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Hydrogen trioxide (HO_3) has long been postulated as a key intermediate in important atmospheric processes but has proved difficult to detect. The molecule was unequivocally detected in experiments based on neutralization-reionization and neutralization-reionization/collisionally activated dissociation mass spectrometry, using protonated ozone (HO_3^+) as the charged precursor. Hydrogen trioxide is a relatively stable species and has a H-O-O-O connectivity and a lifetime exceeding 10^{-6} seconds at ambient temperature.

Hydrogen trioxide (HO_3) is a species that has been long postulated in atmospheric chemistry as a sink for hydroxyl radicals (*1, 2*) and a key intermediate in the H + O_3 reaction, the source of vibrationally excited hydroxyl radicals whose emission spectrum is related to night-sky afterglow (*3–9*). Despite its relevance to atmospheric chemistry and its intrinsic fundamental interest, HO_3 has not been experimentally detected to date, and it has remained open whether it can survive dissociation into O_2 and OH. There is no direct experimental evidence on the existence, stability, and lifetime of HO_3, although thermochemical arguments, based on the known heat of formation of the HO_3^+ ion (*10*), combined with an experimental estimate of its recombination energy (*11*), suggest that HO_3 may be observable at 298 K (*12*).

The relevance of the problem and the lack of direct experimental evidence has stimulated an intense theoretical effort. The results of the numerous studies reported (*2, 6, 13–26*) appear to critically depend on the amount of theory employed and provide contradictory answers regarding the stability of HO_3. The most recent theoretical results (*23–26*), reversing earlier conclusions (*6*), predict that, at 298 K, HO_3 is unstable or marginally stable (*23*) and should not be observable, owing to prompt dissociation into O_2 and OH.

Here, we provide experimental evidence for the existence of the elusive HO_3 radical, based on its actual detection as an isolated gaseous species. On the basis of our previous study on the preparation of protonated ozone, HO_3^+ (*10*), we used this cation as the charged precursor in neutralization-reionization (NR) mass spectrometry (*27, 28*) experiments, implemented on the last generation of dedicated instruments, whose improved performances (in particular, the higher sensitivity in the detection of weak peaks from the reionization step) promise to overcome problems encountered with earlier spectrometers.

Protonated ozone was generated in the chemical ionization source of a multisector mass spectrometer (Fig. 1) by the reaction

$$AH^+ + O_3 \rightarrow HO_3^+ + A \qquad (1)$$

where AH^+ denotes a gaseous acid of adequate strength. The exothermicity of reaction 1 depends on the acid used and amounts to 48.6 and 19.6 kcal mol^{-1} for A = H_2 and A = CH_4, respectively (*29*). The HO_3^+ ions, mass-to-charge ratio (m/z) = 49, were accelerated to kinetic energies between 4 and 8 kV and were mass-selected before undergoing two consecutive collision events in two separate cells located along the beam path and containing suitable target gases. A fraction of the HO_3^+ ions was neutralized in the first cell by electron transfer from target gas molecules, yielding the corresponding neutral species, HO_3, together with charged and neutral fragments. The parent ions that escaped neutralization and any charged fragments that formed were removed by a deflecting electrode, leaving a beam containing only fast-moving neutral species that entered the second gas cell. In this cell, reionization occurred either by electron loss from the neutral species, yielding cations (NR^+ mass spectrometry), or by electron transfer from target gas molecules, yielding anions (NR^- mass spectrometry). In either case, the charged species were mass-selected, and their mass spectrum was recorded. Detection of a "recovery" signal that has a peak at the same m/z as that of the original ions (HO_3^+ in the case of interest) would indicate that they survived the sequence of NR events and, hence, that neutral HO_3 has a lifetime exceeding the time interval between the neutralizing and the reionizing collisions ($\sim 10^{-6}$ s in our experimental setup). A substantial "recovery" peak at m/z = 49, the same ratio as that of the HO_3^+ cations, was observed in the NR^+ spectra (Fig. 2A). Recovery signals at m/z = 49, although less intense, are also present in the NR^- spectra, corresponding to HO_3^- ions, which are formally the anions of the H_2O_3 acid (Fig. 2B). Reaction 1 was also performed with D_3^+ rather than H_3^+ as the acid. The DO_3^+ ions of m/z = 50 thus obtained were assayed by NR^+ mass spectrometry, and we obtained a recovery signal at m/z = 50 (Fig. 3), in agreement with the results concerning HO_3^+. These results indicate that a neutral HO_3 does indeed exist as an isolated species, characterized by a relatively long lifetime at 298 K (*30*), and hence is located in

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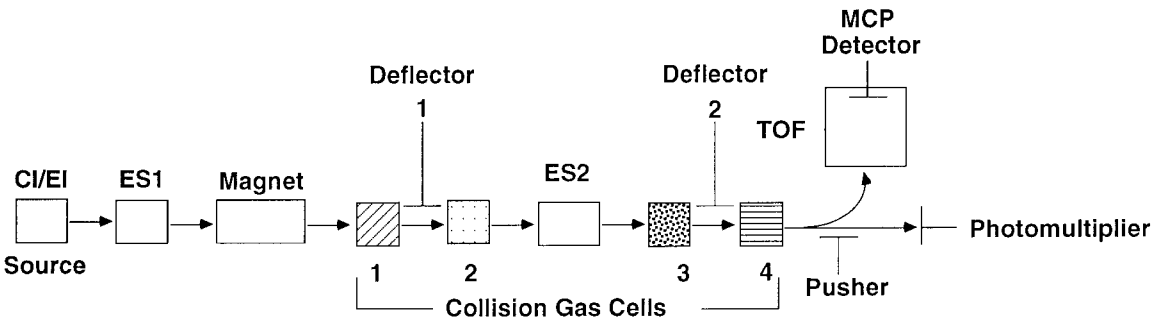

Fig. 1. Schematic illustration of the experimental setup. CI/EI, combined chemical ionization/electron impact source; ES1 and ES2, electrostatic sector analyzers; 1, collision cell containing the neutralization gas; 2, collision cell containing the reionization gas; deflectors, 1-kV electrodes to remove any charged species; 3 and 4, collision cells, either one containing He (for the CAD experiments only); pusher, deflecting electrode to drive the mass-selected ions into the TOF spectrometer equipped with the microchannel plate (MCP) detector.

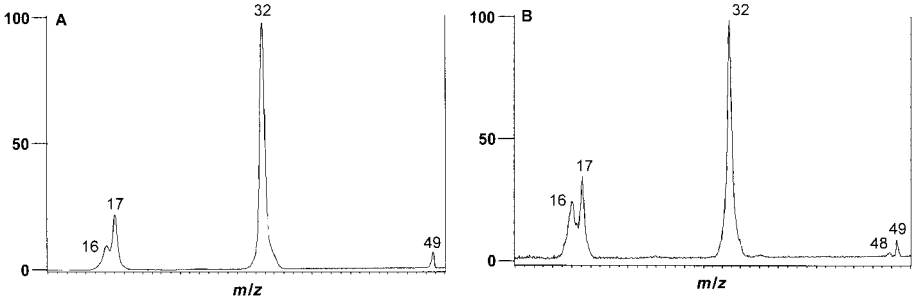

Fig. 2. (**A**) NR^+ spectrum of HO_3^+ ions. $m/z = 49$ and kinetic energy is 4 kV. Neutralizing and reionizing gases are Xe and O_2, respectively. (**B**) NR^- spectrum of HO_3^+ ions. Kinetic energy is 8 kV and neutralizing and reionizing gas is CH_4.

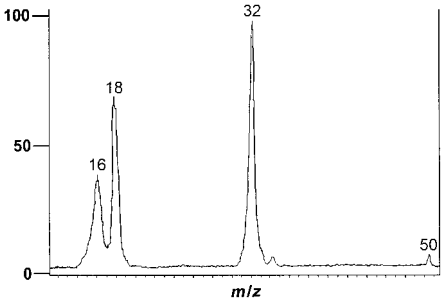

Fig. 3. NR^+ spectrum of DO_3^+ ions. $m/z = 50$, kinetic energy is 8 kV, and neutralizing and reionizing gases are Xe and O_2, respectively.

an energy well sufficiently deep to prevent prompt dissociation into O_2 and OH.

To confirm these conclusions, we exploited the fact that the absolute intensity of the recovery signal of the ion at $m/z = 49$ is sufficiently high to allow its further manipulations and structural assay in neutralization-reionization/collisionally activated dissociation (NR/CAD) mass spectrometry (*27, 28*). The HO_3^+ cations from the reionization of HO_3 were mass-selected and driven into a third gas cell that contained He as the collider, recording the CAD spectrum with the orthogonal time-of-flight (TOF) spectrometer (Fig. 4A). A comparison with the conventional CAD spectrum of HO_3^+ ions from reaction 1, recorded under the same conditions (Fig. 4B), shows that the spectra are very similar. This demonstrates that the ion of $m/z = 49$ displayed by the NR spectra is indeed pure HO_3^+, excluding the admittedly remote possibility of contamination by isobaric ions. Furthermore, the nature of the charged fragments from the dissociation of the cation obtained upon reionization of HO_3 and the likeness of its CAD spectrum with that of protonated ozone from reaction 1 allow the HO_3 radical to be assigned as having H-O-O-O connectivity. This is not unexpected because the same connectivity characterizes the parent HO_3^+ cations (*31*), and it cannot change during the extremely fast (10^{-15} s) neutralization event (*28*). The additional information from the NR/CAD experiments, however, is that the HO_3 radical undergoes no connectivity changes during the relatively long time (10^{-6} s) required for its reionization.

Our results end the long search for the elusive HO_3 radical, characterized as a species of the expected H-O-O-O connectivity and as being relatively stable, with a lifetime in excess of 10^{-6} s at room temperature. Characterization of HO_3 as an intermediate, rather than as a fleeting HO/O_2 complex or a transition state, has a direct bearing on atmospheric chemistry, in particular concerning its role in night-sky afterglow and regarding the accurate kinetic modeling of the $H + O_3$ reaction and the collisional quenching of vibrationally excited hydroxyl radicals by O_2, two processes of current interest (*7, 24*), owing to their importance in atmospheric chemistry.

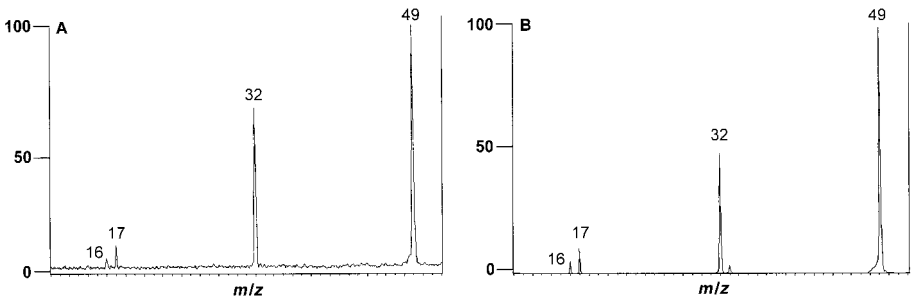

Fig. 4. (**A**) CAD spectrum of $m/z = 49$ ions (kinetic energy is 0.800 keV and target gas is He) obtained by neutralization and consequent reionization of HO_3^+ ions. (**B**) CAD spectrum of HO_3^+ ions from the protonation of ozone, recorded under the same conditions as those in (A).

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30. Strictly, one cannot define the "temperature" of the HO_3 radical obtained from the neutralization process as an isolated translationally excited species that is not thermally equilibrated with the surroundings and does not obey a Boltzmann distribution. Under the circumstances, one can only refer to the temperature of a hypothetical HO_3 population obeying the Boltzmann distribution and having the same average internal energy, the only one that influences the unimolecular dissociation rate. In this sense, the reported value of 298 K, which reflects the measurable apparatus temperature, is given only as a conservative lower limit, in that the HO_3 radicals detected are undoubtedly imparted excess internal energy by the neutralizing-reionizing collisions, and hence their temperature, as defined above, is undoubtedly higher. It follows that if HO_3 survives dissociation at such a higher temperature, it certainly does so at 298 K.
31. Apart from the CAD results from this study, the assignment of the H-O-O-O connectivity to HO_3^+ is based on earlier CAD evidence (*11*) and theoretical results [C. Meredith, G. E. Quelch, H. F. Schaefer III, *J. Am. Chem. Soc.* **113**, 1186 (1991), and references therein].

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