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Experimental and theoretical studies of the gas-phase reactivity of the $(\text{HO})_2\text{P}=\text{O}^+$ phosphonium ions towards methanol

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Abstract

Ion–molecule reactions between the $(\text{HO})_2\text{P}=\text{O}^+$ phosphonium ions and methanol were performed in a quadrupole ion trap mass spectrometer. The $(\text{HO})_2\text{P}=\text{O}^+$ phosphonium ions, formed by electron impact from neutral trimethyl phosphite ions were found to react with methanol according to three consecutive reactions, via sequential methanol addition/water elimination, to yield protonated trimethyl phosphate. To confirm the experimental results, and to state the mechanism for the formation of the ionic species, a theoretical study by using the density functional theory (DFT) approach has been carried out. According to calculations performed at the B3LYP/6-311+G(2df,p) over B3LYP/6-31G* optimized geometries, the overall reaction leading to protonated trimethyl phosphate occurs by an exothermic process of 365 kJ/mol. The isomerization barriers connecting the different intermediates have been also calculated in order to have a more complete description of the reaction processes. In addition, the proton affinity (PA) and the gas-phase basicity (GB) of the molecular species related to the reactions of the $(\text{HO})_2\text{P}=\text{O}^+$ cations with methanol namely: monomethyl phosphate, dimethyl phosphate, and trimethyl phosphate (TMP) have been evaluated to be 855, 875, and 892 kJ/mol (for PAs) and 823, 843, and 862 kJ/mol (for GBs), respectively. The excellent agreement between the theoretical (892 kJ/mol) and the experimental value (891 kJ/mol) of the PA of TMP shows the reliability of our DFT calculations. (Int J Mass Spectrom 195/196 (2000) 545–563) © 2000 Elsevier Science B.V.

Keywords: Ion–molecule reactions; DFT calculations; Proton affinity; Phosphorus ions

1. Introduction

Organophosphorus compounds (OPCs) are an important class of chemicals that have been used widely in agriculture and industry as pesticides, fertilizers, plasticizers, flame-retardants, and extraction solvents. Some of these compounds or their degradation products are highly toxic and they adversely affect the

environment. Their detection and identification, particularly at trace levels, are high-priority concerns within various regulatory and consumer protection agencies. With this in mind, an approach that considers fundamental aspects of the structure and reactivity of organophosphorus ions in the gas phase has been adopted during the last decade.

Nevertheless, although OPCs have been analyzed by mass spectrometry by using a full range of ionization techniques [1], few results about gas-phase chemistry of these compounds have been reported. The ion–molecule reactions between several phosphorus

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Dedicated to Bob Squires for his many seminal contributions to mass spectrometry and ion chemistry.

ions and trimethyl phosphite have been studied by ion cyclotron resonance (ICR) [2] and Fourier transform ICR [3]. For example, Hodges et al. [2] have shown that the principal reaction of $\text{O}=\text{P}(\text{OCH}_3)_2^+$ with trimethyl phosphite leads to a phosphonium ion $:\text{P}(\text{OCH}_3)_2^+$ and neutral trimethyl phosphate together with a trace of tetramethyl phosphonium ion and OPOCH_3 . Zeller et al. [3] have described the formation of the most abundant product ions as a function of time in reaction of neutral trimethyl phosphite with protonated trimethyl phosphate. They reported that protonated trimethyl phosphate protonates neutral (TMP). The study of the gas-phase reactivity of long-lived radical cation of trimethylphosphine oxide has demonstrated that this ion is a Brønsted acid and likely to have a distonic structure with a carbon radical center [4]. The kinetic method has been applied to order the relative affinities of substituted pyridines towards PCl_2^+ and to seek relationships with the affinities towards other chlorinated cations [5]. The proton affinity and the gas phase basicity of orthophosphoric acid have been determined experimentally and estimated theoretically [6]. The gas-phase reactivity of $:\text{P}(\text{OCH}_3)_2^+$ ions with stereoisomeric diols has been studied by Thoen et al. [7] by Fourier transform ICR techniques. The authors showed that $:\text{P}(\text{OCH}_3)_2^+$ provides a powerful chemical ionization reagent for the mass spectrometric determination of diols. Recently, the reactions of 1,2-dioxolane-3-phosphonium ions with diastereomeric diamines has been reported by Thompson et al. [8]. With regard to the gas-phase studies of quadrivalent phosphonium ions, we have shown in a previous study [9] that in a quadrupole ion trap (QIT), the phosphonium cations $\text{O}=\text{P}(\text{OCH}_3)_2^+$ formed by electron impact with neutral trimethyl phosphite, were subject to nucleophilic attack from residual water, present in the QIT, to give a stable adduct. Such reaction has also been reported for the $\text{O}=\text{P}(\text{OCH}_3)_2^+$ species formed upon electrospray ionization of TMP in a LCQ ion trap mass spectrometer [10].

In this article, we present the ion–molecule reactions between the $(\text{HO})_2\text{P}=\text{O}^+$ phosphonium ion and the simplest alcohol reagent: methanol. This study

was performed in a QIT mass spectrometer, which is proving to be an effective device for studying ion–molecule reactions [9,11,12].

The phosphonium $(\text{HO})_2\text{P}=\text{O}^+$ ions were found to react with methanol according to three consecutive reactions, via sequential methanol addition/water elimination, to yield protonated trimethyl phosphate. In order to confirm the experimental results, and to state the mechanism for the formation of the ionic species, we have carried out a theoretical study using the density functional theory (DFT) approach. As evidenced by our previous works [6,9], this method was found to be reliable in the prediction of geometries and energetics for oxygen-containing phosphorus compounds. We have also considered it of interest to evaluate the proton affinity (PA) and the gas-phase basicity (GB) of the molecular species related to the reactions of the $(\text{HO})_2\text{P}=\text{O}^+$ cations with methanol namely: monomethyl phosphate (MMP), dimethyl phosphate (DMP) and TMP. These data are valuable not only in understanding the fundamental nature of the acid–base interactions but also in predicting the intrinsic reactivity of the protonated species.

2. Experimental

Triethyl phosphate (TEP), TMP, and methanol were purchased from Fluka and used without further purification. TEP and TMP were diluted in pentane to a concentration of 100 ppm. All experiments were carried out with a QIT Varian Saturn 3 coupled with a Varian Star 3400 CX gas chromatograph. A $30\text{ m} \times 0.25\text{ mm}$ i.d. DB 5 fused-silica capillary column with a $0.25\text{ }\mu\text{m}$ film thickness was used for all analyses. The helium flow was adjusted to give a column head pressure of 10 psi. The transfer line temperature from the gas chromatograph to the QIT was held at $260\text{ }^\circ\text{C}$. The QIT manifold temperature was $170\text{ }^\circ\text{C}$. The ion–molecule reactions were carried out under the following conditions: $1\text{ }\mu\text{L}$ of the diluted solution of TEP or TMP was injected in the chromatograph in splitless mode with the injector held at $185\text{ }^\circ\text{C}$. The GC was held at $50\text{ }^\circ\text{C}$ for 5 min and ramped to $100\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C}/\text{min}$ and held at that temperature for 5 min.

The data acquisition sequence was composed of: (1) 70 eV electron impact of the neutral precursor, (2) isolation of the ion of interest with a mass isolation window of 3 u and adjustments of the amplitude of the 1.05 MHz rf voltage, applied to the ring electrode so as to store ions at a q_z value of 0.4 (3) reaction time up to 50 ms with methanol, introduced into the ion trap via the calibration gas inlet, and neutral precursor, as it eluted from the GC column (4) ejection and detection (MS^2 spectra) of product ions using the mass-selective instability scan [13] and axial modulation [14] of 2 V for improved resolution. MS^3 experiments using the software “toolkit” were performed to characterize the ion–molecule reaction products.

3. Computational details

3.1. Method

The theoretical study was performed with the GAUSSIAN 94 program package [15]. All geometries were fully optimized using the DFT approach with non local corrections (B3LYP), using a split valence basis set with polarization functions included for heavy atoms (6-31G*). In this method, the Becke three parameter exchange functional, including a mixture of Hartree-Fock, Slater, and Becke exchange functional (B3), are combined with the nonlocal correlation functional of Lee et al. (LYP) [16,17]. The harmonic vibrational frequencies evaluated at the same level of theory were used to characterize the stationary points of the potential energy surfaces: all frequencies being real values indicate a minimum, and one imaginary frequency is characteristic of a transition state. The evaluation of the vibrational frequencies allows us also to correct for zero point energies (ZPE).

In order to have as reliable energetics as possible, we performed single point calculations on all B3LYP/6-31G* optimized geometries at the triply split valence 6-311+G(2df,p) basis set [18] which includes polarization functions on hydrogens and diffuse functions on heavy atoms. Moreover, since thermody-

amic values are generally measured at 298 K, we have also included the corresponding thermal corrections in relative energies.

3.2. Calculations of proton affinities and gas-phase basicities

The PA of a base B at 298 K is defined as negative of the change in enthalpy for



For evaluating the absolute proton affinity, the following expression was used:

$$PA_B = -(\Delta E_{elec} + \Delta(ZPE) + \Delta E_c)$$

The first term represents the difference in electronic energies between protonated and unprotonated species, and the second term is the difference in ZPE of BH^+ and B. The overall ΔE_c is equal to

$$\Delta E_c = \Delta E_{vib} + \Delta E_{trans} + \Delta E_{rot} + \Delta nRT$$

The ΔE_{vib} term appears because of a change in population of vibrational levels with a change in temperature (0–298 K). The two other terms introduce the correction for translational and rotational energy changes. Assuming classical behavior, ΔE_{trans} and ΔE_{rot} are, respectively, equal to $-\frac{3}{2}RT$ and zero (since B and BH^+ have the same structural features). The last term ΔnRT [with $\Delta n = -1$ for reaction (1)] is required to convert an energy to enthalpy assuming ideal gas behavior.

The gas-phase basicity of B, defined as negative of the change in free energy for reaction (1), is related to PA_B by the following equation:

$$GB_B = PA_B - T\Delta S$$

Where ΔS is defined as negative of the change in entropy for reaction (1). This term is the sum of translational, vibrational, rotational, and electronic terms:

$$\Delta S = \Delta S_{trans} + \Delta S_{vib} + \Delta S_{rot} + \Delta S_{elec}$$

Each of these terms can be evaluated by using statistical mechanistic procedures. Nevertheless, it is

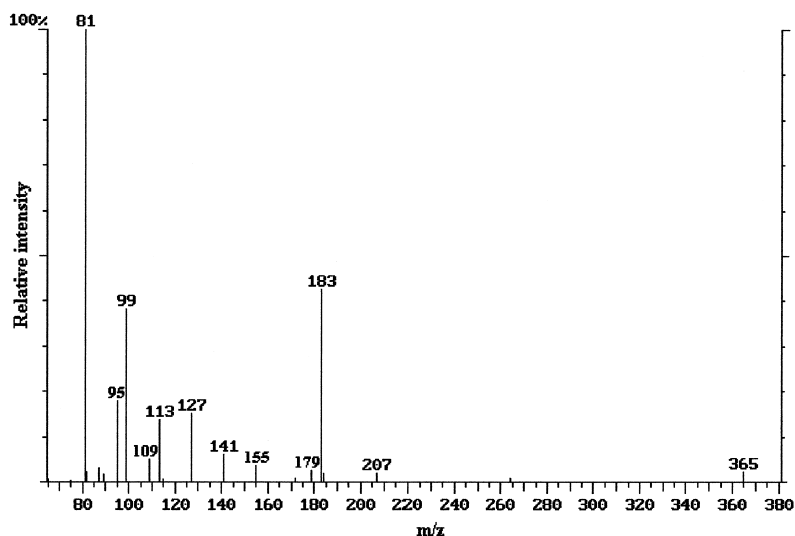


Fig. 1. MS² product spectrum for the ion-molecule reactions of mass-selected m/z 81 ions with methanol for 50 ms.

usually assumed that the only significant contribution to the total entropy change (ΔS) would arise from the ΔS_{rot} term. In such a case, the rotational symmetry change plus the entropy term for a free proton (108.9 J/mol) gives ΔS :

$$\Delta S = R \ln(\sigma_{\text{BH}^+}/\sigma_{\text{B}}) + 108.9$$

where the σ 's are the symmetry numbers of the designated species from reaction (1). ΔS can also be estimated from frequency calculations.

4. Results and discussion

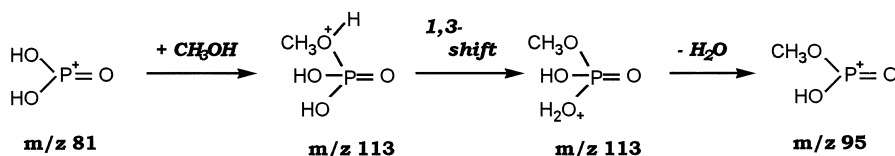
4.1. Gas-phase ion-molecule reactions of $(\text{HO})_2\text{P}=\text{O}^+$ ions towards MeOH

Phosphonium ions $(\text{HO})_2\text{P}=\text{O}^+$ (m/z 81) are formed by dissociative ionization of TEP cation radical. As described previously [19] ionized TEP^{•+}

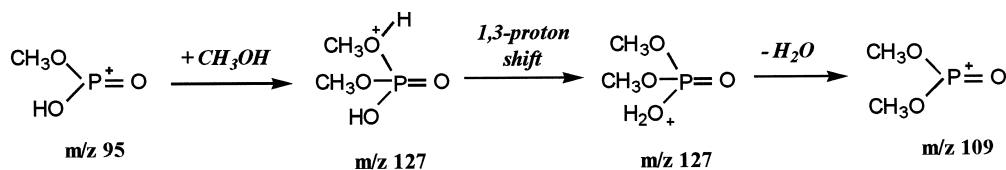
eliminates successively a vinyl radical and two ethylene molecules to give protonated orthophosphoric acid $\text{P}(\text{OH})_4^+$, which in turn dissociates by loss of water yielding the $(\text{HO})_2\text{P}=\text{O}^+$ species.

The isolated m/z 81 ions were allowed to react with methanol for 50 ms. The mass spectrum resulting from ion-molecule reactions is presented in Fig. 1.

The $(\text{HO})_2\text{P}=\text{O}^+$ phosphonium cations rapidly react with methanol to form a stable adduct ion at m/z 113 which corresponds to the protonated monomethyl phosphate. The m/z 113 species spontaneously dissociate by loss of water via a 1,3-proton shift, yielding the $(\text{HO})(\text{CH}_3\text{O})\text{P}=\text{O}^+$ phosphonium ions (m/z 95). These three sequential processes are summarized in Scheme 1. Consecutively the m/z 95 phosphonium cations react with methanol according to an addition reaction to give the protonated dimethyl phosphate at m/z 127. The loss of water from the m/z 127 species yields the $(\text{CH}_3\text{O})_2\text{P}=\text{O}^+$ phosphonium ions of m/z 109 (Scheme 2).



Scheme 1.



Scheme 2.

In order to confirm these results, the m/z 95 cations generated from TMP upon electron ionization were allowed to react with methanol for 50 ms. The resulting spectrum is presented in Fig. 2.

The spectrum clearly shows the formation of protonated dimethyl phosphate (m/z 127) and consecutive water loss (m/z 109 phosphonium ions) which confirms our assumption. It is worth noting that these ions also react with background water to form stable adduct at m/z 113 and with neutral precursor TMP to yield the m/z 141, 155, 235, and 281 ionic species. The m/z 249 ions result from a consecutive addition reaction between the m/z 109 ions and TMP.

The m/z 141 species observed in Fig. 1 correspond to the protonated TMP and are due to the addition reaction between the m/z 109 phosphonium cations and methanol (see Scheme 3). The m/z 141 ions observed in Fig. 2 correspond to the protonated TMP and are the results of (1) a proton transfer reaction

from the m/z 95 ions to neutral TMP, (2) an addition reaction between the m/z 109 ions and methanol.

In summary, we have performed in the gas-phase a three-stage synthesis of protonated TMP from the $(\text{HO})_2\text{P}=\text{O}^+$ phosphonium ions and methanol, as illustrated in Scheme 4.

4.2. Gas-phase ion–molecule reactions of $(\text{HO})_2\text{P}=\text{O}^+$ ions toward neutral precursor TEP

In addition to the previous ion–molecule reaction products, Fig. 1 displays other ions which are the result of reactions between m/z 81 phosphonium ions and the neutral precursor TEP. In order to confirm its origin, these ions were isolated for 50 ms in the absence of methanol and the resulting ion–molecule reaction products are shown in Fig. 3.

As previously reported by Hodges et al. [2], the main reaction between the mass selected ion at m/z 81

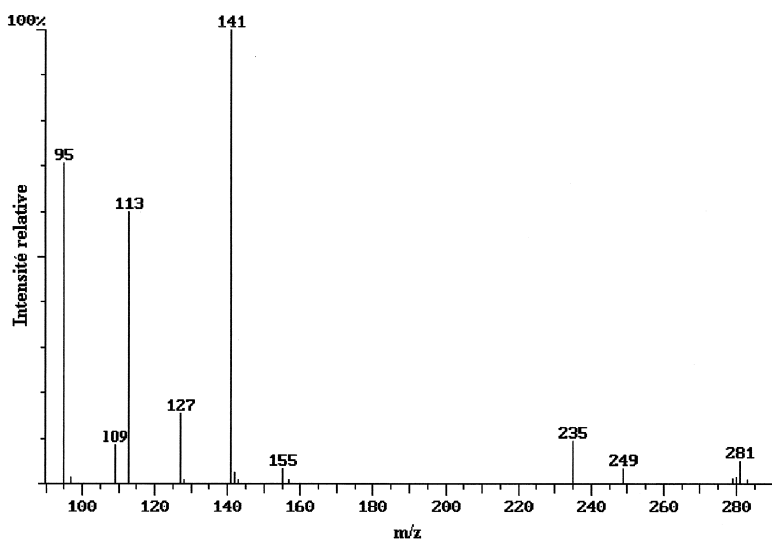
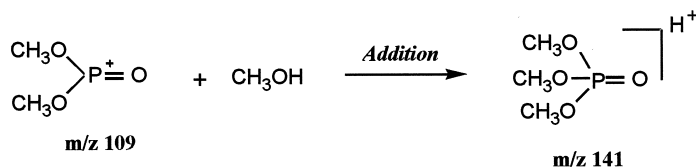


Fig. 2. MS^2 product spectrum for the ion–molecule reactions of mass-selected m/z 95 ions with methanol for 50 ms.



Scheme 3.

and the neutral TEP is a proton transfer reaction, yielding the protonated TEP (m/z 183). This species rapidly reacts again with the neutral TEP, giving the proton-bound dimer $(\text{TEP})_2\text{H}^+$ at m/z 365 (Scheme 5).

Nevertheless, the conditions in the QIT [9,11] differ sufficiently to produce other reaction products at m/z 99, 155, 179, and 207. Protonated orthophosphoric acid $(\text{HO})_4\text{P}^+$ (m/z 99) is the result of an addition reaction between the m/z 81 phosphonium ions and the background water. The three other product ions at m/z 155, 179, and 207 cannot be the direct result of ion–molecule reactions between m/z 81 and neutral TEP. The suggested origin for the m/z 155 ions relies on the results of Cload and Hutchinson [20]. These authors reported the formation of m/z 155 ions by ethylene loss from protonated TEP generated by ammonia chemical ionization. Since the PA of metaphosphoric acid HPO_3 (PA = 712 kJ/mol) [6] is smaller than PA of ammonia (PA = 854 kJ/mol) [21] m/z 183 species in Fig. 3 are expected to eliminate an ethylene molecule, yielding the m/z 155 ions (see Scheme 6).

Although we do not observe any of the adduct ion (m/z 263) between m/z 81 and TEP, the formation of m/z 179 and 207 could arise from two and three sequential ethylene elimination from this adduct, respectively. In order to confirm our assumption, we have performed ion–molecule reactions between

$(\text{CH}_3\text{O})_2\text{P}=\text{O}^+$ phosphonium ions and TEP. These ions were generated by electron ionization induced dissociation of the trimethyl phosphate and were allowed to react with TEP for 50 ms (TEP was introduced into the ion trap via the calibration gas inlet). The resulting spectrum resulting from ion–molecule reaction is presented in the in Fig. 4.

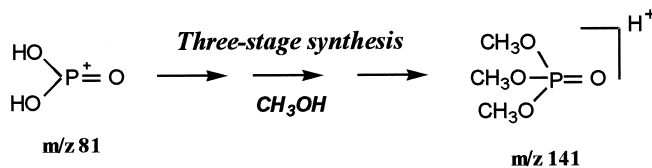
The spectrum clearly shows the formation of an adduct ion at m/z 291 and three other ions at m/z 207, 235, and 263 which come from sequential ethylene eliminations. As a result, these experimental findings confirm the occurrence of such a reaction (addition followed by ethylene losses) in the case of m/z 81 phosphonium ions to yield the m/z 179 and 207 ions.

It is worth noting that MS^3 experiments have shown that m/z 179 and 207 ions undergo proton transfer with neutral TEP to give m/z 183 ions. The result of these reaction channels is summarized in Scheme 7.

5. DFT calculations

5.1. Structure and stability of the different adducts

In order to substantiate the experimental conclusions, the energy profiles corresponding to the three reactions depicted in Schemes 1–3 were explored. The structures of the phosphonium ions were opti-



Scheme 4.

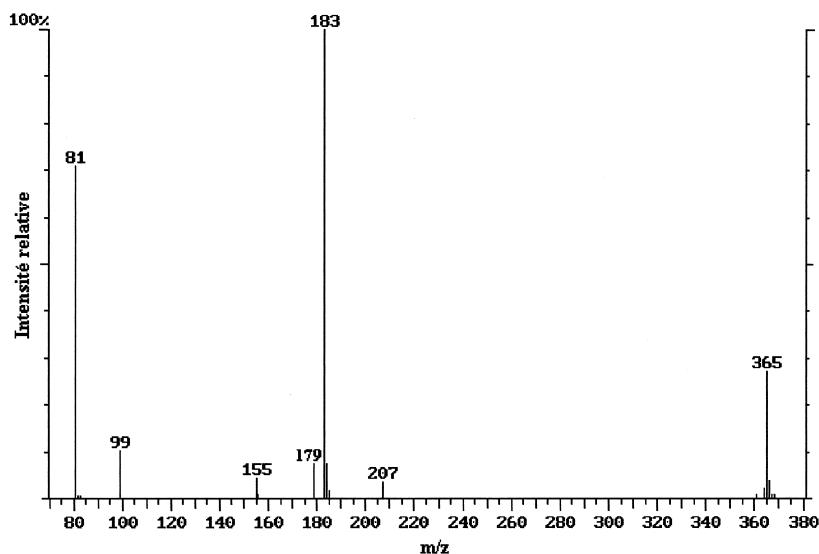
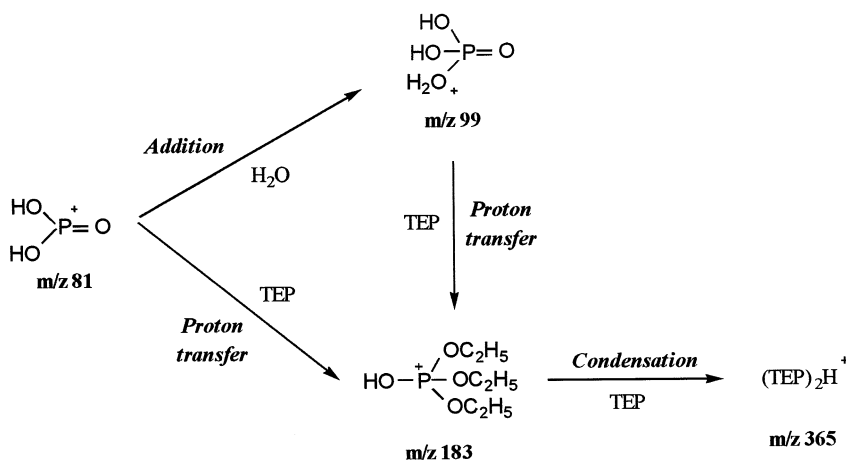


Fig. 3. MS² product spectrum for the ion-molecule reactions of mass-selected m/z 81 ions with TEP for 50 ms.

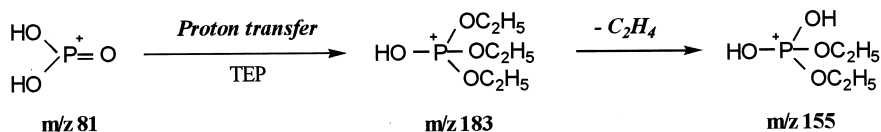
mized at the B3LYP/6-31G* level of theory, their geometries are presented in Fig. 5. As we can see, the three phosphonium ions have a planar conformation [with C_{2v} symmetry for the $(\text{CH}_3\text{O})_2\text{P}=\text{O}^+$ and $(\text{HO})_2\text{P}=\text{O}^+$ ions]. The methanol approach can yield two different conformations **a** and **b** for these adducts ions (see Scheme 8). The B3LYP/3-21G*//B3LYP/3-21G* relative energies of both conformers are reported in Table 1. At this level of theory, we can note that in each case the two conformers **a** and **b** are

almost energetically degenerated. So, the two adducts ions can exist in our experimental conditions. Thus, for the sake of simplicity, the calculations only will refer to species having conformation **a** where the methyl group eclipses the phosphoryl oxygen. The B3LYP/6-31G* optimized structures are drawn in Fig. 6.

In order to state the mechanism for the evolution of the three cationized species, which correspond to the MMP, DMP, and TMP protonated on a methoxy-



Scheme 5.



Scheme 6.

oxygen atom, the structure and stability of the respective isomeric forms have been investigated. The optimized B3LYP/6-31G* geometries of the most stable conformers of $(\text{MMP} + \text{CH}_3\text{OH})^+$, $(\text{DMP} + \text{CH}_3\text{OH})^+$, and $(\text{TMP} + \text{CH}_3\text{OH})^+$ species, are shown in Fig. 7.

An important aspect of Fig. 7 is that an elongation of the $\text{P}-\text{OH}_2^+$ bond follows the protonation on the oxygen of the hydroxyl. Thus, these species may be regarded as strongly bonded complexes between a phosphonium cation and a molecule of water. This elongation suggests that these ions dissociate directly into the products (water and phosphonium ion), without any barrier for the reverse reaction. Note that we have previously described its implementation for such compounds [6,9].

The calculated total and relative energies of the isomeric protonated forms of MMP, DMP, and TMP are reported in Table 2. The results clearly show that

phosphoryl–oxygen protonation is thermodynamically favored over oxygen of the O–R group ($\text{R} = \text{H}$ or CH_3). This is due to the fact that in the former phosphonium ion, the positive charge is largely shifted from phosphorus to the oxygen atoms through the contribution of five bonds. The phosphoryl–oxygen protonation is about 120 kJ/mol more favorable than the methoxy–oxygen one, which in turn is more stable of 20 kJ/mol than the hydroxy–oxygen protonation.

5.2. Description of the gas-phase reaction profiles

The calculated total energies and relative energies of species related to the reaction of the $(\text{HO})_2\text{P}=\text{O}^+$, $(\text{HO})(\text{CH}_3\text{O})\text{P}=\text{O}^+$, and $(\text{CH}_3\text{O})_2\text{P}=\text{O}^+$ phosphonium cations with methanol are reported in Table 3. The geometries of the transition states are presented in

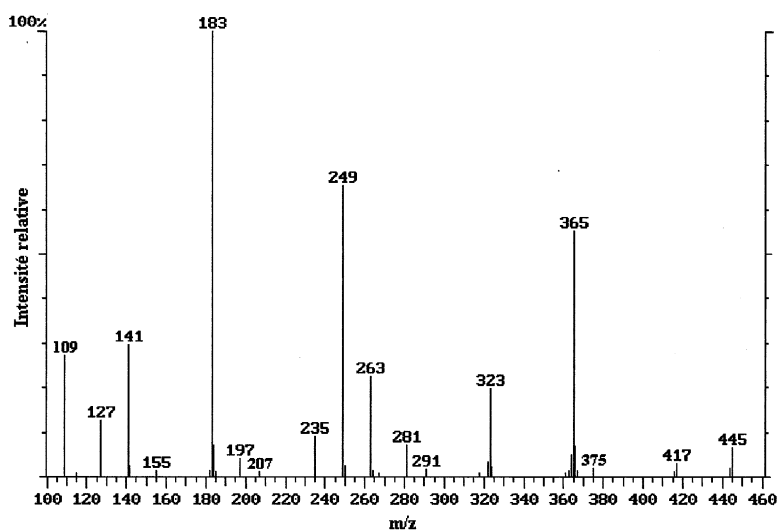
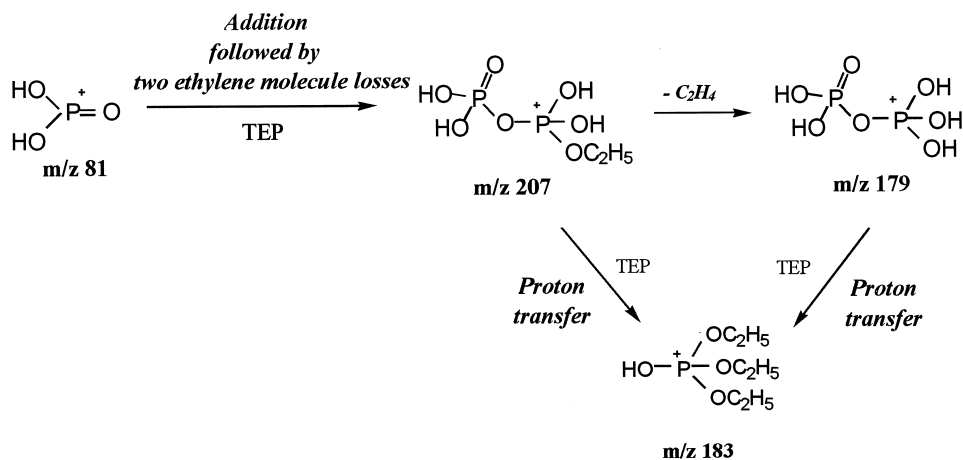


Fig. 4. MS^2 product spectrum for the ion-molecule reactions of mass-selected m/z 109 ions with TEP for 50 ms.



Scheme 7.

Fig. 8. The corresponding gas-phase energy profiles are drawn in Figs. 9–11.

As is shown in Figs. 9–11, our DFT calculations are in agreement with the experimental findings: the

reactions between the $(\text{HO})_2\text{P}=\text{O}^+$ (m/z 81) and $(\text{HO})(\text{CH}_3\text{O})\text{P}=\text{O}^+$ (m/z 95) phosphonium cations and methanol are exothermic about 47 and 41 kJ/mol, respectively. When the $(\text{CH}_3\text{O})_2\text{P}=\text{O}^+$ (m/z 109)

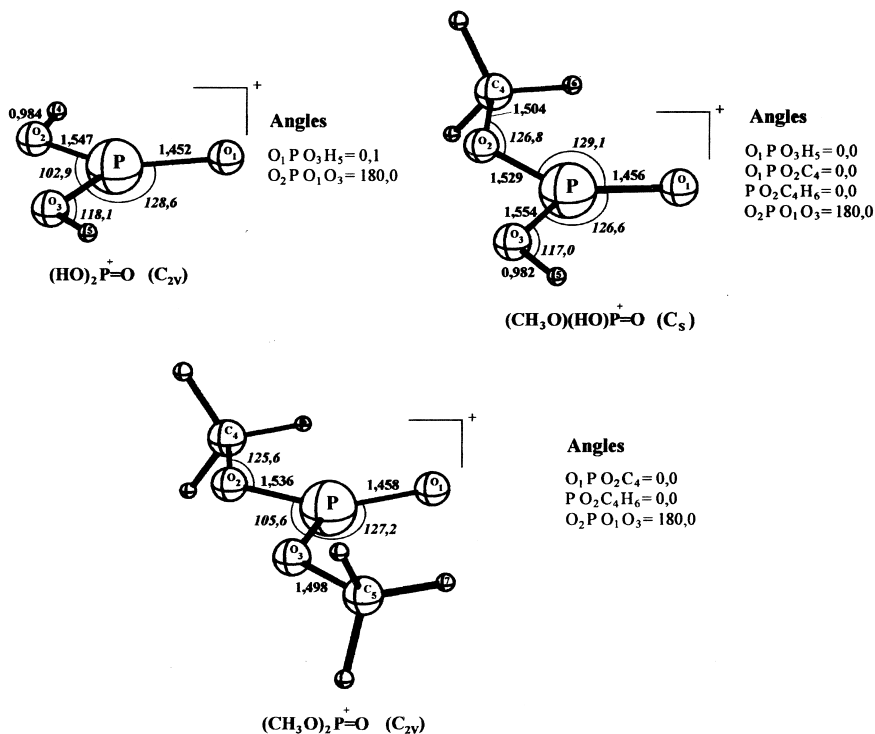
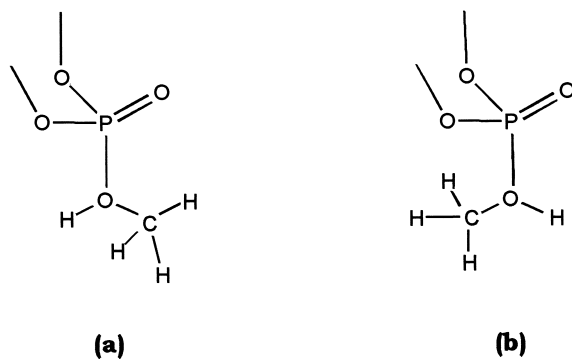


Fig. 5. Equilibrium geometries of phosphonium cations optimized at the B3LYP/6-31G* level. Bond lengths are in angstroms and angles in degrees.



Scheme 8.

phosphonium ions were found to react with methanol according to a substantial exothermic process of about 277 kJ/mol, to yield protonated trimethyl phosphate. Note that all protonated structures and their interconnecting transition structures, which are typical four-membered-ring compounds resulting from a 1,3-shift proton, lie well below the minimum energy for dissociation path reaction. This feature in the potential energy surface explains the rapid and spontaneous 1,3-migration of a proton within the isomers and proves that all isomers can exist in the gas phase. As we can see in Figs. 9 and 10, the adduct ions resulting from the addition of methanol to the $(\text{HO})_2\text{P}=\text{O}^+$ (m/z 81) and $(\text{HO})(\text{CH}_3\text{O})\text{P}=\text{O}^+$ (m/z 95) phosphonium cations can evolve along two competitive pathways. The most favorable reaction, involving TS_2 and TS_4 , yield to the formation of protonated mono- and dimethyl phosphate. These species are calculated to be the most stable structures on the different potential energy surfaces here explored. The less favorable processes lead, after the proton migration of the OCH_3 group to the OH group (via TS_1 and TS_3), to stabilized

intermediate structures where again, a molecule of water is predissociated as described previously.

In summary, the phosphonium ions $(\text{HO})_2\text{P}=\text{O}^+$ react with methanol according to three consecutive reactions via sequential methanol addition/water elimination to yield protonated trimethyl phosphate. This overall reaction occurs by an exothermic process of 365 kJ/mol.

5.3. Proton affinities and gas-phase basicities of orthophosphate esters

Having ascertained the significantly larger stability of the phosphoryl–oxygen atom protonated species we decided to calculate the PA of these orthophosphate esters. We have preliminarily investigated the structure and stability of neutral species MMP, DMP, and TMP by optimizing their geometries at the B3LYP/6-31G* level of theory, which are displayed in Fig. 12. The corresponding structural parameters and total energies together with vibrational and thermal corrections are collected in Tables 4 and 5, respectively.

As is shown in Fig. 12, the structure of lowest energy for both compounds corresponds to a conformation in which the methoxy and hydroxy groups are gauche respect to the $\text{P}=\text{O}$ bond. Table 4 indicates that the geometrical parameters of the three neutral compounds are very similar. This implies that the structures do not vary significantly with methyl substitution (replacing a hydrogen atom by a methyl group). Another feature that emerges from Table 4 refers to the good agreement between the structural parameters of TMP calculated at the B3LYP/6-31G* and those previously obtained at the MP2/6-31G** [22]. More-

Table 1

Relative energies at the B3LYP/3-21G* (kJ/mol) of the conformers which are the result of an addition between phosphonium ions and methanol

	$\text{CH}_3\text{OH}+$		
	$(\text{HO})_2\text{P}=\text{O}^+$	$(\text{CH}_3\text{O})(\text{HO})\text{P}=\text{O}^+$	$(\text{CH}_3\text{O})_2\text{P}=\text{O}^+$
Conformation (a)	0.0	0.0	0.0
Conformation (b)	2.4	3.0	3.1

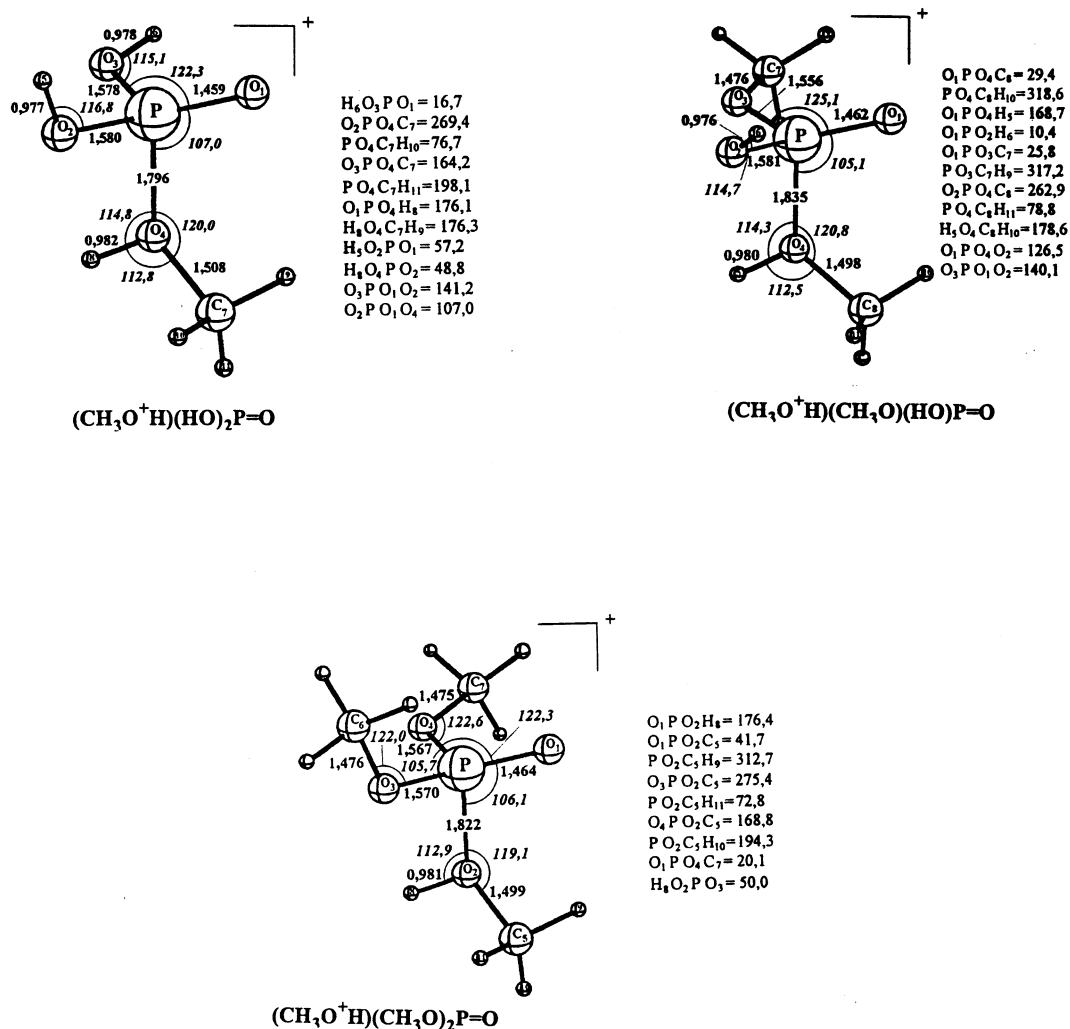


Fig. 6. B3LYP/6-31G* optimized geometries of the three adducts. Bond lengths are in angstroms and angles in degrees.

over, the conformation of TMP, although we strictly find a C_1 symmetry, is very close to a C_3 symmetry as previously described by George et al. [22]. As a result, the use of the B3LYP functional with a 6-31G* basis set is suited for the description of these structures. In order to check the reliability of our DFT calculations and because of the lack of gas-phase experimental data on MMP and DMP, we have considered it of interest to list the computed unscaled B3LYP vibrational frequencies together with experimental [23] and calculated values obtained at the MP2/6-31G* level [22] for TMP (see Table 6). Note

that values given in this table are restricted to the main modes involving only the P=O, P–O–H, and P–O–C vibrations. It must be noted that experimental vibrational frequencies values for TMP are very similar to those calculated at the MP2 and B3LYP levels. This agreement with previous experimental and ab initio results demonstrates the strength of DFT approach in predicting molecular properties for compounds of this type. Another interesting feature that emerges from Table 6 lies in the variations in the P=O stretching values. Replacing one hydrogen atom by a methyl group produces a decrease in P=O stretching value

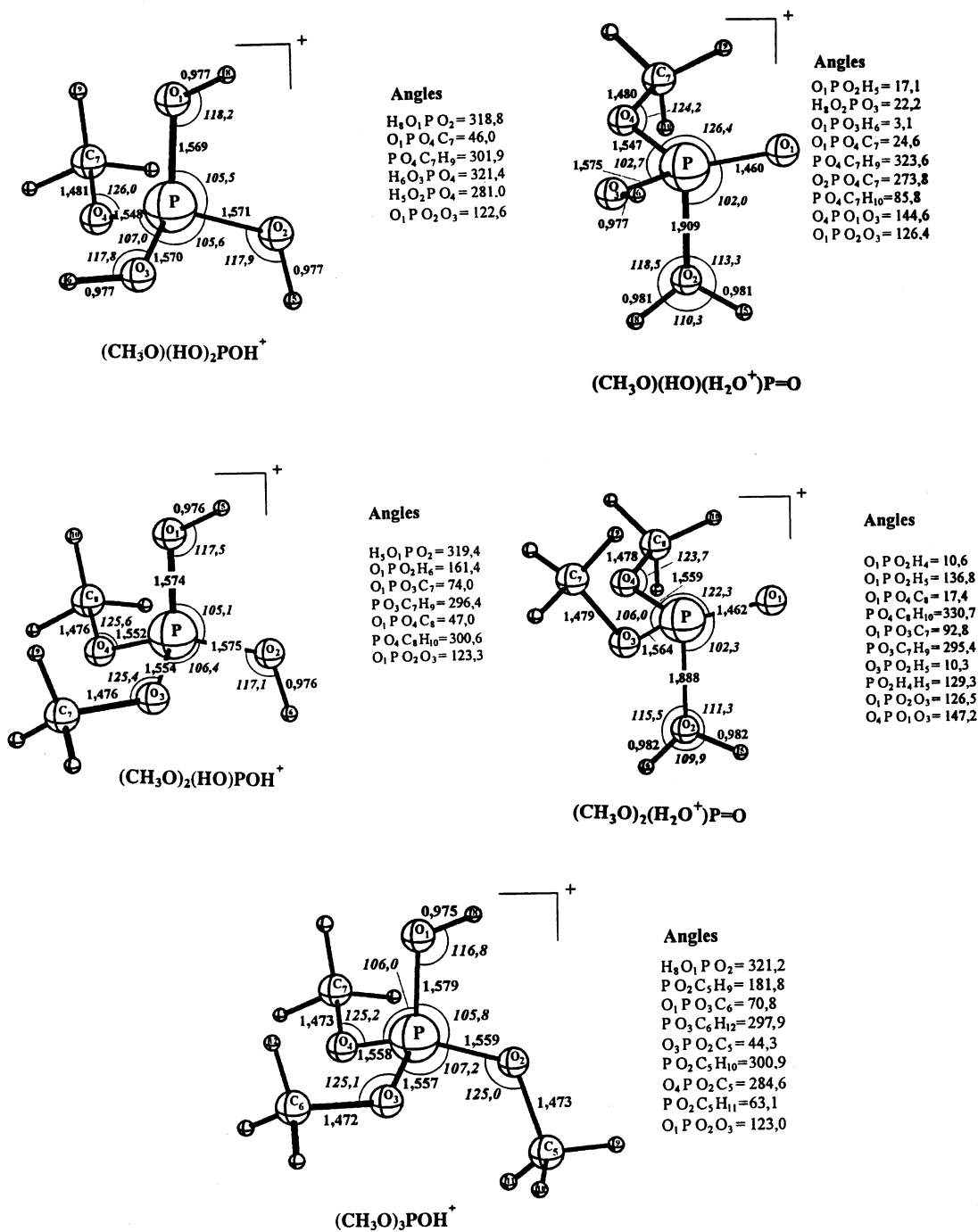


Fig. 7. Equilibrium geometries of the conformers of (MMP + CH₃OH)⁺, (DMP + CH₃OH)⁺, and (TMP + CH₃OH)⁺ cations optimized at the B3LYP/6-31G* level. Bond lengths are in angstroms and angles in degrees.

Table 2

Total (Hartree) and relative energies (kJ/mol) at the B3LYP/6-311+G(2df,p) level for the isomeric protonated forms of MMP, DMP, and TMP

	Total energies	ZPE	Enthalpy correction	Relative energies
<i>(MMP)H</i>				
(CH ₃ O)(HO) ₂ P ⁺ OH	−683.979 167	0.088 354	0.009 024	0
(H ₂ O ⁺)(CH ₃ O)(HO)P=O	−683.927 769	0.088 420	0.009 503	136
(CH ₃ O ⁺ H)(HO) ₂ P=O	−683.933 623	0.088 505	0.009 270	121
<i>(DMP)H⁺</i>				
(CH ₃ O) ₂ (HO)P ⁺ OH	−723.297 529	0.117 302	0.010 809	0
(H ₂ O ⁺)(CH ₃ O) ₂ P=O	−723.244 524	0.117 606	0.011 130	141
(CH ₃ O ⁺ H)(CH ₃ O)HOP=O	−723.251 911	0.117 378	0.011 038	121
<i>(TMP)H⁺</i>				
(CH ₃ O) ₃ P ⁺ OH	−762.614 829	0.146 442	0.012 456	0
(CH ₃ OH ⁺)(CH ₃ O) ₂ P=O	−762.568 709	0.146 582	0.012 652	122

because of the polarization enhancement induced by the methyl group. Note that for each methyl substitution, the P=O stretching decreases of a constant value of about 10 cm^{−1}. This decreasing is also observed when one compares the P=O stretching values of orthophosphoric acid (1322 cm^{−1}) [6] and MMP

(1311 cm^{−1}). The PA and GB of MMP, DMP, and TMP have been calculated at B3LYP/6-311+G(2df,p) level of are listed in Table 7.

It must be noted that the excellent agreement between the theoretical (892 kJ/mol) and the experimental value (891 kJ/mol) [21] of the PA of TMP

Table 3

Total (hartree) and relative energies (kJ/mol) at the B3LYP/6-311 + G(2df, p) level for species related to the reaction of the (HO)₂P=O⁺, (HO)(CH₃O)P=O⁺, and (CH₃O)₂P=O⁺ phosphonium ions with methanol

	Total energies B3LYP/6-311+G(2df,p)	Corrections (vib. + ther.)	Relative energies B3LYP/6-311+G(2df,p)
(HO) ₂ P=O ⁺ + CH ₃ OH	−683.854 180	0.094 709	0
(CH ₃ O ⁺ H)(HO) ₂ P=O	−683.933 623	0.097 775	−200
(CH ₃ O)(HO) ₂ PO ⁺ H	−683.979 167	0.097 378	−321
TS ₁	−683.888 826	0.093 015	−95
TS ₂	−683.901 326	0.092 619	−129
(CH ₃ O)(HO)(H ₂ O ⁺)P=O	−683.927 769	0.097 923	−185
(CH ₃ O)(HO)P=O ⁺ + H ₂ O	−683.872 057	0.094 574	−47
(CH ₃ O)(HO)P=O ⁺ + CH ₃ OH	−723.181 521	0.125 330	0
(CH ₃ O ⁺ H)(CH ₃ O)(HO)P=O	−723.251 665	0.128 636	−175
(CH ₃ O) ₂ (HO)PO ⁺ H	−723.297 529	0.128 111	−297
TS ₃	−723.208 196	0.123 903	−74
TS ₄	−723.220 713	0.123 554	−107
(CH ₃ O) ₂ (H ₂ O ⁺)P=O	−723.244 524	0.128 736	−156
(CH ₃ O) ₂ P=O ⁺ + H ₂ O	−723.196 860	0.125 157	−41
(CH ₃ O) ₂ P=O ⁺ + CH ₃ OH	−762.506 324	0.155 913	0
(CH ₃ O ⁺ H)(CH ₃ O) ₂ P=O	−762.568 709	0.159 234	−155
TS ₅	−762.539 127	0.154 187	−91
(CH ₃ O) ₃ (HO)P ⁺	−762.614 829	0.158 898	−277

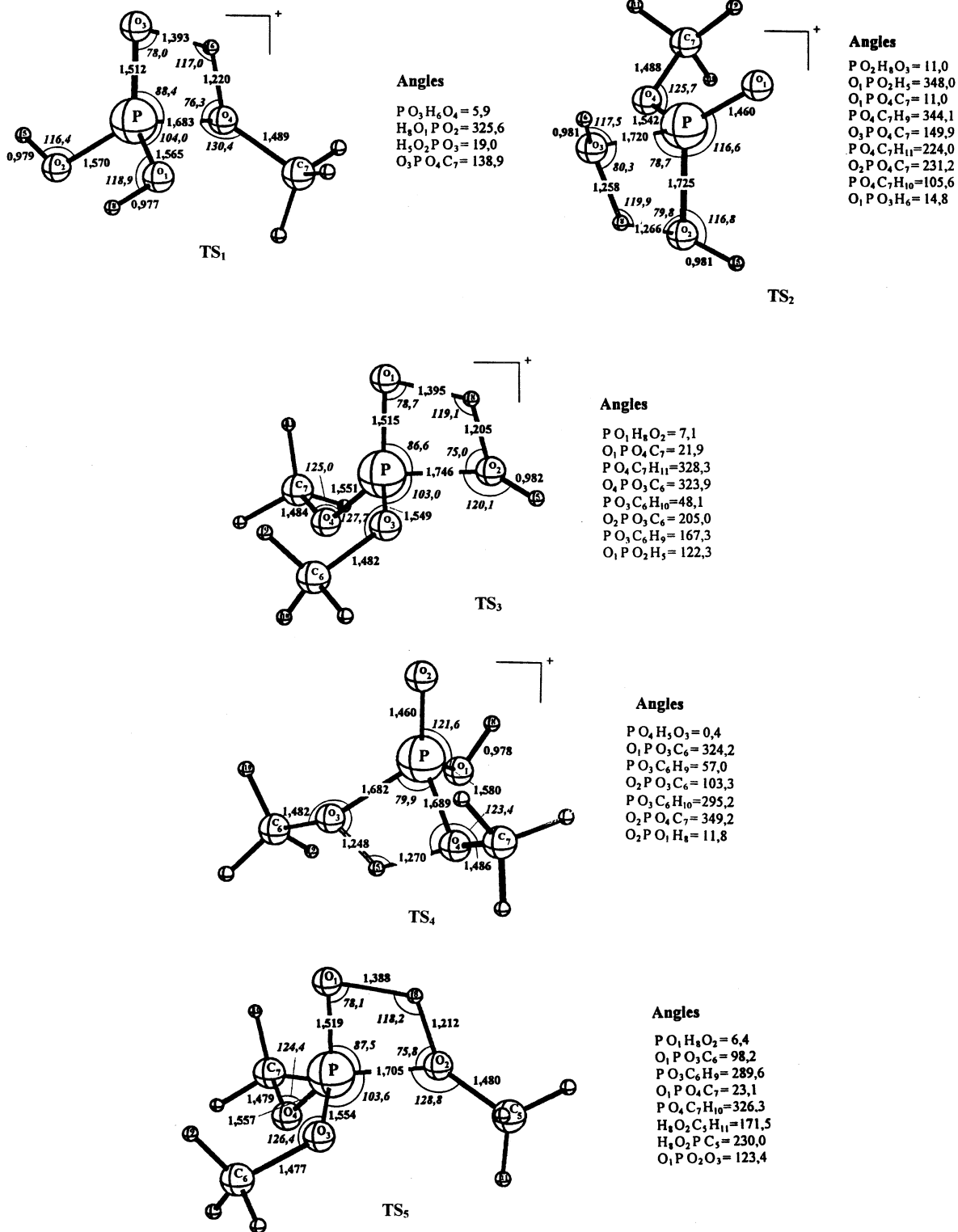
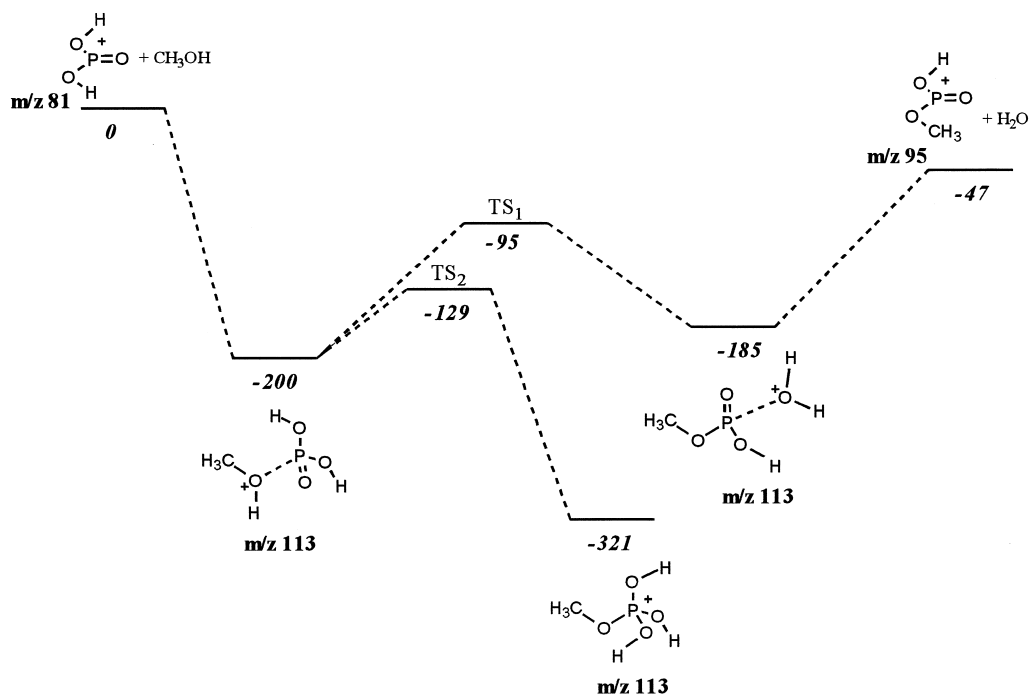
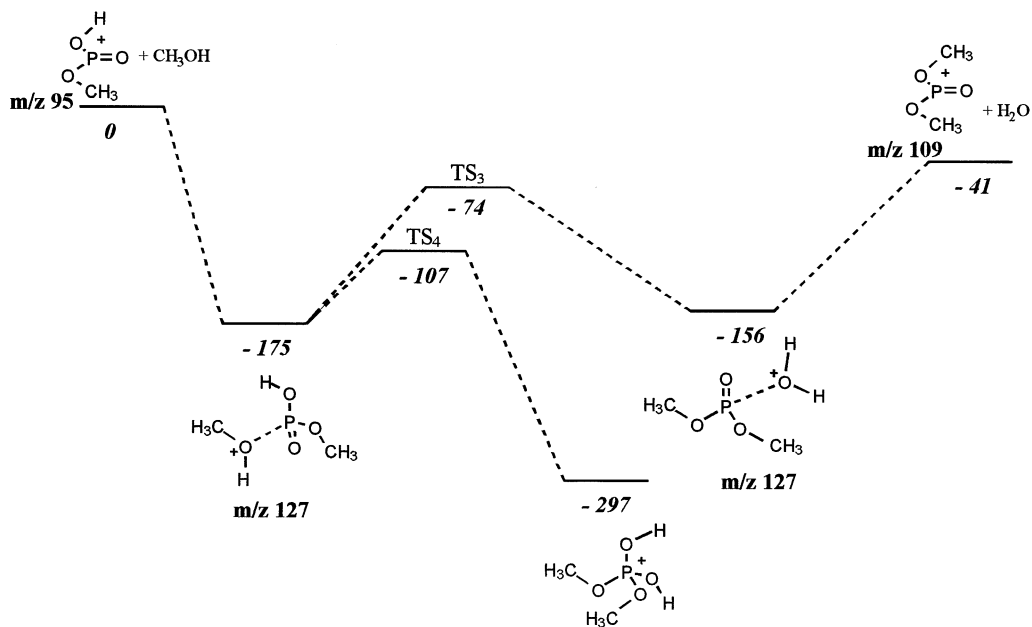


Fig. 8. Equilibrium geometries of transition states corresponding to the 1,3-H transfert optimized at the B3LYP/6-31G* level. Bond lengths are in angstroms and angles in degrees.

Fig. 9. Potential energy surface for the reaction of $(\text{HO})_2\text{P}=\text{O}^+$ phosphonium cations with methanol.Fig. 10. Potential energy surface for the reaction of $(\text{HO})(\text{CH}_3\text{O})\text{P}=\text{O}^+$ phosphonium cations with methanol.

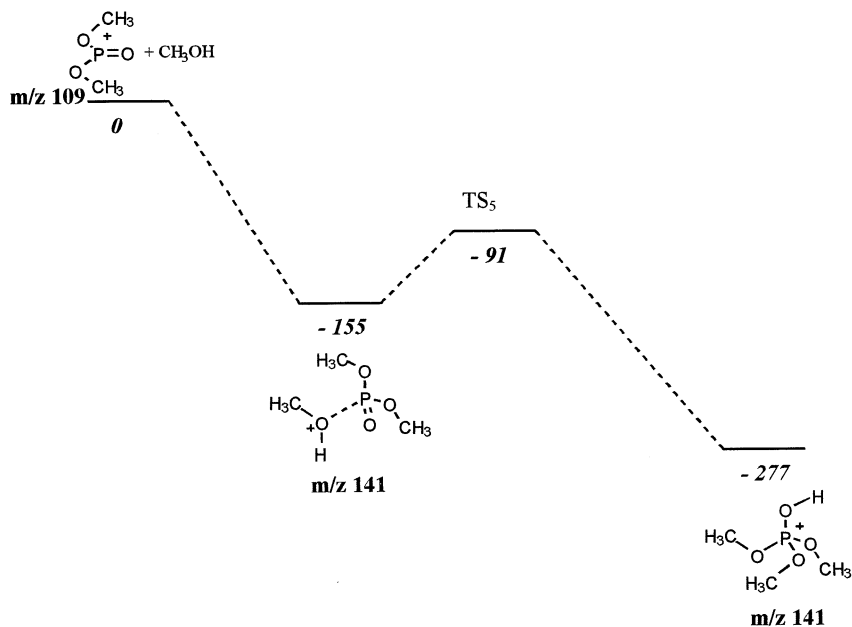


Fig. 11. Potential energy surface for the reaction of $(\text{CH}_3\text{O})_2\text{P}=\text{O}^+$ phosphonium cations with methanol.

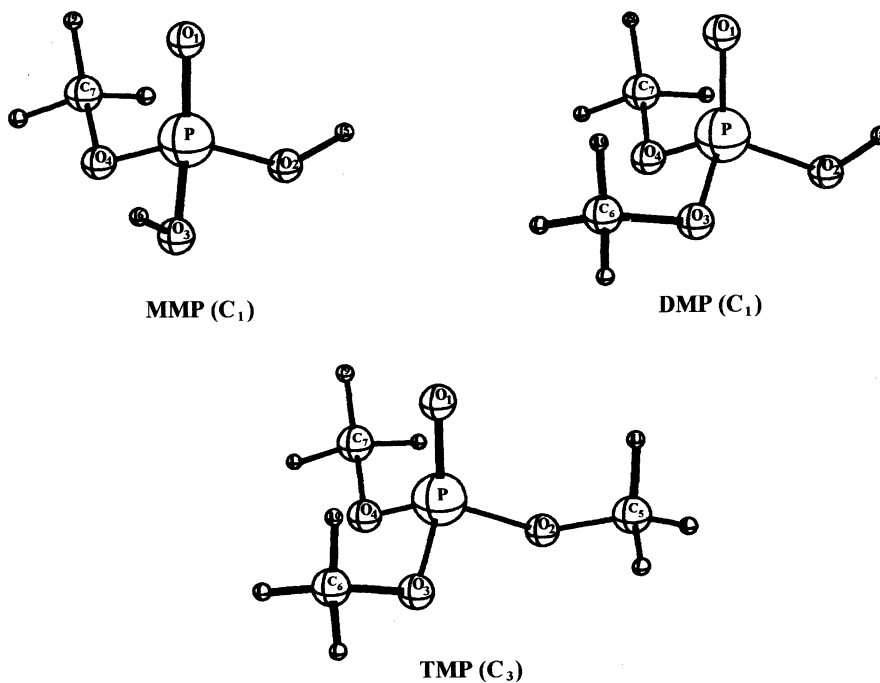


Fig. 12. Equilibrium geometries of MMP, DMP, and TMP optimized at the B3LYP/6-31G* level. Bond lengths and angles are given in Table 4.

Table 4
Structural parameters of MMP, DMP, and TMP computed at the B3LYP/6-31G* level of theory; bond lengths are in angstroms and angles are in degrees

Parameters	MMP	DMP	TMP	TMP ^a
Bond lengths				
PO ₁	1.480	1.481	1.481	1.485
PO ₂	1.616	1.616	1.606	1.608
PO ₃	1.612	1.602	1.606	1.608
PO ₄	1.601	1.606	1.606	1.608
O ₂ C ₅	1.440	1.444
O ₃ C ₆	...	1.440	1.440	1.444
O ₄ C ₇	1.441	1.440	1.440	1.444
O ₂ H ₅	0.971	0.971
O ₃ H ₆	0.971
Angles				
O ₁ PO ₂	115.6	114.9	116.3	116.4
O ₁ PO ₃	115.3	117.3	116.3	116.4
O ₁ PO ₄	117.7	116.6	116.3	116.4
PO ₂ C ₅	118.8	116.6
PO ₃ C ₆	...	118.5	118.7	116.6
PO ₄ C ₇	118.5	118.7	118.8	116.6
PO ₂ H ₅	110.3	109.7
PO ₃ H ₆	109.8
Dihedral angles				
O ₁ PO ₂ C ₅	44.8	45.2
O ₁ PO ₃ C ₆	...	51.9	44.9	45.2
O ₁ PO ₄ C ₇	52.3	44.9	44.3	45.2
O ₁ PO ₂ H ₅	30.2	24.2
O ₁ PO ₃ H ₆	27.4
PO ₂ C ₅ H ₁₁	311.6	...
PO ₃ C ₆ H ₁₀	...	309.1	311.0	...
PO ₄ C ₇ H ₉	306.8	309.7	311.5	...
O ₂ PO ₁ O ₄	120.3	120.6	120.0	120.0
O ₃ PO ₁ O ₄	-119.6	-120.1	-120.0	-120.0

^a Values obtained at the MP2/6-31G** [22] level.

checks again the reliability of our DFT calculations. Another interesting feature that emerges from Table 7 lies in the variations in predicted basicities. Not

Table 5
B3LYP/6-311+G(2df,p) total energies (Hartree) for MMP, DMP, and TMP; vibrational and thermal corrections are in Hartree

	Total energies 6-311+G(2df,p)	Corrections	
		Vibrational	Thermal
MMP	-683.644307	0.077277	0.008695
DMP	-722.955118	0.106277	0.010201
TMP	-762.265520	0.135080	0.011837

unexpectedly, replacing a hydrogen atom by a methyl group increases the basicity, again because of the polarization enhancement due to the methyl group. At our highest level of theory [B3LYP/6-311+G(2df,p)], DMP is found to be 20 kJ/mol more basic than MMP, and TMP, 17 kJ/mol more basic than DMP, i.e. the effect of the second methyl substitution is only slightly smaller than the first one.

6. Conclusion

In this article, we have presented the ion–molecule reactions between methanol and the (HO)₂P=O⁺ phosphonium ions. The experimental study performed in a QIT mass spectrometer has shown that both species react according to three consecutive reactions, via successive methanol addition/water elimination, to yield protonated trimethyl phosphate. Thus, we have performed in the gas phase a three-stage synthesis of protonated trimethyl phosphate from the (HO)₂P=O⁺ phosphonium ions and methanol. We have also investigated the reactions between the (HO)₂P=O⁺ phosphonium ions and its neutral precursor TEP. The main observed is a proton transfer reaction, yielding the protonated TEP. This species rapidly reacts again with the neutral TEP, giving the proton-bound dimer. (TEP)₂H⁺, which decomposes by three ethylene molecules losses yielding to the formation of protonated orthophosphoric acid dimer (HO)₂P(=O)–O–P(OH)₃⁺.

In order to state the mechanism for the evolution of the three cationized species, which correspond to the MMP, DMP, and TMP protonated on a methoxy–oxygen atom, the structure and stability of the respective isomeric forms have been investigated. The results show that phosphoryl–oxygen protonation is thermodynamically favored over oxygen of the O–R group (R = H or CH₃). The phosphoryl–oxygen protonation is about 120 kJ/mol more favorable than the methoxy–oxygen one, which in turn is more stable of 20 kJ/mol than the hydroxy–oxygen protonation. Concerning the reactivity of the adduct ions, the theoretical study is in agreement with the experimental findings: the reactions between the (HO)₂P=O⁺

Table 6

Computed unscaled vibrational frequencies (cm^{-1}) of MMP, DMP, and TMP at the B3LYP/6-31G* level of theory

	MMP	DMP	TMP		Expt.
	B3LYP/6-31G*	B3LYP/6-31G*	B3LYP/6-31G*	MP2/6-31G* ^a	
P–O–(C)	769	748 (s.)	738 (s.)
...	...	851 (as.)	852 (as.)	866	...
P–O–(H)	887	916
...	932
O–C	1092	1077 (as.)	1074 (as.)	1048	1060
...	...	1102 (s.)	1111 (s.)
P=O	1311	1301	1289	1287	1291
O–H	3757 (as.)	3758
...	3760 (s.)

^a Values from [22].

(m/z 81) and $(\text{HO})(\text{CH}_3\text{O})\text{P}=\text{O}^+$ (m/z 95) phosphonium cations and methanol are exothermic about 47 and 41 kJ/mol, respectively. When the $(\text{CH}_3\text{O})_2\text{P}=\text{O}^+$ (m/z 109) phosphonium ions were found to react with methanol according to a substantial exothermic process of about 277 kJ/mol, to yield protonated trimethyl phosphate. This feature in the potential energy surface explains the rapid and spontaneous 1,3-migration of a proton within the isomers and proves that all isomers can exist in the gas phase. Thus, the phosphonium ions $(\text{HO})_2\text{P}=\text{O}^+$ react with via sequential methanol addition/water elimination to yield protonated trimethyl phosphate. This overall reaction occurs by an exothermic process of 365 kJ/mol.

We have also calculated the PA and GB of the molecular species related to the reactions of the $(\text{HO})_2\text{P}=\text{O}^+$ cations with methanol namely: MMP, DMP, and TMP. At our highest level of theory the calculated values are found to be 855, 875, and 892

kJ/mol for PAs and 823, 843, and 862 kJ/mol for GBs, respectively. The excellent agreement between the theoretical (892 kJ/mol) and the experimental value (891 kJ/mol) of the PA of TMP shows the reliability of our DFT calculations.

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References

- [1] R.A.J. O'Hair, in *The Chemistry of Organophosphorus Compounds*, Vol. 4, F.R. Hartley (Ed.), Wiley, Chichester, 1996, pp. 731–765.
- [2] R.V. Hodges, T.J. McDonnell, J.L. Beauchamp, *J. Am. Chem. Soc.* 102 (1980) 1327.
- [3] L. Zeller, J. Farrell Jr., P. Vainiotalo, H.I. Kenttämä, *J. Am. Chem. Soc.* 114 (1992) 1205.
- [4] R. Li, A. Schweighofer, H. Keck, W. Kuchen, H.I. Kenttämä, *Int. J. Mass Spectrom. Ion Processes* 157/158 (1996) 293.
- [5] S. Ma, P. Wong, R.G. Cooks, F.C. Gozzo, M.N. Eberlin, *Int. J. Mass Spectrom. Ion Processes* 163 (1997) 89.
- [6] S. Gevrey, A. Luna, V. Haldys, J. Tortajada, J-P. Morizur, *J. Chem. Phys.* 108 (1998) 2458.
- [7] (a) K.K. Thoen, L. Gao, T.D. Ranatunga, P. Vainiotalo, H.I. Kenttämä, *ICR/Ion Trap Newsletter* 47 (1997) 15; (b) K.K. Thoen, L. Gao, T.D. Ranatunga, P. Vainiotalo, H.I. Kenttämä, *J. Org. Chem.* 62 (1997) 8702.
- [8] R.S. Thompson, Y-Q. Yu, H.I. Kenttämä, in *Proceedings of*

Table 7

PA and GB values (kJ/mol) for MMP, DMP, and TMP obtained at the B3LYP/6-311+G(2df,p)

	PA (kJ/mol)		Rot. sym. numbers		GB (kJ/mol)
	6-311+G(2df,p)	Exp ^a	σ_N	σ_P	
MMP	855	...	1	1	823
DMP	875	...	1	1	843
TMP	892	891	3	1	862

^a Experimental value from [21].

- the 47th ASMS Conference on Mass Spectrometry and Allied Topics, Dallas, TX, 1999, p. 2650.
- [9] J-P. Morizur, S. Gevrey, A. Luna, M-H. Taphanel, *J. Mass Spectrom.* 32 (1997) 550.
- [10] A.J. Bell, D. Despeyroux, J. Murrell, P. Watts, *Int. J. Mass Spectrom. Ion Processes* 165/166 (1997) 533.
- [11] S. Gevrey, M-H. Taphanel, J-P. Morizur, *J. Mass Spectrom.* 33 (1998) 399.
- [12] R.E. March, R.J. Hughes, *J. Mass Spectrom.* 32 (1997) 351.
- [13] G.C. Stafford Jr., P.E. Kelley, J.E.P. Syka, W.E. Reynolds, J.F.J. Todd, *Int. J. Mass Spectrom. Ion Processes* 60 (1984) 85.
- [14] D.B. Tucker, C.H. Hameister, S.C. Bradshaw, D.J. Hoekam, M. Weber-Grabau, in *Proceedings of the 36th ASMS Conference on Mass Spectrometry and Allied Topics*, San Francisco, CA, 1988, p. 620.
- [15] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Peterson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewsky, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, GAUSSIAN 94, revision D.1, Gaussian, Inc., Pittsburgh, PA, 1995.
- [16] (a) A.D. Becke, *J. Chem. Phys.* 96 (1992) 2155; (b) 98 (1993) 5648.
- [17] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [18] (a) R. Krishnan, J.S. Binkley, R. Seeger, J.A. Pople, *J. Chem. Phys.* 72 (1980) 650; (b) A.D. McLean, G.S. Chandler, *ibid.* 72 (1980) 5639.
- [19] F. Tureček, M. Gu, C.E.C.A. Hop, *J. Phys. Chem.* 99 (1995) 2278.
- [20] P.A. Cload, D.W. Hutchinson, *Org. Mass Spectrom.* 18 (1983) 57.
- [21] E.P. Hunter, S.G. Lias, *Proton Affinity Evaluation in NIST Standard Reference Database Number 69*, W.G. Mallard, P.J. Linstrom (Eds.), National Institute of Standards and Technology, Gaithersburg, MD, 1998 (<http://webbook.nist.gov>).
- [22] L. George, K.S. Viswanathan, S. Singh, *J. Phys. Chem.* 101 (1997) 2459.
- [23] G. Lisa, K. Sankaran, K.S. Viswanathan, C.K. Mathews, *Appl. Spectrosc.* 47 (1994) 8.