COMMENTS

Stable vs Metastable HOOO. An Experimental Solution for an Evergreen Theoretical Dilemma

Maurizio Speranza

Dipartimento di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Università degli Studi di Roma "La Sapienza", P.le A. Moro 5, 00185 Rome, Italy

Hydrogen trioxides, H_nO_3 ($n = 1, 2$), are suspected to be pivotal intermediates in atmospheric and combustion chemistry, as well as in chemical and biological oxidation. Owing to their elusive nature, many important features of these species are unknown and can be predicted only on theoretical grounds. Recently, some papers appeared in the literature concerning the thermochemistry of HOOO and HOOOH[1,2] and the HOOO potential energy surface (PES),[3,4] estimated by high-level theoretical procedures. The authors sometimes complain for the lack of quantitative experimental data against which to gauge their theoretical predictions.[1,2] Nevertheless, they[1] just overlooked the sole experimental study wherein to find the desired checking. This state of affair demands a brief outline of the experimental evidence available on this matter and its comparison with the salient conclusions reached in the latest theoretical investigations.

The experimental study in question deals with the stability and reactivity of gaseous $H_nO_3^+$ ($n = 1, 2$), evaluated by Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS). The results lead to $H°_{298}(HOOO) = -1 \pm 5$ kcal mol^{-1} and to an upper limit for $H°_{298}(HOOOH)$ ($< -26 \pm 3$ kcal mol^{-1}).[5] These values arise from an accurate analysis of the efficiency of the gas-phase electron (ET) and hydride (HT) transfers from a host of neutral donors to thermal HOOO$^+$. The shaded area of Figure 1 corresponds to the onset of the observable ET processes and provides a measure of the 298 K ionization enthalpy of HOOO (IE(HOOO$^+$) = 253 ± 4 kcal mol^{-1}). This value, combined with $H°_{298}(HOOO^+) = 252 \pm 3$ kcal mol^{-1},[6] leads to $H°_{298}(HOOO) = -1 \pm 5$ kcal mol^{-1}. Accordingly, HOOO is a relatively stable intermediate, lying 10 ± 5 kcal mol^{-1} *below* the HO + O$_2$ dissociation limit ($H°_{298}(HO) = 9.3 \pm 0.3$ kcal mol^{-1}).[7] Evaluation of the upper limit of $H°_{298}(HOOOH)$ ($< -26 \pm 3$ kcal mol^{-1}) is based instead on the appreciable HT efficiency from methane to thermal HOOO$^+$ (eff = 0.12), which can be justified only if the process is thermochemically allowed.

Prior to this experimental study, assessment of the stability of the HOOO and HOOOH species has been the object of reiterated, though inconclusive, theoretical efforts. Indeed, computation of $H°_{298}(HOOO)$ and $H°_{298}(HOOOH)$ provided scattered values depending upon the level of theory employed ($-13 < H°_{298}(HOOO)$ (kcal mol^{-1}) $< +27$; $-34 < H°_{298}(HOOOH)$ (kcal mol^{-1}) $< +30$) (Figure 2).[8−18] Those more consistent with the experimental measurements are the MCHF/DZP estimate of $H°_{298}(HOOO) = -3.1$ kcal mol^{-1} by Dupuis, Fitzgerald, Hammond, Lester, and Schaefer (DFHLS)[11] and the
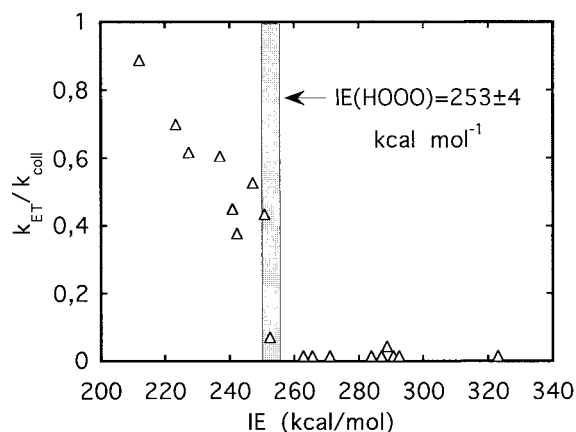

Figure 1. Collision efficiency (k_{ET}/k_{coll}) for the electron transfer to HO$_3^+$ from gaseous donors with increasing standard ionization energies (IE). Donors (from left to right): fluorobenzene, allene, cyclopropane, 1,1-difluoroethene, hydrogen sulfide, ethene, hydrazoic acid, formaldehyde, propane, ethyne, ethane, fluorotrichloromethane, sulfur dioxide, methyl fluoride, methane, water, malononitrile, and carbon monoxide. k_{ET} denotes the experimental electron-transfer rate constant and k_{coll} the corresponding collison rate constant, estimated according to the trajectory calculation method (Su, T.; Chesnavich, W. *J. J. Chem. Phys.* **1982,** 76, 5183). The plot includes data from ref 5. The onset of the observable ET reactions falls in the shaded area.

MP4//MP2/6-31++CG* evaluation of $H°_{298}(HOOOH) = -26.0$ kcal mol^{-1} by Koller and Plesnicar.[18]

In 1996, Junkamp and Seinfeld (JS) computed the standard heat of formation of HOOO and HOOOH at various levels of theory.[2] A value of $+6.1$ kcal mol^{-1} was obtained at the CBS-QCI/APNO level of theory, which increases to $+8.0$ kcal mol^{-1} at the G2M(RCC,MP2) level of theory. At the same computational levels, $H°_{298}(HOOOH)$ amounts to -23.5 and -21.3 kcal mol^{-1}, respectively. According to JS, dissociation of HOOO into HO + O$_2$ requires only $1-3$ kcal mol^{-1} and involves a small activation barrier. Therefore, HOOO would be hardy observable at normal temperatures because the fast HOOO $\leftrightarrow$ HO + O$_2$ equilibrium would be strongly shifted toward dissociation.

One year later, Lay and Bozzelli (LB) indirectly reached the same conclusion.[1] Unfortunately, they did not take the advantage of discussing their results in light of the FTICR-MS experimental data. LB estimated the enthalpy of formation of HOOOH ($H°_{298}(HOOOH) = -23$ kcal mol^{-1}) and its O−H and O−O bond dissociation enthalpies (DH$°_{298}$(HOOO−H) = 82.6 kcal mol^{-1}; DH$°_{298}$(HOO−OH) = 35.8 kcal mol^{-1}) at the G2 levels of theory. From these values, $H°_{298}(HOOO)$ is calculated as large as $+7.5$ kcal mol^{-1}, in excellent agreement with JS's prediction.[2]

In the meanwhile, Varandas and Yu (VY) were constructing a single-valued double many-body expansion (DMBE) potential energy surface (PES) for [H,O$_3$].[3,4] The results are consistent with HOOO as a metastable species placed 2.3 kcal mol^{-1} *above* the HO + O$_2$ dissociation limit ($H°_{298}(HOOO) = +11.6$ kcal mol^{-1}). HOOO dissociation is computed to proceed via a loose HO···O$_2$ transition structure involving a very small activation barrier. Also in this case, HOOO is expected to be a metastable
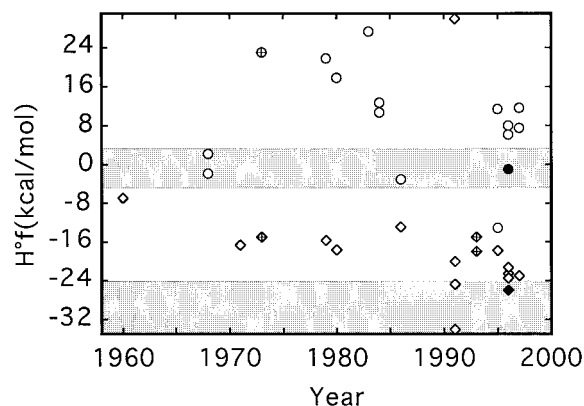
Figure 2. Plot of the calculated heat of formation of HOOO (circles) and HOOOH (diamonds) against the year of publication of the calculation. Circles (year, calculation method, source): 1968, empiric, Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1968; 1973, RHF/4-31G, ref 8; 1979, empiric, Nangia, P. S.; Benson, S. W. *J. Phys. Chem.* **1979**, *83*, 1138; 1980, empiric, Nangia, P. S.; Benson, S. W. *J. Am. Chem. Soc.* **1980**, *102*, 3105; 1983, RHF/4-31G, ref 9; 1984, CCI, ref 10 (higher); 1984, CAS SCF, ref 10 (lower); 1986, MCHF/DZP, ref 11; 1995, BD(T)/6-31G**, ref 12 (higher); 1995, B-LYP/6-31G**, ref 12 (lower); 1996, G2M(RCC, MP2), ref 2 (higher); 1996, CBS-QCI/APNO, ref 2 (lower); 1996, FTICR-MS experimental, ref 5 (full circle); 1997, DMBE, refs 3 and 4 (higher); 1997, G2, ref 1 (lower). Diamonds (year, calculation method, source): 1960, empiric, Benson, S. W. *J. Chem. Phys.* **1960**, *33*, 306; 1971, LCAO-6-31G, ref 13; 1973, RHF/4-31G, ref 8; 1979, empiric, Nangia, P. S.; Benson, S. W. *J. Phys. Chem.* **1979**, *83*, 1138; 1980, empiric, Nangia, P. S.; Benson, S. W. *J. Am. Chem. Soc.* **1980**, *102*, 3105; 1986, CI(SDQ), ref 14; 1991, HF/6-31G**, ref 15 (highest); 1991, MP3/6-31G**, ref 15 (second highest); 1991, MP4/6-31G**, ref 15 (second lowest); 1991, MP2/6-31G**, ref 15 (lowest); 1993, RHF/6-31G**, ref 16 (higher); 1993, MP2/6-31G**, ref 16 (lower); 1995, QCISD/6-311++G(2d,p), ref 17; 1995, B-LYP/6-31G**, ref 12 (lower); 1996, G2M(RCC, MP2), ref 2 (highest); 1996, MP2/6-31G++G*, ref 18 (second highest); 1996, FTICR-MS experimental, ref 5 (full diamond); 1996, CBS-QCI/APNO, ref 2 (second lowest); 1996, MP4//MP2/6-31++CG*, ref 18 (lowest); 1997, G2, ref 1. The crossed symbols refer to approximate values calculated from isodesmic reactions at 0 K without zero-point corrections. The shaded areas refer to the uncertainty ranges of the corresponding FTICR-MS experimental values.

species completely dissociated under normal conditions and, therefore, virtually unobservable. As happened to LB, VY did not critically contrast their computational results with the accessible FTICR-MS evidence.

From the above considerations, the following seem clear:

(A) The alleged lack of experimental data on the thermochemistry of H_nO_3 ($n = 1, 2$), critized by LB,[1] is not borne out by a careful examination of the available literature.

(B) JS's, LB's, and VY's estimates of H°_{298}(HOOO) appear too high relative to the FTICR-MS experimental value[5] and DFHLS's prediction at the MCHF/DZP level of theory.[11] As admitted by JS[1] and VY,[3,4] this is likely due to the difficulty in reproducing the enthalpy of formation of species with O−O bonds with the computational approaches employed. In addition, as pointed out by VY[3] and DFHLS,[11] the MCHF/DZP

calculations probably overestimate bonding in HOOO. In light of these converging considerations, the most reliable value for the standard enthalpy of formation of HOOO remains that measured by the FTICR-MS technique (H°_{298}(HOOO) = −1 ± 5 kcal mol^{-1}). This implies that HOOO is a relatively stable intermediate, which should be observable even at room temperature.[19]

(C) VY's estimate[3,4] of H°_{298}(HOOO) = +11.6 kcal mol^{-1} significantly departs not only from the experimental FTICR-MS value but also from the high-level JS's, LB's, and DFHLS's theoretical estimates. In VY's paper, assessment of the actual stability of HOOO seems to be only a minor problem. Indeed, the authors feel satisfied with the good agreement between the thermal rate coefficients, calculated for the very exothermic process 1 ($\Delta H^{\circ} = -77$ kcal mol^{-1}) on the grounds of their DMBE PES and the experimentally determined values.

$$H + O_3 \rightarrow [HOOO] \leftrightarrow HO + O_2 \qquad (1)$$
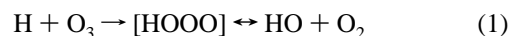
Nevertheless, this agreement should not divert one from considering that a more precise description of the [H,O$_3$] PES around the HOOO critical structure is essential for good-quality dynamics studies[20] and for rationalizing key atmospheric phenomena. Thus, a stable HOOO intermediate can affect the energy partitioning in the products of reaction 1 and, therefore, be responsible for the night-sky airglow.[10,11,20] Furthermore, its role as a stable sink for the HO/O$_2$ pair accounts for the O$_2$ depletion observed in the upper atmosphere.[10]

References and Notes

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