Chemical Activation during Photodifluoroamination

By CARL L. BUMGARDNER,* ERNEST L. LAWTON, and HALBERT CARMICHAEL
(*Department of Chemistry, North Carolina State University, Raleigh, North Carolina* 27607)

RECENTLY several groups[1] reported the loss of HF from a variety of chemically activated fluorohydrocarbons. We describe a case where an excited nitrogen-containing molecule, difluoroaminomethane ($MeNF_2$), is converted into HCN by elimination of HF.†

When NF_2 is photolysed (2537 Å) at room temperature with alkanes, alkyldifluoroamines are produced, probably by the sequence.[2]

$$NF_2 \xrightarrow{h\nu} F + NF$$
$$RH + F \longrightarrow HF + R$$
$$R + NF_2 \longrightarrow RNF_2$$

In the reaction involving methane, HCN was also formed. According to carbon mass balances, $MeNF_2$ and HCN accounted for (105 ± 5%) of the methane consumed. At first the HCN was believed to arise from initially formed $MeNF_2$ by bimolecular elimination reactions. However, the ratio HCN : $MeNF_2$ was found to be time independent (Figure 1) and pressure dependent (Figure 2).

If an excited $MeNF_2$ molecule is the common precursor of stable $MeNF_2$ and HCN then the pressure dependence of the product ratio can be expressed quantitatively in the form:

$$MeNF_2^* \xrightarrow{k_r} HCN + 2HF$$
$$MeNF_2^* \xrightarrow[k_d]{M} MeNF_2$$
$$\frac{[HCN]}{[MeNF_2]} = \frac{k_r}{k_d}\frac{1}{[M]}$$

The linear plot of product ratio against reciprocal pressure has a zero intercept.

Similar straight line graphs were also obtained when the inert gases N_2 and CF_4 were used to establish the pressure. The slopes (k_r/k_d) were different for the three lines, which converged to a common point at zero pressure. Comparison of the ratio of rate constants in the Table shows that

Comparison of k_r/k_d

Deactivator	$k_r/k_d \times 10^{-2}$ Torr
CF_4	1·0
CH_4	2·9
N_2	8·6

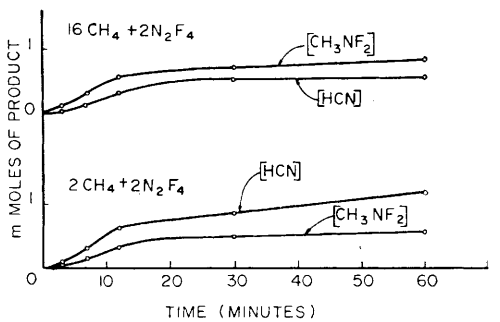

FIGURE 1. *Product dependence on time.*

the pentatomic CF_4 is a more efficient deactivator than diatomic N_2. As anticipated, CH_4 occupies an intermediate position.

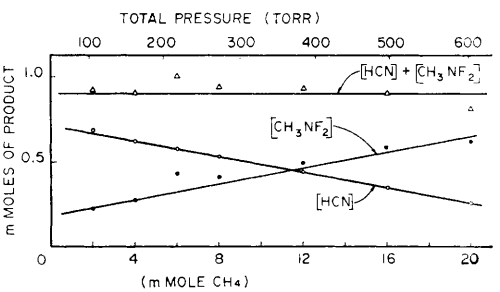

FIGURE 2. *Product dependence on pressure.*

(*Received, June 24th,* 1968; *Com.* 838.)

† Whether the loss of HF occurs stepwise is not known. However, a search in the mass spectra failed to provide any evidence for CH_2NF, the expected intermediate of a multi-step process. This compound is unknown so whether it would survive the reaction conditions cannot be determined at this time.

[1] J. A. Kerr, A. W. Kirk, B. V. O'Grady, and A. F. Trotman-Dickenson, *Chem. Comm.*, 1967, 365; D. C. Phillips and A. F. Trotman-Dickenson, *J. Chem. Soc.* (*A*), 1968, 1144; G. O. Pritchard and J. T. Bryant, *J. Phys. Chem.*, 1968, **72**, 1603; W. G. Alcock and E. Whittle, *Trans. Faraday Soc.*, 1965, **61**, 244.
[2] C. L. Bumgardner, *Tetrahedron Letters*, 1964, 3683.