[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, COLUMBIA UNIVERSITY, AND FROM THE DEPARTMENT OF CHEMISTRY, THE CITY COLLEGE, COLLEGE OF THE CITY OF NEW YORK]

The Synthesis of the Sodium Salt of Tetradecamethylene Disulfonic Acid

BY GILBERT C. H. STONE

In a previous paper by the author,[1] a method for the synthesis of the sodium salts of alkane-α,ω-disulfonic acids by means of the Strecker reaction[2] was described. In each run the reaction had been followed by means of an argentometric titration of aliquot portions of the reaction mixture. And in each case the reaction was found to go to completion if given sufficient time. Table I gives the number of carbons in the alkane-α,ω-disulfonate and a rough estimate of the time for complete conversion.

TABLE I

Carbons	Time for complete conversion, hrs.
2	12
3	18
4	24
5	36
6	60
10	168

It can be inferred that for the preparation of higher members of this series, by means of the same method, an unduly long period of heating would be required. Reactions of this nature have been carried out successfully in short periods of time by using an autoclave to obtain high temperatures.[3,4,5] In order to obviate the use of the autoclave, which is inconvenient in the preparation of large quantities of material, other methods were sought.

A solvent in which both the initial materials are soluble was employed. The dibromide reacted with various simple sulfur-containing compounds yielding terminal carbon–sulfur linkages. In most cases such substances can be oxidized to the sulfonic acid stage. Because of the possibility of forming sulfides, which would yield sulfones upon oxidation, the synthesis of mercaptans was avoided. Preparation of a dithiocyanate met with no success. A dixanthate, however, could be made and oxidized to the sulfonic acid. The following synthesis of the sodium salt of tetradecamethylene disulfonic acid serves as an example of the method whereby the higher homologs of this series may be prepared.

Experimental Part

Tetradecamethylene Glycol.—This was prepared by means of the Grignard reaction from decamethylene dibromide[1] and ethylene oxide, by an adaptation of the method of Dreger.[6] After washing, drying and then vacuum distilling the crude glycol, the properties checked fairly well with those reported by P. Chuit.[7] The yield was 40% of the theoretical amount.

Tetradecamethylene Dibromide.—290 g. (1.26 moles) of the above glycol was treated with gaseous anhydrous hydrogen bromide according to the method of Ruhoff, Burnett and Reid.[8] The resulting dibromide, dissolved in twice its weight of ethylene chloride, was washed and then dried over calcium chloride. After decolorizing with Norite and then removing the solvent, the residue was distilled *in vacuo* and the fraction coming over at 172–175° under 2–3 mm. pressure was collected. The yield was 65% of the theoretical.

Anal. Calcd. for $C_{14}H_{28}Br_2$: C, 47.18; H, 7.93. Found: C, 47.60; H, 7.78.

Sodium Tetradecamethylene Disulfonate.—A solution of 402 g. (one mole) of tetradecamethylene dibromide in 2 liters of hot ethyl alcohol was added slowly to a solution of 480 g. (3 moles) of potassium ethylxanthate in 2 liters of ethanol. The mixture was refluxed with stirring for twenty-four hours. After completely removing the alcohol by distillation, the residual yellow liquid was dissolved in a minimum quantity of ether, well washed with water, and dried with calcium chloride. After removal of the ether, the residual yellow liquid was taken up in redistilled dioxane, and water added until a slight turbidity resulted; 2720 g. (17 moles) of bromine and 1000 ml. of water were added in alternate small portions with shaking. After several hours, excess bromine was removed on a steam-bath, and finally hydrogen bromide and other volatile substances were driven off under reduced pressure by repeated distillations. The liquid remaining was diluted with water and an aqueous solution of silver nitrate added until no more silver salts precipitated. The suspension was brought to a boil and filtered hot. In order to remove any of the silver disulfonate, which is soluble in hot water, from the silver bromide, the precipitate on the Buchner funnel was extracted repeatedly with boiling water. After combining the filtrates and evaporating down to incipient precipitation, the solution was allowed to cool. The silver salt was filtered off and washed with cold water. Further evaporation of the resulting filtrate gave another crop of crystals.

---

(1) Stone, THIS JOURNAL, **58**, 488 (1936).

(2) Strecker, *Ann.*, **148**, 90 (1868).

(3) Reed and Tartar, THIS JOURNAL, **57**, 570 (1935).

(4) Norris, *J. Chem. Soc.*, **121**, 2161 (1922).

(5) Collins, Hilditch, Marsh and MacLeod, *J. Soc. Chem. Ind.*, **52**, 272T (1933).

(6) Dreger, "Organic Syntheses," Coll. Vol. I, p. 299.

(7) Chuit, *Helv. Chim. Acta*, **9**, 264 (1926).

(8) Ruhoff, Burnett and Reid, THIS JOURNAL, **56**, 2784 (1934).

The silver disulfonate was suspended in water, and the silver removed as the sulfide. The yellowish brown filtrate was evaporated down to 2000 ml., exactly neutralized with sodium hydroxide, and concentrated to incipient crystallization. The sodium salt of tetradecamethylene disulfonic acid crystallized out in the ice-box overnight. Several crops of the salt were so obtained. The crystals were purified by dissolving them in a minimum of hot water and adding twice the volume of redistilled acetone. This process of purification was repeated five times. The resulting crystals were white with a slight grayish cast and were not very soluble in water. A solution of the salt was neutral to alizarin. Like the other sodium disulfonates,[1] it showed no tendency to hydrolyze. The yield was 54% of the theoretical.

Anal. Calcd. for $NaO_3S(CH_2)_{14}SO_3Na$: C, 41.76; H, 7.01; Na, 11.43. Found: C, 41.74; H, 6.99; Na, 11.48.

The author wishes to express his thanks to Prof. H. T. Clarke of Columbia University for his kind advice and help during the course of this work; and to Mr. W. Saschek for performing the analyses.

Summary

A method for the preparation and purification of the sodium salts of the higher members of the series of the alkane-α,ω-disulfonic acids has been described. Details were given in regard to the synthesis and properties of the sodium salt of tetradecamethylene disulfonic acid.

NEW YORK, N. Y. RECEIVED NOVEMBER 20, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CITY COLLEGE, COLLEGE OF THE CITY OF NEW YORK, AND FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, COLUMBIA UNIVERSITY]

The Activity Coefficient of Thallous Iodate in Solutions of Alkane-α,ω-disulfonates

BY GILBERT C. H. STONE

The alkane-α,ω-dicarboxylic acids have been studied extensively by Gane and Ingold,[1] Greenspan,[2] and others, with the view of ascertaining the fine structure and dimensions of the aliphatic chain in such molecules. Their results, which indicate that the chain has a rigidly extended zigzag configuration, check well with X-ray data.[3,4,5] These compounds are weak acids, not completely dissociated in aqueous solution. They do not lend themselves to studies, such as activity coefficient measurements from solubility data, which are made on the basis of theories developed on the assumption of complete dissociation. Strong dibasic acids of similar structure would be necessary. With this in mind, a series of alkane-α,ω-disulfonic acids with from one to fourteen carbons were prepared by the author.[6,7] Titration curves of these acids indicated that they are at least as strong as sulfuric acid.

It was desired to determine the qualitative and, if possible, the quantitative effect which would be obtained by increasing the distance between the two strongly polar groups; and the saturated straight aliphatic chain seemed ideal as a separating medium, especially since its normal length and diameter are known. It was hoped that by increasing the distance of separation of these polar groups a point might be found where the molecule ceased to behave as bivalent or dibasic and perhaps functioned as two univalent ions. A study of this nature might throw some light on the structure of large-sized multicharged ions, such as the proteins, which behave as multivalent ions despite the relatively large distances which separate the charged groups.[8]

By taking advantage of the Debye–Hückel relationship

$$-\log \gamma_{\pm} = \frac{0.5056\sqrt{\mu}}{1 + a \times 0.3286 \times 10^8 \sqrt{\mu}} \text{ at } 25^\circ$$

and that $\log S/S_0 = -\log \gamma_{\pm}$, solubility measurements seemed one way of attacking the problem. The "a" value gives an estimate of the *average* ion parameter. While the *average* distance of closest approach might not be expected to check with the actual size of the alkane-α,ω-disulfonate ion, as other ions are present in the solution, nevertheless, since these other ions remain the same, qualitatively and quantitatively, throughout the series of measurements, the a value should increase as the chain length increases.

In the calculations of the ionic strength

$$\mu = \frac{1}{2}\Sigma m_i z_i^2$$

---

(1) Gane and Ingold, *J. Chem. Soc.*, 1594 (1928); 2267 (1928); 1691 (1929); 1375 (1930).

(2) Greenspan, *Chem. Rev.*, **12**, 339 (1933).

(3) Bragg and Bragg, "X-Ray and Crystal Structure," G. Bell and Sons, Lockerbie, Scotland, 1925, p. 294.

(4) Muller, *Proc. Roy. Soc.* (London), **114**, 542 (1927).

(5) Caspari, *J. Chem. Soc.*, 3289 (1928).

(6) Stone, THIS JOURNAL, **58**, 488 (1936).

(7) Stone, *ibid.*, **62**, 571 (1940).

(8) Stone and Failey, *J. Phys. Chem.*, **37**, 935 (1933).