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Linking Ion and Neutral Chemistry in C–H Bond Electrophilic Activation: Generation and Detection of $HO_2^\bullet$ Reactive Radicals in the Gas Phase**

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The activation of inert C–H bonds by charged electrophiles is the subject of extensive investigation mainly motivated by one of the most widely debated questions, that is, the conversion of alkanes into more valuable compounds. Studies of ion-molecule reactions in the idealized gaseous state have provided insightful information on this elementary step, thus lending models and concepts which span from the molecular level to the borders of the nanoscale size.[1] These studies have shown the enhanced ability of oxygen-centered radical cations to activate C–H bonds;[2] the inventory of $XO^{\bullet+}$ reactants now available includes metal oxides and oligomeric cluster ions, mixed metal/nonmetal cluster ions,[2] and also effective metal-free oxide ions.[3]

As a result of the H abstraction, the charge and spin of $XO^{\bullet+}$ are separated in the products [Eqs. (1) and (2)], that is, depending on whether one or two electrons are formally transferred in the process, the $XOH^+/R^\bullet$ or $XOH^\bullet/R^+$ products are formed, respectively (RH = alkane).[4]

$$XO^{\bullet+} + RH \rightarrow XOH^+ + R^\bullet \quad (1)$$

$$XO^{\bullet+} + RH \rightarrow XOH^\bullet + R^+ \quad (2)$$

A very important implication of these thermal ionic reactions is therefore the formation of reactive radicals. The most striking example is the production of methyl radical $CH_3^\bullet$,[2a–c,e–j,3a,b] which can dimerize to give ethane. Likewise, processes of the type shown in Eq. (2) produce oxygen-centered radicals, which can undergo oxyfunctionalization in condensed and gas phases.[11,5,6] It is worth noting that surface-generated $CH_3^\bullet$ and $HO^\bullet$ radicals have been detected in the catalyzed oxidation of methane.[7] Accordingly, the nature and fate of the radicals formed are central to the evolution of the environment or microenvironment where they are generated, a concept that can easily be extended to biological and atmospheric systems.

In this light, the reactivity of $XO^{\bullet+}$ radical cations, so far investigated with alkanes and also alkenes, indicates the formation of many radicals and neutral species in addition to $CH_3^\bullet$: $C_2H_5^\bullet$,[2i,3c] $C_2H_3^\bullet$,[2i,k,3d] $P_4O_9(OH)^\bullet$,[3c] C_2H_4,[2i,3e] C_2H_4O,[1c,2d,k] CH_3OH.[2b,j] While a number of mechanistic details have been elucidated by mass spectrometric experiments, the nature of the uncharged products has never been experimentally probed.[8] This lack becomes a significant limitation when the C–H bond is activated by the two-electron channel [Eq. (2)], as the signature of the H transfer rests on the radical product of the reaction.

In this work, we provide direct experimental evidence for the radical produced by an ion-molecule C–H activation reaction. The reaction between $O_2^{\bullet+}$ and CH_2F_2 was chosen as a model of a two-electron process leading to an oxygen-centered radical. $O_2^{\bullet+}$ is the prototype of metal-free oxygen-centered radical cations, CH_2F_2 (HFC-32; HFC = hydrofluorocarbon) is a methane derivative having a C–H bond strength (102.7 kcal mol^{-1}) quite close to that of CH_4,[9] and a global warming potential approximately 30 times higher for which it is covered by the Kyoto protocol.[10,11] The radical detected is the hydroperoxy radical $HO_2^\bullet$ that can dimerize to H_2O_2. $HO_2^\bullet$ is a known important player in atmospheric ozone cycles,[10] biochemical systems,[12] solution chemistry,[13] and also suggested to be involved in catalyzed oxidation of alkanes.[7d–e] The reactions of $O_2^{\bullet+}$ with some HFCs have previously been studied,[14] whereas to the best of our knowledge no data is available for CH_2F_2. Among the oxide ions, only the vanadium oxide cluster cations have been assayed with CH_2F_2; in these experiments O transfer and C–F activation products were observed.[15]

In our experiments performed under the pressure of approximately 10^{-8} Torr, the reaction between isolated $O_2^{\bullet+}$ ions and CH_2F_2 gives CHF_2^+ as the only charged product of the C–H bond activation.

$$O_2^{\bullet+} + CH_2F_2 \rightarrow CHF_2^+ + HO_2^\bullet \quad (3)$$

The other product observed, the CH_2F^+ ion, cannot be traced to C–F activation by $O_2^{\bullet+}$. The kinetics exhibits the time profile typical of a consecutive reaction (Figure 1), thus showing that the primary product CHF_2^+ subsequently reacts activating the C–F bond of CH_2F_2.

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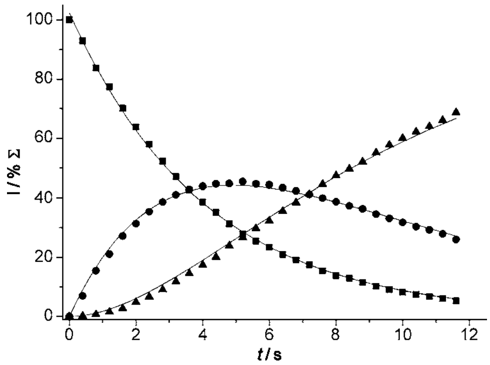

Figure 1. Time profiles and best-fit lines of the $O_2^{\bullet+}$ (■, $R^2=0.999$), CHF_2^+ (●, $R^2=0.994$) and CH_2F^+ (▲, $R^2=0.997$) ions from the reaction of $O_2^{\bullet+}$ with CH_2F_2. P $CH_2F_2 = 2.4\times10^{-8}$ Torr.

$$CHF_2^+ + CH_2F_2 \rightarrow CH_2F^+ + CHF_3 \qquad (4)$$

Accordingly, $O_2^{\bullet+}$ selectively activates the C–H bond of CH_2F_2 with a rate constant $k_3 = 3.3\times10^{-10}$ (± 30 %) cm^3 s^{-1} molecule^{-1}, which corresponds to the efficiency $k/k_{coll} = 17\,\%$ (k_{coll} = collision rate). The rate constant of the consecutive reaction [Eq. (4)], k_4, amounts to 2.2×10^{-10} (± 30 %) cm^3 s^{-1} molecule^{-1}, which is in excellent agreement with the value obtained by experiments independently performed with isolated CHF_2^+ ions, $k = 2.1\times10^{-10}$ (± 30 %) cm^3 s^{-1} molecule^{-1}.

The formation of $HO_2^\bullet$ has been directly probed by experiments, performed at high pressure, that allow detection of the intermediate of the reaction shown in Eq. (3). The stabilization and observation of these intermediates are very rare; in a few cases reported only the ionic products have been characterized.[3a,16] Here, the intermediate formally denoted as $[C, H_2, F_2, O_2]^{\bullet+}$ has been obtained by ionization of O_2/CH_2F_2 mixtures, using $^{18}O_2$ to avoid mixing of the isobaric O_2 and CHF groups. The high-resolution collisionally activated dissociation (CAD) spectrum of isolated $[C, H_2, F_2, {}^{18}O_2]^{\bullet+}$ ions shows two main peaks (Figure 2a): CHF_2^+ and $^{18}O_2^{\bullet+}$. This pattern would indicate the presence of two complexes, $[H^{18}O_2^\bullet\text{-}CHF_2^+]$ and $[^{18}O_2^{\bullet+}\text{-}CH_2F_2]$. Alternatively, the latter complex could account for both the CHF_2^+ and $^{18}O_2^{\bullet+}$ fragments, considering the quite close ionization energies of O_2 and CH_2F_2 and the easy dissociation of $CH_2F_2^{\bullet+}$ into CHF_2^+ + $H^\bullet$ ($\Delta H^\circ = 11.8$ kcal mol^{-1}).[9] The latter is actually consistent with the very low $CH_2F_2^{\bullet+}$ signal observed in the chemical ionization (CI) spectrum. The analysis of the neutral species coming from the dissociation of the reaction intermediate clarifies the issue, showing the nature of the radical formed in the reaction.

To this end, all neutral fragments have been separated from all charged species and reionized by the neutral fragments reionization (N_fR) technique.[17] The spectrum of Figure 2b shows an intense peak at m/z 37 corresponding to the $H^{18}O_2^+$ ion, that can only be formed by reionization of the $H^{18}O_2^\bullet$ radical. Notably, the failure to detect $CH_2F_2^{\bullet+}$, from reionization of the neutral counterpart of $^{18}O_2^{\bullet+}$, confirms its easy dissociation into CHF_2^+. An intense peak at m/z 37 has also been obtained by negative reionization to $H^{18}O_2^-$ (inset of Figure 2b). Accordingly, the positive detection of $H^{18}O_2^+$ and $H^{18}O_2^-$ unambiguously demonstrates that the ionic population contains a detectable amount of reaction intermediate that dissociates into CHF_2^+ and $H^{18}O_2^\bullet$.

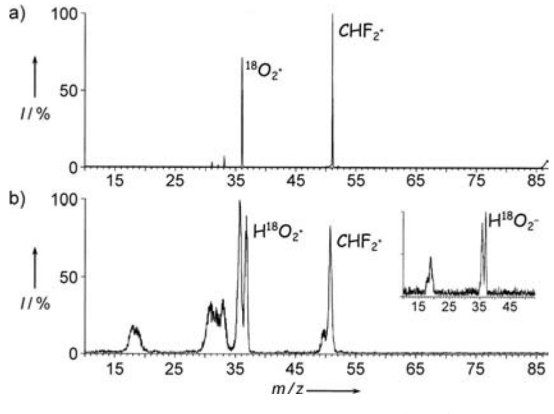

Figure 2. High-resolution CAD spectrum (a) and $^+N_fR^+$ spectrum (b) of $[C, H_2, F_2, {}^{18}O_2]^{\bullet+}$ ions. The inset shows the $^+N_fR^-$ spectrum with the $H^{18}O_2^-$ peak at m/z 37. Unresolved peaks at m/z 50 ($CF_2^{\bullet+}$), 33 (CH_2F^+), 32 ($CHF^{\bullet+}$), 31 (CF^+), 19 (F^+, $H^{18}O^+$), and 18 ($^{18}O^{\bullet+}$). The $^+N_fR^+$ spectrum of unlabeled $[C, H_2, F_2, O_2]^{\bullet+}$ ions display an intense signal corresponding to the HO_2^+ ion superimposed to CH_2F^+ (m/z 33).

Quantum chemical calculations performed at the CCSD(T)/6-311++G(3df,3pd)//B3LYP/6-311+G(d) level of theory are in very good agreement with the experimental evidence. The reaction shown in Eq. (3) is computed to be exothermic by 25.5 kcal mol^{-1}, a value quite close to that evaluated from experimental available data ($\Delta H^\circ = -24$ kcal mol^{-1}).[9] According to the energy profile picture in Figure 3, the reactants generate an encounter complex $[O_2\text{-}CH_2F_2]^{\bullet+}$ (**A**) where $O_2^{\bullet+}$ interacts at a distance of 2.345 Å with the fluorine atom of CH_2F_2. The binding energy of $[O_2\text{-}CH_2F_2]^{\bullet+}$ is 13.3 kcal mol^{-1}.

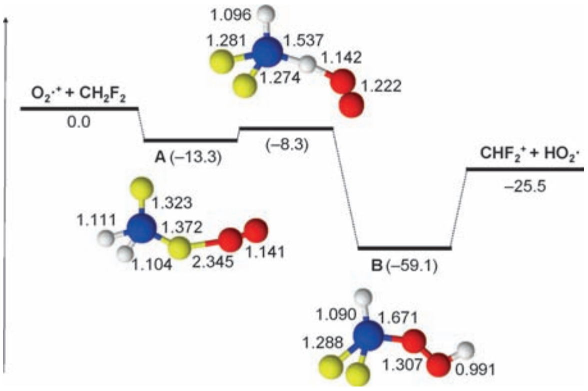

Figure 3. Energy profile of the reaction between $O_2^{\bullet+}$ and CH_2F_2. ΔH° values at 298 K in kcal mol^{-1}, bond lengths in Å.

The encounter complex **A** easily isomerizes to $[HO_2\text{-}CHF_2]^{\bullet+}$ (**B**), where the unpaired electron is entirely located on the newly formed $HO_2^\bullet$ moiety interacting through the oxygen atom with the carbon atom of CHF_2^+. The structures of the two intermediates are consistent with the experimental observations; in particular, the deep well of **B**, 59.1 kcal mol^{-1} below the reactants, accounts for the experimental detection of the $[HO_2\text{-}CHF_2]^{\bullet+}$ complex in sufficient amounts to identify its dissociation radical product. Along the double-well path, the encounter complex **A** is expected to undergo back dissociation in competition with the isomerization, which is consistent with the moderate efficiency of the reaction at room temperature. The rate constant is likely to be sensitive to temperature, as observed for instance with the analogue reaction of $O_2^{\bullet+}$ with CH_4.[18]

In conclusion, in this study we have given direct experimental evidence for an oxygen-centered radical formed by electrophilic C–H bond activation in the gas phase. This is the first experimental detection of both the ion and radical formed in this elementary step. The model reaction also shows that two-electron processes can generate species potentially relevant to functionalization or other chemical cycles. The ensuing chemistry strictly depends on the thermodynamic and kinetic constraints of the reaction pathways; nonetheless this result brings into sharp focus the intimate link existing between ion and neutral chemistry.

Experimental Section

The N_fR experiments were performed using a modified ZABSpec oa-TOF instrument (VG Micromass) of EBE-TOF configuration described elsewhere.[19] High-resolution CI spectra were recorded at 25000 full width at half maximum (fwhm) at the first detector, to rule out isobaric contaminations and assign the elemental composition $[C, H_2, F_2, {}^{18}O_2]^{\bullet+}$. High-resolution CAD spectra of mass- and energy-selected ions were recorded in a gas cell located in the TOF sector (0.8 keV, collision gas: Helium, transmittance $T = 80\,\%$). The N_fR spectra were recorded in a pair of cells located after the magnet: i) the mass-selected ions underwent high-energy (8 keV) CAD in the first cell by collision with He ($T = 80\,\%$); ii) the charged fragments were removed at the exit of the cell by a pair of high-voltage deflecting electrodes; iii) a beam containing only neutral fragments entered the second cell, where they were reionized by collision either with O_2 (${}^{+}N_fR^{+}$) or with Xe (${}^{+}N_fR^{-}$) ($T = 80\,\%$). No signal was observed by switching the deflector on in the absence of the reionizing gas.

The kinetics of the ion-molecule reactions was studied by an EXTREL FTMS 2001 double-cell mass spectrometer. The $O_2^{\bullet+}$ ions were generated in the "source cell" by electron impact (EI) (50 ms, 30 eV) ($P\ O_2 = 1.0 \times 10^{-7}$ Torr). After a cooling period of 4.1 seconds, they were isolated and transferred to the "analyzer cell" containing CH_2F_2 ($P\ CH_2F_2 = 2.3\text{–}9.1 \times 10^{-8}$ Torr). The pressure calibration was carried out using the known rate constant of the reference reaction $CH_4^{\bullet+} + CH_4 \rightarrow CH_5^{+} + CH_3$ ($k = 1.1 \times 10^{-9}$ (± 15 %) cm^3 s^{-1} molecule^{-1}),[20] and the reading was further corrected for the response factor of CH_2F_2.[21] The $O_2^{\bullet+}$, CHF_2^{+} and CH_2F^{+} intensities fit the equations derived by consecutive kinetics, where $O_2^{\bullet+}$ fits a pseudo-first order kinectics.[22] In independent experiments, the CHF_2^{+} ions were generated in the analyzer cell by EI (50 ms, 18 eV) of CH_2F_2 ($P\ CH_2F_2 = 2.1\text{–}11 \times 10^{-8}$ Torr), isolated after a cooling time of 1.5 seconds and allowed to react. The bimolecular rate constants k (cm^3 s^{-1} molecule^{-1}) were obtained by the pseudo-unimolecular rate constants $k_{(obs)}$ (relative square deviation 5 %) and the neutral reactant density. The reaction efficiency k/k_{coll} (k_{coll} = collision rate constant) was calculated according to the ADO theory.[23]

Calculations were performed by locating the lowest stationary points at the B3LYP[24] level of theory with the 6-311+G(d) basis set. Intrinsic reaction coordinate (IRC) calculations were used for the assignment of the saddle points.[25] The energy of all the stationary points was computed at the higher level of calculation CCSD(T)[26] using the 6-311++G(3df,3pd) basis set and the CCSD(T) energies were corrected to 298.15 K by adding the zero point energy correction and the thermal correction computed using the scaled harmonic vibrational frequencies evaluated at B3LYP/6-311+G(d) level. All calculations were performed using Gaussian 03.[27]

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