure 1 shows that the translational and vibra-

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[1] This work was carried out under Army Ordnance Contract W-01-021-ORD-334.

[2] C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 514.

[3] We are indebted to Mr. Al Kennedy and Miss Annie Smelley for analytical data.

TABLE I

ESTIMATION OF STANDARD ENTROPIES[a] $S^0_{298(g)}$

	σ	X = H S^0(obsd.)	Y = F S^0(calcd.)	X = H S^0(obsd.)	Y = Cl S^0(calcd.)	X = H S^0(obsd.)	Y = Br S^0(calcd.)	X = F S^0(obsd.)	Y = Cl S^0(calcd.)
CX_4	12	44.50	...	44.50	...	44.50	...	62.7	...
CX_3Y	3	53.30	53.43	55.97	56.23	58.74	59.14	...	69.89
CX_2Y_2	2	...	58.17	64.68	63.80	70.16	69.62	...	72.90
CXY_3	3	...	62.53	70.86	70.95	79.18	79.68	74.06	75.51
CY_4	12	62.7	...	73.95	...	85.6	...	73.95	...

[a] All of the observed entropy values were taken from the National Bureau of Standards, Circular 500, Washington, D. C., 1952.

tional contributions when added together become an approximately linear function of the composition of the compound. The rotational entropy contribution, however, deviates considerably from linearity since it depends on the symmetry number σ, of the various molecules. The symmetry number arises through the term $- R \ln \sigma$ in the equations for the evaluation of the rotational entropy by statistical thermodynamics.

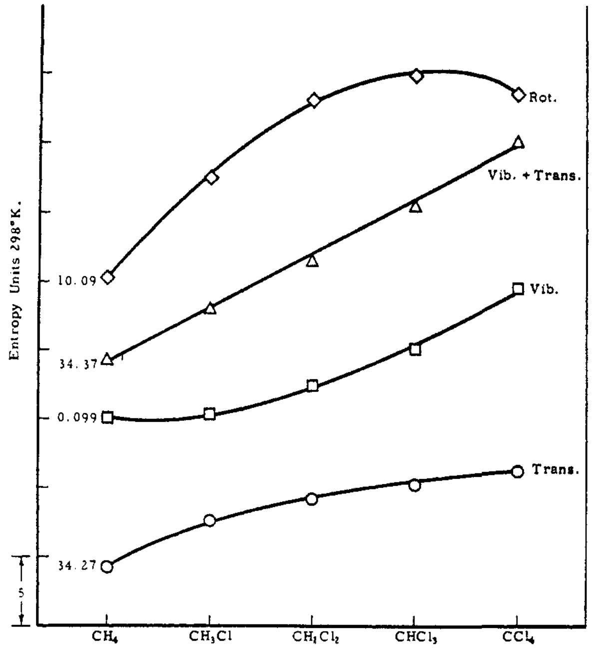

Fig. 1.—Contributions to the standard entropy S°_{298}(g).

Consequently, linear interpolation of $S^0(g) + R \ln \sigma$ leads to satisfactory agreement with observed values for the type of series herein considered (Table I). The average deviation between observed and calculated values for the compounds in Table I is 0.5 entropy unit.

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Distribution of 8-Quinolinol between Water and Chloroform as a Function of pH

BY THERALD MOELLER AND FRED L. PUNDSACK

RECEIVED DECEMBER 20, 1952

The extensive use of 8-quinolinol as an analytical reagent is dependent upon its ability to form with many metal ions water-insoluble chelates which are applicable to both gravimetric and colorimetric determinations. For determinations of the latter type, a number of procedures based upon extraction of metal ions from aqueous solutions into chloroform solutions of 8-quinolinol and subsequent spectrophotometric examinations of the extracts have been proposed.[1-6] These extractions are dependent upon the pH of the aqueous phase, and their usefulness is limited somewhat by the concentration of free 8-quinolinol in the chloroform phase, a large excess of free 8-quinolinol interfering markedly with spectrophotometric determinations of the metal chelate concentrations. Inasmuch as the quantity of 8-quinolinol in the chloroform phase is itself pH dependent, it would help in establishing optimum conditions for quantitative extraction of metal chelates to evaluate the distribution of the reagent between water and chloroform as a function of pH.

From concentration measurements at 18°, Lacroix[2] has calculated a distribution coefficient

$$c_{CHCl_3}/c_{H_2O} = 720 \qquad (1)$$

for molecular 8-quinolinol. In addition, he has evaluated a theoretical distribution curve, based upon data for two extractions, which shows extraction into chloroform to be complete in the pH range *ca.* 4–11, but has offered only limited experimental support. No equilibrium studies on this distribution appear to have been made.

Experimental

Reagents.—The 8-quinolinol was an Eastman Kodak Co. product which had been recrystallized from ethanol. Other chemicals were of reagent quality.

Apparatus.—Spectrophotometric measurements were made with a Beckman model DU spectrophotometer. A Beckman model G pH meter, the glass electrodes of which were calibrated frequently against suitable buffers, was used for all pH measurements.

Procedure.—Twenty-five ml. portions of a chloroform solution of accurately known 8-quinolinol concentration were agitated with 25-ml. volumes of aqueous solutions of known pH values in a constant temperature bath at 25.0 ± 0.1°. The concentration of the original chloroform solution was determined spectrophotometrically, using the 3154 Å. absorption peak of 8-quinolinol in this solvent.[7] The pH of the aqueous phase was adjusted by using sulfuric acid, sodium acetate and sodium hydroxide as required.

Contact between aqueous and chloroform phases for 24 hours was shown to be sufficient to ensure complete concentration equilibration. After a 24-hour contact period in each instance, the total 8-quinolinol content of the aqueous phase was determined spectrophotometrically on an aliquot, using the light absorption at 2505 Å. for acidic solu-

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