

induction-period region, is greater than this. The relative increase, therefore, would be less than  $10^2$ , and this probably is not enough to cause a shift in the induction-period reaction from the characteristics of a univalent ion reaction to those of a bivalent ion reaction.

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### The Molar Refraction of Sulfonyl Chlorides

BY EDWARD F. LANDAU<sup>1</sup>

Except for the early work of Nasini,<sup>2</sup> there is little published information regarding the molar refraction of tetravalent compounds of sulfur. In a previous publication,<sup>3</sup> we evaluate the molar refraction of the  $-\text{SO}_2\text{O}-$  group in a series of ethylenesulfonic esters. This value was  $9.7 \pm 0.2$ .

In the course of this investigation several liquid aliphatic sulfonyl chlorides were prepared. Their molar refractions were determined and the value of the sulfonyl chloride group compared with two other liquid sulfonyl chlorides. The molar refraction of the sulfonyl chloride group as determined from the five compounds listed, is  $15.40 \pm 0.07$ .

TABLE I

MOLAR REFRACTION OF SULFONYL CHLORIDES

Compound	°C. B. p.,	Mm.	$n_D^{20}$	$d_4^{20}$	$M_D^a$ (obs.)	$M_D-\text{SO}_2\text{Cl}^b$
2-Bromoethanesulfonyl chloride <sup>c</sup>	82	5	1.5227	1.894	33.44	15.31
2-Chloroethanesulfonyl chloride	68	5	1.4920	1.555	30.72	15.52
Ethylenesulfonyl chloride	52-56	10	1.4686	1.393	25.31	15.45
Benzenesulfonyl chloride			1.5505 <sup>e</sup>	1.378 <sup>e</sup>	40.73	15.35
<i>i</i> -Butylenesulfonyl chloride <sup>d</sup>	68-70	8	1.4779	1.2704	34.43	15.36

<sup>a</sup> "Landolt-Börnstein Tabellen," Vol. II, p. 986, Bruel values. <sup>b</sup> Evaluated by difference. <sup>c</sup> Marvel, Bailey and Sparberg, *THIS JOURNAL*, **49**, 1833 (1927). <sup>d</sup> Suter, Malkemus and Archer, *ibid.*, **63**, 1596 (1941). <sup>e</sup> At 23°.

### Experimental

**Ethylenesulfonyl Chloride.**—Powdered phosphorus pentachloride (22 g.) was added in small portions to a rapidly agitated suspension of 12.5 g. ammonium ethylenesulfonate<sup>3</sup> in 100 ml. of chloroform. The temperature of this suspension was maintained at 30-40° for two hours. The chloroform was removed by distillation and the residue dissolved in 50 ml. of ether. After three washings with 50-ml. portions of water, the ethereal solution was dried and distilled. Two fractions were obtained. Fraction I, 4 g.; b. p. 52-56° (1 mm.);  $n_D^{20}$  1.4686;  $d_4^{20}$  1.393.

*Anal.* Calcd. for  $\text{C}_2\text{H}_3\text{O}_2\text{ClS}$ : S, 25.34; sapn. equiv., 63.3. Found: S, 25.62, 25.51; sapn. equiv., 64.5. Fraction II, 4 g., b. p. 70-72° (5 mm.);  $n_D^{20}$  1.4740;  $d_4^{20}$  1.439; sapn. equiv., 67.7. This fraction was possibly a polymeric vinyl sulfonyl chloride.

CHEMICAL LABORATORY  
POLYTECHNIC INSTITUTE OF BROOKLYN  
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(1) Present address: Celanese Corporation of America, Newark, New Jersey.

(2) Nasini, *Ber.*, **15**, 2844 (1882).

(3) Whitmore and Landau, *THIS JOURNAL*, **68**, 1797 (1946).

### 4-Quinolinemethanol

BY S. F. MACDONALD

As lepidine undergoes a condensation of the Mannich type with an aldehyde and an amine,<sup>1</sup> 4-quinolinemethanol was prepared in the hope that it would do likewise. Unfortunately, we have been unable to condense it with cotarnine or with formaldehyde and piperidine. Such a condensation would have provided an attractive theory as to the biogenesis of the cinchona alkaloids: a Mannich condensation between 4-quinolinemethanols and one<sup>2</sup> of the stereoisomeric aldehydes of meroquinene; the latter possibly formed from 6-keto-decahydroisoquinoline, by a photolytic reaction analogous to the conversion of cyclohexanone into hexenal.<sup>3</sup>

The preparation of quinoline-4-aldehyde<sup>4</sup> was modified to eliminate difficulties due to bumping and the tedious steam distillation; using acetic acid as solvent we got the same yields with freshly prepared and with year-old selenium dioxide.

### Experimental

**Quinoline-4-aldehyde (Anhydrous).**—A mixture of 40 g. of lepidine, 400 ml. of acetic acid, and 80 ml. of acetic anhydride was stirred at 85-90° and 45 g. of powdered selenium dioxide added over one and a quarter hours. The mixture was heated one and a half hours longer, cooled and filtered. The filtrate was treated with

70 ml. of concentrated hydrochloric acid, allowed to stand at 10° overnight and filtered. The aldehyde in the filtrate was isolated by steam-distilling off the excess acetic acid, neutralizing the remainder with sodium hydroxide then magnesium oxide, and distilling the aldehyde over in steam. The hydrochloric acid precipitate, containing most of the aldehyde, was dissolved in water, filtered, treated with excess sodium hydroxide and the aldehyde filtered off. The two lots of aldehyde were combined, dehydrated by heating *in vacuo* in the distilling flask and distilled *in vacuo*, collecting at 98-108° (ca. 0.1 mm.); yield 50-60%, m. p. 48-49° (uncor.).

**Quinoline-4-methanol.**—A mixture of 30 g. of quinoline-4-aldehyde, 200 ml. of anhydrous *i*-propyl alcohol, and 6.3 g. of aluminum *i*-propylate was distilled slowly through a Widmer column until the temperature at the top of the column rose to 82°, the volume being kept constant by the occasional addition of *i*-propyl alcohol. Thirty ml. of water was then added to the contents of the flask, and water and *i*-propyl alcohol removed by heating *in vacuo*.

(1) Heou-Feo, *Bull. soc. chim.*, [5] **2**, 96 (1935).

(2) King, *J. Chem. Soc.*, 523 (1946).

(3) Ciamician and Silber, *Ber.*, **41**, 1071 (1908).

(4) Kwartler and Lindwall, *THIS JOURNAL*, **59**, 524 (1937); Kaplan, *ibid.*, **63**, 2654 (1941).