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The impervious route to the elusive $HOOO^-$ anion

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Dedicated to Helmut Schwarz, on occasion of his 60th birthday and to honor his outstanding contributions to mass spectrometry and to chemistry in general.

Abstract

The $HOOO^-$ anion, the conjugate base of dihydrogen trioxide, HOOOH, is suggested as a key intermediate in ozonation reactions relevant to atmospheric chemistry, water purification, preparative organic chemistry, etc. Whereas recent theoretical calculations characterize $HOOO^-$ as a long-lived metastable species, so far the anion proved experimentally elusive, defying attempts at its direct detection even in solution, where it should be stabilized by solvation. We report the preparation and the proof-positive detection of $HOOO^-$ as an isolated species with a lifetime >0.8 μs. The preparation proved particularly difficult, since the only viable approach is the indirect route involving the preliminary formation of $HOOO^\bullet$ upon neutralization of $HOOO^+$, followed by electron attachment to the radical, utilizing neutralization–reionization ($^+NR^-$) mass spectrometry. Direct two-electron reduction of the $HOOO^+$ cation to the $HOOO^-$ anion by the vertical process typical of charge reversal (CR) experiments proved inefficient. This observation, and application of neutral and ion decomposition difference (NIDD) mass spectrometry, pioneered by Schwarz and coworkers [Int. J. Mass Spectrom. Ion Processes 172 (1998) 181] suggest that the geometries of $HOOO^+$ and $HOOO^-$ are significantly different, whereas that of the $HOOO^\bullet$ radical is structurally intermediate between them, which accounts for the diversity of the Franck–Condon factors characterizing the mutual vertical transitions of the three species. This inference is consistent with the available optimized geometries of $HOOO^\bullet$ and $HOOO^+$, computed at various levels of theory, and with that of the anion recently reported by Plesničăr et al. [J. Am. Chem. Soc. 124 (2002) 8462].

Keywords: Anion; Ozonation; Tropospheric pollution

1. Introduction

The unabated interest for $HOOO^-$ is motivated by its potential role [1] as a key intermediate in ozonation reactions relevant to atmospheric chemistry, particularly tropospheric pollution [2], drinking water and wastewater purification [3], as well as preparative organic chemistry [4]. The $HOOO^-$ anion has been the subject of several theoretical investigations [5]. In particular, a recent computational study at the CCSD(T)/6-311++G (3df, 3pd) level of theory [5c] predicts the ion to be a planar singlet with an exceptionally long covalent HO–OO bond. Nevertheless, the ion is calculated to be sufficiently stable towards

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dissociation into OH^- and $O_2(^1\Delta_g)$ to be observable by experiment.

However, as far as experimental evidence is concerned, the $HOOO^-$ ion still is a truly elusive species. There is no direct evidence for its existence, although its presence has been inferred from indirect, if reasonable, arguments based on the mechanistic analysis of the water-catalyzed ozonation of 1,3-dioxolanes in polar solvents [1d]. It should be noted that direct detection, e.g., by spectroscopic techniques, of $HOOO^-$ in solution is still lacking, and in any case would fall short of demonstrating the existence of the anion as an isolated species, since its solvation is reported to have a strongly stabilizing effect [5c].

In summary, the need to demonstrate the existence of the $HOOO^-$ anion in the gas phase is currently acute, and indeed four different experimental ways to achieve this goal have been suggested in the most recent theoretical study [5c].

This recent upsurge of interest for the $HOOO^-$ anion has prompted us to revisit certain earlier results, regarded as an aside in a study primarily aimed at detecting the $HOOO^\bullet$ radical [6]. The results point to the potential usefulness of appropriate mass spectrometric techniques to achieve proof-positive demonstration of the existence of the $HOOO^-$ anion in the gas phase.

2. Experimental section

2.1. Materials

CH_4, O_2, He and the other gases used were research-grade products, with a stated purity exceeding 99.95 mol%, and were used without further purification. O_3 was prepared by passing UHP O_2 through a commercial ozonizer, collected in a silica trap cooled to 77 K, and released upon gradual warming. Due to its unavoidable decomposition, O_3 was invariably contaminated by O_2.

2.2. Instruments

The experiments were performed using a modified ZAB Spec oa-TOF instrument (VG Micromass) of EBE-TOF configuration, where E and B stand for electrostatic and magnetic sectors and TOF for orthogonal time-of-flight mass spectrometer. The instruments was fitted with a chemical ionization (CI) ion source, a gas-collision cell located in the first field-free region, and two pairs of gas-collision cells located after the magnet along the beam path. Typical operating conditions of the CI source were as follows: temperature, 400 K; repeller voltage, 0 V; electron energy, 50 eV; emission current, 1 mA. The ions were mass selected and the HO_3^+ cations were assayed by $^+CR^-$ and $^+NR^-$ mass spectrometry utilizing the collision cells pair located between the magnet and the second electrostatic sector. In all experiments the collision gas was admitted into the cell to such a pressure as to achieve a 80% trasmission of the beam. In the $^+NR^-$ experiments CH_4 and O_2 were used as the neutralizing and the reionizing gas, respectively, and the NR spectra were averaged over 100 acquisitions to improve the signal-to-noise ratio. The $^+CR^-$ experiments were performed in the second cell of the pair located immediately after the magnet, utilizing O_2 as the collision gas and 80% beam trasmission. In order to verify the applicability of the neutral and ion decomposition difference (NIDD) mass spectrometry, $^+CR^-$ experiments were performed also under exactly the same set of conditions as in the $^+NR^-$ experiments, except as concerns the high-voltage deflecting electrode, that was grounded. The influence of the collision gas pressure on the $^+CR^-$ spectra was also investigated.

3. Results and discussion

The association process

$$HO^- + O_2(^3\Sigma_g{}^-) \rightarrow [HO-O_2]^- \qquad (1)$$

explored under typical negative-ion CI conditions as a possible route to generate a $HOOO^-$ anion and to investigate its stability has proved fruitless. The failure can be traced to back dissociation of the adduct under these conditions, i.e., pressures $\leq$0.1 Torr and a temperature $\geq$400 K prevailing in the ion source. This inference is consistent with the remarkably low theoretically computed binding energy of the monomers in the triplet $[HO–O_2]^-$ adduct, <3 kcal mol^{-1} [5c].

We have also tried the hydride-ion abstraction from CH_4 by $O_3{}^-$, suggested on theoretical grounds [5c], but this too proved unsuccessful under our experimental conditions.

We therefore have turned to the third conceivable route, i.e., the electron capture by the hydrogen trioxide radical.

$$HOOO^{\bullet} + e \rightarrow HOOO^- \qquad (2)$$

At first sight, this approach is not particularly attractive, since it requires that the elusive target anion is formed by ionization of another transient, unbottleable species. However, the preliminary results obtained in the search for the $HOOO^{\bullet}$ radical [6] inspired us to reinvestigate its anion by neutralization–reionization $^+NR^-$ mass spectrometry [7] via the sequence:

$$O_3 + HA^+ \rightarrow HO_3{}^+ + A \qquad (3)$$

$$HO_3{}^+ \xrightarrow{M_1,+e} HO_3{}^{\bullet} \qquad (4)$$

$$HO_3{}^{\bullet} \xrightarrow{M_2,+e} HO_3{}^{\bullet} \qquad (5)$$

To this end, $HO_3{}^+$ has been obtained by CH_4/CI of ozone, according to Eq. (3), A = CH_4, a process exothermic by 19.6 kcal mol^{-1} [8]. The cation, $m/z = 49$, has been mass selected, neutralized upon collision with CH_4, and the $HO_3{}^{\bullet}$ radical formed has been reionized utilizing O_2 as the stationary target. The $^+NR^-$ spectrum illustrated in Fig. 1a displays a significant peak of $m/z = 49$, showing that the $HOOO^-$ anion is formed in the negative reionization step and survives the flight from the gas-collision cell containing O_2 to the electrostatic sector analyzer. Based on the mass of the anion, 49 D, its kinetic energy, 4 keV, the lowest accelerating voltage utilized, and the geometry of the mass spectrometer, the lifetime of $HOOO^-$ can be estimated to exceed 0.8 μs. The assignement of the peak as $HOOO^-$ is consistent by its CAD spectrum recorded in the orthogonal TOF analyzer, that displays $O_2{}^-$ ($m/z = 32$) as the major fragment.

The successful $^+NR^-$ experiments have suggested, as an attractive alternative, the utilization of CR mass spectrometry, where the two-electron reduction of $HO_3{}^+$ to $HO_3{}^-$ occurs in a single collisional event by a vertical transition, without the intermediate formation of neutral $HO_3{}^{\bullet}$, at variance with the two-step sequence typical of $^+NR^-$ spectrometry.

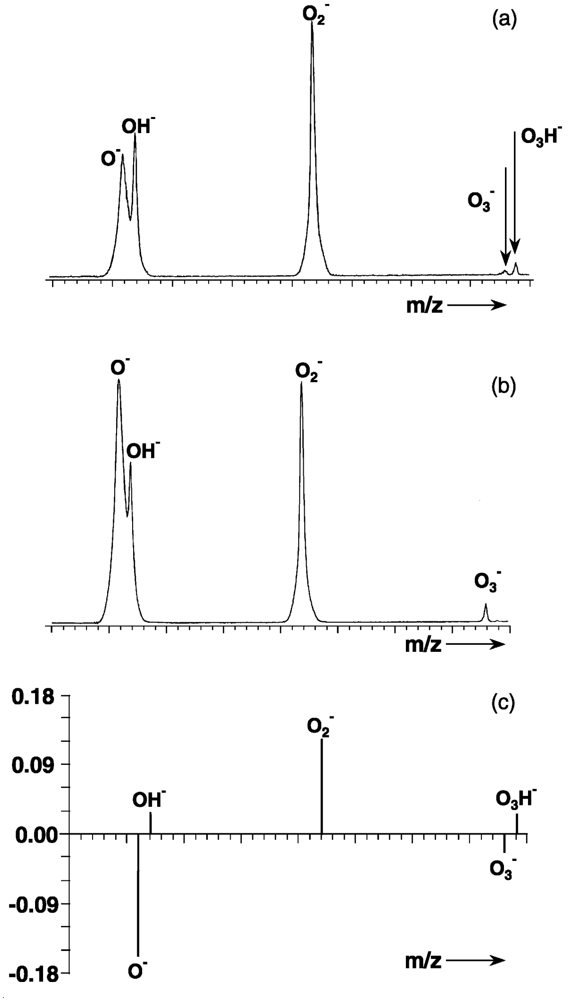

Fig. 1. (a) $^+NR^-$ mass spectrum (CH_4, 80% T, O_2, 80% T), (b) $^+CR^-$ mass spectrum (O_2, 80% T), and (c) $^+NIDD^-$ spectrum of O_3H^+ ion.

As shown by the typical spectrum illustrated in Fig. 1b, $^+CR^-$ is a remarkably inefficient process, pointing to the difficulty of achieving the direct $HOOO^+ \rightarrow HOOO^-$ conversion via a single, vertical transition. To further investigate this point, we have utilized the NIDD mass spectrometry, a technique, introduced by Schwarz and coworkers [9], aimed at a clear-cut assignment of the contribution of neutral and charged species to the total fragmentation. Preliminary tests have been performed, in order to ascertain whether the conditions required to apply the NIDD approach could be met in the specific system of interest, particularly as concerns the reproducibility of the experiments and their scarce sensitivity to changes of the pressure of the target gas in the collision cell. The $^+$NIDD$^-$ spectrum (Fig. 1c) displays the HO_3^-, O_2^- and OH^- peaks on the positive scale, and the O_3^- and O^- peaks on the negative scale. These results can be rationalized assuming that the $HOOO^\bullet$, O_2^- and OH^- anions arise exclusively, or at least predominantly, from the reionization of the corresponding neutrals, including the undissociated $HOOO^\bullet$ radical and the O_2 and OH fragments. The latter species are the neutral counterparts of the OH^+ and O_2^+ ions, formed by collisional dissociation processes that occur together with reaction (4) in the neutralization cell. Another likely source of the O_2^- and OH^- fragments is the dissociation of the $HOOO^-$ anion formed by electron transfer to the $HOOO^\bullet$ radical in the negative reionization step. Whereas this channel contributes only to a limited extent to the total number of fragmentations observed in most NR experiments, it could be significant in the case of interest, owing to the relatively low endothermicity of the dissociation of $HOOO^-$ into OH^- and O_2, 14.3 kcal mol^{-1}, combined with the relatively large electron affinity, 1.118 eV, of the $HOOO^\bullet$ radical, computed in the most recent theoretical study [5c]. From these data, the overall process

$$HOOO^\bullet + e \rightarrow HO^- + O_2(^1\Delta_g) \qquad (6)$$

is estimated to be exothermic by 13.1 kcal mol^{-1}. This result cannot rigorously be applied to the collisional reduction of the radical, that does not involve the capture of a free, thermal electron. However, it underlines the tendency of the $HOOO^-$ anion to undergo dissociation by the facile fission of its exceptionally long, and consequently weak, HO–O_2 bond.

In the above outlined scheme, the O_3^- and O^- anions, whose peaks are on the negative scale in the NIDD spectrum, are assumed to arise from fragmentation processes activated by the collision of $HOOO^+$ with the O_2 in the $^+$CR$^-$ experiments. Formation of O^- and O_3^-, typical products of high-energy, unselective dissociation channels, does not occur at all, or only to a relatively insignificant extent, from the reionization of the uncharged species formed in the neutralization cell.

The situation is different in the case of the O_2^- fragment, formed in the $^+$CR$^-$ experiments as it appears

Table 1
Geometries of neutral and charged HO_3 species computed at various levels of theory. Distances in Å, angles in degrees

Species	$R(O_a–O_b)$	$R(O_b–O_c)$	$R(O_c–H)$	α (O–O–O)	θ (O–O–H)	Method	Reference
cis-$HO_3^\bullet$	1.243	1.433	0.975	111.4	98.6	MP2	[10]
	1.268	1.461	0.970	110.9	98.6	QCISD	[10]
	1.251	1.503	0.970	112.6	99.5	B3LYP	[10]
	1.229	1.75	0.976	113.4	94.3	CASSCF	[10]
HO_3^-	1.321	1.803	0.964	107.8	84.3	CCSD(T)	[5c]
HO_3^+	1.147	1.330	0.972	118.1	107.6	DZ+PSCF	[11]
	1.209	1.384	0.999	117.5	105.8	CCSD	[11]
	1.189	1.407	1.016	118.7	106.7	LCGTO-DF	[12]

		Computed $R(O_b–O_c)$, α and θ differences[a]		
		H_3O^+ vs. HO_3^-	HO_3^+ vs. $HO_3^\bullet$	HO_3^- vs. $HO_3^\bullet$
Δ	$R(O_b–O_c)$	0.419	0.366	0.053
Δ	α	9.7	4.1	5.6
Δ	θ	21.5	11.5	10.0

[a] Absolute differences calculated from the CASSCF [10], the CCSD(T) [5c] and the CCSD [11] results.

on the positive scale in the NIDD spectrum because its major source is the reionization of neutral species ($HOOO^\bullet$, O_2).

The summary of the experimental evidence from NR, CR and NIDD mass spectrometry is that, whereas both the $HOOO^+ \rightarrow HOOO^\bullet$ and $HOOO^\bullet \rightarrow HOOO^-$ vertical transitions do occur, the direct $HOOO^+ \rightarrow HOOO^-$ vertical transition is not observed. The discrepancy can be traced to the different Franck–Condon factors of the transitions involved, which in turn suggest that the $HOOO^\bullet$ structure is to some extent intermediate between those of $HOOO^+$ and $HOOO^-$ that are considerably different from each other.

This inference is born out by a comparison of the geometries of the $HOOO^{+/\mathbf{0}/-}$ species, reported by the available theoretical studies (Table 1). Focusing attention on length of the bond joining the HO–OO units [$R(O_b–O_c)$], as the key parameter to evaluate its strength, and on the OOO and OOH angles, we note that there are indeed large structural differences between $HOOO^+$ and $HOOO^-$, whereas those between $HOOO^+$ and $HOOO^\bullet$, and between $HOOO^-$ and $HOOO^\bullet$ are considerably less pronounced. This provides a satisfactory explanation for the inefficiency of the vertical, two-electron collisional reduction of $HOOO^+$ to $HOOO^-$, and hence for the essential intermediate role of the $HOOO^\bullet$ radical.

4. Conclusion

The present results positively show that the $HOOO^-$ anion does exist as an isolated species in the dilute gas state, with a relatively long lifetime, whose lower limit is estimated around 10^{-6} s. The anion, the corresponding radical and cation, have the H–O–O–O connectivity, as deduced from the results of structurally diagnostic collisional techniques. The preparation, and hence the detection of $HOOO^-$ is particularly difficult, in that the only viable approach requires the preliminary formation of the $HOOO^\bullet$ radical, followed by its stepwise reduction in two separate collisional events, according to the sequence typical of $^+NR^-$ mass spectrometry. The two-electron reduction of $HOOO^+$ to $HOOO^-$ in a single, vertical collisional event, typical of $^+CR^-$ mass spectrometry, is inefficient. These findings, and the application of the NIDD technique, suggest that the structure of the $HOOO^+$ cation and the $HOOO^-$ anion are significantly different, which adversely affects the Franck–Condon factors for their vertical interconversion, whereas the process is possible if mediated by the $HOOO^\bullet$ radical, whose structure is intermediate between those of the cation and the anion.

This interpretation is consistent with the theoretically computed geometries of the $HOOO^{+/\mathbf{0}/-}$ species involved. More generally, the agreement between theory and experiment is quite satisfactory. In particular, we note that the barrier computed by Plesničar et al. [5c] for the dissociation of the $HOOO^-$ anion into OH and $O_2(^1\Delta_g)$, $15.4\,\mathrm{kcal\,mol^{-1}}$, is sufficiently high to provide a rationale for the experimental detection of the anion.

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