

CFCl_2SCl , rather than trichloromethanesulfonyl fluoride, CCl_3SF , as reported by Kober.²

In the Raman spectrum of the yellow reaction product, I find that the most prominent line (532 cm.^{-1}) also occurs in the Raman spectrum of trichloromethanesulfonyl chloride (535 cm.^{-1}), where it has been assigned to the stretching vibration of the S-Cl bond.³ This observation is strong confirmatory evidence for the retention of the S-Cl bond during fluorination.

(2) E. Kober, *J. Am. Chem. Soc.*, **81**, 4810 (1959).

(3) J. Duchesne, *Bull. Soc. roy. Sci. Liege*, **11**, 61 (1942); F. Feher, *Z. anorg. allgem. Chem.*, **284**, 60 (1956).

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THE ISOLATION OF ETHERATED CARBONIC ACID Sir:

M. Schmidt¹ isolated thiosulfuric acid by the low temperature reaction of $\text{Na}_2\text{S}_2\text{O}_3$ with HCl in ether. It was thought that carbonic acid might also be prepared at low temperatures in a similar manner.

All reactions were conducted under anhydrous conditions using anhydrous reagents. Finely divided NaHCO_3 was dispersed in ether and cooled to -30° . Freshly prepared HCl in ether, also at -30° , then was added with stirring to an excess of this mixture. The addition was not accompanied by gas evolution. Analysis of a sample of the ether did not show the presence of chloride ions.

The cold ether solution was decanted from the solids, consisting of unreacted NaHCO_3 and product NaCl, and cooled to -78° . At this temperature white, snow-like crystals were precipitated slowly from solution. They began to decompose rapidly at -10° with evolution of carbon dioxide and formation of water (ice).

Quantities of this product were allowed to decompose and the products of decomposition allowed to pass through two weighed U-tubes containing anhydrous $\text{Mg}(\text{ClO}_4)_2$ and soda lime, respectively. The molar ratio of the decomposition products, namely, H_2O and CO_2 , was thus established as being approximately 1:1.

A U-tube fitted with a fritted-glass filter and which could be disconnected below the disk was used to determine the extent of etherification of the carbonic acid at low temperatures. The joined U-tube was completely immersed in a bath kept at -78° and a quantity of the precipitated crystals was then collected onto the filter disk. They were dried by a stream of precooled nitrogen. The leg containing the dry sample was then connected to a gas-measuring buret. The carbon dioxide evolved from the decomposition of the compound on warming to room temperature was measured over mercury at constant pressure. The liquid products were weighed by difference. Corrections were made for temperature, pressure and vapor pressure of water and ether. The increase in weight corresponded to a molar quantity of water

(1) M. Schmidt, *Z. anorg. und allgem. Chem.*, **289**, 141 (1957).

(expected) plus a molar quantity of ether approximately equal to the molar quantity of carbon dioxide measured.

The analyses of two preparations are given: (1) CO_2 evolved = 24.6 ml. (0.0011 mole) corrected; weight of liquid products, $(\text{C}_2\text{H}_5)_2\text{O} + \text{H}_2\text{O}$ = 0.0938 g. corrected; weight of ether = 0.0938 g. - 0.0198 g. (weight of 0.0011 mole H_2O assumed = CO_2) = 0.0740 g. (0.0010 mole); molar ratio $\text{CO}_2:\text{Et}_2\text{O}$ = 0.0011:0.0010. (2) CO_2 evolved = 9.3 ml. (0.00041 mole) corrected; weight of liquid products, $(\text{C}_2\text{H}_5)_2\text{O} + \text{H}_2\text{O}$ = 0.0407 g. corrected; weight of ether = 0.0407 g. - 0.0074 g. (weight of 0.00041 mole H_2O assumed = CO_2) = 0.0333 g. (0.00045 mole); molar ratio $\text{CO}_2:\text{Et}_2\text{O}$ = 0.00041:0.00045.

When a stream of precooled ammonia was passed through an ether solution of the compound at -30° a voluminous white precipitate immediately formed. An infrared spectrogram of this solid was identical with one of known pure $(\text{NH}_4)_2\text{CO}_3$.

An ether solution of carbonic acid was found to react generally with strong bases to form carbonates and bicarbonates.

From these preliminary experiments it can be concluded that anhydrous carbonic acid, H_2CO_3 , may be prepared and exists in ether solution at -30° as a stable entity. As such it reacts with strong bases to form carbonates and bicarbonates. In addition, the monoetherate of carbonic acid, $\text{H}_2\text{CO}_3\cdot\text{Et}_2\text{O}$, may be precipitated from ether solution at -78° filtered and analyzed.

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STRUCTURE AND NATURE OF BONDING OF $\text{C}_5\text{H}_5\text{Co}(\text{CH}_3\text{C}_2\text{CH}_3)_2\text{CO}^1$

Sir:

The reactions of certain metal carbonyls and their derivatives with alkynes have resulted in new types of complexes²⁻¹² whose exact nature, although inferred from chemical evidence, as yet is unknown.

A single crystal X-ray investigation of one of these compounds, $\text{C}_5\text{H}_5\text{Co}(\text{CH}_3\text{C}_2\text{CH}_3)_2\text{CO}$, has yielded results of definite structural interest. This compound formed by the reaction of dimethylacetylene with $\text{C}_5\text{H}_5\text{Co}(\text{CO})_2$ was first pre-

(1) Presented in part before the Division of Physical Chemistry, American Chemical Society Meeting, April 5-14, 1960.

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(4) G. N. Schrauzer, *Chem. and Ind.*, 1403 (1958); 1404 (1958).

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(6) W. Hübel and E. H. Braye, *ibid.*, **10**, 250 (1959).

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(8) J. R. Leto and F. A. Cotton, *J. Am. Chem. Soc.*, **81**, 2970 (1959).

(9) G. N. Schrauzer, *ibid.*, **81**, 5307 (1959).

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