Protonated Ozone: Experimental Detection of O_3H^+ and Evaluation of the Proton Affinity of Ozone

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The elusive protonated ozone ion (O_3H^+) has been long postulated as a reactive intermediate but never experimentally observed. This ion has been detected here in mass spectrometric experiments with the use of Fourier transform ion cyclotron resonance. In these experiments, ozone (O_3) was protonated by strong acids—for example, H_3^+, KrH^+, XeH^+, and CH_5^+. The hitherto experimentally unknown proton affinity of O_3 was evaluated by a "bracketing" technique and determined to be 148 ± 3 kilocalories mole^{-1} at 298 kelvin, in excellent agreement with a value determined in a recent theoretical study of the O_3/O_3H^+ system, which was 148 kilocalories mole^{-1} at zero temperature (~149.5 kilocalories mole^{-1} at 298 kelvin).

Because of its unshared electron pairs, O_3 tends to react as a nucleophile; yet, it also has a typical electrophilic character, best exemplified by its insertion into the π bond of alkenes. Whereas the ability of O_3 to behave as a Lewis base (entering into coordination with typical Lewis acids such as $AlCl_3$) is well documented (*1*), little is known of the Brønsted-base character of O_3 because of the elusive nature of its conjugate acid O_3H^+. The only experimental indication for the existence of the latter dates back to 1976, when Olah and coworkers suggested that the acid-catalyzed ozonolysis of alkanes involves electrophilic insertion of O_3H^+ into a σ bond (*2–4*). However, attempts at detecting O_3H^+ directly by means of nuclear magnetic resonance spectroscopy were unsuccessful, and no further experimental evidence on the existence of protonated O_3 in solution, or in the gas phase, has subsequently been reported.

Apart from being an intrinsically interesting object of research, O_3H^+ is related to a fundamental and hitherto unknown property of O_3—namely, its proton affinity (PA), which quantitatively defines the basicity of the O_3 molecule. Given the interest of the problem and the lack of experimental information, theoretical methods have been used to establish the existence, structure, and the relative stability of isomeric O_3H^+ ions. Although the results depend considerably on the theoretical approach and on the size of the basis set used, these studies consistently assign a terminally protonated, open-chain structure to the most stable O_3H^+ protomer, the theoretically computed PA of O_3 ranging from 124 to 157 kcal mol^{-1} (*5–8*).

Having recently examined (with a combination of theoretical and mass spectrometric techniques) protonated nitrosyl fluoride [$(FNO)H^+$] (*9, 10*), we decided to extend our experimental investigation to the isoelectronic O_3H^+ ion. We found that O_3H^+ can successfully be obtained by the general reaction

$$AH^+ + O_3 \rightleftharpoons A + O_3H^+ \qquad (1)$$

where AH^+ denotes a Brønsted acid of adequate strength—for example, A = H_2, PA = 101.2 (where PA is measured in kilocalories per mole); A = Kr, PA = 101.6; A = Xe, PA = 120.3; and A = CH_4, PA = 130.2 (*11, 12*). In a typical experiment, the external chemical ionization ion source of an APEX 47e FT-ICR mass spectrometer (Bruker Spectrospin) operated at 25°C was fed with CH_4 (the reactant gas) at 1×10^{-4} torr and a O_2/O_3 mixture (nominal molar ratio = 10:1) at a pressure of 3×10^{-6} torr. Under these conditions, both O_3^+ ions [mass-to-charge ratio (m/z) = 48] and O_3H^+ ions (m/z = 49) are formed (Fig. 1) (*13*). The assignment of the observed O_3H^+ peak is supported by accurate mass measurements and by formation of O_3D^+ ions (m/z = 50) when AH^+ acids are replaced in reaction 1 by the corresponding AD^+ acids.

The experimental evaluation of the PA of O_3 proved difficult. Application of the accurate method based on the evaluation of prototropic equilibria (*1*) was found to be impossible because all attempts at introducing and maintaining adequate O_3 concentrations in the reaction cell invariably failed (*14*); in any case, it would have been impossible to measure the actual O_3 pressure with any degree of accuracy. We therefore used a "bracketing" technique based on the measurement of the rate constant k of the process

$$O_3H^+ + B \rightarrow O_3 + BH^+ \qquad (2)$$

where B is a gaseous base of appropriate strength. The collision efficiency of the reaction is conveniently expressed by the k/k_{ADO} ratio, where k_{ADO} denotes the rate of collision of O_3H^+ with the various neutral species, calculated according to the ADO theory (*15*). A high collision efficiency of the deprotonation process is taken as an indication that the PA of the reference base B exceeds that of O_3, whereas the inefficiency of reaction 2 is taken as evidence that the PA of B is lower than the PA of O_3. Strictly speaking, the latter inference is not rigorous, because the inefficiency of reaction 2 could reflect the operation of kinetic, rather than thermochemical, factors. This, however, seems unlikely in our case, because exothermic proton-transfer reactions that involve, as in reaction 2, sterically unhindered n-type bases are generally observed to occur at, or nearly at, the collision rate (*16*). The results of the bracketing experiments (Fig. 2) show that the PA of O_3 is intermediate between that of CH_3F [145.0 kcal mol^{-1} (*11*), k/k_{ADO} = 0.05] and that of SO_2 [150.9 kcal mol^{-1} (*12*), k/k_{ADO} = 0.56] and hence can be assigned a value of 148 ± 3 kcal mol^{-1} at 298 K, leading to a value for H_f° (standard formation enthalpy) for O_3H^+ of 252 ± 3 kcal mol^{-1}.

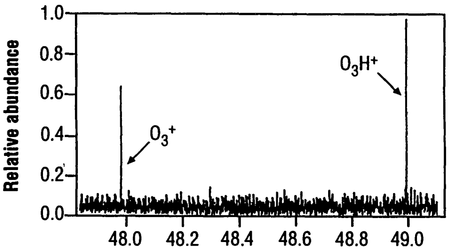

Fig. 1. Partial mass spectrum showing the O_3^+ ion (m/z = 47.984195) and the O_3H^+ ion (m/z = 48.992020) obtained from reaction 1 (A = CH_4, at a total pressure of 2×10^{-5} torr).

These results are in excellent agreement with those of ab initio calculations at the CCSDT-1 level of theory, the most sophisticated so far used in the study of O_3H^+, leading to a value for the PA of O_3 of 148

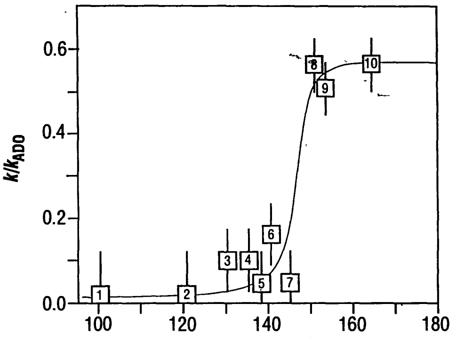

Fig. 2. Collision efficiency of proton transfer reaction 2 versus the PAs of the reference bases B: 1, Kr; 2, Xe; 3, CH_4; 4, NF_3; 5, N_2O; 6, CO; 7, CH_3F; 8, SO_2; 9, C_2H_2; and 10, H_2O.

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kcal mol^{-1} at zero temperature, corresponding to ~149.5 kcal mol^{-1} at 298 K (*7*). Although such a remarkable agreement can be partially fortuitous, the substantial accord established by our work between high-level ab initio calculations and mass spectrometric results in the O_3/O_3H^+ system is reassuring.

A preliminary survey of the gas phase chemistry of O_3H^+ has revealed several interesting aspects. In one of these, by allowing isolated O_3H^+ ions to react with methane, we observed the exothermic process

$$O_3H^+ + CH_4 \rightarrow CH_3^+ + H_2O + O_2 \quad (3)$$

where $\Delta H^\circ_3 = -31 \pm 3$ kcal mol^{-1}. This is followed by the well-known addition process

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \quad (4)$$

The above sequence is the gas phase counterpart of the oligomerization of CH_4 observed by Olah and co-workers in cold solutions of O_3 in "magic acid" (HSO_3F-SbF_5); our ion cyclotron resonance results here substantiate their mechanistic hypothesis based on the intermediacy of O_3H^+ (*2*).

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12. For recently reevaluated PA values, see J. E. Szulejko and T. B. McMahon, *J. Am. Chem. Soc.* **115**, 7839 (1993).
13. Hydrogen abstraction by O_3^+ from CH_4 could conceivably contribute to the formation of O_3H^+. Ion cyclotron resonance experiments involving isolated O_3^+ ions have shown that the process is too slow in comparison with reaction 1 to contribute to the formation of O_3H^+.
14. Despite the careful choice of the experimental conditions, extensive decomposition (more than 90%) of O_3 occurs before the ion source of the spectrometer is entered.
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16. The efficiency can be depressed if proton transfer is nearly thermoneutral or if hindered bases are involved (*15*) [H. Bücker and H.-F. Grützmacher, *Int. J. Mass Spectrom. Ion Processes* **109**, 95 (1991)].

17. Financial support from Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST) and from Consiglio Nazionale delle Ricerche (CNR) is gratefully acknowledged. F. Angelelli performed the ion cyclotron resonance experiments with customary skill.

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The Abundance of Heavy Elements in Interstellar Gas

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The Goddard high-resolution spectrograph aboard the Hubble Space Telescope has been used to produce interstellar abundance measures of gallium, germanium, arsenic, krypton, tin, thallium, and lead, the heaviest elements detected in interstellar gas. These heavy elements arise from stellar nuclear processes (slow- and rapid-process neutron capture) that are different from those that produce zinc and the lighter elements previously observed. These data allow investigators to study how the heavy elements chemically interact with interstellar dust and to compare interstellar heavy element abundances in the current galactic epoch to those present at the time of the formation of the solar system. For example, the data indicate that the abundance of atoms in interstellar dust cannot be explained by simple condensation models alone and must be heavily influenced by chemistry in the interstellar medium. Also, the data for some elements suggest that their true galactic cosmic abundances may be different from the "fossil" abundances incorporated into the solar system 4.6 billion years ago.

The abundances of atomic elements in the galaxy are expected, on average, to reflect the history of galactic chemical evolution produced through a wide range of stellar nuclear processes. The study of elemental abundances in the interstellar medium (ISM) through absorption line spectroscopy affords an opportunity to explore (i) the efficiency with which heavy elements produced by local events (for example, supernovae and evolving moderate to low mass stars) mix with the existing gas and (ii) the nature of the condensation of elements from the gas phase onto dust.

Of particular interest are atomic transitions that arise from elements in the dominant state of ionization in the ISM that are heavier than Zn (atomic number $Z = 30$), the heaviest element previously detected in the ISM gas (*1*, *2*). The solar system abundances of these elements, obtained from both the sun and meteorites (C1 chondrites) (*3*), are very low; even the strongest absorption lines are so weak that observing them requires the use of the moderate to high-resolution gratings and the high signal-to-noise (S/N) (>>100/1) capabilities of the Goddard high-resolution spectrograph (GHRS) (*4*–*6*) aboard the Hubble Space Telescope (HST). By exploiting these capabilities, the GHRS has been used to obtain interstellar absorption line data for Ga ($Z = 31$), Ge ($Z = 32$), As ($Z = 33$), Kr ($Z = 36$), Sn ($Z = 50$), Tl ($Z = 81$), and Pb ($Z = 82$) in the spectra of several background stars (*4*, *7*, *8*). However, the entire ensemble of elements has thus far only been observed toward ζ Ophiuchi, a bright O-star at a distance of about 200 pc.

These heavy elements are significant because they derive from nuclear processes [slow (*s*) and rapid (*r*) neutron capture onto lighter elements arising in a diverse range of stellar progenitors] that differ from those that produce Zn and the lighter elements (nuclear statistical equilibrium and lighter element burning occurring at high temperatures). Specifically, *s*-process nucleosynthesis arises whenever the time between successive neutron captures is much longer than the relevant beta decay time scale, whereas *r*-process nucleosynthesis arises from neutron capture on time scales of the order of 10^{-5} s (for example, supernovae). Consequently, a comparative study of heavy elements allows us to explore the possible effects of local chemical enrichment and mixing in the interstellar gas and the efficiency with which heavy elements are bound into interstellar dust. In addition, for some elements, these data represent the first abundance measurements outside of the solar system. Thus, these data can also provide the opportunity to probe the nature of the solar system abundances with respect to the possible influence of local chemical enrichment on the presolar nebula. This is particularly relevant considering that solar system abundances are commonly used as the cosmic reference standard in general abundance studies.

In the study of interstellar heavy element abundances, the critical atomic transitions arise from the ground state of atoms in their dominant ionization state, and the vast majority of these transitions corre-

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