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Elementary Reaction of $CF_2(\tilde{X})$ with O_3 : **Primary Products**

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The reaction of $CF_2(\tilde{X})$ with O_3 has been investigated in a discharge flow reactor at room temperature and low pressure (p = 2.5 mbar). $CF_2(\tilde{X})$ was produced by a microwave discharge of a mixture of CF₂Br₂/He. The reactants and products were detected by mass spectrometers (MS), which were connected to the flow systems via a continuous molecular beam sampling system.

The following primary products were observed (CF₂O₃ (m/z = 98); CF₂O (m/z = 47, 66); O_2 (m/z = 32)). The reaction mechanism:

 $CF_2(\tilde{X}) + O_3 \rightleftharpoons CF_2O_3^{\#} \rightarrow CF_2O_3$ \rightarrow CF₂O+O₂

(1)

explains the observed primary products. The molecule with the empirical formula CF₂O₃ has been observed directly by MS; the structure is discussed.

1. Introduction

Difluorcarbene (CF₂($\tilde{X}^{1}A_{1}$)) is a radical, albeit not a very reactive one, and therefore it may play an important role as a fluorine-containing intermediate in the degradation of fluorinated compounds in the upper atmosphere and stratosphere. Also in plasma etching systems $CF_2(\tilde{X})$ can be regarded as a fluorine-containing reservoir.

In the plasma etching processes of Si and SiO₂ surfaces, used in the fabrication of micron-size features in semiconductor devices, CF4 discharges are applied. In models to understand these processes, CF_x radicals and F atoms are involved [1-3]. The addition of a small amount of O_2 to the CF₄ plasma is known to increase significantly the etching rate. The main etching species are assumed to be F atoms, the concentration of which is increased by O atom reactions [4]. Stable O3 molecules, which can be added

to the system in large quantities compared to the concentration at labile O atoms available, might also cause an increase in the F atom concentration in the C-F-O system. One possible pathway is the reaction of $CF_2(\tilde{X})$ with ozone.

 $CF_2(\tilde{X})$ is formed in the atmospheric chemistry by photolysis of CFCls such as CF_2Cl_2 , which accumulate in the earth's atmosphere and stratosphere [5-8]. Since the reactivity of $CF_2(\tilde{X})$ in its electronic ground state with atmospheric gases like O_2 , N_2 , CO_2 is very low, the concentration of $CF_2(\tilde{X})$ could reach higher values than that of other reactive intermediates.

The reaction of O_3 with $CF_2(\tilde{X})$

 $CF_2(\tilde{X}) + O_3(\tilde{X}^1A_1) \rightarrow \text{products}$

(1)

is therefore of great interest. Under atmospheric conditions, reaction (1) is not very fast. At room temperature approximately one million CF_2 -O₃ collisions are needed before reaction occurs with an activation energy of 25 kJ/ mol [9]. The products of the gas phase reaction (1) have not previously been measured directly. In an argon matrix a CF_2 -O₃ complex was observed by IR-spectroscopy [10, 11].

The oxidation reaction of $CF_2(\tilde{X})$ with NO₂, which leads to CF_2O and NO (1), has been studied directly [12]. The oxidation reaction with O(³P) atoms

$$CF_2(\tilde{X}) + O({}^{3}P) \rightarrow FCO + F$$
 (5)

which is a fast process [13] leads to the formation of FCO radicals and F atoms [14, 15].

The aim of this work was to measure directly the products of the reaction (1). As the reaction is very slow under experimental conditions, only very low product concentrations are to be expected. The ideal method for the sensitive detection of all products is a flow reactor combined with a mass spectrometer.

2. Experimental

The experimental arrangements, as described in detail elsewhere [12, 16], consisted of an isothermal discharge flow reactor at low pressure and a molecular beam sampling device connecting the flow reactor to a magnetic deflection type mass spectrometer with electron impact ionisation. This experimental arrangement is shown in Fig. 1. The second detection device used was a time of flight mass spectrometer which had a choice of electron impact ionisation.

The experimental study of the primary products of the reaction (1), CF_2 + O_3 , is complicated by the fact that reaction (1) is very slow (i.e. low product concentrations) compared to possible other reactions like secondary reactions and heterogeneous reactions of O_3 , products, and impurities. The





Fig. 1. Experimental arrangement: Flow reactor connected with a magnetic deflection type mass spectrometer via a molecular beam sampling system; by choice: analog ion current or synchronous single ion counting.

aging of the reactor and the accumulation/desorption of products at/from the reactor wall were investigated using the time of flight mass spectrometer. Time resolved mass spectra (m/z = 2-300) are obtained to assess the temporal behaviour of the reactor. The low signal-to-noise ratio of the spectra had to be accepted for the sake of good time resolution. No interfering accumulation of products was observed between the normal cleaning intervals. Therefore quantitative measurements were performed by coupling the flow reactor with the magnetic deflection mass spectrometer, along with analogous amplification or digital single ion counting of the signal. This arrangement brought about a substantial enhancement of the signal-to-noise ratio and the extension to the low energy impact ionisation near threshold.

The CF₂ radicals were produced by the dissociation of CF₂Br₂ by a microwave discharge in the side arm of a fast flow reactor, operating at a pressure in the range $0.5 \le p/mbar \le 10$. The CF₂(\tilde{X}) yield from the dissociation of CF₂Br₂ depends on the concentration of CF₂Br₂ as shown in Fig. 2. The dissociation (followed at m/z = 129 and 131, respectively) is complete ($\ge 99\%$) if a mole fraction of x(CF₂Br₂) = $2.6 \cdot 10^{-3}$ was used in the experiments (see Fig. 2).

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Fig. 2. $CF_2(\tilde{X})$ yield versus mol fraction of CF_2Br_2 in discharge: $\gamma = \{[CF_2Br_2]_{-E} - [CF_2Br_2]_{+E}\}/[CF_2Br_2]_{-E} [CF_2Br_2]_{+E} = concentration of <math>CF_2Br_2$ with discharge on and off, followed as CF_2Br^+ on m/z = 129 and 131 respectively; IE = 100 eV; p = 2.5 mbar. $\bar{v} = 26.6 \text{ m/s}.$

The $CF_2(\tilde{X})$ source is characterized by the time of flight mass spectrum taken at an ionisation energy of IE = 100 eV in the mass range $60 \le m/z \le 206$ as shown in Fig. 3. The depletion of CF_2Br_2 , which is detected as the CF_2Br^+ ion (m/z = 129, 131), is obvious. The increase at m/z = 158, 160 and 162 is due to the formation of $Br_2(^{79,79}Br_2^+, ^{79,81}Br_2^+ \text{ and } ^{81,81}Br_2^+)$. The formation of m/z = 79, 81 (Br⁺) is independent of the discharge situation, i.e. the fragmentation of CF_2Br_2 or of Br_2 forming Br^+ ions is equal at the high ionisation energy. The peak at m/z = 69 is due to the CF_3 radical from the combination reaction $F + CF_2 \xrightarrow{M} CF_2$ (2). The formation of F atoms in the CF_2Br_2 discharge was found and characterized in [17]. The F atom concentration is of minor importance ($0.01 \le [F]/[CF_2] \le 0.001$). At the masses m/z = 179 and 181 only marginal increases were found when the discharge was switched on and off, respectively. From the absence of





Fig. 3. Time of flight mass spectra in the mass range $28 \le m/z \le 131$; IE = 100 eV, O₃ absent. \bar{v} (flow reactor) = 20.3 m/s, p = 1.7 mbar, $\Delta t = 8.6$ ms (transfer time from discharge to the tip of the expansion nozzle in the flow reactor). a) discharge "on"; b) discharge "off".

 $C_2F_4Br^+$ it can be concluded that CF_2Br radicals, which would combine to form $C_2F_4Br_2$ in a fast reaction (k = $1.0 \cdot 10^{13} \text{ cm}^3/\text{mol s}$ [18], were not present in the discharge system, since $C_2F_4Br^+$ (m/z = 179, 181) is the main fragment ion of $C_2F_4Br_2$. No signal was found at m/z = 100 ($C_2F_4^+$) indicating that the combination reaction $CF_2 + CF_2 \xrightarrow{M} C_2F_4$ (3) is too slow under the experimental conditions given in Fig. 3 (k₃ = $2.6 \cdot 10^{10} \text{ cm}^3/\text{mol s}$ [19].

The reactant O_3 was injected into the main flow by a movable inlet probe. The different positions of the probe correspond to different reaction times. The O_3 concentration was obtained by the titration reaction:

$$O_3 + F \rightarrow OF + O_2 \tag{6}$$

with a known F atom concentration.

The samples were withdrawn continuously by a molecular beam sampling device. The ions are produced by electron impact with variable electron impact ionisation energies (10-30 eV, 70 eV, 100 eV) and analysed by the mass spectrometer with high resolution. High ionisation energies were applied to obtain high sensitivity whereas at low ionisation energies ion fragmentation was reduced or suppressed. Sensitive detection was accomplished by synchronous single ion counting combined with chemical

modulation of the reaction by switching the microwave discharge on/off and gating the two-channel counter to the conditions " $CF_2 + O_3$ "/"· $CF_2Br_2 + O_3$ " in the reactor.

Gases of the highest commercially available purity were used without further purification (He 99.996%, Messer Griesheim, CF_2Br_2 (\geq 98%) Merck-Schuchardt). Ozone was produced from O_2 (\geq 99.996% UCAR) with a commercially available ozonizer (Argentox GI 10). O_3 was adsorbed on silicagel at the temperature of $CO_2(s)$ in two traps and thus separated from the oxygen. The ozone was desorbed from the silicagel and transfered by He into the reactor.

3. Results

The mass spectra of the products of the reaction:

 $CF_2(\tilde{X}) + O_3(\tilde{X}) \rightarrow \text{products}$ (1)

were taken at high (70 eV) and low ionisation energy. Three overview spectra in the mass ranges $15 \le m/z \le 50$, $40 \le m/z \le 50$ and $60 \le m/z \le 100$ are shown in Figs. 4, 5, and 6. The interpretation of the mass spectra was performed with the data summarized in Table 1.

The depletion of $CF_2(\tilde{X})$ due to reaction (1) is seen in Fig. 4 (m/z = 50, CF_2^+). The increase of the peaks m/z = 44 and 47 cannot be assigned to the products CO_2 and COF since they are fragment ion peaks (see below). The increase at m/z = 48 is simply caused by the added O_3 .

From the depletion of CF_2 observed at m/z = 50 as a function of reaction time a rate constant k_1 could be obtained from the simple expression:

$$\ln\{[CF_2](t_R)/[CF_2]_0\} = k [O_3] t_R,$$
(I)

if the CF_2 depletion in the system was only due to reaction (1). The sensitivity of the CF_2 detection, however, is not sufficient to use such small initial CF_2 concentrations that parallel reactions are suppressed:

$$CF_2 + Br_2 \rightarrow \text{products}$$
 (7)

and

$$CF_2 + CF_2 \xrightarrow{M} C_2F_4$$
 (3)

For the determination of k_1 the reactions (7) and (3) have to be taken into account ($k_7 = 1.6 \cdot 10^9 \text{ cm}^3/\text{mol s}$ [27] $k_3 = 2.6 \cdot 10^{10} \text{ cm}^3/\text{mol s}$ [19]). The rate for the removal at the wall:

 $CF_2 \xrightarrow{\text{wall}} \text{products}$ (8)

was determined separately to be $k_w = 10 \text{ s}^{-1}$ under the experimental conditions. From the CF₂ depletion in the flow reactor in the presence of O₃ an upper limit for k_1 was obtained, which is higher than that determined di-





Fig. 4. Mass spectrum for the reaction $CF_2 + O_3 \rightarrow \text{product}$; IE = 70 eV, $[CF_2]_0/[O_3]_0 \approx 1/2O$. a) in the absence of O_3 ; b) in the presence of O_3 .

rectly at very low CF_2 concentrations; where reactions (3) and (7) can be neglected [9]. As the derived value in (a) is an upper limit only, it does not contradict the results given in (a). A computer simulation of the full mech-

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Fig. 5. Mass spectrum for the reaction $CF_2 + O_3 \rightarrow \text{product}$; IE = 17 eV. a) discharge "on"; b) discharge "off".

anism resulted the total depletion of CF_2 obtained under our experimental conditions due to reaction (1). Expressed in molefraction this reads as: $\Delta x (CF_2) \cong 4 \cdot 10^{-5}$).

The mass spectrum at low masses in the range $16 \le m/z \le 50$ and at an ionisation energy of IE = 17 eV is shown in Fig. 5. The peak m/z = 48(O₃) decreased due to reaction (1). The formation of O₂ (m/z = 32, O₂⁺) was observed. The mass peak m/z = 32 (O₂⁺) is a fragment peak of O₃, too, and thus should decrease by reaction (1); the observed increase indicates, however, that O₂ is a reaction product. The discrimination between the two electronic states of the oxygen molecule O₂ (O₂ ($X^3\Sigma_g^-$) and O₂ ($a^1\Delta_g$)] was not obtained (see Discussion). The mass peak m/z = 16 (O⁺) is a fragment of O₃ as well as of O₂ and the signal height was found to be unchanged. The signals with m/z = 32 and 50 increased when the discharge was switched on and the signals at m/z = 48 decreased. The peaks m/z = 48 and 50 are due to the reactants O₃ and CF₂, respectively; CF₂⁺ was observed only if the discharge was on and therefore is not a fragment ion from CF₂Br₂.

The product spectrum for the mass range $60 \le m/z \le 102$ taken with the magnetic deflection type mass spectrometer at IE = 17 eV is shown in





Fig. 6. Reaction product spectrum of reaction (1); IE = 17 eV. a) absence of O_3 , b) presence of O_3 . [CF₂]₀ = $1.4 \cdot 10^{-11}$ mol/cm³, [O₃] = $9 \cdot 10^{-10}$ mol/cm³; $\bar{v} = 26.6$ m/s; t_R = 5.9 ms, p = 2.5 mbar.

Fig. 6. For the registration of the background mass spectrum, the O_3 flow was substituted by an equivalent He flow in order to keep the flow conditions unchanged.

Signal increases were observed for the peaks at m/z = 95, 96, 97 and 98. The mass peaks m/z = 95 and 97 can be attributed to the ion BrO⁺. The ratio of the peak heights is 1:1 due to the ⁷⁹Br and ⁸¹Br isotope abundance ratio. The increases at m/z = 96 and 98 are due to HOBr (⁷⁹Br and ⁸¹Br). The increase of the signal of the peak m/z = 98 was larger than the increase of m/z = 96 even after subtraction of the mass spectrometric background at m/z = 98. Thus it is concluded that the mass peak m/z = 98 is due not only to HO⁸¹Br⁺ but also the ion CF₂O₃ from the initial complex CF₂O₃ formed in reaction (1):

$$CF_2(\tilde{X}) + O_3(\tilde{X}) + M \rightarrow CF_2O_3 + M.$$
 (1)

The decrease of the peaks with m/z = 79 and 81 belonging to Br atoms and the observation of BrO⁺ can be interpreted by the reaction of Br atoms with O₃ forming BrO:

$$Br + O_3 \rightarrow BrO + O_2. \tag{9}$$

The peak at m/z = 100, which results from $C_2F_4^+$, is more or less unchanged.

Table 1. Mass spectra, electron impact ionisation around 70 eV, if not stated otherwise and thermodynamic data of some compounds. I \triangleq intensities relative to the main peak (I = 1).

 CF_2Br_2 ; M = 208/210/212, $H^0_{f,298}$ = -380.7 kJ/mol [20] 129 79 131 31 81 50 191 12 [21] m/z I 1.0 0.973 0.261 0.258 0.251 0.188 0.67 0.59 $(CF_2Br)_2$; M = 258/260/262, $H^0_{f, 298} = -790.8 \text{ kJ/mol}$ [20] 179 181 [21] m/z 129 131 100 31 260 50 I 1.00 0.974 0.340 0.331 0.170 0.134 0.124 0.75 $F_2CO; M = 66, H^0_{f,298} = -607.9 \text{ kJ/mol} [22]$ 47 28 50 19 48 m/z 66 31 16 [21] Ι 1.00 0.548 0.136 0.44 0.24 0.10 0.09 0.09 C_2F_4 ; M = 100, $H^0_{f,298}$ = -661.1 kJ/mol [20] m/z 31 81 100 50 12 69 24 19 [21] I 1.00 0.731 0.431 0.308 0.77 0.36 0.24 0.14 O_3 ; M = 48, $H^0_{f,298}$ = +132.3 kJ/mol [20] 32 m/z 16 48 I 1.00 0.53 0.37 (17 eV) (this study) 48 32 m/z1.00 0.69 (14 eV) (this study) I FCO; M = 47, $H_{f;298}^0 = -152.1 \text{ kJ/mol} [22]$ $CF_2(\tilde{X}); M = 50, H_{f;298}^0 = -205.0 \text{ kJ/mol} [23, 24, 25]$ 50 19 [23, 24, 25] m/z31 I 1.00 0.87 0.59 (70 eV) 50 31 (17 eV) m/z I 1.00 0.31 50 m/z 31 (70 eV) (approximate, this study) 0.7 I 1.00 $CF_{3}(\tilde{X}); \ M = 69, \ \ H^{0}_{\rm f,298} = \ -460.2 \ kJ/mol \ [24, \ 25]$ 50 31 69 19 m/z 1.00 0.89 0.50 0.46 (70 eV) [23, 24, 25] I m/z 69 50 31 19 1.00 (17 eV) I _ FO_2 ; M = 51, $H_{f,298}^0 = +12.6 \text{ kJ/mol}$ [20] CF₂Br; M = 129/131, $H_{f,298}^0 = -220 \text{ kJ/mol}$ (estimated) $H_{f,298}^0 = +125.9 \text{ kJ/mol}$ BrO; M = 95/97,[20] HOBr M = 96/89, $H_{f,298}^0 = -37.6 \text{ kJ/mol}$ [26]

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This indicates that at the high CF_2 concentrations, which are needed in order to observe a reaction effect, the combination reaction (3) contributes to the CF_2 radical consumption.

The mass peaks m/z = 80 and 82 are due to HBr, which is formed in the heterogeneous reaction of Br atoms from the CF_2Br_2 discharge and traces of adsorbed water.

The mass spectral range around m/z = 66 was examined in detail as inserted in Fig. 6. A small increase was found at m/z = 66 (the mass peak of CF_2O^+) at low ionisation energy (17 eV). This indicates that the CF_2O_3 complex that was formed initially decomposes via:

$$CF_2 O_3^{\#} \to CF_2 O + O_2 \tag{1b}$$

leading to the formation of CF_2O (m/z = 66, CF_2O^+) and O_2 (m/z = 32, O_2^+) as observed in the spectrum (Fig. 5). The signal at m/z = 69 (CF_3^+) did not change by the addition of O_3 . Thus the CF_3 reaction with O_3 was unimportant in the system studied.

The assignment of the primary products of reaction (1) (CF₂O₃, CF₂O, O₂) was deduced from the overview mass spectra recorded as the analogous ion currents with the inherent limits of mass spectrometric detectability. In order to enhance the confidence level of the ion current measurements and to further unravel the fragment ion formation of the products CF₂O₃, CF₂O, O₂ and of byproducts use has been made of the synchronous single ion counting technique together with a systematic variation of the ionisation energy ($10 \le IE/eV \le 70 \text{ eV}$).

The results obtained at IE = 17 eV are shown in Fig. 7. The peaks were measured by single ion counting and corrected for the mass spectrometric background. In this spectrum the formation of m/z = 32 (O₂) was observed. The formation of CF₂O was detected (m/z = 66, CF₂O⁺) directly by the parent ion and by the fragment m/z = 47 (FCO⁺). The formation of the initial complex CF₂O₃ was detected directly by its CF₂O₃⁺ ion (m/z = 98). The contribution of HO ⁸¹Br isotope to the peak at m/z = 98 (CF₂O₃⁺ + HO ⁸¹Br⁺) can be subtracted via the signal of HO ⁷⁹Br isotope (m/z = 96), taking into account the known natural isotope abundance $(^{79}Br/^{81}Br =$ 1.028). The formation of BrO (m/z = 95, 97) and the heterogeneous formation of HBr (m/z = 80, 82), as well as the consumption of Br/Br_2 (m/z = 79, 81; Br⁺) do not influence the deduction of the mechanism of reaction (1). In this more sensitive experiment a consumption of CF_3 (m/z = 69, CF_3^+) was also observed. A significant increase was observed at m/z = 50 (CF_2^+) where a decrease due to the consumption of CF_2 would be expected. This signal at m/z = 50 is explained as a fragment ion of CF_2O_3 at the low ionisation energy (IE = 17 eV). At high ionisation energy (IE = 70 eV) a decrease was observed (Fig. 4) due to the dominant CF⁺₂ ion formation from the $CF_2(\tilde{X})$ radical.





Fig. 7. Product spectrum of the reaction (1); IE = 17 eV, p = 1.9 mbar, T = 298 K, $\bar{v} = 21.6$ m/s, $t_R = 6.5$ ms, $[CF_2]_0 = 9.6 \cdot 10^{-11}$ mol/cm³, $[O_3]_0 = 1.1 \cdot 10^{-9}$ mol/cm³.

In order to prove that CF_2O is a direct product of reaction (1) at the low pressures applied in the present experiments (i.e. that m/z = 47 and 66 is not only a fragment ion of CF_2O_3) the products were compared with the products of the reaction:

$$CHF_2 + O_3 \rightarrow CHF_2O^{\#} + O_2 \tag{10}$$

$$CHF_2O^{\#} \rightarrow CF_2O + H.$$

This is a fast reaction $k_{10}(298 \text{ K}) = 1.4 \cdot 10^{12} \text{ cm}^3/\text{mol s}$ in which CF₂O is formed as the main product [28]. The results obtained for four different ionisation energies are shown in Fig. 8. The peaks m/z = 66 and 47 are compared. For the reaction (10) it is known that m/z = 66 is the parent peak of CF₂O and m/z = 47 the fragment peak of CF₂O. In the CF₂/O₃ system both could be fragment peaks of CF₂O₃. The appearance potential of FCO⁺ from CF₂O was determined to be 14.736 eV [22]. At low ionisation energy (i.e. 17 eV) the fragment patterns obtained in the reaction CF₂ + O₃ and CHF₂ + O₃ were identical. At this ionisation energy the formation of the fragment ion CFO⁺ (m/z = 47) from CF₂O₃ is of no importance. For





Fig. 8. The products of reaction (1) and the reaction $CHF_2 + O_3 \rightarrow CF_2O + HO_2$ at different ionisation energy. \blacksquare , $CF_2 + O_3$; \Box , $CHF_2 + O_3$ under otherwise identical experimental conditions. Magnetic deflection type mass spectrometer ion signals obtained by single ion counting.

higher ionisation energies the fragmentation forming CFO⁺ is increased and thus the number of counts for m/z = 47 increased relative to m/z = 66. Thus, it is concluded that in the reaction (1) CF₂O and CF₂O₃ are formed both as primary products.

Experimental results of the systematic variation of the ionisation energy for four examples are also shown for m/z = 44 (CO₂⁺) in Fig. 8 as observed in the CF₂/O₃ system. As the signal at m/z = 44 depends strongly on the ionisation energy and decreases relative to the signal of the primary products CF₂O₃, CF₂O, and O₂, it can be concluded that CO₂ is not a primary reaction product, but a fragment ion formed via CF₂O₃ $\xrightarrow{e^-}$ CO₂⁺ + F₂O.

Therefore, the following mechanism is proposed:

$$CF_2(\tilde{X}) + O_3(\tilde{X}) \stackrel{\text{\tiny M}}{\rightleftharpoons} CF_2O_3^{\#} \to CF_2O_3$$

 $\to CF_2O + O_2$ (1)

i.e. $CF_2O_3^{\#}$ isomerizes or decomposes prior to collision stabilisation under the experimental conditions at a pressure of p = 2.5 mbar and forms CF_2O and O_2 molecules.

The depletion of CF_2 occurs not only via the very slow reaction (1) but also via the fast combination reaction (3). With this mechanism all observed mass peaks and fragment ion formation can be explained.

4. Discussion

The rate of reaction (1) has been determined in a flow reactor with LIF detection of CF_2 under pseudo first order conditions ($[CF_2]_0 \ll [O_3]_0$). The rate constant was determined with the assumption that the stoichiometry of the reaction is unity [9]. The products had not previously been determined directly. With the determination of the products in the present work the stoichiometry can be derived to be unity since none of the reaction products further react fast with $CF_2(\tilde{X})$ under the conditions of the investigation of the rate coefficient. Thus the rate coefficient:

$$k_1(T) = 1.9 \cdot 10^{12} \exp(-25 \text{ kJ/mol}^{-1}/\text{RT}) \text{ cm}^3/\text{mol s}$$

given in (9) evaluated from the disappearance rate of the CF_2 radicals can be associated with the reaction:

$$CF_2(\tilde{X}) + O_3 \rightarrow \text{products.}$$
 (1)

In the first step a complex $CF_2O_3^{\#}$ is formed:

$$\operatorname{CF}_2(\tilde{X}) + \operatorname{O}_3(\tilde{X}) \rightleftharpoons \operatorname{CF}_2\operatorname{O}_3^{\#}.$$
 (1a)

The complex $CF_2O_3^{\#}$ contains sufficient energy to decompose

$$CF_2O_3^{\#} \to CF_2O(\tilde{X}) + O_2(X^3\Sigma_g^-)$$
 (1b)

in a highly exothermic reaction ($\Delta_{R}H = -545.2 \text{ kJ/mol}$).

The experimental findings of this work on the formation of the primary products of the reaction $CF_2 + O_3 \rightarrow \{CF_2O_3; CF_2O + O_3\}$ (compound of the empirical molecular formula CF_2O_3) together with the following information related to the $CF_2 + O_3$ reaction make a detailed picture of the dynamics of the reaction feasible beyond the above given considerations resulting from the energetics. These informations are:

(i) Ab initio calculations of the CF_2 -O₃ complex and matrix isolation IR spectroscopy [10, 11] led to the identification of a weakly bound complex





Fig. 9. Energy diagram for the reaction $CF_2 + O_3$. Primary complex structure as given in (10) (k_{ass} , k_{rediss} , k_{diss} ,

 CF_2 -O₃ with various structures (Fig. 9). Structure (1): Electrostatic interaction of the two terminal oxygen atoms equally with the carbon atom, giving rise to a binding energy of $E_{01} = 16.2$ kJ/mol. Structure (3): one terminal oxygen atom interacts with the C atom with a binding energy of $E_{03} = 9.7$ kJ/mol.

(ii) A long lived species FC(O) OOF, different from the described CF_2 -O₃ complex, has been identified by NMR spectroscopy and was described to be stable for more than 8 h at 100 mbar and room temperature [29].

(iii) The rate coefficient of the reaction $CF_2 + O_3$, k(T), exhibits a high temperature dependence, represented by an activation energy of $E_a = 25 \text{ kJ/mol} [9]$.

The dynamics of the reaction $CF_2 + O_3$ is described as a complex forming bimolecular reaction with a loose entrance and rigid exit channel [30]

for which the energetics are displayed in Fig. 9. Assuming independent channels for the association (rate constant k_{ass}), redissociation of the complex (specific rate constant, $k(E) = k_{rediss}$), stabilization by collisions with M (rate constant k_{stab}), isomerisation of the complex (k_{iso}), and dissociation of the complex to the products $CF_2O + O_2$ (k_{diss}), a semiquantitative calculation of the complex life time $\tau(E)$ is possible following the procedures of Troe [31]. The difference of the thermal energy $(H_{300}-H_0)$ of the reaction is given by the levels $CF_2 + O_3$ (300 K) and $CF_2 + O_3$ (0 K). The binding energies and the frequencies are taken from (10), the total energy $E = E_0 + E_0$ $(H_{300}-H_0)$, $(E_0 = 16.2$ and 9.7 kJ/mol, respectively). The frequencies used are: 1221, 1102, 668, 1080, 1078, 707, 1224, 1109, 15 $(4 \times)$ cm⁻¹). The specific rate constant k(E) for the redissociation of the complex is found to be the fastest process (k(E) $\approx 2 \cdot 10^{10} \, \text{s}^{-1}$). The value is thought to be reliable within a factor of 5, considering the uncertainties in the transition state. At the experimental conditions of this work (a pressure of 1.3 mbar, main carrier gas: He) the rate constant for the stabilization $k_{stab} = Z_{LJ} \cdot [M]$ $(Z_{LJ}$ = Lenard-Jones collision frequency) is of the order of $k_{stab} \cong$ $2.4 \cdot 10^7 \, \text{s}^{-1}$. Thus in a step ladder model of redissociation/deactivation by an average transfered energy down of $-\langle \Delta E \rangle \approx 200 \text{ cm}^{-1}$, complete redissociation and no stabilisation to the structures (1), (3) are to be expected. The observed species of empirical formula (CF_2O_3) may be formed by an independent isomerisation channel of the complex CF2O3 over a barrier to a structure like FC(O)OOF, different from the noted species (1), (3) (Fig. 9). In the presented flow reactor experiments also a heterogeneous process might be responsible for the FC(O)OOF formation. But it is noteworthy to state that the time resolved experiments with the arrangement flow reactor/ time of flight mass spectrometer the product signals followed immediately the reaction conditions "on"/"off" and did not point to a slow desorption process for (CF_2O_3) formation. Thus it can be concluded that no indication to a heterogeneous contribution to the CF₂O₃ formation was observed.

The small amount of the primary dissociation products $(CF_2O + O_2)$ is explained by the high barrier (represented by the measured activation energy) leading to $k_{diss} \ll k_{rediss}$, making the redissociation process (k_{rediss}) the major process. A direct abstraction route ($CF_2O_3 \rightarrow CF_2O + O_2$) is thought to be negligible, as the complex (CF_2O_3) is substantiated by the ab initio calculations and the experimentally proven existence of a species (CF_2O_3).

From the energetics it can be discussed in which electronic state O_2 is formed. The dissociation of the complex CF_2O_3 (1b) is highly exothermic $(\Delta_R H = -450 \text{ kJ/mol})$ even if O_2 is formed in its first electronically excited singlet state O_2 ($^1\Delta_g$), as one would expect from spin conservation rules. In the dissociation pathway (1b) the CF_2O has sufficient internal energy, to decompose further via:

$$CF_2O(\tilde{X}) \rightarrow FCO + F \qquad \Delta_R H = 535 \text{ kJ/mol.}$$

Elementary Reaction of $CF_2(\tilde{X})$ with O_3 : Primary Products

This pathway is, however, energetically accessible only if O_2 is formed in the spin forbidden triplet electronic ground state $(X^3\Sigma_g^-)$. No indications were found that either FCO or F atoms are formed in the system, this might point to the formation of O_2 in the metastable exited singlet state.

Other reaction channels can be excluded from the energetics and from the observed products. The formation of F atoms via the reaction:

$$CF_2 + O_3 \rightarrow CO_2 + O + 2F$$

is endothermic by $\Delta_R H = 64.8$ kJ/mol. Moreover this reaction would also be in disagreement with the observed formation of CF₂O and O₂. A direct formation of CO₂ via:

$$CF_2 + O_3 \rightarrow CO_2 + F_2O$$
 $\Delta_R H = -322.5 \text{ kJ/mol}$

is, however, highly exothermic, and could be followed by the slightly exothermic subsequent reaction:

 $F_2O + O_3 \rightarrow 2 F + 2 O_2$ $\Delta_R H = -3.2 \text{ kJ/mol}$

in which the F atoms and O_2 molecules are formed. This reaction sequence, which would require a significant amount of rearrangement in the CF_2O_3 complex, does not, however, explain the observed formation of CF_2O .

A formation of difluordioxirane:

$$CF_2(\tilde{X}) + O_3(\tilde{X}) \rightarrow CF_2O_2(\tilde{X}^1A_1) + O(^3P)$$

is very endothermic by approximately $\Delta_R H = +317$ kJ/mol [32], even if the O atoms are formed in the spin forbidden triplet electronic ground state. This reaction and in particular the spin allowed reaction forming O(¹D) are of no importance in the thermal system CF₂/O₃.

Thus it can be concluded that the dynamics sketched in Fig. 9 represent the mechanism of reaction (1).

The reactions of odd oxygen O and O_3 lead to very different products. In the case of $O({}^{3}P)$ two reactive F atoms are formed

$$O + CF_2 \rightarrow FCO + F. \tag{5}$$

$$O + FCO \rightarrow CO_2 + F. \tag{11}$$

whereas in the reaction (1) two stable molecules, CF_2O and O_2 , together with CF_2O_3 result.

From the presented results O_3 is unlikely to be considered as an additive in the etching process since no actived F atoms are formed, needed to accelerate the process.

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