

# Notes

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

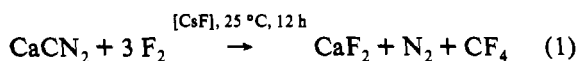
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Carbon tetrafluoride is an exceptionally stable gas with a melting point close to that of CH<sub>4</sub>.<sup>1</sup> CF<sub>4</sub> is therefore an excellent inert solvent for both low-temperature reactions and fluorine chemistry (e.g. low-temperature solution Raman and NMR spectroscopy). It can be prepared on a laboratory scale by reacting C (carbon soot),<sup>2</sup> SiC,<sup>1</sup> or CO<sub>2</sub> with F<sub>2</sub> at temperatures as high as 400–500 °C. Industrially it is prepared by the aggressive reaction of F<sub>2</sub> on CF<sub>2</sub>Cl<sub>2</sub> or CF<sub>3</sub>Cl or by electrolysis of metal fluorides using a C anode.<sup>1</sup> 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<sub>2</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub>.<sup>2</sup> We now report on a simple one-step and high-yield synthesis of pure CF<sub>4</sub> on a laboratory scale.

Graphite-free calcium cyanamide, CaCN<sub>2</sub>,<sup>2,3</sup> reacts stoichiometrically with F<sub>2</sub> according to eq 1. The presence of trace



amounts of CsF suppresses the formation of NF<sub>3</sub>, which is formed as a side product in the absence of CsF up to 5%.<sup>4</sup> CF<sub>4</sub> is readily separated from solid CaF<sub>2</sub>, and N<sub>2</sub> can easily be pumped off at

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- (4) As CsF catalyzes the isomerization of FNCNF to give F<sub>2</sub>CN<sub>2</sub>,<sup>7</sup> both species are likely to be intermediates in the fluorination pathway of CaCN<sub>2</sub>. Whereas the first step (formation of FNCNF or F<sub>2</sub>CN<sub>2</sub>) is a slow reaction, the fluorination of F<sub>2</sub>CN<sub>2</sub> to give CF<sub>4</sub> and N<sub>2</sub> is apparently a fast reaction. (N.b. Difluorodiazirine, F<sub>2</sub>CN<sub>2</sub>, can be decomposed to difluorocarbene and N<sub>2</sub> either by thermal or by ultraviolet irradiation.<sup>8</sup>) If FNCNF is not converted into F<sub>2</sub>CN<sub>2</sub> (by CsF catalysis) the formation of NF<sub>3</sub> as a side product is in agreement with the N–F bonded precursor.

–196 °C. The yield of the crude product (which is essentially pure) is quantitative. After purification by fractional condensation, pure CF<sub>4</sub> is obtained in 85–90% yield. Vibrational (IR, Raman), analytical, and mass spectral data for CF<sub>4</sub> are, without any reservation, nicely in agreement with those reported in the literature.<sup>2,5,6</sup> The use of commercially available CaCN<sub>2</sub> (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<sub>4</sub>.

### 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<sub>2</sub> 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<sub>3</sub> was loaded with 3.0 g (37.5 mmol) carbon-free CaCN<sub>2</sub>,<sup>2,3</sup> 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<sub>3</sub> is most convenient, F<sub>2</sub> can be used for deactivation.] F<sub>2</sub> (115 mmol, 4.4 g) was condensed at –196 °C onto the CaCN<sub>2</sub>. 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<sub>4</sub> 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<sup>-1</sup>): 2565 m, 2193 s, 1945 m, br, 1540 s, 1283 vvs ( $\nu_3$ ), 631 s ( $\nu_4$ ); cf. ref 6. Raman (647.09 nm, 50 mW, –110 °C, liquid under pressure,  $\Delta\nu$  in cm<sup>-1</sup>, relative intensities in parentheses): 1281 (1),  $\nu_3$ ; 908 (10),  $\nu_1$ ; 633 (1),  $\nu_4$ ; 438 (2)  $\nu_2$ ; cf. ref 6. Bp: –130 ± 3 °C (lit.<sup>1,2</sup> –128.5 °C). Mp: –185 ± 5 °C (lit.<sup>1,2</sup> –183.5 °C). MS (EI, 70 eV, 25 °C):  $m/e$  = 88 (M<sup>+</sup>).

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**Registry No.** CaCN<sub>2</sub>, 156-62-7; F<sub>2</sub>, 7782-41-4; CF<sub>4</sub>, 75-73-0.

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