INORG. NUCL. CHEM. LETTERS Vol. 8, pp. 469-475, 1972. Pergamon Press. Printed in Great Britain.

THE PHOTOCHEMICAL FLUORINATION OF CYANOGEN CHLORIDE

E. V. Oexler and E. H. Staricco

Departamento de Fisicoquimica, Facultad de Ciencias Quimicas
Universidad Nacional de Cordoba, Cordoba (32), Argentina

(Received 12 January 1972)

Some attention has been devoted to the fluorination of cyanogen chloride (1-5). When silver difluoride was used as a fluorinating agent at room temperature (1), CF_3NNCF_3 was produced in high yield. However, at 100°C (2), besides this compound were also found N_2, CF_3Cl, CF_4, CF_2Cl_2, $CFCl_3$ and CF_3NNCF_2Cl. A variety of products were obtained when other fluorides were employed at higher temperatures (3,4), but in none of these cases were compounds with N-F bonds isolated. At 94°C (5), in the reaction between ClCN and F_2 among many compounds a small quantity of CF_2ClNF_2 and CF_3NFCl were obtained.

We wish to report that in an attempt to have an insight into the mechanism of the fluorination of ClCN a study of this system was undertaken. It was found that no thermal reaction occurs between ClCN and F_2 up to 45°C, but when the gaseous mixture was irradiated with light of 3660 Å, a reaction takes place, CF_3Cl, CF_2Cl_2 and N_2 being the major products.

Experimental

ClCN was prepared according to Klemenc (6), and then trap to trap distilled at low temperature. F_2 (Air Products) was twice distilled between liquid oxygen and liquid nitrogen temperatures and stored in a trap cooled with liquid nitrogen. Nitrogen (99,9%) and Argon (99,9%) were used without further purification.

The reactor was a quartz cylinder 10 cm long; it was connected to a quartz spiral manometer used as the reference instrument of a mercury manometer. Aluminum valves with nickel needle stems and Teflon gaskets were employed. The source of light was a HBO 500 Osram lamp and by means of quartz lens, diaphragms and Schott filters a parallel beam of 3360 Å was obtained. The intensity of incident light, measured with a Kipp compensated thermopile and a Microva Galvanometer, was $4,54.10^{15}$ quantum $minute^{-1}cc^{-1}$.

Procedure: Most of the experiments were carried out to only few percent conversion. After the period of illumination the gaseous mixture was expanded into a trap containing mercury. A U-trap cooled with liquid nitrogen was placed between the reactor and the trap. In that way, unreacted fluorine was eliminated by reaction with mercury and the products not condensed in liquid nitrogen could be analyzed with a Molecular Sieve 5A column of 1/4 in. x 5 ft. with helium as carrier gas in a chromatograph

fitted with a gas density detector. Condensable products were analyzed in every run with a column of dinonylphthalate 28% on Chromosorb P (60-80 mesh) of 1/4 in. x 8 ft. and nitrogen as carrier gas.

All compounds were identified by I.R. spectra.

Results and Discussion

Runs were performed at -4, 10 and 30°C with variation of the initial pressure of F_2 between 40-400 Torr and that of ClCN between 5-40 Torr. In a typical run with 200 Torr of F_2 and 20 Torr of ClCN at 30°C and 5% conversion, it was found that products were CF_3Cl:N_2:CF_2Cl_2:CF_3NNCF_3 in a ratio 4:2.5:1:0.5 and traces of SiF_4 and COF_2.

In the range of pressure studied the ratio, CF_3Cl/CF_2Cl_2, was found to depend to some extent on the initial pressure of F_2 when the ratio of F_2/ClCN was less than 5, and became independent of F_2 for F_2/ClCN higher that value (Table I).

The relation CF_3Cl/CF_2Cl_2 diminished with increasing initial ClCN pressure and also with increasing temperature, but the addition of argon increased the ratio CF_3Cl/CF_2Cl_2 (Fig. I).

From the information presently available a realiable mechanism seems far from being assessed, however, a tentative approach may be suggested.

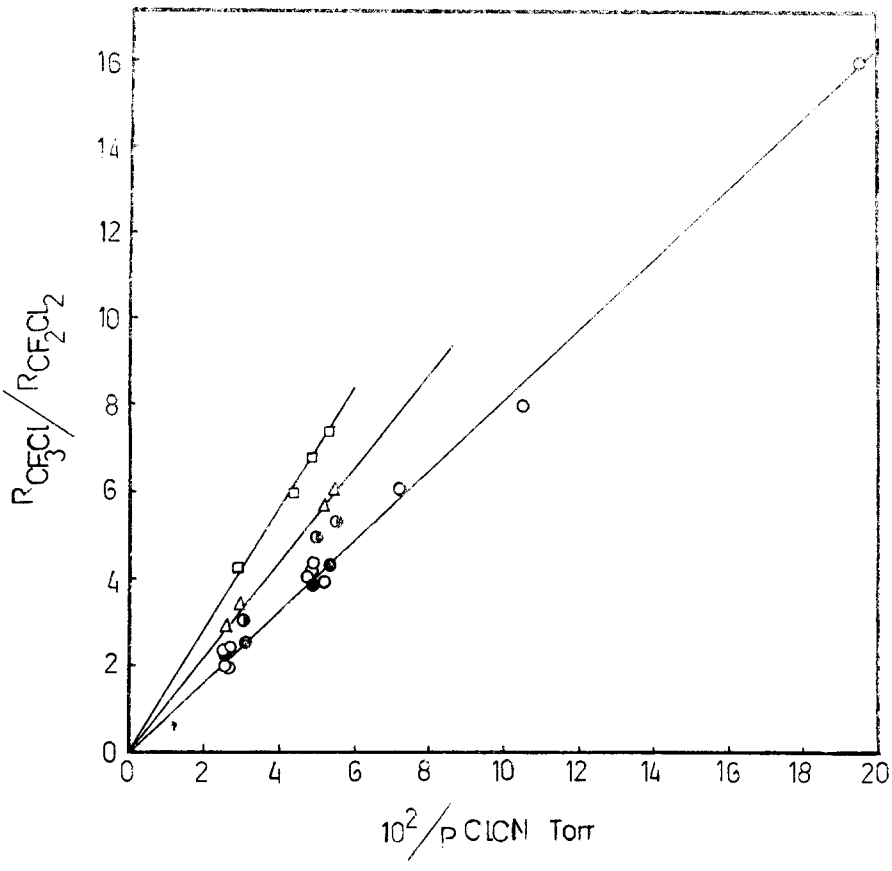

FIG. I

Dependency of $R_{CF_3Cl}/R_{CF_2Cl_2}$ with the pressure of cyanogen chloride

circles, F_2 only, half filled circles (with addition of 400 Torr Argon) and full filled circles (with addition of 400 Torr Nitrogen), 30°C;

triangles, 10°C; squares, -4°C

Initial pressure of fluorine = 200 Torr.

TABLE I

p F_2, Torr	CF_3Cl/CF_2Cl_2
40	2.8
60	3.4
80	3.7
100	3.9
200	4.0
200 +	3.9
400	4.1

Initial pressure of ClCN = 20 Torr; time of photolysis 25 minutes; temp. 30°C.
+, the incident light was 50% less than in the other runs.

From light measurements and from the absorption coefficient of F_2 (7), the quantum yield of CF_3Cl at 30°C with 200 Torr of F_2 and 200 Torr of ClCN was calculated to be 4 (molecules CF_3Cl/absorbed h.ν), indicating a chain mechanism.

The absorption of light of 3660 Å by F_2 produces atoms of fluorine (8) that reacts with ClCN giving:

$$F + ClCN \rightarrow FClCN \qquad (I)$$

These radicals react with F_2 giving CF_2Cl radicals which, in turn, react with F_2 forming CF_3Cl, or abstract Cl from ClCN giving CF_2Cl_2.

$$FClCN + F_2 \rightarrow CF_2Cl + NF \qquad (II)$$

$$CF_2Cl + F_2 \rightarrow CF_3Cl + F \qquad (III)$$

$$CF_2Cl + ClCN \rightarrow CF_2Cl_2 + CN \qquad (IV)$$

Reaction IV, may be supported by the fact that under different conditions the ratio CF_2Cl_2/CF_3NNCF_3 was always 2, suggesting that CF_3NNCF_3 is formed by subsequent reactions of CN with fluorine.

Moreover the abstraction of Cl from ClCN can be supported by experiments formed in this laboratory that showed that in the photolysis of CF_3I in presence of ClCN the major product is CF_3Cl (9).

The formation of N_2 may be explained on the basis of:

$$2\ NF \rightarrow N_2 + 2\ F \qquad (V)$$

a reaction indeed reasonable since Diesen (10) has found that (V) occurs in shock wave experiments. So it could be said that the reaction

$$NF + F_2 \rightarrow NF_2 + F$$

does not occur. As a matter of fact no traces of N_2F_4, NF_3 or some other compound containing N-F bond were found despite exhaustive searching.

Acknowledgment

We thank the Consejo Nacional de Investigaciones Cientificas y Tecnicas (Republica Argentina) for financial support.

References

1. O. GLEMSER, H. SCHROEDER und H. HAESELER, Z. anorg. allgem. Chem., 282, 80 (1955).
2. H. L. CRAIG, Diss. Abst., 16, 862 (1956).
3. H. J. EMELEUS and G. L. HURST, J. Chem. Soc., 396 (1964).
4. W. J. CHAMBERS, C. W. TULLOCK and D. D. COFFMAN, J. Am. Chem. Soc., 84, 2337 (1962).
5. J. B. HYNES, B. C. BISHOP and L. BIGELOW, Inorg. Chem., 6, 417 (1967).
6. A. KLEMENC und G. WAGNER, Z. anorg. allgem. Chem., 233, 427 (1938).
7. R. GATTI, E. H. STARICCO, J. E. SICRE und H. J. SCHUMACHER, Z. Physik. Chem., 35, 343 (1962).
8. G. HERZBERG, Spectra of Diatomic Molecules, p. 389. D. Van Nostrand Co., Princeton, N.J., 2nd Edition (1950).
9. E. V. OEXLER and E. H. STARICCO, not yet published.
10. R. W. DIESEN, J. Chem. Phys., 45, 759 (1966).