

## Short Communication

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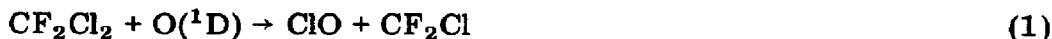
### Relative rate constants for the reactions of O(<sup>1</sup>D) atoms with fluorochlorocarbons and with N<sub>2</sub>O

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The possibility that stratospheric ozone may be depleted by a catalytic chain cycle involving Cl and ClO has recently been explored in detail (see Molina and Rowland [1] for a review). Sources of the Cl (or ClO) radicals include photolysis, in the stratosphere, of man-made chlorofluorocarbons (FCCs). An alternative route for production of ClO from the FCCs is chlorine abstraction by excited atomic oxygen, O(<sup>1</sup>D). This process may be exemplified for CF<sub>2</sub>Cl<sub>2</sub>:



The O(<sup>1</sup>D) in the lower stratosphere is largely formed as a product of ozone photolysis at  $\lambda < 310$  nm.

To correctly model the effects on atmospheric ozone concentrations of release of FCCs, it is clearly necessary to know the rate constants for the reactions of O(<sup>1</sup>D) with the FCCs. In the present communication, we describe determinations of the rate constants for the reactions of O(<sup>1</sup>D) with nine fluoro (chloro) carbons. The rate constants were measured, in a static, competitive, experiment, relative to the rate constants for the reaction of O(<sup>1</sup>D) with N<sub>2</sub>O.

### *Experimental*

Excited oxygen atoms, O(<sup>1</sup>D), were usually generated by the photolysis of NO<sub>2</sub> at  $\lambda = 229$  nm, although, in a few experiments, the atoms were produced by O<sub>3</sub> photolysis at  $\lambda = 254$  nm. A pair of Cd lamps (Philips 93107E) with Cl<sub>2</sub> filters (5 cm path, 1 atm. pressure) were used as the source of  $\lambda = 229$  nm radiation, while a low pressure Hg lamp (Hanovia) with a similar Cl<sub>2</sub> filter was used as the  $\lambda = 254$  nm source.

The photolyses were conducted in an X-shaped reaction cell; it was equipped with Suprasil windows for photolysis and NaCl windows for infrared absorption measurements.

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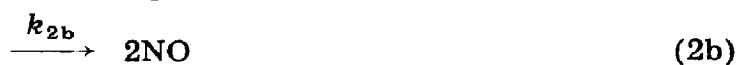
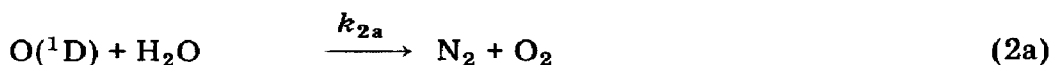
Nitrogen dioxide and nitrous oxide were obtained from cylinders (BDH); the stated purities were:  $\text{NO}_2 > 99.5\%$ ,  $\text{N}_2\text{O} > 98\%$ . Ozone was prepared by the action of an electric discharge in  $\text{O}_2$ , followed by adsorption on silica gel at 196K and subsequent desorption at room temperature. Purities (measured from the optical absorption) were typically 90%. Halocarbon purity was checked by gas chromatography and mass spectroscopy and was  $>99.7\%$  (except  $\text{CF}_3\text{CHCl}_2$ , whose purity was 98%). All reactions were carried out at room temperature ( $297 \pm 3\text{K}$ ). Typical reaction conditions used were:  $\text{NO}_2$ ,  $\sim 5$  Torr; total pressure, 10 Torr (made up of  $\text{N}_2\text{O}$  and halocarbon). The ratio of halocarbon to  $\text{N}_2\text{O}$ ,  $[\text{HC}]/[\text{N}_2\text{O}]$ , was varied between 0.5 and 3.0.

Concentrations of halocarbon and of  $\text{N}_2\text{O}$  remaining in the cell were followed, as a function of time, by infra-red spectrometry (Perkin-Elmer model 257 spectrometer).

### Results and Discussion

With the exception of experiments with  $\text{CF}_4$  (where no reaction was observed), changes in halocarbon and  $\text{N}_2\text{O}$  concentrations were followed for photolysis times between 20 and 60 hours. Product peaks were also observed by infra-red absorption, and identified [2, 3] as  $\text{COF}_2$ . No halocarbon was lost when halocarbon alone was irradiated.

If the only loss process for  $\text{N}_2\text{O}$  and for halocarbon is reaction with  $\text{O}(^1\text{D})$  atoms:



then the loss of halocarbon,  $\Delta[\text{HC}]$ , is related to the loss of  $\text{N}_2\text{O}$ ,  $\Delta[\text{N}_2\text{O}]$ , and the original concentrations of halocarbon and  $\text{N}_2\text{O}$  by:

$$\frac{\Delta[\text{HC}]}{\Delta[\text{N}_2\text{O}]} = \frac{k_{1a}}{k_2} \frac{[\text{HC}]}{[\text{N}_2\text{O}]}$$

where  $k_2 = k_{2a} + k_{2b}$ .

Values of  $\Delta[\text{HC}]/\Delta[\text{N}_2\text{O}]$  and  $[\text{HC}]/[\text{N}_2\text{O}]$  are plotted in Fig. 1. The least squares gradients,  $k_{1a}/k_2$ , are shown in Table 1. No change in the value of  $k_{1a}/k_2$  could be detected on (a) increase in total gas pressure, up to a maximum of 30 Torr; (b) addition of a six-fold excess of  $\text{NO}_2$ ; (c) addition of 5 Torr of  $\text{NO}$  (a product of  $\text{NO}_2$  photolysis) to a standard  $\text{CF}_2\text{Cl}_2/\text{N}_2\text{O}$  mixture.

Trial experiments with  $\text{CF}_2\text{Cl}_2$  using photolysis of ozone ( $\lambda = 254 \text{ nm}$ ) as the source of  $\text{O}(^1\text{D})$  gave  $k_{1a}/k_2$  equal to  $1.1 \pm 0.3$  and  $1.6 \pm 0.3$  for values

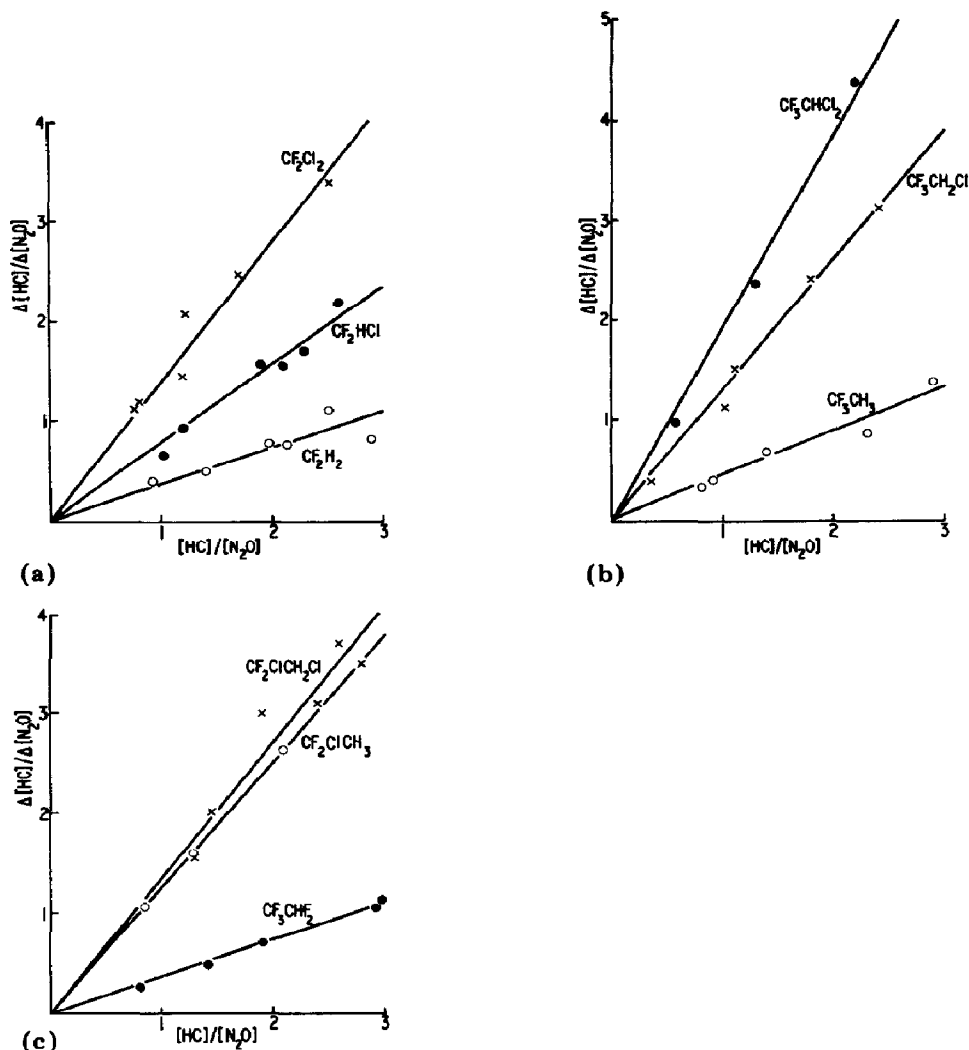


Fig. 1. Plots of the ratio of the changes in halocarbon and in nitrous oxide concentrations as a function of the initial halocarbon to nitrous oxide concentration ratio. (a): x,  $\text{CF}_2\text{Cl}_2$ ; ●,  $\text{CF}_2\text{HCl}$ ; ○,  $\text{CF}_2\text{H}_2$ . (b): ●,  $\text{CF}_3\text{CHCl}_2$ ; x,  $\text{CF}_3\text{CH}_2\text{Cl}$ ; ○,  $\text{CF}_3\text{CH}_3$ . (c): x,  $\text{CF}_2\text{ClCH}_2\text{Cl}$ ; ○,  $\text{CF}_2\text{ClCH}_3$ ; ●,  $\text{CF}_3\text{CHF}_2$ .

of our work and that of Pitts *et al.* [2], on the one hand, with that of Jayanty *et al.* and Fletcher and Husain, on the other, is also of limited validity. of  $[\text{HC}]/[\text{N}_2\text{O}]$  of 1.1 and 1.7. These results are thus identical, within the experimental error, to those obtained using  $\text{N}_2\text{O}$  photolysis of the  $\text{O}(^1\text{D})$  source.

Other published data are compared with our own in Table 1. The experiments of Jayanty *et al.* [4], and the direct  $\text{O}(^1\text{D})$  quenching measurements of Fletcher and Husain [5], yield rate constants,  $k_1 (= k_{1a} + k_{1b})$ , for overall deactivation of  $\text{O}(^1\text{D})$ . Since only lower limits are available for the ratio  $k_{1a}/k_1$  ( $\geq 0.33$  for  $\text{CF}_3\text{Cl}$  and  $\text{CFCl}_3$ ,  $\geq 0.40$  for  $\text{CF}_2\text{Cl}_2$  [6]), comparison

TABLE 1

Rate data for the reaction of O(<sup>1</sup>D) with halocarbons

| Compound                              | $k_{1a}/k_2$ |                         | $k_1/k_2$                 |                          | $10^{10}k_{1a}/\text{cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$ |
|---------------------------------------|--------------|-------------------------|---------------------------|--------------------------|--|
|                                       | This work    | Pitts <i>et al.</i> [2] | Jayanty <i>et al.</i> [4] | Fletcher and Husain [5]† |  |
| CF <sub>4</sub>                       | No reaction  | 0.1                     |                           | 0.14 ± 0.1               |  |
| CF <sub>3</sub> Cl                    |              |                         | 0.52                      | 1.1 ± 0.1                |  |
| CF <sub>2</sub> Cl <sub>2</sub>       | 1.4 ± 0.3    | 2.4 ± 0.3               | 1.3 ± 0.1                 | 2.2 ± 0.1                | 3.1 ± 0.7  |
| CFCI <sub>3</sub>                     |              | 2.65 ± 0.4              | 1.5                       | 2.5 ± 0.2                |  |
| CCl <sub>4</sub>                      |              |                         | 2.1                       | 3.9 ± 0.4                |  |
| CHF <sub>2</sub> Cl                   | 0.8 ± 0.2    | 1.6 ± 0.2               |                           | 1.1 ± 0.1                | 1.8 ± 0.4  |
| CHFCl <sub>2</sub>                    |              |                         |                           | 2.2 ± 0.1                |  |
| CHF <sub>3</sub>                      |              |                         |                           | 0.44 ± 0.04              |  |
| CH <sub>2</sub> F <sub>2</sub>        | 0.4 ± 0.2    |                         |                           |                          | 0.8 ± 0.4  |
| CF <sub>2</sub> Cl-CF <sub>2</sub> Cl |              | 1.5 ± 0.2               |                           | 1.7 ± 0.1                |  |
| CF <sub>2</sub> Cl-CFCl <sub>2</sub>  |              | 2.5 ± 0.3               |                           | 2.4 ± 0.2                |  |
| CF <sub>2</sub> Cl-CH <sub>2</sub> Cl | 1.4 ± 0.3    |                         |                           |                          | 3.0 ± 0.7  |
| CF <sub>3</sub> -CH <sub>2</sub> Cl   | 1.3 ± 0.3    |                         |                           |                          | 2.9 ± 0.7  |
| CF <sub>3</sub> -CH <sub>3</sub>      | 0.5 ± 0.1    |                         |                           |                          | 1.0 ± 0.2  |
| CF <sub>3</sub> -CF <sub>2</sub> H    | 0.4 ± 0.1    |                         |                           |                          | 0.8 ± 0.2  |
| CF <sub>3</sub> CHCl <sub>2</sub>     | 1.9 ± 0.3    |                         |                           |                          | 4.3 ± 0.7  |
| CH <sub>3</sub> CF <sub>2</sub> Cl    | 1.2 ± 0.3    |                         |                           |                          | 2.7 ± 0.7  |

†Based on  $k_2 = (2.2 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [7].

Nevertheless, where comparisons are possible (CF<sub>2</sub>Cl<sub>2</sub> and CHF<sub>2</sub>Cl), our values of  $k_{1a}/k_2$  and those of Fletcher and Husain suggest that  $k_{1a}/k_1$  is, in fact, at least as large as 0.6 - 0.7.

The last column of Table 1 gives our values for  $k_{1a}$  derived from a value of  $k_2 = 2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [7]. It is apparent that for species such as CF<sub>2</sub>Cl<sub>2</sub> or CF<sub>3</sub>CHCl<sub>2</sub> the rate constant is approaching the gas kinetic limit. As might be expected, presence of chlorine in the halocarbon favours the reaction, and the presence of fluorine tends to reduce  $k_{1a}$ .

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