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The Fluorination of Carbon Monoxide, Carbonyl Chloride, and Carbonyl Fluoride[*1]

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This paper will deal with the electrochemical fluorination of carbon monoxide, carbonyl chloride, carbonyl fluoride, cyanogen, and hydrogen cyanide. These gaseous compounds have been subjected to fluorination by various methods,[1] but no work has yet been published on their electrochemical fluorination. The primary objective of this work was to extend the scope of the technique of electrochemical fluorination for gaseous compounds,[2] previously used mostly in the fluorination of organic gases,[3] to inorganic gases containing a carbon-oxygen or carbon-nitrogen multiple bond, and to clarify the behavior of these compounds in the fluorination.

The method of the fluorination involves the bubbling of metered starting materials through a bubbler into anhydrous liquid hydrogen fluoride in an electrolytic cell.[2] The fluorinated products were freed from hydrogen fluoride and then analyzed. It was found that carbon monoxide, carbonyl chloride, and carbonyl fluoride were fluorinated to give the anticipated products, while cyanogen and hydrogen cyanide were cleaved extensively by the fluorination. The reaction conditions for the electrochemical fluorination of carbon monoxide, carbonyl chloride, and carbonyl fluoride, and the results obtained are shown in Table 1.

In addition, oxygen difluoride was always found in the products. Small amounts of perfluorodimethyl ether and carbon dioxide were present in the products obtained from carbon monoxide. From carbonyl chloride, a considerable amount of chlorine was identified, besides a trace of chlorotrifluoromethane. This indicates the ease of the removal of chlorine of carbonyl chloride in the electrochemical process.[*2]

The electrochemical fluorination of carbon dioxide was also examined. The bulk of the starting material was recovered unchanged; traces of carbon tetrafluoride, hexafluoroethane, trifluoromethane, and a highly explosive product, which was not identified, were also found.

TABLE 1. FLUORINATION OF CARBON MONOXIDE, CARBONYL CHLORIDE AND CARBONYL FLUORIDE

Sample	Sample feed rate m*l*/min	Total amount of sample fed mol	Electrolysis condition[a)]	Product composition %				Total Yield[b)] %
				CF_4	COF_2	CF_3OF	CF_3OOCF_3	
CO	51	0.416	A	15	71	8	6	58
$COCl_2$	25	0.201	B	8	82	10	—	72
COF_2	49	0.197	C	10		73	17	74

a) A: HF 1 *l*, NaF 10 g, He 20 m*l*/min, anodic current density 2.2 A/dm², cell voltage 5.5—6 V, electricity passed 61 A. hr, cell temperature 7—8°C.
B: HF 300 m*l*, He 20 m*l*/min, anodic current density 1.7 A/dm², cell voltage 7—8 V, electricity passed 30 A. hr, cell temperature 12—13°C.
C: HF 1 *l*, NaF 10 g, He 20 m*l*/min, anodic current density 2.2 A/dm², cell voltage 5.5—6 V, electricity passed 30 A. hr, cell temperature 7—8°C.
b) Calculated on the basis of the amount of the starting material fed.

[*1] "Electrochemical Fluorination of Gases." Part VII.

[1] For example, a detailed study of the catalytic fluorination of carbon monoxide has recently been reported; M. Wechsberg and G. H. Cady, *J. Amer. Chem. Soc.*, **91**, 4432 (1969).

[2] Part VI of this series: S. Nagase, T. Abe and H. Baba, This Bulletin, **42**, 2062 (1969).

[3] See, for example, S. Nagase, T. Abe and H. Baba, *ibid.*, **40**, 684 (1967).

[*2] Under pressure, carbonyl chloride is known to react with anhydrous hydrogen fluoride to yield carbonyl chlorofluoride and carbonyl fluoride, together with hydrogen chloride. [J. H. Simons, D. F. Herman and W. H. Pearlson, *J. Amer. Chem. Soc.*, **68**, 1672 (1946)]. This reaction was examined under the conditions used for the present work. When carbonyl chloride was bubbled into anhydrous hydrogen fluoride in a cell kept at 7°C without passing a current through, small amounts of carbonyl chlorofluoride and hydrogen chloride were produced.

The electrochemical fluorination of cyanogen and hydrogen cyanide resulted in an extensive cleavage of the carbon-nitrogen multiple bond, giving fragmented fluorinated products.[4] We will now give examples of the composition of the products obtained from the electrochemical fluorination of cyanogen and hydrogen cyanide, which was carried out under conditions similar to those described above. Cyanogen (feed rate, 56 m*l*/min; hydrogen fluoride, 1 *l*; temperature, 5—6°C) gave 59% nitrogen trifluoride, 35% hexafluoroethane, and 6% carbon tetrafluoride. From hydrogen cyanide (feed rate, 37 m*l*/min; hydrogen fluoride 1 *l*; temperature, −5°C), 48% nitrogen trifluoride, 42% carbon tetrafluoride, 7% trifluoromethane, and 3% trifluoromethyldifluoroamine were formed. The evolution of nitrogen was also observed.

Experimental

Materials. Carbon monoxide and carbonyl chloride from a commercial cylinder were used. The carbonyl fluoride[5] and cyanogen[6] were prepared by the methods described in the literature. The hydrogen cyanide was synthesized by a conventional method.

Procedures. The fluorination procedures used were essentially the same as those described in a previous paper.[2] Product identification and analysis were performed by means of gas chromatography,[*3] infrared spectroscopy (Hitachi EPI-S2 spectrometer), and mass spectrometry (Hitachi RMU-7 spectrometer).

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[4] T. Abe, S. Nagase and K. Kodaira, *ibid.*, **43**, 957 (1970).

[*3] Gas chromatography was carried out with a Shimadzu GC-2C model chromatograph using a 0.3 cm i.d.×6 m column packed with 66% FC 43 (Minnesota Mining & Manufacturing Co.) on 60/80 mesh Celite 545 SK (Gaschro-Kogyo Co.). Column temperature, 0°C; carrier gas, helium.

In preliminary experiments, an attempt was made to analyze the products by a modification of Hempel's gas analysis, but the method was found not to be suitable for this purpose because of the reaction of carbonyl fluoride and trifluoromethyl hypofluorite with glass and with mercury covered with fluorocarbon oil respectively.

[5] F. S. Fawcett, C. E. Tullock and D. D. Coffman, *J. Amer. Chem. Soc.*, **84**, 4275 (1962).

[6] T. Moeller, "Inorganic Syntheses," Vol. V., p. 43 (1957).