

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. - 0.0193 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.

(2) W. Reppe and H. Vetter, *Ann.*, **582**, 133 (1953).

(3) H. W. Sternberg, R. Markby and J. Wender, *J. Am. Chem. Soc.*, **80**, 1009 (1958).

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

(5) W. Hübel, E. H. Braye, A. Clauss, E. Weiss, U. Krüerke, D. A. Brown, G. S. D. King and C. Hoogzand, *J. Inorg. Nucl. Chem.*, **9**, 204 (1959).

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

(7) R. Markby, H. W. Sternberg and J. Wender, *Chem. and Ind.*, 1381 (1959).

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

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

(10) E. R. H. Jones, P. C. Wailes and M. C. Whiting, *J. Chem. Soc.*, 4021 (1955).

(11) W. Hübel and E. Weiss, *Chem. and Ind.*, 703 (1959).

(12) P. L. Pauson, *Proc. Chem. Soc.*, 297 (1960).

pared by Markby, Sternberg and Wender,⁷ who generously supplied us with crystals. The monoclinic crystals have lattice constants $a = 8.18 \text{ \AA}$., $b = 13.37 \text{ \AA}$., $c = 11.02 \text{ \AA}$., and $\beta = 91^\circ 44'$. The probable space group is $P2_1/n$. For four molecules per unit cell the calculated density is 1.43 g./cc. in agreement with the experimental density 1.46 g./cc. determined by the flotation method. Weissenberg intensity data involving 890 independent reflections were obtained photographically with $\text{MoK}\alpha$ radiation. A three-dimensional structural analysis of the data including least squares refinement yielded refined positional and thermal parameters. The final discrepancy factor for individual isotropic thermal parameters is 8.1%; for anisotropic thermal parameters, 5.1%.

The molecular structure can be described as a sandwich in which the cobalt lies between a cyclopentadienyl ring and a tetramethylcyclopentadienone ring. The most interesting feature is that all the C—C bonds in the tetramethylcyclopentadienone ring are essentially equal, thus indicating complete delocalization of the four π -electrons. The stabilization of the complex then is accomplished in part by an electron transfer from the cobalt to give aromatic character in which the cobalt in effect becomes bonded to two cyclopentadienyl rings. Strong π -bonding between the rings and the cobalt, resulting in the use of all the low energy bonding orbitals of the metal, increases stability. Hence, this aromaticity gives rise to a mesoionic structure proposed by others.^{7,13} A qualitative M.O. treatment of this type compound has been done.¹⁴

Of considerable interest is the fact that the cyclopentadienone ring is not planar; the carbonyl group is tipped out of the plane of the other atoms away from the cobalt such that the resulting angle of tilt is 9° . It is difficult to rationalize this effect as being electronic in origin, especially in the crystalline state where intermolecular forces must be considered. As expected, the cyclopentadienyl ring is planar although distorted.

The perpendicular distance from the cobalt to the cyclopentadienyl ring is 1.67 \AA .; to the substituted ring 1.63 \AA .. Hence, the planes, if parallel, are 3.3 \AA . apart. Actually, the calculated angle between the planes is approximately 3° , so they are almost parallel.

Another feature of the molecule is that the five carbon atoms of the two rings are eclipsed with respect to one another, that is, four of the corresponding C...C distances are 3.3 \AA . apart.

Of prime interest is the comparison of these structural results with those for biscyclopentadienyl iron, better known as ferrocene.¹⁵ The average C—C distance in the cyclopentadienyl ring in ferrocene is 1.40 \AA .; in the cobalt compound 1.43 \AA .. The Fe—C distance in ferrocene of 2.05 \AA .. is comparable with a Co—C distance of 2.07 \AA .. The distance between the rings in ferrocene is also 3.3 \AA ..

(13) E. Weiss and W. Hübel, *J. Inorg. Nucl. Chem.*, **11**, 42 (1959).

(14) D. A. Brown, *ibid.*, **10**, 39, 49 (1959); **13**, 212 (1960).

(15) J. D. Dunitz, L. E. Orgel and A. Rich, *Acta Cryst.*, **9**, 373 (1956).

However, the rings in ferrocene are staggered rather than eclipsed.

This structural determination represents the first direct X-ray diffraction evidence for the existence of a sandwich complex involving a cyclopentadienone ring and clearly substantiates chemical evidence given independently by other workers⁴⁻⁹ for these type compounds.

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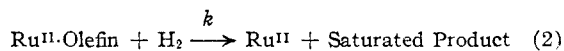
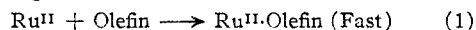
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HOMOGENEOUS CATALYTIC HYDROGENATION OF α -OLEFINIC COMPOUNDS

Sir:

Although a variety of metal ions and complexes are now known¹ which activate molecular hydrogen homogeneously in solution and catalyze the reduction of inorganic substrates such as $\text{Cr}_2\text{O}_7^{2-}$ and Fe^{3+} , these have not, in general, proved effective catalysts for the hydrogenation of olefinic compounds. We now wish to report the successful hydrogenation, under homogeneous conditions, of several olefinic compounds including maleic, fumaric and acrylic acids, using chlororuthenate(II) complexes as catalysts.

Most of the experiments were made in aqueous 3 *M* HCl solution using maleic acid as substrate. Ru^{II} was generated by reduction of $(\text{NH}_4)_2\text{RuCl}_6$ with TiCl_3 . With maleic acid in excess over Ru^{II} , hydrogenation to succinic acid proceeded at conveniently measurable rates over the temperature range 70 to 90° , according to the rate law, $k[\text{H}_2] \cdot [\text{Ru}^{\text{II}}]_{\text{Total}}$ with $\Delta H^* = 19 \text{ kcal./mole}$ and $\Delta S^* = -2 \text{ e.u.}$ The reaction apparently involves the formation of a Ru^{II} -olefin complex which reacts with hydrogen, *i.e.*



In the case of maleic acid, the formation of a 1:1 complex with Ru^{II} , with a stability constant of 5×10^3 (3 *M* HCl, 20°), was confirmed spectrophotometrically.

Measurements of the uptake of ethylene and propylene by Ru^{II} solutions, and of the accompanying spectral changes, confirm that these olefins also form stable 1:1 complexes with Ru^{II} , but attempts to hydrogenate these under homogeneous conditions have not, thus far, proved successful.

These appear to be the first examples of Ru^{II} monoolefin complexes, although a diolefin (norbornadiene) complex, $\text{C}_7\text{H}_8\text{RuCl}_2$, believed to have a polymeric halogen-bridged structure, has been reported recently.²

(1) J. Halpern, *J. Phys. Chem.*, **63**, 398 (1959); *Advances in Catalysis*, **11**, 301 (1959).

(2) E. W. Abel, M. E. Bennett and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).