# Isotope Exchange in Ionized $O_3/O_2$ Mixtures: The Role of $O_5^+$, a Unique $O_n^+$ Complex

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A hitherto unknown reaction, the isotope exchange between oxygen and ozone, accompanies formation of the latter upon ionization of $O_2$ or air, a long-known process widely utilized for the production of ozone and of great relevance to atmospheric chemistry. The isotope exchange was demonstrated and its mechanism established by mass spectrometric techniques that allowed identification of the charged intermediate, the $O_5^+$ ion, characterized by the joint application of theoretical and experimental methods as truly unique among all known $O_n^+$ complexes. The results are of interest to atmospheric chemistry, bearing on the problem related to the widely different extent of $^{18}O$ enrichment of ozone in the stratosphere and in the troposphere.

## Introduction

The isotopic composition of atmospheric $O_3$ has received much attention after the discovery that it is highly enriched in $^{18}O$ in the stratosphere, whereas a lower enrichment is observed in the troposphere.[1,2] As a part of our interest in the ionic chemistry of $O_3$,[3] we report here the first observation of the isotopic exchange in ionized $O_3/O_2$ mixtures and a study of its mechanism which led to the identification of $O_5^+$ as the charged exchange intermediate. The results are of interest to atmospheric chemistry, since the higher $^{18}O$ content of stratospheric than of tropospheric ozone may reflect not only different formation routes but also different efficiencies of isotopic mixing processes, and $O_n^+$ clusters are present in air ionized by cosmic rays, UV radiation lightning, and radioactive emanation.[4]

In this study the isotope exchange was examined by Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. Briefly, $O_3^+$ ions, produced in the external chemical ionization (CI) source of the spectrometer upon ionization of $O_3$, were driven into the resonance cell and isolated by selective ejection techniques, removing all other charged species. The $O_3^+$ ions were then allowed to react with $^{18}O_2$, contained in the cell at pressures ranging from $10^{-8}$ to $10^{-7}$ Torr.

The charged products were unequivocally identified by accurate mass measurements, and the time profile of their intensity was established, in order to evaluate the efficiency of their formation processes relative to the ion−molecule collision rate. The latter was calculated from the pressure of the neutral reagent according to the ADO theory[5] or the trajectory algorithm,[6] which in this case led to the same results.

The structural study of the $O_5^+$ ion, the charged exchange intermediate not directly observable in the low-pressure range typical of FT-ICR experiments, was performed by collisionally activated dissociation (CAD) mass spectrometry, utilizing a reverse geometry instrument. Labeled $O_5^+$ ions were successfully generated in the high-pressure CI source of the mass spectrometer upon ionization of $^{18}O_2/O_3$ gaseous mixtures, and their CAD spectra were recorded utilizing He as the collision gas.

Finally, additional evidence on the structure and the stability of relevant $O_5^+$ species was sought by computational methods in the framework of the density functional theory.

## Results

**FT-ICR Mass Spectrometry.** $O_3^+$ ions, prepared and isolated as discussed in the previous section, were found to undergo, in addition to charge exchange, the following isotope exchange processes when allowed to react with labeled oxygen at 25 °C in the pressure range from $10^{-8}$ to $10^{-7}$ Torr.

$$^{16}O_3^+ + {}^{18}O_2 \longrightarrow {}^{16}O^{18}O_2^+ \quad (+\ {}^{16}O_2) \qquad (1a)$$

$$^{16}O_3^+ + {}^{18}O_2 \longrightarrow {}^{16}O_2^+ \quad (+\ {}^{16}O^{18}O_2) \qquad (1b)$$

These reactions are relatively efficient, for example, $k_{1a}$ amounts to about 10% of $k_{coll}$, the ion−molecule collision rate, whereas the $k_{1a}/k_{1b}$ branching ratio is about 1:5, the higher rate of reaction 1b being consistent with the lower ionization potential of $O_2$ than of $O_3$. As could be expected, the $^{16}O^{18}O_2^+$ ions formed from reaction 1a, reisolated and allowed to react again with the labeled oxygen present in the cell, were observed to undergo further isotope exchange according to the processes

$$^{16}O^{18}O_2^+ + {}^{18}O_2 \longrightarrow {}^{18}O_3^+ \quad (+\ {}^{16}O^{18}O) \qquad (2a)$$

$$^{16}O^{18}O_2^+ + {}^{18}O_2 \longrightarrow {}^{16}O^{18}O^+ \quad (+\ {}^{18}O_3) \qquad (2b)$$

whose efficiency and branching ratio seem similar to those of reactions 1a and 1b, although accurate measurements are prevented by the low intensity of $^{16}O^{18}O_2^+$.

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**Table 1.** CAD Spectra of $O_5^+$ and $O_4^+$ Ions

| species | rel intensities of fragments (%) | | |
|---|---|---|---|
| | *m/z* 32 | *m/z* 34 | *m/z* 36 |
| $^{16}O_2{}^{18}O_2{}^{+\,a}$ | 47 | | 53 |
| $^{16}O_2{}^{18}O_2{}^{+\,b}$ | 33 | 29 | 38 |
| $^{16}O_5{}^{+\,c}$ | 100 | | |
| $^{16}O_3{}^{18}O_2{}^{+\,c}$ | 30 | 58 | 12 |
| $^{16}O_4{}^{18}O^{+\,c}$ | 66 | 34 | |
| $^{16}O_4{}^{+\,a,b,c}$ | 100 | | |
| $^{18}O_4{}^{+\,a}$ | | | 100 |

[a] CI of $^{16}O_2/^{18}O_2$. [b] CI of $^{16}O_2/^{18}O_2/^{16}O^{18}O$. [c] CI of $^{16}O_3/^{16}O_2/^{18}O_2$.

**CAD Mass Spectrometry.** The $^{16}O_3{}^{18}O_2{}^+$ ions formed from the reaction

$$^{18}O_2{}^+(^{18}O_2) + {}^{16}O_3(^{16}O_3{}^+) \rightarrow {}^{16}O_3{}^{18}O_2{}^+ \qquad (3)$$

promoted by ionization of a $^{16}O_3/^{18}O_2$ mixture (0.5 Torr) were analyzed by CAD mass spectrometry, utilizing the lowest pressure of the collider (He) required to cause measurable dissociation of the $O_5^+$ ions (Table 1). The CAD spectra show that $O_2^+$ is the only significant fragment and denote extensive isotope scrambling within the $^{16}O_3{}^{18}O_2{}^+$ ions from process 3, the relative abundances of the $^{16}O_2{}^+$, $^{16}O^{18}O^+$, and $^{18}O_2{}^+$ being very close to those expected for a statistical $^{18}O$ distribution. Such a behavior sets $O_5^+$ apart from all known $O_n^+$ complexes, whose monomers retain their initial structure and bonding through the association/dissociation sequence undergoing no isotopic mixing, as shown by the CAD spectra of the $^{16}O_2{}^{18}O_2{}^+$ adducts obtained upon ionization of an $^{16}O_2/^{18}O_2$ mixture (Table 1). This is consistent with the structure currently assigned to $O_4^+$, the most simple $O_n^+$ complex and the core ion in larger $O_n^+$ clusters,[7,8] viewed as a complex formed by two distant, weakly interacting $O_2$ units.[9,10]

## Theoretical Calculations

The evidence for the intermediacy of $O_5^+$ in the isotope exchange prompted its study at the B3LYP/6-31G(d) and B3LYP/6-311G(d) levels of theory, with single-point CCSD(T) calculations.[11] The 2A″ surface was identified as the most stable at the B3LYP/6-31G(d) level, examining both planar and nonplanar structures on the doublet and on the quartet surfaces. The geometries, optimized at the B3LYP/6-311G(d) level of theory, of the first-order saddles **1**−**3** and the minima **4**−**6** identified in the 2A″ surface are illustrated in Figure 1 and in Table 2, which reports the CCSD(T) energies, the 0 point corrections, and the $O_3{-}O_2^+$ binding energies (BE) of the minima.

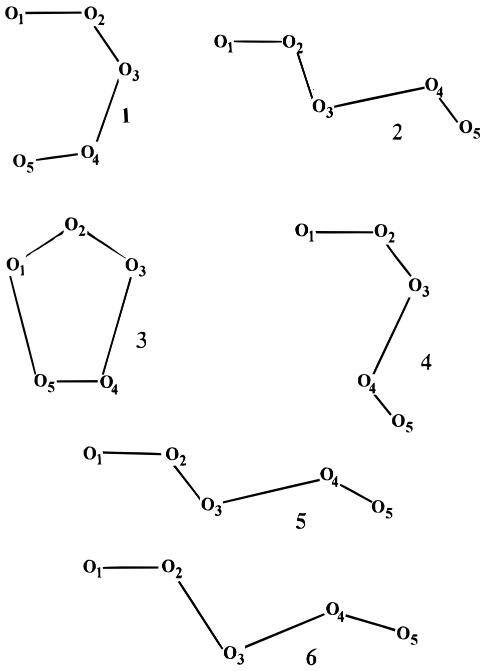

**Figure 1.** Stationary points on the 2A″ surface identified at the B3LYP/311G(d) level of theory. The numbers correspond to those of Table 2.

The most stable species **6** has a symmetrical structure whereby the central atom has lost memory of its former bonding in $O_3$, being linked to two equivalent, relatively distant (2.073 Å) $O_2$ units. Remarkably, despite such a strong structural deformation suggestive of a significant covalent interaction, the $O_3{-}O_2^+$ BE in **6** is only slightly larger than the $O_2{-}O_2^+$ BE in $O_4^+$, that is, 12.1 versus 9.1 kcal mol$^{-1}$.[12] From the computed BE and the heats of formation of the monomers,[13] one obtains $\Delta H_f°(O_5^+) = 300.4$ kcal mol$^{-1}$, whose comparison with the values from photoionization experiments ranging from 295.4 to 299.5 kcal mol$^{-1}$ provides a useful estimate of the experimental and theoretical uncertainty ranges.

## Discussion

The experimental and theoretical results outline a coherent picture of the mechanism of the isotope exchange, in particular as concerns the intermediacy of $O_5^+$. The FT-ICR results, which unequivocally demonstrate the occurrence of the exchange and allow its efficiency to be evaluated, provide only indirect evidence for the role of $O_5^+$, which (as most adducts from ion neutral association) is too short-lived to be detectable in ICR experiments, characterized by very low pressures and hence by a most inefficient collisional stabilization. Fortunately, $O_5^+$ can easily be obtained in CI experiments, whose upper pressure limit, about 0.5 Torr, exceeds that typical of ICR mass spectrometry by some 6 orders of magnitude. The actual detection of $O_5^+$ in $O_2/O_3$ CI plasmas and especially the CAD results, pointing to extensive isotope mixing in labeled $O_5^+$ ions, provide

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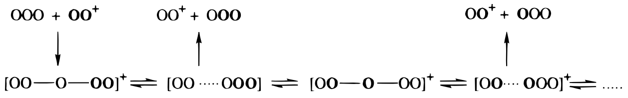
**Table 2.** Optimized Geometries, at the B3LYP/6-311G(d) Level, and CCSD(T) Energies of the Stationary Points Localized on the $O_5^+$ 2A″ Surface[a]

| | saddle | | | minimum | | global minimum |
|---|---|---|---|---|---|---|
| | **1**[b] | **2** | **3** | **4** | **5** | **6** |
| $r(O_1O_2)$ | 1.241 | 1.186 | 1.265 | 1.237 | 1.233 | 1.164 |
| $r(O_2O_3)$ | 1.295 | 1.564 | 1.265 | 1.299 | 1.320 | 2.073 |
| $r(O_3O_4)$ | 2.146 | 2.110 | 2.459 | 2.193 | 2.112 | 2.073 |
| $r(O_4O_5)$ | 1.149 | 1.155 | 1.142 | 1.149 | 1.141 | 1.164 |
| $\angle(O_1O_2O_3)$ | 119.6 | 114.0 | 114.7 | 119.3 | 115.0 | 115.5 |
| $\angle(O_2O_3O_4)$ | 131.9 | 103.5 | 107.0 | 118.6 | 107.4 | 99.5 |
| $\angle(O_3O_4O_5)$ | 129.3 | 113.5 | 101.6 | 110.9 | 111.4 | 115.5 |
| $\angle(O_1O_2O_3O_4)$ | 0.0 | 180.0 | 30.0 | 0.0 | 180.0 | 180.0 |
| $\angle(O_2O_3O_4O_5)$ | 0.0 | 180.0 | −16.0 | 180.0 | 180.0 | 180.0 |
| $E_{CCSD(T)}$ | −374.604 183 | −374.598 172 | −374.612 099 | −374.608 111 | −374.607 816 | −374.613 129 |
| relative energies[c] | 5.6(6.2) | 9.4(9.2) | 0.7(1.3) | 3.1(3.9) | 3.3(4.1) | 0(0) |
| binding energy[d] | 5.8(5.9) | 2.0(2.9) | 10.7(10.8) | 8.3(8.2) | 8.1(8.0) | 11.4(12.1) |

[a] Bond lengths in Å, angles in deg, total energies in hartree, relative and binding energies in kcal $mol^{-1}$. [b] The numeration follows that of Figure 1. [c] Values in parentheses include 0 point correction to the energy, evaluated at the B3LYP/6-311G(d) level. [d] Binding energy evaluated with respect to $O_3 + O_2^+$ in their ground state. Values in parentheses include 0 point energy.

**Scheme 1**



compelling evidence for the intermediacy of the complex in the isotope exchange reaction.

The theoretical description of $O_5^+$ characterizes the ion as a species endowed with a unique combination of features that set it apart from all other known $O_n^+$ complexes. Since $O_5^+$ is the first, and so far the only, complex containing an odd number of oxygen atoms, it is conceivable that its features are peculiar of the entire class of odd-membered $O_n^+$ ions. Remarkably, the monomers undergo a profound structural change upon association into $O_5^+$, that is, their bonding is not a purely electrostatic interaction between distant and structurally unchanged $O_2$ units, as in $O_4^+$ and larger even-membered clusters, yet the $O_3-O_2^+$ BE is remarkably low. Another feature of the 2A″ $O_5^+$ surface is the presence of energetically well accessible saddle points for structural rearrangement, for example, **2** connects minima **5** and **6**, **3** is the TS for the transfer of an $O_2$ unit from $O_3$ to $O_1$, etc.

The symmetrical structure, the low $O_3-O_2^+$ BE, and the facile rearrangement of $O_5^+$ accord well with its role of intermediate in the isotope exchange. A likely mechanism involves reversible conversion of **6** into the electrostatic complexes **4** and/or **5**, sufficiently long-lived on the time scale of the CAD experiments (ca. 10 $\mu$s) to undergo repeated association/dissociation processes, which, coupled with the mutual rotation of the monomers within the charged cluster, account for the observed $^{18}O$ randomization, for example, according to Scheme 1.

The larger BE of $O_2^+$ to $O_3$ than $O_2$ makes $O_5^+$ a species of interest to atmospheric chemistry in that its formation from the reaction of ozone with $O_4^+$ and larger clusters present in ionized air[4] is energetically allowed.

As a final remark, and a stimulus for future experimental work, we suggest that the most intense infrared frequencies of the global minimum **6**, centered at 1564.7, 1628.7, 311.5, and 263.2 $cm^{-1}$ according to the results of B3LYP/6-311G(d) calculations scaled by the recommended 0.95 factor,[14] be matched with those measured by IR spectroscopy of $O_5^+$ ions prepared upon ionization of $O_3/O_2$ mixtures and codeposited with excess Ne, according to the matrix isolation technique applied to $O_4^+$.[7]

## Experimental Section

**Materials.** The gases used and the $^{18}O_2$ sample (99.1 atom %) were obtained from Matheson Gas Products Inc. as research-grade products with a stated purity of 99.95 mol %. Ozone was prepared from dry $O_2$ in a commercial ozonizer and collected in a silica trap cooled to −196 °C. $O_3$ was recovered by controlled warming of the trap and invariably contained $O_2$.

**FT-ICR Experiments.** The spectra were recorded utilizing a Bruker Spectrospin Apex TM 47e instrument, equipped with an external ion source and a cylindrical "infinity" cell[15] located within the poles of a superconducting magnet (4.7 T). For the determination of the rate constants, the readings of the Bayard−Alpert ionization gauge of the reaction cell were corrected according to the procedure recommended by Bartmess and Georgiadis.[16]

**CAD Spectrometry.** The measurements were performed utilizing a VG Micromass ZAB 2F spectrometer, whose CI source was equipped with a thoriated iridium filament, capable of sustained operation in $O_2/O_3$ mixtures at pressures up to 0.5 Torr, under conditions where tungsten or rhenium filaments are rapidly destroyed. Typical operating conditions were as follows: emission current, 1 mA; repeller voltage, 0 V; source temperature, 150 °C; accelerating voltage, 8 kV. In order to record CAD spectra, He was admitted into the collision cell of the spectrometer, using the minimum pressure necessary to produce measurable intensities of the fragments.

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