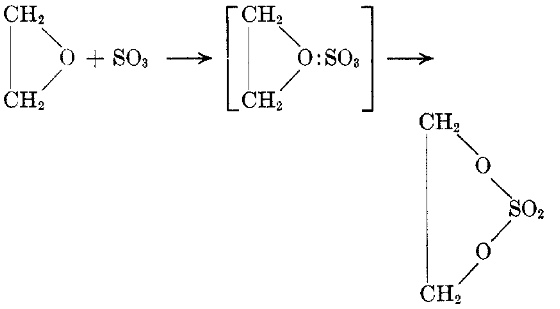
Reaction of Ethylene Oxide with Sulfur Trioxide

G. E. Ham

Received November 30, 1959

The reaction of certain aliphatic ethers with sulfur trioxide has been found to result in formation of the corresponding dialkyl sulfate. For example, Suter and Evans[1] report a yield of 85 to 90% of bis-(2-chloroethyl) sulfate from bis(2-chloroethyl) ether and sulfur trioxide. They describe the reaction as proceeding through the formation of the ether coordination compound which undergoes rearrangement to the sulfate on heating. Should it be possible to form the sulfur trioxide–ethylene oxide coordination compound, one might expect this to rearrange easily to the five-membered ring compound, ethylene sulfate.



(I)

Ethylene oxide was treated with sulfur trioxide under a variety of conditions in an attempt to prepare ethylene sulfate. The only reaction system which did not result in excessive charring involved the use of 1,4-dioxane–sulfur trioxide addition compound in 1,4-dioxane. When one mole of ethylene oxide was treated with one mole of sulfur trioxide in 1,4-dioxane, a homogeneous solution was obtained which when mixed with cold water gave no acid. Removal of the solvent *in vacuo* gave a slightly colored, very viscous liquid. All attempts to crystallize this material failed. However, a 9.5% yield of the expected white crystalline ethylene sulfate could be sublimed *in vacuo* from the viscous liquid. On continued heating the heavy viscous liquid decomposed.

EXPERIMENTAL

To 200 ml. of dry redistilled 1,4-dioxane was added dropwise with cooling and stirring 19.3 g. (0.242 mole) of sulfur trioxide. By careful control of the temperature (*ca.* 10°) and rate of addition the sulfur trioxide could be added without charring. During addition the dioxane–sulfur trioxide addition compound precipitated from solution. After addition of sulfur trioxide was complete, ethylene oxide was passed slowly through the mixture which was stirred and cooled. When 0.25 mole of ethylene oxide had been added, the dioxane–sulfur trioxide addition compound had completely dissolved. The final volume of the reaction mixture was 210 ml.

A 5-ml. aliquot of this solution was added to about 50 ml. of water at room temperature and shaken vigorously. An oily layer separated from solution. This mixture was neutralized with less than 1 ml. of 0.100*N* sodium hydroxide solution.

The dioxane solution (50 ml.) was distilled under vacuum (2 mm.) until a pot temperature of 50° was reached. The residue (10.5 g.) was a dark viscous liquid. This material (1.69 g.) was heated to 70–80° in a micro sublimation apparatus at 2 mm. There was obtained 110 mg. (9.5%) of white crystalline ethylene sulfate, m.p. 96–97° (lit.,[2] m.p. 99°).

Anal. Calcd. for $C_2H_4O_4S$: C, 19.35; H, 3.25. Found: C, 19.86; H, 3.36.

Acknowledgment. The author wishes to thank Dr. O. C. Dermer for helpful discussions and S. A. Sims for able assistance.

Organic Process Development Laboratory
The Dow Chemical Company
Freeport, Tex.

---

[1] C. M. Suter and P. B. Evans, *J. Am. Chem. Soc.*, 60, 536 (1938).

[2] Wilson Baker and F. B. Field, *J. Chem. Soc.*, 86 (1932).

Relative Basicities in the Series Dialkyl Sulfide, Sulfoxide, and Sulfone Toward Boron Trifluoride

Robert G. Laughlin

Received November 2, 1959

Strong evidence has been obtained that in the series R-S-R′, R-SO-R′, R-SO$_2$R′ ($R = n\text{-}C_{12}H_{25}$, $R' = CH_3$ or C_2H_5) the sulfoxide is considerably more basic toward the Lewis acid boron trifluoride than either the sulfide or sulfone. Each formed a 1:1 complex on passing boron trifluoride into a cold benzene solution, as indicated by abrupt saturation of the solution when close to one molar equivalent had been added. The benzene was then evaporated at aspirator pressure at or below room temperature. Only the sulfoxide formed a vacuum-stable complex. The starting sulfide and sulfone were recovered in the other two cases. Thus the dissociation of the sulfoxide complex must be much lower than that of the sulfide and sulfone complexes, *i.e.*, the sulfoxide is the strongest base towards boron trifluoride.

The order of basicity in this series toward boron trifluoride and toward protons will not necessarily correspond, especially if steric factors are involved.[1] However, Wimer[2] has obtained results from nonaqueous titrations which indicate that the order is the same. His data, combined with the known pK_A of protonated phosphine oxides (R_3POH^+),[3] would

---

[1] E. A. Braude and F. C. Nachod, ***Determination of Organic Structures by Physical Methods***, Academic Press, Inc., N. Y., (1955), pp. 634ff.

[2] D. C. Wimer, *Anal. Chem.* **30**, 2060 (1958).