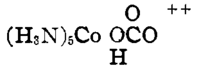
A conclusion about mechanism which applies to the results for $CO_3^=$ attached as a chelate, bound at one position, or not bound at all, is that there is no transfer of oxygen from the solvent to C at any stage on the release of CO_2. Thus it seems likely that the activated complex which in the case of $Co(NH_3)_5CO_3^+$ has the composition $Co(NH_3)_5CO_3H^{++}$, does not have the structure reasonable for this complex ion, but rather has the proton on the oxygen bridging cobalt and carbon



$$(H_3N)_5Co\underset{H}{O}\overset{O}{C}O^{++}$$

Since new Co(III) bonds are established during the release of CO_2 from $Co(NH_3)_4CO_3^+$, it will be of interest to learn whether groups besides water (*e.g.*, Cl^-, $SO_4^=$) can enter during this rapid process. It was this possibility that attracted interest to the aquation of $Co(NH_3)_5CO_3^+$, but could not be realized in this reaction since oxygen is left attached to Co(III).

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Some Esters of Unsaturated Acids

BY V. SATTA,[1] M. L. FEIN AND E. M. FILACHIONE

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In connection with a study of the preparation of co-polymers of acrylic esters, various esters of unsaturated acids (listed in Table I) were required. Though several of these esters are available commercially, their physical properties are either not found in the permanent chemical literature or these are insufficiently reported. *n*-Butyl maleate[2,3] and fumarate[2,3] and 2-chloroethyl maleate[4] and fumarate[5] have been most completely reported; for butyl fumarate, however, the previously reported constants and those of this paper are not in good agreement. The patent literature reports only the boiling point of 2-ethylhexyl maleate,[3] and the refractive index for *n*-butyl aconitate[6] and 2-ethylhexyl aconitate.[7] This paper reports the preparation, boiling point, refractive index and density of various esters of several unsaturated acids.

Experimental

Samples of 2-chloroethyl crotonate, butyl maleate, 2-ethylhexyl maleate, butyl itaconate, butyl aconitate and 2-ethylhexyl aconitate were available commercially; these were redistilled and the constants determined.

The other esters of Table I were prepared by the usual esterification procedure, glass equipment with ground glass joints being employed.[8] A mixture of acid or anhydride, an excess of the alcohol, sulfuric acid catalyst and entraining agent was refluxed, and water was continuously removed in a separating trap. Benzene or toluene was used as the entraining agent except in the preparation of the butyl esters, in which the excess of butyl alcohol served as the entraining agent. After esterification was complete, the catalyst was neutralized with sodium acetate, and the ester isolated by vacuum distillation. A 35-mm. by 50-cm. Vigreux or an alembic-type still,[9] mounted to permit agitation of the still pot contents, was used in the distillation. Center fractions were collected for determination of the various constants. Results are shown in Table I.

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TABLE I

PROPERTIES OF SOME ESTERS OF UNSATURATED ACIDS

Ester	Yield, %	B.p., °C.	B.p., mm.	$n^{20}D$	d^{20}_4	Carbon, % Found	Carbon, % Calcd.	Hydrogen, % Found	Hydrogen, % Calcd.	Chlorine, % Found	Chlorine, % Calcd.	Sapn. equiv. Found	Sapn. equiv. Calcd.
2-Chloroethyl crotonate[a]		58–60	3.5	1.4599	1.1185					23.72	23.86		
n-Butyl maleate[a]		124–125	3.4	1.4451	0.9964								
n-Hexyl maleate	97	127	0.7	1.4499	.9583	68.20	67.57	10.48	9.92			142.1	142.2
2-Ethylhexyl maleate[a]		156	0.7	1.4548	.9437								
2-(2-Chloroethoxy)-ethyl maleate	86	197	1.0	1.4858	1.2738					21.70	21.54		
n-Butyl fumarate	80	117	2.5	1.4429	0.9775	63.12	63.13	8.77	8.77			113.9	114.1
2-Ethylhexyl fumarate	87	160	0.5	1.4570	0.9398	70.53	70.55	10.58	10.66			171.4	170.2
2-(2-Chloroethoxy)-ethyl fumarate	83	182	0.3	1.4863	1.2673					21.83	21.54		
n-Butyl chloromaleate	83	112	1.2	1.4558	1.0756	54.86	55.10	7.29	7.23	13.50	13.31		
2-Chloroethyl chloromaleate	75	138	1.2	1.4983	1.4047					38.44	38.60		
n-Butyl itaconate[a]		82	0.2	1.4450	0.9839								
n-Butyl aconitate[a]		155	.5	1.4553	1.0184								
2-Ethylhexyl aconitate[a]		170[b]	.07[b]	1.4620	0.9589								

[a] The commercially available esters were redistilled. [b] Distilled in an alembic-type still.

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[1] Foreign trainee from Italy.

[2] G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, 658 (1948).

[3] W. O. Kenyon and C. C. Unruh, U. S. Patent 2,448,531, September 7, 1948.

[4] M. E. Synerholm and A. Hartzell, *Contrib. Boyce Thompson Inst.*, **14**, 79 (1945); *C. A.*, **40**, 669 (1946).

(5) D. Vorländer, *Ann.*, **280**, 200 (1894).

(6) P. M. Kirk, U. S. Patent 2,375,563, May 8, 1945.

(7) E. R. Meincke, U. S. Patent 2,475,629, July 12, 1949.

(8) P. A. Shearer and A. M. Pardee, *Proc. S. Dakota Acad. Sci.*, **15**, 24 (1935); *C. A.*, **30**, 2550 (1936).

(9) W. P. Ratchford and C. E. Rehberg, *Anal. Chem.*, **21**, 1417 (1949).

(10) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

Sulfatoalkyl Amines

BY WILSON A. REEVES AND JOHN D. GUTHRIE

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Although a number of investigators have reported the preparation and use of 2-aminoethyl sulfuric acid[1,2] other aminoalkyl sulfates have received very little attention. Apparently, most interest in these sulfates has been for the production of

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[1] Sigmund Fränkel and Martha Cornelius, *Ber.*, **51**, 1654 (1918).

[2] John D. Guthrie, *Textile Research J.*, **17**, 625 (1947).

TABLE I

SULFATOALKYL AMINES

Name (formula)	M.p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found	Potassium, % Calcd.	Potassium, % Found	Chloride, % Calcd.	Chloride, % Found
Sulfatoalkyl ethylenediamine hydrochloride ($HO_3SOCH_2CH_2NHCH_2CH_2NH_2 \cdot HCl$)	192	12.70	13.19	14.53	14.20			16.07	16.18
2-Sulfato 1,3-diaminopropane hydrochloride [$H_2NCH_2CH(OSO_3H)CH_2NH_2 \cdot HCl$]	270	13.56	13.71	15.52	15.00			17.17	17.20
Potassium (disulfatoethyl)-amine monohydrate ($KO_3SOCH_2CH_2NHCH_2CH_2OSO_3H \cdot H_2O$)	127.5	4.37	4.36	19.90	19.73	12.17	12.16		
1-Sulfato-2-diethylaminopropane [$HO_3SOCH_2CH(CH_3)N(C_2H_5)_2$]	228.5	6.60	6.61	15.08	14.85				
2-(2-Sulfatoethyl)-pyridine ($HO_3SOCH_2CH_2NC_5H_4$)	167	6.90	6.73	15.76	15.31				
2-Sulfatoethyldimethylamine hemihydrate [$HO_3SOCH_2CH_2N(CH_3)_2 \cdot {}^1/_2H_2O$]	Anh. 253	7.90	7.90	18.05	18.15				
3-Sulfatopropylamine ($HO_3SOCH_2CH_2CH_2NH_2$)	230.5	9.03	8.97	20.65	20.71				

either ethylenimine or substituted ethylenimines by the method of Wenker[3] or similar methods.[4] Saunders[5] prepared a number of sulfuric acid esters of the simple monohydroxyethylarylamines. Aminized cotton is produced by allowing 2-aminoethylsulfuric acid to react with cotton in the presence of sodium hydroxide.[6] A number of other sulfatoalkyl amines, some of which have not previously been reported, were made (see Table I) for use in determining their reactivity with cotton and evaluating the chemically modified cottons produced by such reactions.

In each case the sulfates were prepared from the corresponding aminoalkyl alcohol by allowing the alcohol to react with chlorosulfonic acid in carbon tetrachloride. With carbon tetrachloride as the solvent or as the suspending agent the solution or the mixture is stirred and maintained near 0°. A cooled mixture of chlorosulfonic acid in carbon tetrachloride is initially added dropwise and later aliquot additions are increased as the reaction becomes less vigorous. Under these conditions there is no charring, and the product separates out either as a viscous liquid or a granular mass. The monosulfato monoamines may be obtained as inner salts, and the monosulfato diamines are easily isolated as hydrochlorides, whereas the disulfato monoamines are readily crystallized as monosodium or potassium salts. These crystalline products generally contain some free sulfate ion, but this contamination can easily be removed by crystallizing from an appropriate aqueous ethanol solution. When the hydrochloride is to be crystallized, the ethanol solution should be acidified with hydrochloric acid.

Since the sulfation of each alcohol was carried out under similar conditions, only one typical preparation will be described.

Experimental

Potassium Acid Disulfatoethyl Amine.—Diethanolamine (210 g.) suspended in 270 ml. of carbon tetrachloride was cooled to near 0° in an ice-salt-bath. Chlorosulfonic acid (466 g.) was added to the cool diol while stirring. At first the addition of chlorosulfonic acid was dropwise and slow; the later additions were larger and more rapid. After all the chlorosulfonic acid had been added, the mixture was removed from the cooling bath and stirred until the contents reached about room temperature. Much of the liberated hydrochloric acid had been removed at this stage. The crude granular disulfato compound separated out as an extremely deliquescent material. The neutral potassium salt was made by dissolving the acid in 500 ml. of water, then adding 30% potassium hydroxide in 50% ethanol until the solution had a *p*H of 7–8. Three liters of 95% ethanol was stirred in and when cooled, 550 g. (86% yield) of potassium acid disulfatoethyl amine separated. To get a highly purified sample, a portion of the above material was dissolved in a minimum of hot 67.5% ethanol and allowed to crystallize slowly.

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[3] Henry Wenker, THIS JOURNAL, 57, 2328 (1935).

[4] H. Schlapfer and A. Margot, U. S. Patent 2,558,273 (1951).

[5] K. H. Saunders, *J. Chem. Soc.*, 121, 2667 (1922).

[6] Wilson A. Reeves and John D. Guthrie, *Textile Research J.*, in press.

[7] One of the Laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

The Electrical Effect of the Trimethylsilyl Group. II.

BY JOHN D. ROBERTS AND CLARE M. REGAN

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In an earlier investigation,[1] we presented evidence based on Hammett[2] σ-constants that the trimethylsilyl [$(CH_3)_3Si-$] group is electron-donating in character as judged by the manner in which it influences the acidity of the carboxyl group in benzoic acid. Since the electrical influence of the group is not apparently clear-cut in other types of compounds[3] we have reinvestigated the reactivities of the trimethylsilyl substituted benzoic acids and have prepared the corresponding ethyl esters and determined their alkaline saponification rates.[4]

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[1] J. D. Roberts, E. A. McElhill and R. Armstrong, THIS JOURNAL, 71, 2923 (1949).

[2] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chap. VII.

[3] H. Soffer and T. DeVries, THIS JOURNAL, 73, 5817 (1951).

[4] We have confined our attention to the acids and esters since Dr. R. A. Benkeser of Purdue University has measured the reactivities of a number of amine derivatives. ADDED IN PROOF.—R. A. Benkeser and H. R. Krysiak, *ibid.*, 75, 2421 (1953). The results of these investigators with benzoic acid derivatives are in good agreement with those given in Table II.