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The photolysis of CF_3COCl in the presence of O_2 and CO: catalytic oxidation of CO to CO_2 and the formation of polyoxygenated intermediates

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Abstract

Photolysis of CF_3COCl in the presence of O_2 yields the radical CF_3O, which then reacts in the presence of CO and O_2 to yield a variety of CF_3-containing species initiated by the following reactions:

$$CF_3O + CO \rightarrow CF_3OCO$$

$$CF_3OCO + O_2 \rightarrow CF_3OC(O)O_2$$

The reactions of various oxygenated CF_3-containing radicals give rise to two different compounds with the general composition $CF_3OC(O)O_yCF_3$ (y=4 and 3) that show increased thermal stability as the number of oxygen atoms in the peroxidic bonding bridge decreases. A further species of the formula $CF_3OC(O)O_2C(O)OCF_3$ is also invoked. Parallel reactions lead to the formation of $CF_3OC(O)O$ radicals that decompose to give CF_3O and CO_2, thus providing a way of maintaining the chain reaction that catalytically converts CO into CO_2. Experimental evidence for the formation and thermal decay of these intermediates is presented.

Keywords: Catalytic oxidation; Polyoxygenated intermediates; Photolysis

1. Introduction

Photolysis of CF_3COCl in the presence of O_2 and CO leads to the formation of CF_2O and Cl_2, and the catalytic conversion of CO to CO_2 [1]. These observations can be understood in terms of the formation of CF_3 radicals in the primary photolytic step. The thermodynamically possible initial photochemical steps for a 254 nm photon are:

$$CF_3COCl + h\nu \rightarrow CF_3 + CO + Cl \quad (1a)$$

$$CF_3COCl + h\nu \rightarrow CF_3 + COCl \quad (1b)$$

$$CF_3COCl + h\nu \rightarrow CF_3CO + Cl \quad (1c)$$

$$CF_3COCl + h\nu \rightarrow CF_3Cl + CO \quad (1d)$$

Of these, channel (1d) is excluded on the basis of our earlier results [1]. We shall show later that channel (1c) also cannot participate. The remaining two pathways, (1a) and (1b), both yield CF_3. The perfluorinated fragment is captured efficiently by O_2 to form CF_3O_2

$$CF_3 + O_2 \xrightarrow{M} CF_3O_2 \quad (2)$$

which then goes on to yield CF_3O either from the radical–radical collision

$$CF_3O_2 + CF_3O_2 \rightarrow CF_3O + CF_3O + O_2 \quad (3)$$

or from the reaction with Cl atoms

$$CF_3O_2 + Cl \rightarrow CF_3O + ClO \quad (4)$$

which are themselves a product of the initial photolytic process (1a).

Reaction (3) has a rate constant of 1.7×10^{-12} cm^3 $molecule^{-1}$ s^{-1} [2], while for reaction (4) the rate constant is 4.5×10^{-11} cm^3 $molecule^{-1}$ s^{-1} [3]. Both reactions are sufficiently rapid to lead virtually exclusively to the formation of CF_3O radicals in our system.

In other experiments, Blesa and Aymonino [4] studied the photolysis of $CF_3O_2CF_3$ in the presence of CO and O_2 and observed that CO was oxidised catalytically to CO_2 and that

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the formation of CO_2 continued even when illumination was discontinued. These workers explained their observations by assuming that an intermediate was formed during photolysis. In our previous experiments [1], we also observed the quantitative conversion of CO into CO_2 in the photolysis of CF_3COCl in the presence of O_2 and CO. In addition, some peaks in the IR spectrum disappeared when the system was left in the dark. We were, therefore, able to corroborate the existence of at least one intermediate, but its identity still remained to be determined.

In the present paper, we describe further investigations of this system, and put forward evidence for the existence of three different species, two of them, with the general formula $CF_3OC(O)O_yCF_3$ (y=4 and 3) possessing different lifetimes (around a minute for the first one and hours for the second), and the third ascribed to the symmetrical peroxide $CF_3OC(O)O_2C(O)OCF_3$.

2. Experimental

2.1. Materials

Commercially available samples of CF_3COCl (PCR Research Chemicals) were distilled in vacuum before use.

Oxygen was condensed by passing O_2 at atmospheric pressure through a trap immersed in liquid air. The condensate was then pumped under vacuum several times and transferred to a glass bulb whilst the trap was immersed in liquid air.

CO was passed through a trap maintained at liquid nitrogen temperature and stored in a glass bulb.

2.2. Procedure

A quartz-walled cell equipped with KCl windows was used to conduct the photochemical experiments. Photolysis was carried out using three low-pressure 10 W Hg lamps arranged around the cell, which was mounted in the light path of a FTIR spectrophotometer to allow us to monitor the appearance of products and the disappearance of reagents as a function of time.

The light path of the cell (23 cm) was chosen in order to fill the available space in the path of the FTIR beam in order to avoid interference of CO_2 in ambient air.

The measurements were performed at room temperature and at low temperatures (close to 5°C); the lower temperatures were employed in experiments aimed at synthesising as much intermediate as possible. The sub-ambient temperatures were obtained by evaporating liquid nitrogen in the cell compartment of the FTIR; good mixing of the gas was obtained with small fans placed in situ. Temperatures were measured with a thermocouple attached to the external walls of the cell. Different temperature ranges were obtained by the use of containers with different thermal insulations. Note that we were interested in the achievement of a temperature range where the decomposition of the intermediate was precluded and not in maintaining a stabilised temperature.

A typical room temperature experiment involved photolysis of the sample for about 2 min, then turning off the light, and continuing to monitor the variation of product concentrations for around 120 min. In the case of low-temperature experiments, we extended the observation time after having turned off the photolysing lamps to up to 2 days.

3. Results

Fig. 1 shows the spectra obtained before and during photolysis, and 10 min after having turned off the photolysis lamps. Several new peaks (indicated with arrows) appear during the photolysis, and disappear when the system is in the dark, thus indicating the existence of at least one intermediate.

A more detailed analysis is shown in Fig. 2, which shows the time variation of the peaks from the spectra obtained following the photolysis of 2.0 torr CF_3COCl in the presence of 5 torr CO and 10 torr O_2. To maximise the yield of intermediates, the photolysis was conducted for 30 min at low temperature (5°C), but the reaction system was warmed to room temperature immediately after photolysis in order to follow the time evolution of the various species. The figure shows the difference spectra after subtraction of the IR absorptions corresponding to the pure reagents and the stable products (CF_2O, CO_2, and $CF_3O_3CF_3$; the latter species is formed only in these very long photolyses). The peaks at 975, 990, 1137 and 1256 cm^{-1} decrease in intensity as time elapses, whereas the intensity of the peak at 1168 cm^{-1} increases at first and then begins to decrease. This observation suggests the formation of two intermediates, the first (peak characteristics at 975 and 1137 cm^{-1}) with a short lifetime (ca. 2 min), and the second (peak at

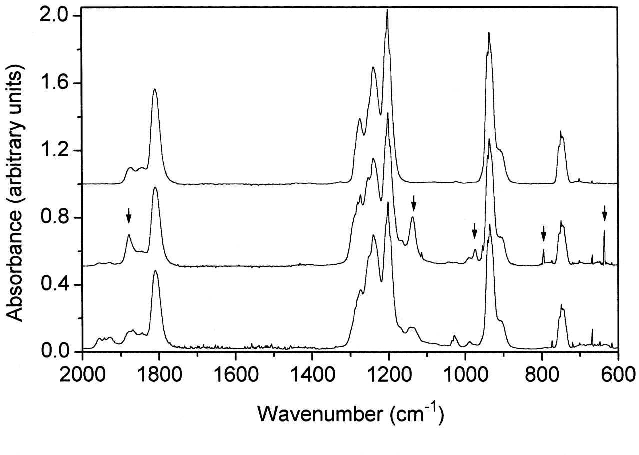

Fig. 1. Spectral sequence in the photolysis of 2 torr CF_3COCl, 5 torr CO and 10 torr O_2. Spectra without manipulation were taken directly from the reaction cell. Upper trace, before photolysis; middle trace, during photolysis; lower trace, 10 min after turning off photolysing lamps.

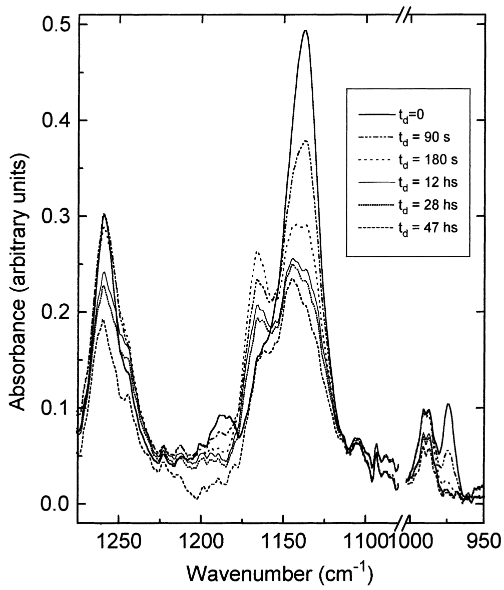

Fig. 2. Detailed view of the temporal variation of some selected bands showing the existence of more than one intermediate. The spectra were taken at different times after turning the lights off and after F_2CO, CO_2, $CF_3O_3CF_3$ and CF_3COCl subtraction. Note that t_d is defined as the time elapsed from the moment that the photolysis lamps are turned off.

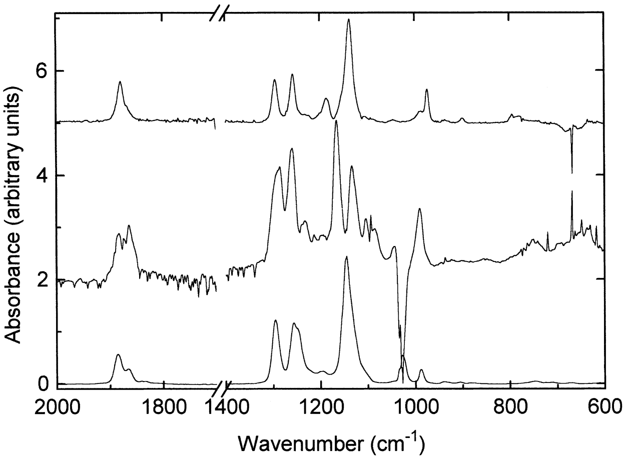

Fig. 3. Spectra of Intermediates I (upper trace), II (middle trace) and III (lower trace) resulting after appropriate subtraction. Note that for Intermediate II, the overall trace has been magnified 10 times. The negative peak corresponding to SiF_4 (1029 cm^{-1}) is a result of succesive subtractions.

1168 cm^{-1}) persisting for hours. We shall henceforth refer to these two intermediates as Intermediates I and II. Increases in the concentration of Intermediate II when the system is in the dark indicates its probable formation from the rupture of Intermediate I.

There is evidence in our spectra of the presence of a third species of higher stability, and that we shall identify as Intermediate III. The shape of the peak initially at 1137 cm^{-1} begins to change; a broadening is observed that corresponds to a new feature at 1143 cm^{-1}. Subsequently, even this peak begins to decay, at times longer than 12 h (possible loss processes are examined in Section 4). However, substantial amounts of Intermediate III remain after periods as long as 47 h, as indicated by the remaining absorbance at 1143 cm^{-1} shown in Fig. 2. Virtually none of the Intermediates I or II can be present at these times, so that the spectrum at 47 h can be identified with that of Intermediate III and the other stable products. The bottom trace of Fig. 3 shows the difference spectrum after absorbances due to CF_2O, CO_2 and $CF_3O_3CF_3$ have been removed. In addition to the absorption feature at 1143 cm^{-1}, there are two additional bands at higher frequencies, 1865 and 1885 cm^{-1}, that appear to be associated with Intermediate III.

The upper two traces of Fig. 3 show the spectra corresponding to Intermediates I and II obtained in the following sequence of four steps.

1. The spectrum obtained at t_d=0 (t_d is the time in the dark after the lamps are turned off) was taken as the starting point. The spectra corresponding to reagents, CF_2O, CO_2 and, if necessary, $CF_3O_3CF_3$ were subtracted. This difference spectrum should contain the bands of the two intermediates as well as a small contribution from Intermediate III which has already been generated at short times.
2. A scaled spectrum corresponding to Intermediate III was removed from the spectrum obtained in step 1. This difference spectrum should contain the bands of the Intermediates I and II.
3. Spectra obtained for t_d between 180 and 3600 s were used to obtain the spectrum of Intermediate II, after subtraction of absorptions due to reagents, stable products, and Intermediate III. As Intermediate I has a short lifetime at room temperature, it is evident that for t_d>180 s, Intermediate I will have decomposed completely, while Intermediate II has a lifetime of several hours.
4. Finally, the spectrum corresponding to Intermediate I was obtained as the difference between the spectrum obtained in step 2 and the spectrum obtained in step 3 (suitably scaled).

Fig. 4 displays the temporal variation of the yields of products and Intermediates I and II, together with the decrease in [CO]. The determination was carried out at room temperature with 5 torr CO in the mixture. The 975 and 1168 cm^{-1} bands were used for the measurement of Intermediates I and II, respectively. Note that the ordinates are arbitrary spectral peak areas, and thus do not indicate the relative concentrations of different species. Intermediate I increases in concentration during photolysis (irradiation time 120 s) but once the system is in the dark, its concentration decreases and at the same time the concentration of CO_2 increases. The figure also shows that the decrease of the peaks from Intermediate I is accompanied by a concomitant increase of Intermediate II and CF_2O.

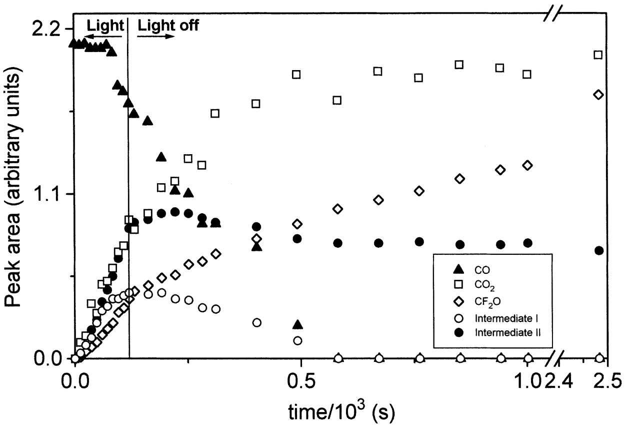

Fig. 4. Room temperature photolysis of 2 torr CF_3COCl, 10 torr O_2 and 5 torr CO. Time variation of the concentration of Intermediates I, and II, CF_2O, CO and CO_2 (see text for details). Note how clearly the catalytic conversion of CO into CO_2 can be seen. After the lights are turned off, CO concentration goes down steadily while the CO_2 sharply increases until Intermediate I has disappeared.

Fig. 5(a) indicates the variation of the relative concentration of Intermediate I as a function of time at different temperatures and initial pressures of CO. It can be seen that the higher concentration of intermediates appear at the lower temperature for a fixed CO pressure, and that the amount formed for a given temperature depends on the pressure of CO added to the system. When photolysis is performed in the presence of 1 torr CO, the disappearance of Intermediate I occurs more rapidly than in the presence of 5 torr CO. Furthermore, the concentration of Intermediate I does not decrease at low temperatures. Fig. 5(b) shows the concentration of CF_2O as a function of time for the same experimental conditions as those indicated for Fig. 5(a). The initial rate of formation of CF_2O is relatively somewhat higher for the higher initial pressure of CO, and the final yield is also higher.

In an attempt to shed further light on the composition of Intermediate III, a special experiment was conducted, in which CF_3COCl was photolysed at low temperature (5°C) in order to maximise initially the yield of Intermediate I. Low-temperature photolysis was carried out for 30 min. After allowing 2 days in the dark to ensure complete decomposition of Intermediates I and II, the different fractions of the stable products were distilled and collected. Firstly, the non-condensible fraction was eliminated from a liquid-nitrogen cooled bath, then the residue was distilled between -100°C and liquid-nitrogen temperature, collecting CO_2 and CF_2O. Lastly, the fraction distilling between -30°C and -80°C was analysed by mass spectrometry. The mass spectrum obtained (Fig. 6) shows a mass peak at $m/z = 129$, which in our system could be assigned to two possible different fragments, $CF_3OC(O)O^+$ and $CF_3C(O)OO^+$.

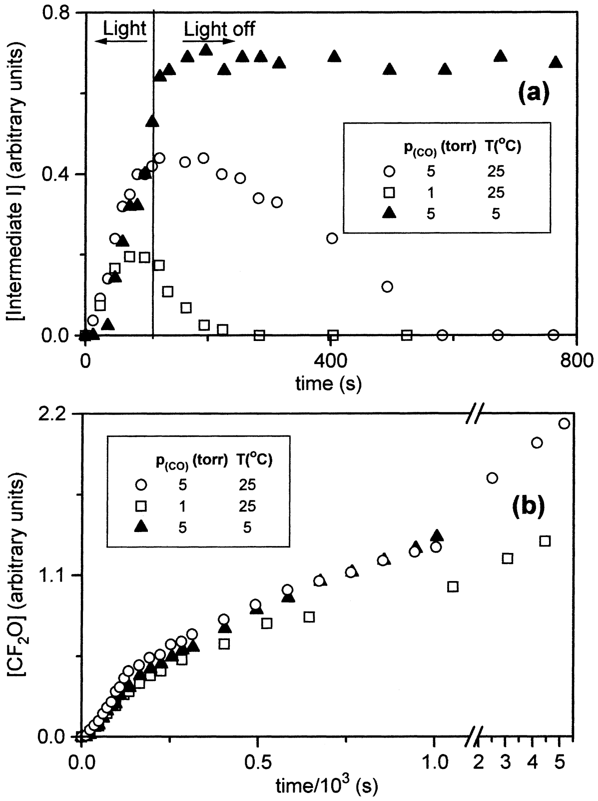

Fig. 5. Time variation of concentration of Intermediate I (a) and CF_2O (b) at different CO initial pressures and temperatures. The symbols reflect the conditions of the experimental run.

4. Discussion

4.1. Nature of the intermediates

Our discussion first deals with the identification of the labile species, Intermediates I, II and III, and then goes on to consider the reaction mechanisms by which they are formed. To expedite our treatment, we first set out our conclusions

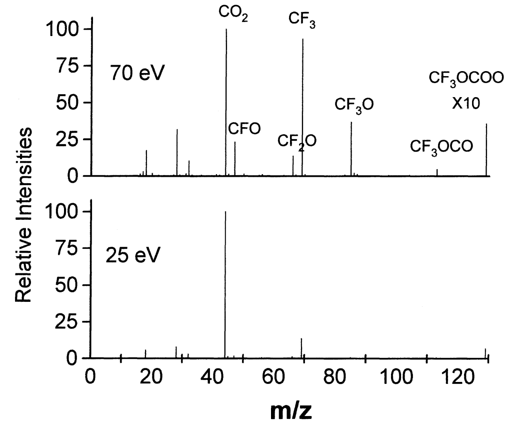

Fig. 6. Mass spectra at two different energies showing the existence of the fragment CF_3OCOO^+ arising from the rupture of Intermediate III which is assigned to $CF_3OC(O)OOC(O)OCF_3$.

about the identities of the three compounds, and then show in the discussion that follows the reasoning that we adopted. Our suggestions are:

Intermediate I=$CF_3OC(O)O_2{\cdot}O_2CF_3$
Intermediate II=$CF_3OC(O)O_3CF_3$
Intermediate III=$CF_3OC(O)O_2C(O)OCF_3$

There are several pieces of information that lead us to these conclusions. They are (i) the ultimate products of the thermal decomposition of these species are probably CF_2O and CO_2; (ii) their relative stabilities; (iii) their IR spectra (see Fig. 3); (iv) the peak observed at 720 cm^{-1} (cf. middle trace Fig. 3) only for Intermediate II and not for Intermediate I or Intermediate III; (v) decomposition of Intermediate I appears to give rise to an increase in the concentration of Intermediate II (although this observation should not be taken to imply that Intermediate II is a direct product of the decomposition of Intermediate I).

The IR spectra themselves indicate the presence of carbonyl groups, and C–F and C–C bonds, while the peak at 720 cm^{-1} suggests, as discussed by Wallington et al. [5], that we are faced with a trioxide for Intermediate II. We shall show later that the structure suggested is the only one consistent with a tenable production mechanism.

We now turn to the evidence for the structure of Intermediate III. We have noted the presence of IR absorptions at 1865 and 1885 cm^{-1} in the spectrum of this species. Meller and Moortgat [6], who studied the reaction of photochemically generated CF_3O radicals with CO, ascribed their bands at 1867 and 1889 cm^{-1} to the carbonyl groups of the peroxide $CF_3OC(O)O_2C(O)OCF_3$. This assignment was based on the results of Aymonino [7] who observed bands in the peroxide at 1867 and 1888 cm^{-1}. It is tempting, therefore, to take our IR spectra as indicating that Intermediate III is this peroxide. However, since the absorption bands could originate from other carbonyl species, we have turned to the mass spectra to provide additional confirmation.

The mass spectra of the product of the special run described earlier, were obtained initially using an electron impact energy of 25 eV. The aim was to detect the molecular ion. Nevertheless, the highest *m*/z peak observed was 129 (Fig. 6). On first inspection, reasonable assignments would be the fragments $CF_3OC(O)O^+$ or $CF_3C(O)O_2^+$. However, the second possibility can be discarded on the basis of the results obtained by Wallington et al. [5]. These workers irradiated mixtures of $CF_3CHO/Cl_2/O_2/N_2$ to generate CF_3CO radicals, which react with the O_2 to form $CF_3C(O)O_2$ radicals. The final products were $CF_3O_3CF_3$, CF_3OH, CO, CO_2 and CF_2O. An unknown product with a lifetime of around 100 s, and with characteristic IR frequencies at 762, 1053, 1298 and 1859 cm^{-1}, was also observed. The authors postulated that this product was CF_3O_3 $C(O)CF_3$. Such IR features are absent in our system. It seems, then, that no CF_3CO radicals are formed. $CF_3C(O)O_2^+$ then has no source. Furthermore, the result shows that the photolytic primary step 1(c) must be at most a minor contributor to the overall decomposition of CF_3COCl.

Identification of the *m*/*z*=129 peak with $CF_3OC(O)O^+$ is consistent with the weakest bond in the molecule being a peroxidic O–O bond. When the excitation energy was increased to 70 eV, the intensity of the ion peak decreased (note that in the upper figure its intensity has been magnified by a factor of 10) at the same time that fragments with lower *m*/*z* increased in intensity. We thus believe that these spectra confirm the existence of $CF_3OC(O)O_2C(O)OCF_3$.

There is a further point of interest in connection with Intermediate III. The unsymmetrical peroxide CF_3OO-$C(O)OCF_3$, bis (trifluoromethyl) peroxy-carbonate, is stable and has been known since 1972 [8]. Its boiling point is 25°C, which ensures that, at the concentrations that could be formed, it will remain in the gas phase even at the low (5°C) temperatures that we used. More important, however, are its IR characteristic frequencies. These are reported as: 1146 (vs.); 1878, 1300, 1250 and 1024 (s); 933, 746, 702 and 580 (m); 607 (w) and 1412 and 637 (vw) cm^{-1}. A close inspection of the lower trace of Fig. 3 shows that the substance represented by the spectrum is not CF_3OO-$C(O)OCF_3$ itself. Nevertheless, there is a close parallel between our observed spectrum and that reported for $CF_3OOC(O)OCF_3$, not only in the position of the absorption bands but also in their relative intensities, which could be taken as indicative that our species and $CF_3OOC(O)OCF_3$ have very similar structures.

We note that the loss processes for Intermediate III could include some hydrolysis inside the cell. This postulate is lent credence, since the products formed at such long times include SiF_4 (not shown in the sequential variation of spectra in Fig. 2), besides CF_2O and CO_2.

4.2. Mechanism and kinetics

Fig. 4 shows clearly that, in agreement with our earlier results [1], CO concentration decreases during photolysis of CF_3COCl, and continues to decrease even when the system is left in the dark; the concentration of CO_2 increases throughout these periods. As explained in Section 1, the initial steps of the reaction (reactions (1a) or 1(b), and (3) or (4)) lead to the formation of CF_3O radicals. The results of Blesa and Aymonino [4] and Meller and Moortgat [6], who photolysed $CF_3O_2CF_3$ in the presence of CO and O_2 make it clear that CF_3O can affect the oxidation. Although, it is also possible that atomic chlorine generated directly in step (1a) or indirectly from step (1b) could initiate oxidation [1,9]; wall removal of Cl will prevent Cl-initiated chains from persisting for the reaction durations examined in the present work.

The pathway which leads to the formation of intermediates begins with the reaction between the radical CF_3O and CO to form CF_3OCO. There are three possible channels

$$CF_3O + CO \xrightarrow{M} CF_3OCO \qquad (5a)$$

$$CF_3O + CO \rightarrow CF_3 + CO_2 \qquad (5b)$$

$$CF_3O + CO \rightarrow CF_2O + FCO \qquad (5c)$$

for the reaction between CF_3O and CO. This reaction has been investigated extensively [10,11]. The rate constant for reaction (5) was first investigated by Saathoff and Zellner [12] who reported a value for a fixed pressure. Czarnowski and Schumacher [11] had suggested earlier that the reaction rate was pressure-dependent, and, subsequently, a pressure dependence for the rate constant has been found [13,14]. The very recent result of Meller and Moortgat [6] for high pressures (1 atm) puts the value at 5×10^{-14} cm^3 molecule^{-1} s^{-1}. The data of Turnipseed et al. [13] indicate that the rate constant for the total pressures in our system (8–17 torr) will lie in the range 1.2–2.5$\times10^{-14}$ cm^3 molecule^{-1} s^{-1}. Once formed, the most probable fate of the CF_3O radicals thus is reaction with CO when pressures higher than 1 torr of CO are used.

Channels (5b) and (5c) appear to make little contribution. Upper limits of $k_{5b}<4\times10^{-16}$ and $k_{5b}+k_{5c}=2\times10^{-15}$ cm^3 molecule^{-1} s^{-1} have been given by Turnipseed et al. [13]. In any case, even if reaction (5b) were to occur, it would also contribute to the catalytic conversion of CO to CO_2, since the CF_3 radicals formed will re-enter the chain at reaction (2). We do not observe any formation of $(FC(O)O)_2$; neither did Wallington and Ball [14] in a system also containing CF_3, CO and O_2. Reaction (5c) thus seems not to be one of the possible channels for the reaction of CF_3O radicals with CO.

Formation of CF_3OCO in reaction (5a) is followed by addition of O_2

$$CF_3OCO + O_2 \xrightarrow{M} CF_3OC(O)O_2 \qquad (6)$$

Although the rate constant for reaction (6) is unknown, it can be assumed to take a value equal to that of the reaction CF_3CO+O_2 (7.3×10^{-13} cm^3 molecule^{-1} s^{-1}) [15]. In our system, the formation of peroxy radicals is thus assured in view of the high concentration of O_2.

There are three possible channels for self-reaction of $CF_3OC(O)O_2$ radicals

$$CF_3OC(O)O_2 + CF_3OC(O)O_2 \rightarrow CF_3OC(O)O_2 \cdot O_2C(O)OCF_3 \qquad (7a)$$

$$CF_3OC(O)O_2 + CF_3OC(O)O_2 \rightarrow CF_3OC(O)O + CF_3OC(O)O + O_2 \qquad (7b)$$

$$CF_3OC(O)O_2 + CF_3OC(O)O_2 \rightarrow CF_3OC(O)O_2C(O)OCF_3 + O_2 \qquad (7c)$$

Reaction (7a) is a simple dimerisation, while reaction (7b) is the analogue of many peroxy radical reactions, including that of $CF_3C(O)O_2$ [15]. Channel (7c) is written as a concerted process yielding the peroxide $CF_3OC(O)O_2C(O)OCF_3$. We do not believe that this peroxide can be formed by the dimerisation of free acyloxy radicals, CF_3O-$C(O)O$, from channel (7b), because these radicals are very likely to dissociate rapidly as do other similar acyloxy species [15]

$$CF_3OC(O)O \rightarrow CF_3O + CO_2 \qquad (8)$$

The CF_3O radicals from reaction (8) can, of course, either continue the chain conversion of CO to CO_2, or alternatively leave the catalytic cycle to yield CF_2O.

The traces for concentrations of Intermediate I in Figs. 4 and 5, and especially that for low temperature in Fig. 5(a), suggest strongly that the intermediate is only produced during the period that the reaction system is illuminated. This result means that the intermediate must be produced from at least one radical that disappears in the dark. The most abundant of these species will be CF_3O_2, and we suggest that the reaction involved is

$$CF_3O_2 + CF_3OC(O)O_2 \rightarrow CF_3OC(O)O_2 \cdot O_2CF_3 \qquad (9)$$

At this stage, we have now written reactions that form two of our intermediates, reaction (9) for Intermediate I and reaction (7c) for Intermediate III. Finally, we suggest that Intermediate II is formed by yet another association reaction between radicals present in the system, $CF_3OC(O)O_2$ and CF_3O

$$CF_3OC(O)O_2 + CF_3O \rightarrow CF_3OC(O)O_3CF_3 \qquad (10)$$

A supply of CF_3O_2 and $CF_3OC(O)O_2$ radicals is maintained in the dark by the thermal decomposition of Intermediate I

$$CF_3OC(O)O_2 \cdot O_2CF_3 \rightarrow CF_3O_2 + CF_3OC(O)O_2 \qquad (-9)$$

This interpretation is entirely consistent with our observation (Fig. 4) that the decrease in concentration in the dark of Intermediate I is accompanied by an increase in the concentration of Intermediate II, since reaction (−9) will provide an additional source of radicals in the dark system. It is evident that Intermediate I does not provide a major reservoir for reactive radicals, since the rate of CF_2O formation is only slightly greater (Fig. 5(b)) at 25°C than at 5°C, while the decay of Intermediate I is much faster (Fig. 5(a)). Similar conclusions can be drawn from the runs performed at 1 and 5 torr of CO at a fixed temperature.

Fig. 5(a) demonstrates that the amount of Intermediate I formed from the photolysis is larger at lower temperatures, which is indicative of its higher stability at low temperatures.

Fig. 5(b) shows clearly the increase of $[CF_2O]$ even during the dark period, showing that the catalytic cycle continues in the absence of new CF_3 radicals. Wallington and Ball [14] employed the photolysis of $CF_3N_2CF_3$ to generate CF_3. In the presence of CO and air, they observed that 96% of the CO that disappeared was converted to CO_2, a value that correlates very well with our findings for room temperature experiments. For the experimental runs carried out by us at low temperatures, the formation of higher quantities of Intermediate III leads to a lower fractional conversion.

The mechanism of formation of CF_2O in systems such as ours itself remains uncertain, despite much effort on the part of several research groups. Fig. 5(b) shows that the rate of formation of CF_2O is perhaps larger by a factor of two during the period of illumination than after it, but that this rate then remains virtually constant for as much as 10^3 s thereafter. At least in the early stages of the dark period, the rates of CF_2O formation are only slightly dependent on the temperature. For low pressures of CO, the rate is also only slightly lower initially, although it begins to drop off as CO is consumed. These results also confirm that CF_2O is largely a product of the main oxidation cycle in the dark (reactions (5), (6), (7b) and (8)), although the small differences between the different curves in Fig. 5(b) probably reflect the supply of additional radicals in the dark from the reservoir of Intermediate I. At the very longest times, Intermediates II and III could also contribute.

A reaction often invoked by Descamps and Forst [16] and Turnipseed et al. [13] to account for the formation of CF_2O is the process

$$CF_3O \rightarrow CF_2O + F \tag{11}$$

However, the reaction is 96 $\mathrm{kJ\,mol^{-1}}$ endothermic, and is likely to be very slow, at least for unexcited CF_3O. A wall reaction

$$CF_3O + \text{wall} \rightarrow CF_2O \tag{12}$$

has been invoked by Meller and Moortgat [6]. In their apparatus, the rate constant was $0.45\ \mathrm{s^{-1}}$. Although not directly relevant to a completely different experimental system, the observations do demonstrate that CF_3O radicals could readily be converted to CF_2O on the vessel surfaces on the time scale of our experiments, which have durations of up to tens of thousands of seconds. It thus seems reasonable to assume that the CF_2O observed derives largely from decomposition of CF_3O, with the intermediate species acting as small reservoirs of various radicals over their respective lifetimes.

5. Conclusions

The present paper dealt with a detailed view of the reactions that the CF_3O radicals present in the presence of CO and CO_2.

Although much work still needs to be done, it seems to be that new intermediates are found in the catalytic reaction that converts CO into CO_2.

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