Direct Experimental Evidence for the $H_2O^+O_2^-$ Charge Transfer Complex: Crucial Support to Atmospheric Photonucleation Theory**

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At the end of the nineteenth century water-vapor photonucleation was thoroughly investigated by Wilson,[1] who observed the formation of droplets upon UV irradiation of supersaturated air and discovered that oxygen plays a role. Although photonucleation, and its atmospheric relevance, has since been the subject of numerous studies,[2] its mechanism remained poorly understood, until Byers Brown[3] proposed a theory based on the excitation by a UV photon of a collision complex ($H_2O \cdot O_2$) to a charge transfer (CT) complex ($H_2O^+O_2^-$). Owing to its large dipole moment, the complex acts as an effective nucleation center, attracting the polar water molecules and promoting the formation of a cluster ("Wilson cluster"). Ab initio[4] and modeling studies[5] provide a sound theoretical foundation to the Byers Brown mechanism, which has so far suffered from a complete lack of experimental evidence for the occurrence of its pivotal intermediate, the CT complex. Here, we report direct experimental evidence for its existence as an isolated species with a lifetime exceeding 0.5 μs in the gas phase. Apart from being of interest to the chemistry of water clusters, this result has a direct bearing on the water-vapor photonucleation in the atmosphere.

To clarify our experimental strategy, it is useful to contrast the salient features of the H_2O/O_2 pairs bound by van der Waals (vdW) or CT interactions, as described by the most recent and reliable theoretical analysis.[4c] The energy separation between the two species is computed to amount to 5.75 eV, corresponding to an excitation wavelength of 215.6 nm. The vdW collision complex is characterized by a large separation of H_2O and O_2 and by an essentially repulsive interaction between them, whereas in the CT complex the H_2O^+/O_2^- separation is much shorter and the binding energy (BE) very large, as expected for the charged fragments of a zwitterion whose dipole moment is computed to be 6.04 D. Furthermore, there is a reasonably good agreement between the calculated UV spectrum of the vdW complex and the experimentally observed photonucleation spectrum.

The large difference between the BE of the H_2O/O_2 pair in the vdW complex and the BE of the H_2O^+/O_2^- pair in the CT complex suggested that the most promising experimental approach could be based on neutralization–reionization (NR) mass spectrometry. This well-established technique[6] is endowed with the ability, essential in the case of interest, of discriminating between strongly bound neutral species, such as the CT complex, and very weakly bound species, such as the vdW water–oxygen complex. The latter would be undetectable by NR mass spectrometry because the energy deposition in the high-energy neutralizing collisions is far too large to result in species with microsecond lifetimes, which are the only ones observed in NR experiments.[7]

Our experimental approach can be outlined as follows. Charged water–oxygen adducts (i.e. $(H_2O \cdot O_2)^+$ or $(H_2O \cdot O_2)^-$ ions) were produced by well-established ion–molecule reactions in the chemical ionization (CI) source of a multisector mass spectrometer. The ions were accelerated to energies of 4–8 kV and 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 ions was neutralized in the first cell by electron transfer reactions, for example according to Equation (1), where M denotes a target gas molecule, accompanied by fragmentation processes. The parent ions that escaped neutralization, the fragment ions, and in general all charged species were removed by a deflecting electrode, leaving a beam containing only fast-moving neutral species to enter the second gas cell. Here reionization occurred either by collision-induced electron loss from the neutral species, yielding cations ($^+NR^+$ variant), or by electron transfer from a molecule of the target gas ($^+NR^-$ variant), yielding anions.

$$(H_2O \cdot O_2)^+ \xrightarrow{+M,\ -M^+} (H_2O \cdot O_2) \qquad (1)$$

In either cases, the reionized species were energy selected and their mass spectra recorded. Detection of a "recovery" signal, a peak of the mass-to-charge ratio (m/z 50) of the original ions, would demonstrate that they survived sequence (2) and hence that the ($H_2O \cdot O_2$) neutral species must have a lifetime exceeding the time interval of the order of one microsecond between the neutralization and the reionization events.

$$(H_2O \cdot O_2)^+ \xrightarrow{\text{Neutralization}} (H_2O \cdot O_2) \xrightarrow{\text{Reionization}} \begin{cases} \rightarrow (H_2O \cdot O_2)^+ & (\mathbf{2a}) \\ \rightarrow (H_2O \cdot O_2)^- & (\mathbf{2b}) \end{cases}$$

The same scheme applies, with obvious modifications, to the experiments involving the $(H_2O \cdot O_2)^-$ ion, where detection of a recovery signal at a mass-to-charge ratio of 50 from sequence (3) would provide independent evidence for the existence of the neutral species of interest.

$$(H_2O \cdot O_2)^- \xrightarrow{\text{Neutralization}} (H_2O \cdot O_2) \xrightarrow{\text{Reionization}} \begin{cases} \rightarrow (H_2O \cdot O_2)^+ & (\mathbf{3a}) \\ \rightarrow (H_2O \cdot O_2)^- & (\mathbf{3b}) \end{cases}$$

Both the $^+NR^+$ and $^+NR^-$ spectra display significant recovery peaks at m/z 50 and the same peaks are also displayed by the $^-NR^+$ and $^-NR^-$ spectra (Figure 1). Although the evidence from these NR experiments appeared hardly questionable, the importance of the problem suggested a confirmatory test to make the conclusions irrefutable. To this end, $^{18}O_2$ and $H_2{}^{18}O$ were used to prepare $(H_2{}^{16}O \cdot {}^{18}O_2)^+$ and $(H_2{}^{18}O \cdot {}^{16}O_2)^+$ adducts with m/z ratios of 54 and 52, respectively, whose NR spectra, illustrated in Figure 2, are fully consistent with those of the unlabeled species.

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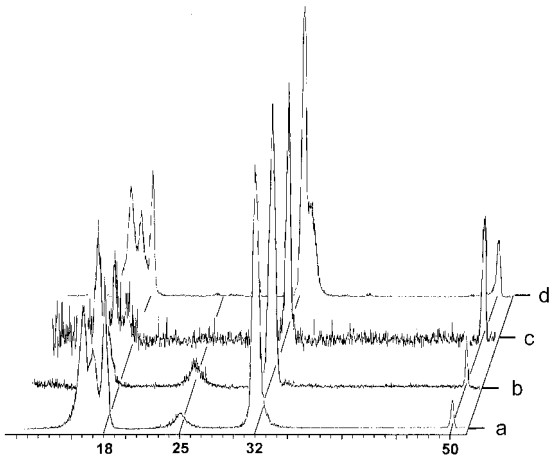

Figure 1. a) $^{+}NR^{+}$ spectrum, b) $^{+}NR^{-}$ spectrum of the $(H_2O \cdot O_2)^+$ ion [Eq. (2)], c) $^{-}NR^{-}$ spectrum, d) $^{-}NR^{+}$ spectrum of the $(H_2O \cdot O_2)^-$ ion [Eq. (3)] (m/z 50). Note the recovery peak at the same m/z ratio from all the sequences.

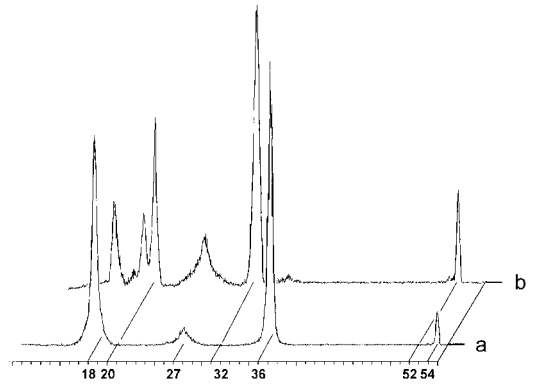

Figure 2. $^{+}NR^{+}$ spectra of a) the $(H_2O \cdot {}^{18}O_2)^+$ ion (m/z 54), b) the $(H_2{}^{18}O \cdot O_2)^+$ ion (m/z 52), both displaying recovery peaks at the expected m/z ratios.

In a separate set of experiments, the fragmentation pattern of the cations from the reionization process was examined by neutralization – reionization/collisionally-activated dissociation (NR/CAD) mass spectrometry utilizing the TOF analyzer. The cation, which is formed from the reionization of the unlabeled neutral species, decomposes exclusively into O_2^+ (m/z 32), without detectable formation of the OH^+ fragment, a result consistent with the expected $H_2O{-}O_2$ connectivity. The only fragments formed from the dissociation of the $(H_2{}^{16}O \cdot {}^{18}O_2)^+$ and $(H_2{}^{18}O \cdot {}^{16}O_2)^+$ recovery ions from the reionization of the corresponding neutral species are $^{18}O_2^+$ (m/z 36) and $^{16}O_2^+$ (m/z 32), respectively, without detectable formation of the isotopically mixed $^{16}O^{18}O^+$ fragment (m/z 34).

The summary of the experimental results is that a neutral $(H_2O \cdot O_2)$ species does exist in the isolated state, and that its lifetime exceeds 0.5 μs, the minimum flight time from the neutralization to the reionization cell of our apparatus for a 50 Da molecule traveling at the speed corresponding to a kinetic energy of 8 keV.

Regarding the nature and the bonding of the neutral species detected, we preliminarily note that the energy deposited into the neutral species by the 8 keV neutralizing collisions prevents survival of neutral species located in shallow energy wells; the detection limit of NR mass spectrometry corresponds to a energy well depth of the order of 10 kcal mol^{-1}.[7] It follows that a sizable barrier must exist for the dissociation of the observed species, be it an H_2O_3 molecule or some $H_2O \cdot O_2$ adduct. As to covalently bound species, the only conceivable candidate, the HOOOH molecule, can safely be excluded, based on the following considerations. First, it is extremely unlikely that ionic species of the H-O-O-O-H connectivity can be formed upon the mere clustering of O_2^{+}/O_2^{-} ions with water in the CI source. Second, the NR/CAD spectrum of the $(HOOOH)^+$ ion from the reionization of HOOOH would be expected to contain a peak for the HO^+ fragment, which was not detected. Finally, the lack of the isotopically mixed $^{16}O^{18}O^+$ fragment in the NR/CAD spectra of the $(H_2{}^{18}O \cdot {}^{16}O_2)^+$ and $(H_2{}^{16}O \cdot {}^{18}O_2)^+$ ions from the reionization of the corresponding neutral species suggests that the oxygen atoms undergo no scrambling, and that the constituent water and oxygen units retain their distinct identity throughout the entire neutralization – reionization sequence.

These results strongly support the existence of a metastable $H_2O \cdot O_2$ adduct that cannot be matched by the vdW collision complex that is formed by H_2O and O_2 molecules and in which the interaction is theoretically characterized as repulsive.[4c] More generally, the theory of intermolecular interactions predicts that the BE of any conceivable adducts formed by neutral, ground-state H_2O and O_2 molecules is many orders of magnitude less than required to survive the neutralization event.[8] It follows that such weakly bound species would invariably dissociate in the picosecond timeframe, and hence would be undetectable by NR mass spectrometry. Based on the above considerations, the neutral species observed must be identified as a metastable adduct formed by *excited* H_2O and O_2 molecules, whose excess energy with respect to the ground state is easily available at the expense of the translational energy of the parent projectile ion.[9] Among such species, the $(H_2O^+O_2^-)$ CT complex, located 5.75 eV above the ground-state vdW complex,[4c] is by far the most likely candidate. Indeed, apart from $(H_2O^+O_2^-)$ being the only excited adduct identified theoretically by the systematic exploration of the H_2O/O_2 system, the BE of its charged fragments is very large,[4c] well above the limit required for detection by NR mass spectrometry.[10] Of course, the CT complex, although stable with respect to dissociation into its charged fragments, can be short-lived owing to fast intramolecular processes, such as fluorescence and intersystem crossing. So far, the lifetime of the CT complex has not been calculated theoretically, but certain spectroscopic features led to an estimated 10^{-9} – 10^{-6} s range.[4b] The lifetime deduced from the present results approaches the upper limit of the above interval, which reinforces the role of the CT complex as a nucleation center, allowing sufficient time for the polar water molecules to organize into a Wilson cluster.

Experimental Section

The experiments were performed with a multisector mass spectrometer of the EBE-TOF configuration (ZAB Spec oa-TOF, VG Micromass Ltd., Manchester, UK), modified by addition of two pairs of collision gas cells and a low-temperature CI source equipped with a thoriated filament.

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Typical CI source conditions were as follows: source temperature 100 °C; repellor voltage 0.0 V; ion-extraction voltage 8 kV; source pressure 0.1–0.3 Torr. The NR experiments were performed in the first of the collision cells positioned between the magnet and the second electrostatic analyzer, using Xe or CH_4 as the neutralizing colliders, at a pressure adjusted to achieve a 80 % transmittance. Reionization was achieved utilizing O_2 as the collider, approximately at the same transmittance. Any ions remaining after the first collision event were deflected from the primary neutral beam using a high-voltage electrode (1 kV), whose efficiency was checked by suitable control experiments. The NR spectra were averaged over 20–50 acquisitions to achieve a satisfactory signal-to-noise ratio.

The gases were of research grade from commercial sources with a stated purity exceeding 99.95 mol % and were used without further purification. Ozone was prepared from dry O_2 in a commercial ozonizer, collected in a silica trap at 77 K and recovered by controlled warming of the trap. $^{18}O_2$ and $H_2{}^{18}O$ (> 99 ^{18}O atom %) were obtained from Isotec (Miamisburg, USA). The $(H_2O \cdot O_2)^+$ ion was prepared by hydration of O_2^+ in the positive O_2/CI of water[11]. Much higher yields were achieved by displacement of O_3 by H_2O in the O_5^+ complex[12], a very efficient process as demonstrated by kinetic experiments performed utilizing a Fourier-transform ion-cyclotron resonance mass spectrometer (47e Apex, Bruker Spectrospin AG, Bremen, Germany). The $(H_2O \cdot O_2)^-$ ion was prepared by hydration of O_2^- in the negative CI of moist oxygen.[13]

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Efficient Hydrolysis of RNA by a PNA–Diethylenetriamine Adduct**

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A few years ago, Komiyama et al. reported[1] that a hybrid composed of diethylenetriamine (DETA) anchored to the 5′-end of DNA by means of a urethane bond (Figure 1a) hydrolyzed linear RNA selectively at the 3′-side of cytosine 22 (C22, marked with an arrow) to give a 22-mer RNA fragment

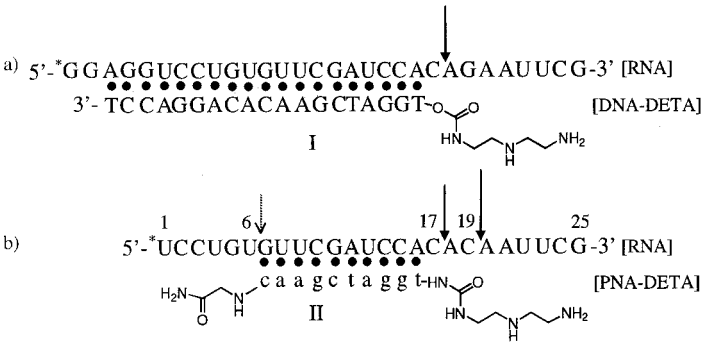

Figure 1. a) Complex **I** of RNA and DNA–DETA as employed by Komiyama et al.; b) complex **II** of RNA and PNA–DETA. Arrows indicate cleavage positions of RNA for hydrolysis by DNA–DETA or PNA–DETA. Nucleotide units are written in uppercase, PNA units in lowercase.

with a 3′-phosphate terminus. This selective scission was ascribed to intramolecular acid–base cooperation of an ammonium ion and a neutral amine in the ethylenediamine moiety $[N(CH_2)_2NH_2]$ of the DNA–DETA adduct.[2] Interestingly, the total conversion for the RNA hydrolysis was only 10 mol % after incubation of the RNA·DNA–DETA complex **I** (Figure 1a) at pH 8 for 4 h at 50 °C. The relatively low conversion of the RNA substrate may be attributed to less effective hydrogen bonding in complex **I**. We surmised that a higher conversion could be attained by decreasing significantly the freedom in dangling motion of the duplex in the complex.

It is generally accepted that peptide nucleic acids (PNAs)[3] nicely mimic the physical properties of DNA. Thus, PNAs hybridize sequence specifically to RNA (DNA). They bind, however, more strongly to RNA (DNA)[4] due to the presence of a neutral polyamide backbone. The latter features, together

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