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The ions $CH_6O^{\bullet+}$ and CH_7O^+

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This contribution is dedicated to the memory of Pierre Longevialle, a fine scientist and educator.

Abstract

The previously unknown ion $CH_6O^{\bullet+}$ was found to be a major product of the dissociation of metastable $[CH_3CHO^{\bullet+}{\cdot}H_2O]$ adduct ions. The single dissociation of the $CH_6O^{\bullet+}$ ion is to H_3O^+ and $CH_3^{\bullet}$, in keeping with its structure being a methyl radical electrostatically bound to protonated water. Ab initio calculations at the B3-LYP and G3 levels of theory showed $[CH_3^{\bullet}{\cdot}H_3O^+]$ to be bound by 58 kJ/mol. Similar calculations on the CH_7O^+ ion showed that it is best described as H_3O^+ bound to a methane molecule. H_3O^+ is bound via one of its hydrogens, to the center of a face of a slightly flattened CH_4 tetrahedron. The calculated binding energy, 35 kJ/mol, is in good agreement with experiment. (Int J Mass Spectrom 217 (2002) 179–184) © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Electrostatically bound, odd and even electron ion/neutral complexes have in the past decade been shown to occupy significant positions in the gas phase ion chemistry of small polyatomic ions [1–4]. The earlier lack of information concerning such species largely arose because although they may be stable, the potential wells that they occupy usually lie above the global minimum. For many years research was focused on global minima and tended to neglect alternative, stable configurations of higher energy. The chemistry of many ion/neutral complexes has been unraveled via their production as stable species from the unimolecular dissociation of polyatomic ions. Their chemistry is closely similar to that of the ion produced by a direct bimolecular reaction [5]. In general, unimolecular dissociations produce ion/neutral pairs, although in some cases, an ion in association with two neutrals has been observed [6,7].

An excellent example of an even electron ion/neutral system is provided by the species $C_2H_7O^+$, which has at least four stable isomers [8]. Two are the covalently bound, protonated molecules $CH_3CH_2OH_2^+$ and $(CH_3)_2OH^+$, and two are electrostatically bound $[CH_3^+{\cdot}CH_3OH]$ [8a–c] and $[C_2H_4{\cdot}H_3O^+]$ [8d]. Although $[C_2H_4{\cdot}H_3O^+]$ is predicted by theory to occupy a shallow potential well, 27 kJ deep, it has eluded direct experimental identification. Nevertheless, its participation in the chemistry of $C_2H_7O^+$ ions is justified by observations of the bimolecular chemistry of $H_3O^+ + C_2H_4$ adduct ions [8d], and from the unimolecular dissociation of deuterium labeled $C_2H_7O^+$ ions [9].

The smaller homologous ion, CH_5O^+, has as its global minimum, the protonated methanol ion,

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$CH_3OH_2^+$; other forms do not occupy significant minima. This metastable ion (MI) dissociates by a simple bond cleavage to $CH_3^+ + H_2O$, in close competition with the elimination of H_2 to yield the CH_2OH^+ ion, a reaction involving a high reverse energy barrier. The intermediate, ion-induced dipole complex $[^+CH_2OH \cdot H_2]$ is but weakly bound, ca. 7 kJ/mol [10].

The ion CH_7O^+, *m/z* 35, was first described long ago as a minor component of the ionized methane–water system [11]. It was described as likely consisting of the formal species $[H_3O^+{\cdot}CH_4]$ and $[CH_5^+{\cdot}H_2O]$ [12]. On the basis of the sum of the enthalpies of these partners, 522 and 671 kJ/mol, respectively, the former was preferred. The binding energy for $[H_3O^+{\cdot}CH_4]$ was evaluated by experiment to be ca. 33 kJ/mol. This number has recently been slightly revised upwards to ca. 42 kJ/mol [13].

The missing ion in this group, $CH_6O^{\bullet+}$, has yet to be described. Ion–molecule reactions between $CH_4^{\bullet+}$ and H_2O (and vice versa) were dominated by proton transfer giving H_3O^+, or electron transfer (ionization energy (IE) $H_2O = 12.61$ eV and $CH_4 = 12.51$ eV) [11,12,14–18]. No adduct ion of *m/z* 34 has yet been reported. From consideration of the sum of the partner enthalpies (for the only reasonable pairs), $\sum \Delta H$, for $[CH_3^{\bullet}{\cdot}H_3O^+]$ $[CH_4^{\bullet+}{\cdot}H_2O]$, $[CH_4{\cdot}H_2O^{\bullet+}]$ and $[CH_5^+{\cdot}{}^{\bullet}OH]$, which are 744, 890, 900 and 952 kJ/mol, respectively, the first promises to be the most suitable pairing for a stable species.

In this work we describe the first experimental identification of the $CH_6O^{\bullet+}$ ion and the first presentation of the optimized structure of CH_7O^+ ion given by ab initio calculations. The benchmark heats of formation and binding energies of the $CH_6O^{\bullet+}$ and CH_7O^+ ions as well as their products were also derived from the calculation. From this perspective, calculations play a unique role in determining the properties of ionic clusters, i.e., geometries, heats of formation and binding energies, etc. because these values are indeed often impossible to measure by experiment. Factors which influence the binding energies in such species will also be discussed in relation to methods currently used to estimate them.

2. Experimental

Experiments were carried out using a modified ZAB-2F mass spectrometer of BEE geometry [19]. MI, and collision-induced dissociation (CID), mass spectra were obtained in the third field-free region of the instrument. The accelerating potential was 8000 V. Helium was used as collision gas at a pressure of $\sim 1 \times 10^{-7}$ mbar, at which the main ion beam was reduced by ca. 10%, single collision conditions.

The proton bound dimer of acetaldehyde and methanol was generated under chemical ionization conditions in the ion source, using approximately equimolar mixtures of CH_3CHO and CD_2HOH at a total pressure of ca. 1×10^{-4} mbar. The ion of $m/z = 79$, $CH_3CHOH^+HOCD_2H$, was selected by the magnet into the second field-free region. There, CID produced the ion $[CH_3CHOHOH]^{\bullet+}$, $m/z = 62$, by loss of a $CD_2{}^{\bullet}H$ radical. (Note that use of CD_3OH would have led to the ambiguous loss of 18 mass units, $CD_3^{\bullet}$ or H_2O.) Labeled analogues were produced using CD_2HOD and CD_3CHO. The resulting acetaldehyde/water ions $[CH_3CHODOD]^{\bullet+}$ and $[CD_3CHODOD]^{\bullet+}$, $m/z = 64$ and 67, respectively, were transmitted into the third field-free region and their MI and CID mass spectra were recorded. Product ions were analyzed by the second electric sector.

Chemicals were purchased from Aldrich (Milwaukee) and from CDN Isotopes (Pointe Claire, Quebec) and used without further purification.

3. Computational procedures

Standard ab initio molecular orbital calculations [20] were carried out using the Gaussian 98 [21] suite of programs. The geometries of all species were optimized at the B3-LYP/6-31+ G(d) level of theory. Vibrational frequencies were also obtained at this level.

Single-point energies on the B3-LYP/6-31+ G(d) geometries were obtained by G3 theory. G3 theory approximates the energy of a species at the QCISD(T)/G3large level of theory by a series of additive corrections to a base MP4/6-31+ G(d) energy.

The G3large basis set is a modified version of the standard 6-311+ G(3df, 2p) basis set in which more polarization functions are added to first-row elements (3d2f), fewer on second-row elements (2df), and core polarization functions are incorporated. Details of the properties of the G3large basis set can be found in the original publication by Curtiss et al. [22]. G3 incorporates a scaled (by 0.9614 [23]) B3-LYP/6-31+ G(d) zero-point vibrational energy (ZPE), spin-orbit corrections for atoms, and the use of the MP2(full)/G3 large calculation to take into account core-correlation contributions. Finally, an empirical higher-level correction (HLC) accounts for residual basis set errors. The G3 total energies were converted to heats of formation according to the atomization method outlined by Nicolaides et al. [23]. Thermal corrections to 298 K employed the scaled B3-LYP/6-31+ G(d) frequencies and known thermal corrections for the elements [24].

Binding energies of the clusters were determined from the difference in energy between the lowest energy dissociation products and the intact cluster.

4. Results and discussion

Recent experiments in this laboratory have used CID of proton bound molecular pairs, explicitly to generate odd electron ion/molecule complexes [25]. The odd electron ions can be in their conventional or distonic forms depending on the choice of appropriate precursor molecules. For example, the ion [$CH_3OD^{\bullet+}{\cdot}CD_3OD$] was generated by the CID loss of $CH_3^{\bullet}$ from [$(CH_3)_2OD^+DOCD_3$], while [$^{\bullet}CH_2OH_2{}^+{\cdot}CH_3OH$] was produced from $(CH_3OH)_2H^+$ by CID loss of $H^{\bullet}$. In a related study of (labeled) acetaldehyde proton-bound to methanol,[1] it was found that the ion lost the methanol CH_3 group under CID, to produce the formal ionized acetaldehyde/water ion pair (see Section 2).

The dissociations of this MI pair are the losses of $CH_3^{\bullet}$, H_2O and the wholly unexpected elimination of CO to produce the ion $CH_6O^{\bullet+}$. The only fragment ion from this latter species was H_3O^+. Although, as is described in detail elsewhere (see footnote 1), there was clear indication that labeled ions of formal structure $CH_3CHO^{\bullet+}$/HOH underwent rearrangement prior to loss of water, the labeled $CH_6O^{\bullet+}$ ions did not arise from any complexes that had undergone H/D positional mixing prior to the CO loss. The labeled H_3O^+ product ions contained no H/D from the original aldehyde methyl group. This is in keeping with the $CH_6O^{\bullet+}$ ions only having the structure $CH_3^{\bullet}{\cdot}H_3O^+$, and moreover, that isomeric forms are not accessible at energies up to that required for the simple bond cleavage. Note that this stricture requires that the electrostatic binding energy in the $CH_4^{\bullet+}{\cdot}H_2O$ and $CH_4{\cdot}H_2O^{\bullet+}$ ions cannot exceed about 150 kJ/mol (see Section 1), a quantity significantly greater than that for proton bound pairs [26], typically 130 kJ/mol for an $O \cdots H^+ \cdots O$ link. The structures and energies of this new ion and CH_7O^+ investigated by the above quantum calculations, are described below.

The geometry of the [$CH_4{\cdot}H_3O^+$] ion deserves comment. The electrostatic bonding does not involve a linear $C \cdots H^+ \cdots O$ orientation, but the binding H from the H_3O^+ ion lies centrally in front of one face of the CH_4 tetrahedron, this latter, in turn, is slightly distorted, with larger H–C–H angles on the bound face (see Table 1). The non-bonded H atoms of the H_3O^+ do not eclipse the H atoms on the (distorted) tetrahedral face.

In the $CH_6O^{\bullet+}$ ion, the methyl radical has become slightly pyramidal, away from the formal (binding) proton of H_3O^+. Note that the shorter $C \cdots H^+ \cdots O$ (C–H) distance implies a stronger bond than that in the CH_7O^+ ion.

Table 2 shows the 0 K binding energies calculated with the G3 and B3-LYP levels of theory, [$CH_3^{\bullet} \cdot H_3O^+$] = 65, 55 kJ/mol and [$CH_4 \cdot H_3O^+$] = 31, 35 kJ/mol, respectively; 298 K values (G3) from the data in Table 1 are 58 and 35 kJ/mol, respectively. The latter is in good agreement with the experimental value of 33 kJ/mol [11] mentioned above.

Also shown in Table 1 are values estimated using the versatile empirical equation of Larson and McMahon [26] which relates the binding energy in species

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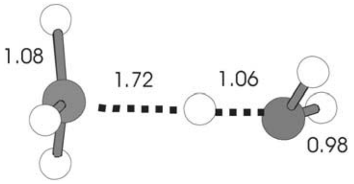
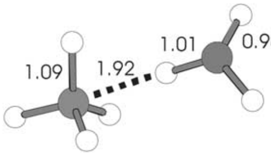
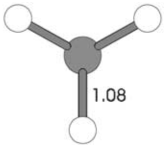
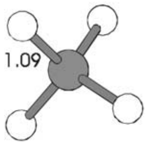
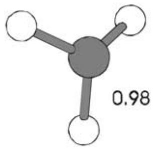
[1] Work in preparation for publication.

Table 1
Geometries and energies for $CH_6O^{\bullet +}$ and CH_7O^+ ions

Species	Geometries	$\Delta_f H^\circ$ (298 K, kJ/mol)	
		G3	[28]
$[CH_3^{\bullet} \cdot H_3O^+]$	The C $\cdots$ H^+ $\cdots$ O angle is ~180°. The $CH_3^{\bullet}$ is not flat having a dihedral angle ∠H–C–H–H ~154°. The complex ion has a 'staggered' conformation shown by Newman projections 	690	(675)
$[CH_4 \cdot H_3O^+]$	The C $\cdots$ H^+–O angle is ~180°. H_3O^+ has a dihedral angle ∠H–O–H–H ~130°. The tetrahedral CH_4 is distorted such that the ∠H–C–H facing the hydrogen bond is larger, ~120° 	494	(456)
$CH_3^{\bullet}$	Planar $CH_3^{\bullet}$, the ∠H–C–H = 120° 	145	146
CH_4	Tetrahedral CH_4 	−74	−74
H_3O^+	Pyramidal H_3O^+, with a dihedral ∠H–O–H–H ~130° 	603	591

Estimated values, see text, are given in parenthesis.

Table 2
Binding energies calculated with the G3 and B3-LYP/6-31+ G(d) levels of theory

Cluster ion	Dissociation products	Binding energies (kJ/mol)[a]		
		B3-LYP/6-31+ G(d)	G3	Experimental values [11–13]
$[CH_3^{\bullet} \cdot H_3O^+]$	$CH_3^{\bullet} + H_3O^+$	65	55 (58)[b]	–
$[CH_4 \cdot H_3O^+]$	$CH_4 + H_3O^+$	31	35 (35)[b]	33, 42

[a] 0 K values unless stated.
[b] 298 K values in parenthesis.

$[AH^+{\cdot}B]$ with the proton affinities (PA) of A and B

$$D[AH^+ \cdot B] = 0.46(PA(B) - PA(A)) + 129\,kJ/mol$$

For the ion $CH_6O^{\bullet+}$, represented as a proton bound methyl radical and water molecule, the binding energy from the above equation is 62 kJ/mol, in surprisingly satisfactory agreement with our calculated 58 kJ/mol. Note that $PA(H_2O) = 691$ kJ/mol [27]; $PA(^{\bullet}CH_3) = 545$ kJ/mol from $\Delta_f H^\circ[CH_4{}^{\bullet+}] = 1132$ kJ/mol [28], $\Delta_f H^\circ[H^+] = 1530$ kJ/mol, $\Delta_f H^\circ[^{\bullet}CH_3] = 146$ kJ/mol [28].

Similar agreement is not obtained for the CH_7O^+ ion, where the corresponding estimated binding energy is significantly high, 61 kJ/mol; $PA(CH_4) = 544$ kJ/mol [27]. At worst, this approach gives an upper limit to the binding energy.

The empirical equation appears to work quite well for heteroatoms with non-bonding electron pairs and also to free radicals. The extended application and limitations of such equations will be discussed in a future publication.

When considering ground state connectivities for complex ions comprising of ion–molecule or ion–radical pairs, the most likely structure can be obtained by considering the sum of energies of the separated components. Binding energies, which can be estimated using the above empirical equation, can roughly define the depth of the potential well of the complex ion with respect to its lowest energy dissociation products. Therefore, an approximate value for $\Delta_f H^\circ$ of the complex ion can be determined therefrom.

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