

Preliminary Note

Reactions of Electronically Excited O(¹D) Atoms with Fluorocarbons

H. L. SANDOVAL, R. ATKINSON and J. N. PITTS, Jr.*

Department of Chemistry and Statewide Air Pollution Research Center, University of California, Riverside, California 92502 (U.S.A.)

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Commercial fluorocarbons are currently being released into the atmosphere at rates of $\sim 6.5 \times 10^5$ tons per year (1970) [1] and their tropospheric sinks are of considerable interest. They appear to be chemically inert in the troposphere [2] and indeed are used as tracers of Man's activities and of global atmospheric motions [3 - 5]. Thus, for example the fluorocarbons CHF₂Cl, CF₂Cl₂, CF₂ClCF₂Cl, CFCl₃ and CF₂ClCFCl₂ were observed to be less reactive than methane towards ground state O(³P) atoms [6], in agreement with their observed tropospheric stability.

Recently, however, it has been postulated [7] that vertical transport of fluorocarbons to the stratosphere with subsequent photodissociation there could lead to ozone destruction *via* a Cl-O₃ chain [7, 8], analogous to the NO-O₃ chain [9]. In this work we have studied the reactions of electronically excited oxygen atoms, O(¹D), with fluorocarbons for both fundamental interest and because of the possible stratospheric implications.

Experimental

The apparatus and experimental technique will be described in detail later, and hence only a brief summary is given here.

O(¹D) atoms were generated by the photolysis of NO₂ at 2288 Å [10] using cadmium resonance lamps. The X shaped 10 cm pathlength reaction cell had Supracil end windows for photolysis and NaCl windows for infra-red absorption measurements. The reactions were monitored by infra-red absorption using a Perkin-Elmer 221 spectrophotometer. NO₂ and fluorocarbons were handled in a conventional high vacuum system, with typical conditions being: 5 Torr NO₂, 5 Torr fluorocarbon, and photolysis times of 20 - 80 hours.

*To whom correspondence should be addressed.

Results and Discussion

In all cases, appreciable reaction of the fluorocarbons was observed. Control runs in which the fluorocarbon alone was irradiated showed no loss of fluorocarbon. Furthermore, the addition of up to 180 Torr of CO_2 , an efficient quencher of $\text{O}(^1\text{D})$ atoms [11], markedly decreased the fluorocarbon loss and product formation rates, while the addition of 100 Torr of He, a very inefficient quencher of $\text{O}(^1\text{D})$ atoms [12], had no observed effect. These observations confirm that the reactions observed are due to $\text{O}(^1\text{D})$ atoms [any $\text{O}(^3\text{P})$ atoms present would react almost exclusively with NO_2 in view of the low reactivity of fluorocarbons with $\text{O}(^3\text{P})$ atoms] [6]. This supports an earlier qualitative observation of $\text{O}(^1\text{D})$ abstraction from CF_3Cl [13].

There are at present no literature data available on the rates or products of $\text{O}(^1\text{D})$ atom reactions with fluorocarbons, and hence initial experiments have been carried out on the determination of reaction rate constants relative to N_2O :



where $k_2 = (k_{2a} + k_{2b}) = (2.2 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [14].

Under these experimental conditions and low conversions the loss of fluorocarbon, $\Delta[\text{FC}]$, is related to the loss of N_2O , $\Delta[\text{N}_2\text{O}]$, by the expression:

$$\frac{\Delta[\text{FC}]}{\Delta[\text{N}_2\text{O}]} = \frac{k_{1a}}{k_2} \frac{[\text{FC}]}{[\text{N}_2\text{O}]} \quad (\text{I})$$

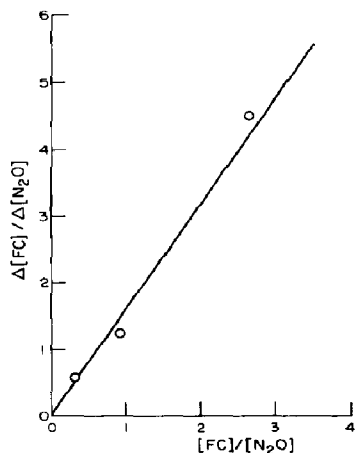


Fig. 1. Plot of equation (I) for the fluorocarbon CHF_2Cl . Pressure NO_2 , 5 Torr; total pressure, 10 Torr.

Figure 1 shows a plot of this expression for the fluorocarbon CHF_2Cl , the ratio k_{1a}/k_2 obtained from the slope being $k_{1a}/k_2 = 1.6 \pm 0.2$, giving $k_{1a} = (3.5 \pm 0.6) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (where the indicated errors are the estimated overall error limits). These rate constants k_{1a} and k_2 are both almost gas kinetic collision frequency. The formation of products *via* reaction (1a) at such a rapid rate suggests that it probably dominates over the quenching reaction (1b) for CHF_2Cl .

Thus if significant vertical transport occurs, in addition to a possible stratospheric sink of fluorocarbons by photodissociation in the wavelength region 1750 - 2000 Å [7], reaction with $\text{O}(^1\text{D})$ atoms could be a further loss process in the stratospheric region above $\sim 20 \text{ km}$ [15].

Further work on the rates, products and possible stratospheric implications of these reactions is currently being carried out.

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