3864 *Inorg. Chem.* **1992**, *31*, 3864

Notes

Fluorination of Calcium Cyanamide: A Convenient Laboratory Scale Synthesis of Carbon Tetrafluoride

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Received February 25, 1992

Carbon tetrafluoride is an exceptionally stable gas with a melting point close to that of CH_4.[1] CF_4 is therefore an excellent inert solvent for both low-temperature reactions and fluorine chemistry (e.g. low-temperature solution Raman and NMR spectroscopy). It can be prepared on a laboratory scale by reacting C (carbon soot),[2] SiC,[1] or CO[2] with F_2 at temperatures as high as 400–500 °C. Industrially it is prepared by the aggressive reaction of F_2 on CF_2Cl_2 or CF_3Cl or by electrolysis of metal fluorides using a C anode.[1] Whereas the laboratory method using CO (yield 15–85%) requires sophisticated equipment, the fluorination of C leads to product mixtures also containing variable amounts of the higher homologues of fluorocarbons, mostly C_2F_6 and C_3F_8.[2] We now report on a simple one-step and high-yield synthesis of pure CF_4 on a laboratory scale.

Graphite-free calcium cyanamide, $CaCN_2$,[2,3] reacts stoichiometrically with F_2 according to eq 1. The presence of trace

$$\mathrm{CaCN_2 + 3\,F_2 \xrightarrow{[CsF],\ 25\ ^\circ C,\ 12\ h} CaF_2 + N_2 + CF_4} \tag{1}$$

amounts of CsF suppresses the formation of NF_3, which is formed as a side product in the absence of CsF up to 5%.[4] CF_4 is readily separated from solid CaF_2, and N_2 can easily be pumped off at −196 °C. The yield of the crude product (which is essentially pure) is quantitative. After purification by fractional condensation, pure CF_4 is obtained in 85–90% yield. Vibrational (IR, Raman), analytical, and mass spectral data for CF_4 are, without any reservation, nicely in agreement with those reported in the literature.[2,5,6] The use of commercially available $CaCN_2$ (Alfa) cannot be recommended as the black material contains up to 10% C from the industrial diazotization process (see below, "*Caution*"). This leads to unstoichiometric fluorination reactions and therefore impure CF_4.

Experimental Section

Caution! Fluorine and chlorine trifluoride are powerful oxidizers, are toxic, and can react violently with most organic substances (e.g. graphite-free $CaCN_2$ has to be used, see above). Suitable shielding is required, and protective clothing and face masks should be worn at all times.

A 120-mL steel reaction vessel (SS-316, deactivated with ClF_3 was loaded with 3.0 g (37.5 mmol) carbon-free $CaCN_2$[2,3] and 0.3 g (2.0 mmol) of CsF. [N.b. The reaction should be carried out in well-passivated metal equipment only. Although ClF_3 is most convenient, F_2 can be used for deactivation.]) F_2 (115 mmol, 4.4 g) was condensed at −196 °C onto the $CaCN_2$. The reaction mixture was warmed within 1 h to room temperature and held at this temperature for 12 h. After the mixture was cooled to −196 °C (or −183 °C), all volatile components were removed in vacuum and pure CF_4 was isolated after fractional condensation at −160 °C in 89% yield (2.9 g, 33 mmol). IR (gas, 25 °C, 0.14 psi, $\tilde{\nu}$ in cm^{-1}): 2565 m, 2193 s, 1945 m, br, 1540 s, 1283 vvs (ν_3), 631 s (ν_4); cf. ref 6. Raman (647.09 nm, 50 mW, −110 °C, liquid under pressure, $\Delta\nu$ in cm^{-1}, relative intensities in parentheses): 1281 (1), ν_3; 908 (10), ν_1; 633 (1), ν_4; 438 (2) ν_2; cf. ref 6. Bp: −130 ± 3 °C (lit.[1,2] −128.5 °C). Mp: −185 ± 5 °C (lit.[1,2] −183.5 °C). MS (EI, 70 eV, 25 °C): $m/e = 88\ (M^+)$.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft (Grant KL 636/2-1) and to the Fonds derChemischen Industrie for financial support of this work.

Registry No. $CaCN_2$, 156-62-7; F_2, 7782-41-4; CF_4, 75-73-0.

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[4] As CsF catalyzes the isomerization of FNCNF to give F_2CN_2[7] both species are likely to be intermediates in the fluorination pathway of $CaCN_2$. Whereas the first step (formation of FNCNF or F_2CN_2) is a slow reaction, the fluorination of F_2CN_2 to give CF_4 and N_2 is apparently a fast reaction. (N.b. Difluorodiazirine, F_2CN_2, can be decomposed to difluorocarbene and N_2 either by thermal or by ultraviolet irradiation.[8]) If FNCNF is not converted into F_2CN_2 (by CsF catalysis) the formation of NF_3 as a side product is in agreement with the N–F bonded precursor.

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