

THE PHOTO-OXIDATION OF 1,3-DICHLOROTETRAFLUORO-ACETONE: MECHANISM OF THE REACTION OF CF_2Cl WITH OXYGEN

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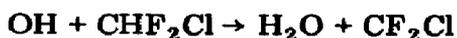
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Summary

The 313 nm photolysis of 1,3-dichlorotetrafluoroacetone in the presence of oxygen was investigated at 298 K. CF_2O and CO_2 were identified as the reaction products, and a mechanism is proposed to explain their formation. Evidence is obtained for the formation of CO_2 by the reaction of CF_2ClO radicals with CO .

1. Introduction

The reaction of the hydroxyl radical with fluorocarbon-22 (CHF_2Cl) provides a tropospheric sink for the latter species:



Seigneur *et al.* [1] have performed a one-dimensional diffusion and reaction calculation in which the flux of fluorocarbon-22 at the tropopause was predicted to be from 4% to 12% of that at ground level. Other evidence [2] suggests that the flux at the tropopause may be a larger fraction of the ground level flux which would fit with current estimates of atmospheric hydroxyl radical concentration that are lower than those available for the 1977 calculation.

The CF_2Cl radicals produced in the troposphere will undoubtedly react immediately with oxygen. In examining the literature, we found that the mechanism of the oxidation of CF_2Cl radicals is not well understood [3 - 9]. In all the work reported to date, CF_2Cl has been produced from the photolysis of CF_2Cl species. The question immediately arises as to whether the halogen atom also produced in the primary process is a complicating factor in these studies.

Photolysis of 1,3-dichlorotetrafluoroacetone (DTA) has been shown to produce CF_2Cl radicals efficiently:



is the exclusive primary photochemical process at 313 nm [10, 11]. In this investigation we have used DTA photolysis at 313 nm as a CF_2Cl source. We report here the results of a mechanistic investigation via end product analysis.

2. Experimental details

2.1. Apparatus

A conventional Pyrex vacuum system capable of achieving 10^{-5} Torr was used. The pressures were measured by a McLeod gauge, a Pirani gauge or a mercury manometer. The cylindrical commercial quartz reaction vessel was 10 cm long by 3.3 cm in diameter with planar Ultrasil end windows. The 313 nm radiation from a high pressure mercury lamp (Osram HBO 500 W) was isolated by a Bausch and Lomb high intensity grating monochromator with a 10 nm bandpass and collimated just to fill the reactor. The relative light intensity was photoelectrically monitored.

2.2. Chemicals

1,3-dichloro-1,1,3,3-tetrafluoroacetone was obtained from Pfalz and Bauer, Inc. It was used after degassing by several freeze-pump-thaw cycles. No impurities could be detected by gas chromatography although it was possible that the sample contained some of the asymmetrical isomeric ketone. CF_2O , purchased from Matheson, had a stated minimum purity of 97.0%. Tetrafluoromethane with a stated minimum purity of 99.7 mol.% was also obtained from Matheson. Helium (Air Products Co., minimum purity 99.9%) and oxygen (Chemetron, purity 99%) were employed without further purification.

2.3. Product analyses

Product analyses were performed on a Perkin-Elmer 810 flame ionization detector-thermal conductivity (FID-TC) gas chromatograph or a Varian 1520 FID-TC gas chromatograph and a Hewlett Packard 3380A integrator. Products of the photolysis of DTA in the absence of oxygen were identified on a Porapak T column 6 ft long with an outside diameter of 1/4 in at 90 °C, while the products of the photo-oxidation were analyzed on a Spherocarb column 6 ft long with an outside diameter of 1/8 in temperature programmed from 10 to 70 °C. All columns were found to convert CF_2O to CO_2 . The analyses were therefore done by both gas chromatography (GC) which gave the sum of CF_2O and CO_2 , denoted CO_2^* , and IR spectroscopy which gave the relative CF_2O and CO_2 yields. Quantitative GC analysis was accomplished by adding known amounts (typically 2%) of the inert

internal standard CF_4 to the reaction mixture before photolysis. The product quantum yields were determined by diethyl ketone actinometry. Positive product identification was by gas chromatography-Fourier transform IR spectrometry and by mass spectrometry. No evidence was found for chlorine or for any chlorine-containing species. All experiments were done at ambient temperature.

3. Results

3.1. Photolysis of 1,3-dichlorotetrafluoroacetone

The products of the photolysis of pure DTA were CO , CF_2Cl_2 , $1,2\text{-C}_2\text{F}_4\text{Cl}_2$ and $1,3\text{-C}_3\text{F}_6\text{Cl}_2$. These are the same products as those reported by Bowles *et al.* [10]. Furthermore, the relative yields were in good agreement with the values reported by these workers. CO quantum yields obtained from the photolysis of 20 Torr DTA with up to 165 Torr He and about 2% - 5% CF_4 are shown in Fig. 1. At lower pressures Φ_{CO} is greater than the value of 0.8 reported by Bowles *et al.* [10] but is in reasonable agreement with the value of 0.9 reported by Majer *et al.* [11]. The CO quantum yields, and hence the quantum yields of CF_2Cl , are relatively insensitive to pressurization with helium. Thus we corroborate earlier work and we do not expect the photo-oxidation to have much pressure dependence.

3.2. Photo-oxidation of 1,3-dichlorotetrafluoroacetone

The only products observed from the photolysis of DTA in the presence of O_2 were CF_2O and CO_2 . Additionally, CO was consumed in the reaction, as were O_2 and DTA. No chlorine-containing chemical species could be found by GC, IR spectrometry or mass spectrometry.

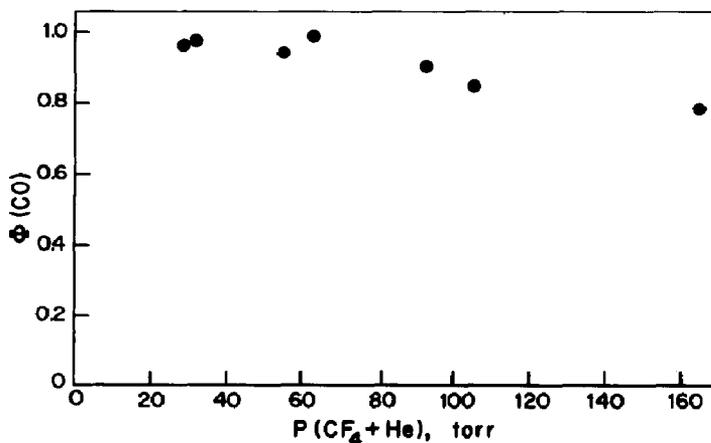


Fig. 1. CO quantum yields in the 313 nm photolysis of 20 Torr DTA in the presence of He.

A series of experiments was done in which the partial pressure of O_2 was varied in mixtures containing 20 Torr DTA and 60 Torr He. Figures 2 and 3 show the product quantum yields as a function of the initial pressure of added O_2 , as well as the quantum yields for O_2 disappearance. Similar results were obtained in experiments with 34 Torr He and 20 Torr DTA with increasing amounts of O_2 . The CO is entirely consumed at O_2 pressures above about 3 Torr, and the quantum yields of CF_2O and CO_2 also appear to become independent of the O_2 pressure above about 3 Torr. The CF_2O -to- CO_2 ratio was 2, independent of the O_2 pressure, the helium pressure and the photolysis time. The photolysis of 20 Torr DTA at a constant O_2 pressure (2.3 Torr) and varying amounts of helium (26 - 93 Torr) showed that product quantum yields and O_2 consumption quantum yields were independent of pressure in this range, consistent with the insensitivity of Φ_{CO} to P_{He} in experiments without O_2 .

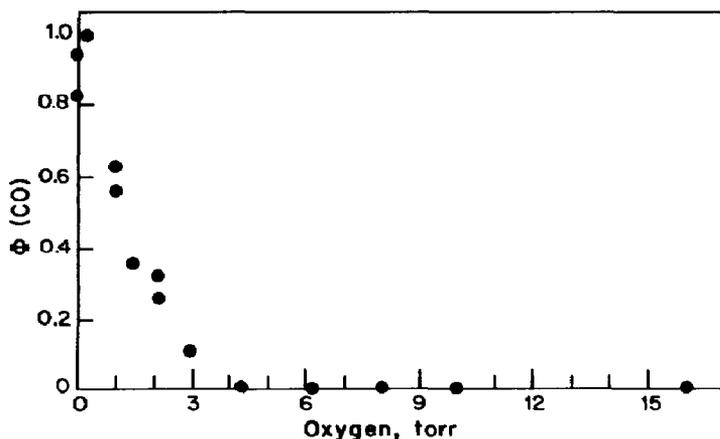


Fig. 2. CO quantum yields in the 313 nm photolysis of 20 Torr DTA in the presence of 60 Torr He as a function of added O_2 pressure.

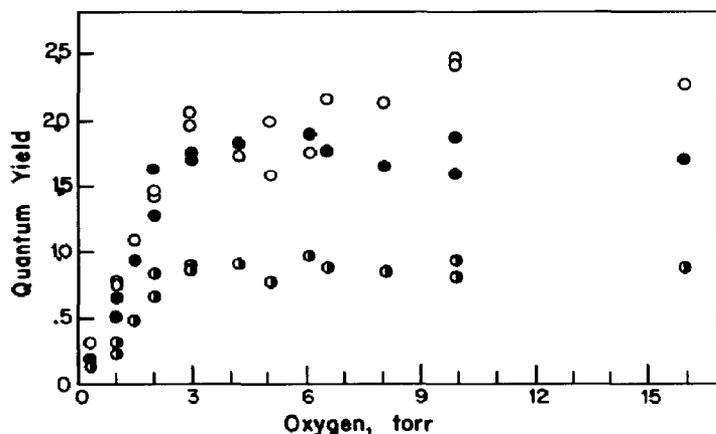


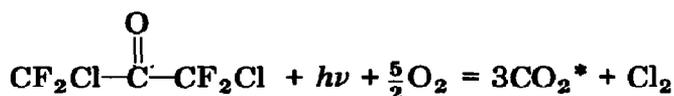
Fig. 3. Quantum yields of CO_2 and CF_2O formation and O_2 disappearance in the 313 nm photolysis of 20 Torr DTA in the presence of 60 Torr He as a function of O_2 pressure.

The yield of CO_2^* (combined CO_2 and CF_2O obtained from GC analysis only) was a linear function of time going through the origin, showing that these products are not formed in secondary reactions. The light intensity was varied by a factor of 20 using calibrated screens. The CO_2 and CF_2O quantum yields were found to be independent of light intensity.

4. Discussion

4.1. Stoichiometry

The results clearly show the consumption of O_2 and CO and the formation of CF_2O and CO_2 . The latter pair are always produced in a 2:1 ratio, although the GC analysis converts CF_2O to CO_2 and the sum of these species are reported as CO_2^* . The overall stoichiometry can be represented by the following equation:

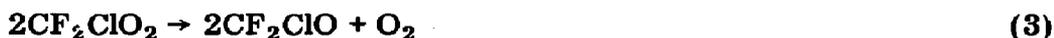


This predicts $\Phi_{-\text{O}_2}/\Phi_{\text{CO}_2^*} = 0.84$. The experimentally determined value of this ratio, obtained from experiments containing enough O_2 to remove CO completely, was 0.79 ± 0.11 . Furthermore, the above stoichiometry predicts $\Phi_{\text{CO}_2^*} = 3\phi$ where ϕ is the primary photodissociation quantum yield. If ϕ is taken as equal to Φ_{CO} ($\langle\Phi_{\text{CO}}\rangle = 0.89 \pm 0.07$), then the prediction is $\Phi_{\text{CO}_2^*} = 2.67$. This can be compared with the experimentally determined value of 2.78 ± 0.32 . Thus the carbon, oxygen and fluorine balance is satisfactory. We conclude that CF_2O results from the oxidation of CF_2Cl radicals formed in the DTA primary process (reaction (1)) and that the CO_2 results from the oxidation of the CO concurrently produced. The overall processes are given by the stoichiometric reactions $\text{CF}_2\text{Cl} + \frac{1}{2}\text{O}_2 \rightarrow \text{CF}_2\text{O} + \text{Cl}$ and $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$. The chlorine presumably ends up as Cl_2 . We are led to this conclusion by the fact that there is a good carbon, fluorine and oxygen balance and that no chlorinated compounds could be detected. Detection of Cl_2 by UV spectrophotometry and mass spectrometry was not possible because of interference from DTA.

4.2. Mechanism

The formation of CF_2O must be initiated by the reaction of O_2 with CF_2Cl radicals from the primary process of DTA. It has been suggested [6] that this occurs by a one-step process: $\text{CF}_2\text{Cl} + \text{O}_2 \rightarrow \text{CF}_2\text{O} + \text{ClO}$. However, this is not supported by observations of ClO formation in the flash photolysis of halomethanes in the presence of O_2 [7]. Further evidence against a direct reaction is provided by the observation that ClO formation is suppressed by added C_2H_6 in the flash photolysis of DTA- O_2 mixtures [12].

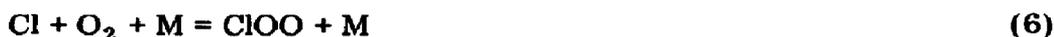
The results of this work are consistent with the following steps initiated by the addition of O_2 and CF_2Cl , as suggested by Jayanty *et al.* [4]:



The reaction of Cl with the peroxy radical



suggested by Gillespie *et al.* [7] to account for observations on the rate of formation of ClO in the flash photolysis of halomethanes in the presence of O_2 is unimportant here, since in steady illumination photolysis the lower free-radical concentrations mean that the rate of reaction of Cl with O_2 [13]



where $k_6 = (2.0 \pm 1.0) \times 10^{-33} (T/300)^{-1.3}$ must be many times faster than the rate of reaction (5), even if reaction (5) occurs with unit collision efficiency.

There is evidence that CO can be converted to CO_2 through reactions involving chlorine atoms. Bodenstein and Onoda [14] and Rollefson [15] found that CO_2 is produced at room temperature in a mixture of Cl_2 , CO and O_2 . Bodenstein *et al.* [16] have suggested that this occurs via the reactions $COCl + O_2 \rightarrow CO_2 + ClO$ and $ClO + CO \rightarrow CO_2 + Cl$. The COCl and ClO may be formed in the present DTA- O_2 system by the reactions



and reaction (6) followed by



However, it was found in the present work that the addition of 5 Torr C_2H_6 , which is sufficient to scavenge the Cl formed in reaction (4) by the reaction $Cl + C_2H_6 \rightarrow HCl + C_2H_5$, produced no change in Φ_{CO} . We must therefore conclude that chlorine atoms are not involved in the oxidation of CO to CO_2 .

This leaves only two possibilities: reaction of CO with either CF_2ClO_2 or CF_2ClO . These can be distinguished by experiments with added CO. A mechanism composed of reactions (1) - (4) and the reaction



predicts that $\Phi_{CF_2ClO} / \Phi_{CO_2} = 1$ at CO pressures that are sufficiently high for the rate of reaction (5) to be much greater than the rate of reaction (3). Alternatively, a mechanism composed of reactions (1) - (4) and the reaction



predicts that $\Phi_{\text{CF}_2\text{O}}/\Phi_{\text{CO}_2} = k_4/k_{10}(\text{CO})$. Figure 4 clearly shows that $\Phi_{\text{CF}_2\text{O}}/\Phi_{\text{CO}_2}$ does not approach unity as P_{CO} increases but decreases to considerably smaller values. Furthermore, a plot of $\Phi_{\text{CF}_2\text{O}}/\Phi_{\text{CO}_2}$ versus P_{CO}^{-1} is linear, as shown in Fig. 5. The slope of this plot gives $k_4/k_{10} = 12.2$ Torr which is consistent with the assignment of reasonable values to k_4 and k_{10} . No information on these rate constants could be found in the literature.

Finally, the surmised formation of Cl_2 most probably occurs by reactions involving ClO [17, 18] and perhaps COCl but not involving CF_2ClO or CF_2ClO_2 .

The finding that CO reacts with CF_2ClO rather than with CF_2ClO_2 is in accord with literature data showing that OH reacts at least a factor of 10^6 faster with CO than HO_2 does [13]. Furthermore, Czarnowski and Schumacher [19] have recently reported that CF_3O reacts with CO .

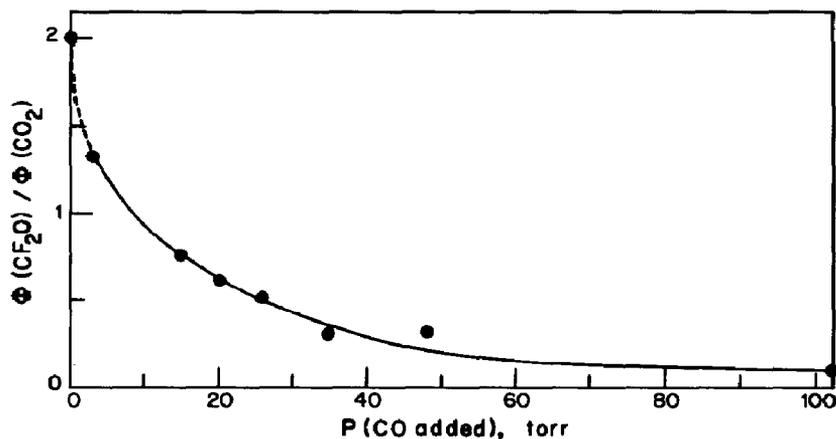


Fig. 4. The ratio $\Phi_{\text{CF}_2\text{O}}/\Phi_{\text{CO}_2}$ obtained in the 313 nm photolysis of 20 Torr DTA in the presence of 15 Torr O_2 as a function of the CO pressure.

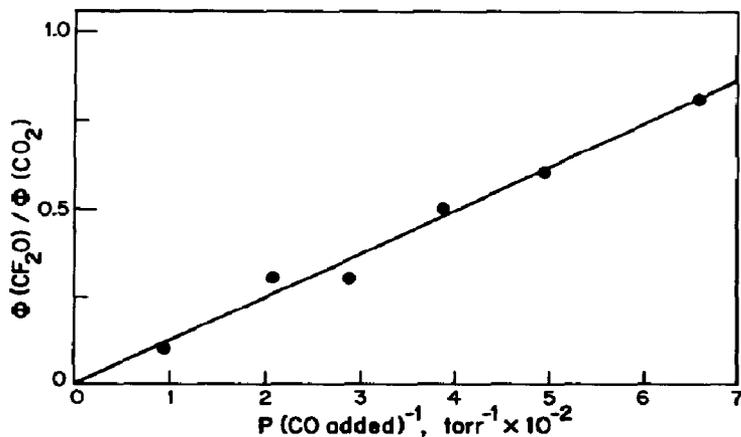


Fig. 5. The ratio $\Phi_{\text{CF}_2\text{O}}/\Phi_{\text{CO}_2}$ as a function of the reciprocal CO pressure.

Acknowledgment

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