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# Ionization of Ozone/Chlorofluorocarbon Mixtures in Atmospheric Gases: Formation and Dissociation of $[CHX_2O_3]^+$ Complexes (X = Cl, F)**

Fulvio Cacace, Giulia de Petris,* Federico Pepi, Marzio Rosi, and Antonio Sgamellotti

The interest in chemical interactions between ozone and halocarbons, and their impact on the ozone layer depletion, has almost exclusively concerned neutral species. Yet, since the advent of rocket-born mass spectrometers, a rich ionic chemistry is known to occur in the atmosphere, and the lifetimes of certain pollutants have been shown to be limited by ionic reactions.[1] This has stimulated the study of ionized halocarbons in atmospheric gases,[2–4] as well as of the ionic chemistry of ozone, leading inter alia to the detection of elusive cations such as $O_3H^+$,[5] whose role in the chemistry of the upper atmosphere had long been postulated.[6, 7] So far, however, ozone and halocarbons have been studied separately, and no information is available on the ionic chemistry of gases containing both species, a serious limitation that contrasts with the approach successfully followed in the study of the corresponding homolytic reactions.

Here we report the highlights of the first study specifically aimed at examining ionic reactions occurring in atmospheric gases ($O_2$, $N_2$) containing both ozone and a halocarbon. Although several halomethanes—including $CHCl_2F$, $CHClF_2$, $CHF_3$, and $CH_3F$—were investigated, we shall concentrate on a typical example, that is, the ionization of $CHCl_2F/O_3$ mixtures diluted in $O_2$. The salient feature of the experiments performed in the chemical ionization (CI) ion source of the spectrometer (see Experimental Section) is the addition to ozone of the $CHClF^+$ ion [Eq. (1)], which is formed in turn by dissociative charge transfer from $O_2^+$ and $O_3^+$ to the halocarbon [Eq. (2)].

$$CHClF^+ + O_3 \rightarrow \underset{\mathbf{1}}{CHClFO_3^+} \qquad (1)$$

$$CHCl_2F + O_n^+ \rightarrow CHClF^+ + O_n + Cl \qquad (2)$$

Occurrence of process (2) was demonstrated by Fourier transform ion cyclotron resonance (FT-ICR) experiments involving the reaction of isolated $O_3^+$ ions with $CHCl_2F$ at $10^{-8}$ to $10^{-7}$ Torr. The inefficient collisional deactivation in this pressure range prevents detection of **1**, since any complex formed would undergo back dissociation. Collisional deactivation is considerably more effective at much higher pressures, up to 0.5 Torr, typical of $O_2$/CI experiments, which allows stabilization and hence detection of **1**. The collisionally activated dissociation (CAD) mass spectra of the stable population of **1** show only the $CHClF^+$ fragment—that is, back dissociation of the complex into its components—as expected for an electrostatic adduct. Ions **1** formed with excess internal energy undergo metastable dissociation, as shown by the mass-analyzed ion kinetic energy (MIKE) spectrum (Figure 1).

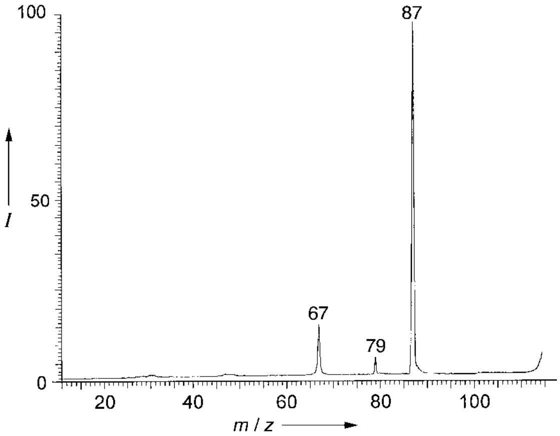

Figure 1. Typical MIKE spectrum of $CH^{35}ClFO_3^+$ ions, displaying the $HFClO_2^+$ fragment (*m*/*z* 87), the $CFO_3^+$ fragment (*m*/*z* 79), and the $CHClF^+$ fragment (*m*/*z* 67). *I* = intensity.

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Among the metastable transitions observed [Eqs. (3)–(5)], process (3), the predominant one, is truly remarkable, involving an exceptional molecular reorganization characterized by

$$\mathrm{CHClFO_3^+}\ \mathbf{1} \xrightarrow{80\%} \mathrm{HClFO_2^+} + \mathrm{CO} \tag{3}$$

$$\mathrm{CHClFO_3^+}\ \mathbf{1} \xrightarrow{5\%} \mathrm{CFO_3^+} + \mathrm{HCl} \tag{4}$$

$$\mathrm{CHClFO_3^+}\ \mathbf{1} \xrightarrow{15\%} \mathrm{HCClF^+} + \mathrm{O_2} \tag{5}$$

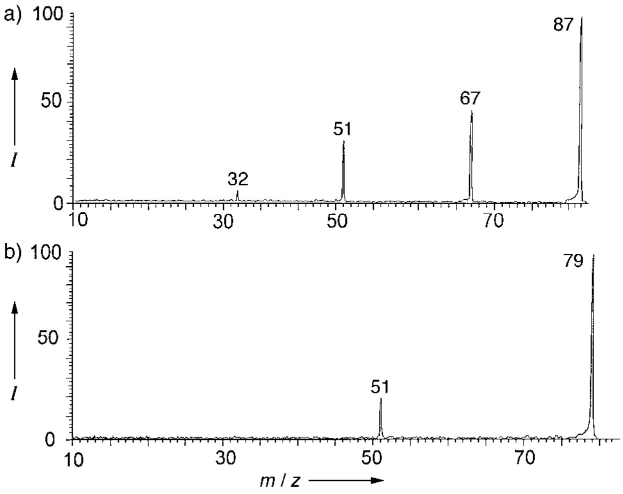

Figure 2. a) Typical CAD spectrum of $HF^{35}ClO_2^+$ ions, showing the $ClO_2^+$ fragment (*m*/*z* 67), the $FO_2^+$ fragment (*m*/*z* 51), and the $O_2^+$ fragment (*m*/*z* 32). b) Typical CAD spectrum of the $CFO_3^+$ ion, displaying the $FO_2^+$ fragment (*m*/*z* 51). *I* = intensity.

the fission of all the bonds initially present in the HCClF moiety. The very observation of fragmentation (3) and, a fortiori, its predominance over competing channels, especially the plain back dissociation (5) of **1** into its components, was so peculiar as to require confirmatory experimental evidence and theoretical support. As to the first point, MS/MS experiments were performed whereby the charged fragments from the metastable transitions (3)–(5) were probed by CAD spectrometry. The results, illustrated in Figure 2, are fully consistent with the assignments based on MIKE spectrometry and provide useful information on the structure of the metastable ions, and hence on their parents. The charged products from reactions (3) and (4) undergo the collision-induced fragmentation processes (6) and (7), respectively. As

$$\mathrm{HClFO_2^+} \xrightarrow{41\%} \mathrm{FO_2^+} + \mathrm{HCl} \tag{6a}$$

$$\mathrm{HClFO_2^+} \xrightarrow{52\%} \mathrm{ClO_2^+} + \mathrm{HF} \tag{6b}$$

$$\mathrm{HClFO_2^+} \xrightarrow{7\%} \mathrm{O_2^{\cdot +}} + \mathrm{HF} + \mathrm{Cl^{\cdot}} \tag{6c}$$

$$\mathrm{CFO_3^+} \xrightarrow{100\%} \mathrm{FO_2^+} + \mathrm{CO} \tag{7}$$

to process (5), the charged fragment $HCClF^+$—isobaric with another conceivable fragment, $ClO_2^+$—was assigned based on the identity of its CAD spectrum with that of the model $HCClF^+$ ion from $CHCl_2F$.

The theoretical analysis was based on density functional theory[8] using the hybrid B3LYP functional[9] to localize the stationary points and to evaluate the vibrational frequencies. Single-point energy calculations at the optimized geometries (Figure 3) were performed according to the CCSD(T) approach.[10, 11] Transition states were located using the synchronous transit-guided quasi-Newton method.[12] The zero-point energies evaluated at the B3LYP/6-311 G (d,p) level were added to the CCSD(T) energies, and the total energies at 0 K of the species of interest were corrected to 298 K by including translational, rotational, and vibrational contributions; all calculations were performed using Gaussian 94.[13]

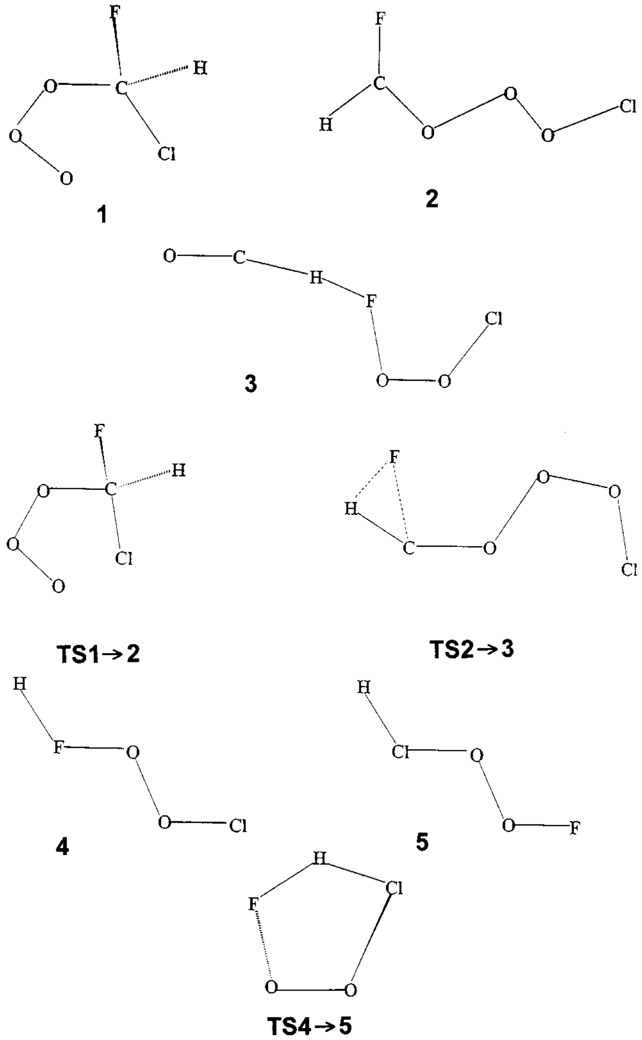

Figure 3. Optimized geometries of relevant ions. Detailed geometrical parameters and energies are given as supporting information.

The product from association (1) is species **1**, where a tetrahedral C atom is bonded to H, F, and Cl atoms and to a slightly distorted $O_3$ molecule. Adduct **1** can undergo back dissociation to its components or evolve into **2**, in essence a formyl fluoride molecule linked, mainly electrostatically, to $ClO_2^+$. The formation of **2**, which occurs via the transition state **TS1**→**2**, is highly exothermic. Ions **2** containing excess internal energy can further evolve into the isomer **3** via **TS2**→**3**, which protrudes by about 25 kcal mol$^{-1}$ above the $CHClF^+/O_3$ asymptote. Species **3**, containing an almost linear OCHF group linked to a $O_2Cl^+$ unit, can lose CO to yield the $HFOOCl^+$ fragment **4**, which is in turn liable to HF loss. As

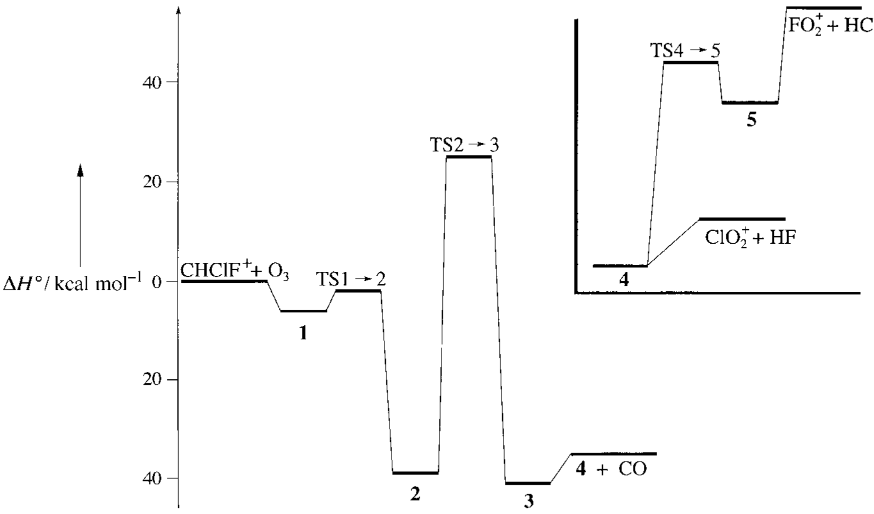

Figure 4. Energy profile ($\Delta H°$, 298 K), based on the thermochemical data of Table 1.

shown in the inset of Figure 4, **4** can also rearrange via **TS4 →5** into isomer **5**, which is liable to HCl loss.

The theoretical results summarized in Table 1 and in Figures 3 and 4 provide a satisfactory explanation for all experimental features, accounting for the CAD spectrum of the adduct **1** and for all fragments resulting from its metastable decomposition. Significantly, the remarkable unimolecular dissociation sequence outlined by the mass spectrometric and theoretical results is not peculiar to complex **1**, representing instead a common, distinctive feature of the entire class of adducts from a variety of $CHX_3$ halocarbons (X = Cl, F), although the rate of the competing fragmentation channels was found to depend to some extent on the nature and the number of the halogen atoms.

Table 1. Relevant thermochemical data [kcal mol$^{-1}$] at 298 K, computed at the CCSD(T) level of theory.

| Process | $\Delta\Delta H°$ | Barrier height |
|---|---|---|
| $CHClF^+ + O_3 \rightarrow$ **1** | −6.1 | |
| **1** → **2** | −31.8 | 5.5 |
| **2** → **3** | −0.8 | 63.0 |
| **3** → **4** + CO | 6.2 | |
| **4** → **5** | 33.6 | 42.1 |
| **4** → $ClO_2^+ + HF$ | 9.4 | |
| **5** → $FO_2^+ + HCl$ | 19.2 | |

## *Experimental Section*

The gases, research-grade products from commercial sources with a stated purity in excess of 99.99 mol%, were used without further purification. Ozone was prepared, trapped over silica, and desorbed as previously reported.[14] The halocarbons and the other chemicals were also commercially available, research-grade products. The FT-ICR experiments were performed with a 47e APEX spectrometer from Bruker Spectrospin, equipped with a Bayard-Alpert ionization gauge and a cylindrical "infinity" cell.[15] The MIKE and CAD spectra were recorded utilizing a hybrid, reverse geometry ZAB Spec oa-TOF spectrometer from Micromass Ltd., whose CI source was fitted with thoriated filaments to operate in a $O_3/O_2$ gaseous environment.

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