

A THEORETICAL APPROACH TO GAS-PHASE ION CHEMISTRY

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Abstract - The use of ab initio molecular orbital theory to study gas-phase ion chemistry is discussed. Particular attention is focussed on distonic radical cations, a recently defined, new class of reactive intermediates in which the charge and radical sites of the radical cation are formally separated. Ylidions, in which the charge and radical sites are on adjacent centers, are examined as a particular sub-class. Distonic radical cations in general (e.g. $\text{CH}_2\text{CH}_2\dot{\text{O}}\text{H}_2$) and ylidions in particular (e.g. $\text{CH}_2\dot{\text{O}}\text{H}_2$) are shown to have special stability. Ylide dications (e.g. $\text{CH}_2\text{OH}_2^{2+}$) are also examined and shown to be generally much more stable than their classical isomers.

INTRODUCTION

The experimental determination of the energies and structures of stable, neutral molecules is generally a straightforward matter. This is not the case, however, for reactive species such as gas-phase ions. Ion energies are in principle available from mass-spectrometry-based techniques (Ref. 1); however, the information obtained is often indirect and the interpretation of the data can therefore be ambiguous. Structures of gas-phase ions represent an even more difficult target and only a handful of polyatomic ions have had their detailed structures experimentally determined to date (Ref. 2).

In contrast, ab initio molecular orbital theory may be applied to reactive species such as ions with no more difficulty than to stable, neutral molecules. Detailed structures may be determined routinely and relative energies of isomeric species obtained. In addition, transition structures for chemical reactions, which are not directly observable experimentally, may be fully characterized. Reaction potential surfaces may thus be derived and reaction mechanisms established.

This presentation illustrates the use of ab initio molecular orbital theory to study gas-phase ion chemistry with examples taken from our recent research. Particular emphasis is placed on the recent discovery of ylidions and ylide dications as two new classes of reactive intermediates of special stability. Extension to the more general class of distonic radical cations is also discussed.

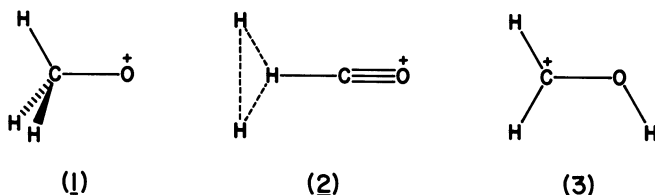
METHOD

The results reported herein are based on ab initio molecular orbital calculations, carried out with modified (Ref. 3,4) versions of the Gaussian 80 (Ref. 5) and 82 (Ref. 6) systems of programs. Such calculations enable the determination of equilibrium and transition structures in the potential energy surface and of their relative energies. Optimized structures were obtained with the 3-21G (Ref. 7), 4-31G (Ref. 8), 6-31G* (Ref. 9) or 6-31G** (Ref. 9) basis sets using gradient procedures. Harmonic vibrational frequencies were evaluated, firstly to characterize rigorously stationary points in the potential surface as minima (representing equilibrium structures) or saddle points (representing transition structures), and secondly, to evaluate zero-point contributions to relative energies. Unless otherwise noted, quoted relative energies refer to 6-31G** calculations with electron correlation incorporated at the third-order Møller-Plesset level of perturbation theory (Ref. 10). Such calculations are denoted MP3/6-31G**.

THE NATURE OF THE CH_3O^+ CATION

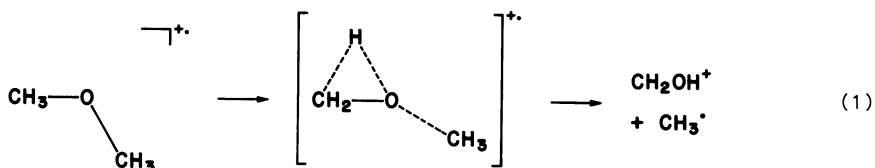
The first problem which we shall discuss concerns the identity of the CH_3O^+ ion formed from dimethyl ether in the mass spectrometer, about which there has been considerable confusion

in the literature. Appearance potential measurements (Ref. 11) yield a heat of formation of -803 kJ mol^{-1} for this ion, i.e. about 96 kJ mol^{-1} above that (707 kJ mol^{-1}) of the well-known hydroxymethyl (CH_2OH^+) cation. The question is: what is the nature of this ion at 803 kJ mol^{-1} ? Three proposals have been advanced over the years. The first (Ref. 12) was that the ion is simply the methoxy cation CH_3OH^+ (1) and that its energy is $\sim 100 \text{ kJ mol}^{-1}$ above that of CH_2OH^+ . This was, however, subsequently shown to be unlikely by theoretical calculations (Ref. 13) which indicated that singlet CH_3O^+ would collapse without activation energy to CH_2OH^+ .



The second possibility to receive support in the literature (Ref. 13,14) was that the ion is the same as that detected in high-pressure mass spectrometric experiments by Kebarle and others (Ref. 15) involving reaction of HCO^+ with H_2 , i.e. a CH_3O^+ structure (2) resembling a complex of HCO^+ with H_2 . This ion (2) was found to have a heat of formation of 810 kJ mol^{-1} , almost exactly what is required to explain the dimethyl ether ionization results.

Finally the suggestion was made (Ref. 16,17) that the ion observed is simply the CH_2OH^+ ion (3), formed with -96 kJ mol^{-1} of excess energy. In this connection, the most plausible proposal came from Dill, Fischer and McLafferty (Ref. 17) who firstly found that the collisionally-activated dissociation (CAD) spectrum of the m/z 31 ion from dimethyl ether to examine also triplet CH_3O^+ but we find that this has a very high energy, corresponding to a heat of formation of $\sim 1090 \text{ kJ mol}^{-1}$. These results rule out either singlet or triplet CH_3O^+ as the species formed at threshold from dimethyl ether radical cation.



This turns out to be closely related to what we find with our detailed calculations (Ref. 18).

Our calculations (Ref. 18) confirm, in the first place, the previous conclusions that singlet CH_3O^+ collapses without activation energy to CH_2OH^+ . We felt it worthwhile to examine also triplet CH_3O^+ but we find that this has a very high energy, corresponding to a heat of formation of $\sim 1090 \text{ kJ mol}^{-1}$. These results rule out either singlet or triplet CH_3O^+ as the species formed at threshold from dimethyl ether radical cation.

What about the suggestion of an $\text{HCO}^+ \dots \text{H}_2$ complex? This was an attractive possibility because the ΔH_f° at 810 kJ mol^{-1} was almost exactly the (apparent) ΔH_f° for the CH_3O^+ ion formed from dimethyl ether. However, we find in agreement with previous work that the complex sits in a very shallow well and is bound with respect to separated $\text{HCO}^+ + \text{H}_2$ by only 16 kJ mol^{-1} . It would seem most unlikely that such a complex could be formed in a dissociation-rearrangement reaction.

Our proposed solution to the problem is summarized in the schematic potential energy diagram displayed in Fig. 1. The dimethyl ether radical cation ($\text{CH}_3\text{OCH}_3^+$, 4) can rearrange by means of a 1,2-hydrogen shift via a transition structure (5) at 146 kJ mol^{-1} to the intermediate oxonium ion, $\text{CH}_2\text{OHCH}_3^+$ (6). The oxonium ion can then undergo a simple bond fission to yield the CH_2OH^+ ion plus methyl radical. Note that because a barrier of 146 kJ mol^{-1} has to be surmounted, the CH_2OH^+ ion is produced with $\sim 110 \text{ kJ mol}^{-1}$ of excess energy. This is in remarkable agreement with the experimental appearance potential results which were consistent with the formation of a CH_2OH^+ ion with -96 kJ mol^{-1} excess energy. Our potential function represents in many respects an explicit text-book example of a fragmentation involving a rate-determining isomerization prior to dissociation to yield product ions with considerable excess energy (Ref. 19).

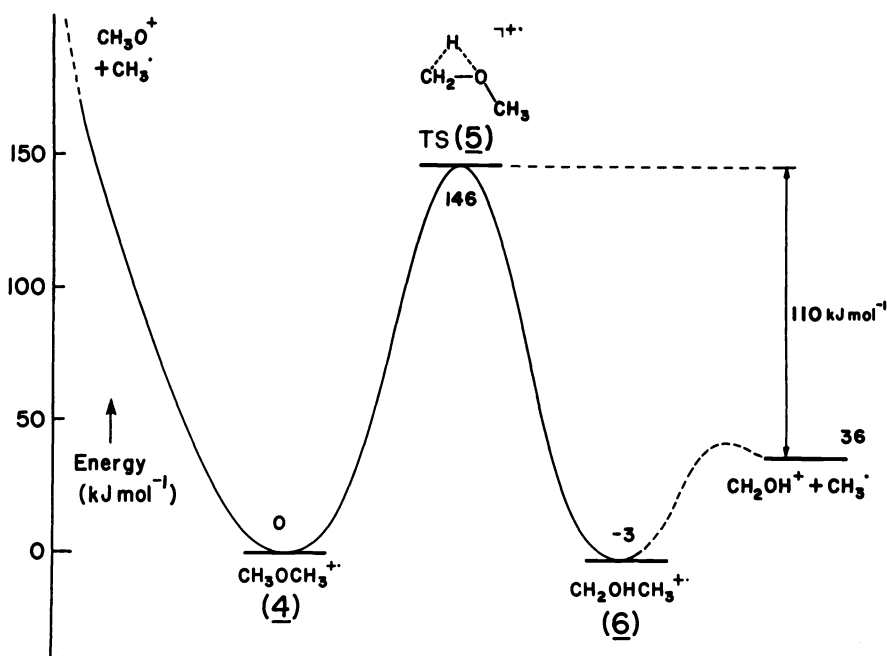


Fig. 1. Schematic potential energy profile for the generation of CH_2OH^+ ions from dimethyl ether radical cation (4).

The oxonium ion $\text{CH}_2\text{OHCH}_3^+$ (6) warrants further comment. It is a new species without a stable neutral counterpart. A striking feature is that its energy is marginally lower than that of the dimethyl ether radical cation (4) itself. It has led us on to some exciting new chemistry which forms the basis of most of the remainder of this paper.

THE CH_3S^+ ION FORMED FROM DIMETHYL SULFIDE

Let us first turn briefly to the sulfur analogue of the methoxy cation problem - namely, what is the nature of the CH_3S^+ ion formed from dimethyl sulfide in the mass spectrometer? There are interesting similarities and differences between this and the oxygen system.

Historically, two structural isomers of composition CH_3S^+ were believed to exist, CH_3S^+ formed from alkyl methyl sulfides, and CH_2SH^+ formed from alkane thiols (Ref. 20). In this way, CD_3SH was considered to produce both CD_3S^+ (by H^+ loss) and CD_2SH^+ (by D^+ loss) with the former appearing at slightly lower energy.

Recent experimental work using a variety of approaches (Ref. 21) has demonstrated, however, that the ion produced from CH_3SCH_3 is CH_2SH^+ and not CH_3S^+ as originally thought. Very little is in fact known about the ion of structure CH_3S^+ . For example, is its energy close to that of CH_2SH^+ or is it very different? There appears to be some confusion, even in the recent literature, on this point and we sought (Ref. 22,23) to clarify this and other issues.

One interesting experimental result is that the observed appearance potential together with other thermochemical data (Ref. 1,20) indicate that CH_2SH^+ is formed from $\text{CH}_3\text{SCH}_3^+$ with only a small amount, -16 kJ mol^{-1} , of excess energy. This contrasts with the large excess energy (-96 kJ mol^{-1}) that we have just seen in the case of CH_2OH^+ produced from CH_3OCH_3 .

What are our theoretical predictions (Ref. 22) for the CH_3S^+ system? First, singlet CH_2SH^+ is clearly the most stable isomer. Triplet CH_3S^+ lies significantly higher ($\geq 113 \text{ kJ mol}^{-1}$) in energy. Singlet CH_3S^+ is not stable but will collapse without activation to singlet CH_2SH^+ . These results are consistent with CH_2SH^+ rather than CH_3S^+ being generally formed at threshold in mass spectrometric fragmentation reactions.

Our mechanism for the formation of CH_2SH^+ from dimethyl sulfide is embodied in the calculated potential energy diagram shown in Fig. 2. Dimethyl sulfide radical cation (7) rearranges by means of a 1,2-shift (via 8) to give a sulfonium ion intermediate $\text{CH}_2\text{SHCH}_3^+$ (9) which then fragments to give CH_2SH^+ plus methyl radical.

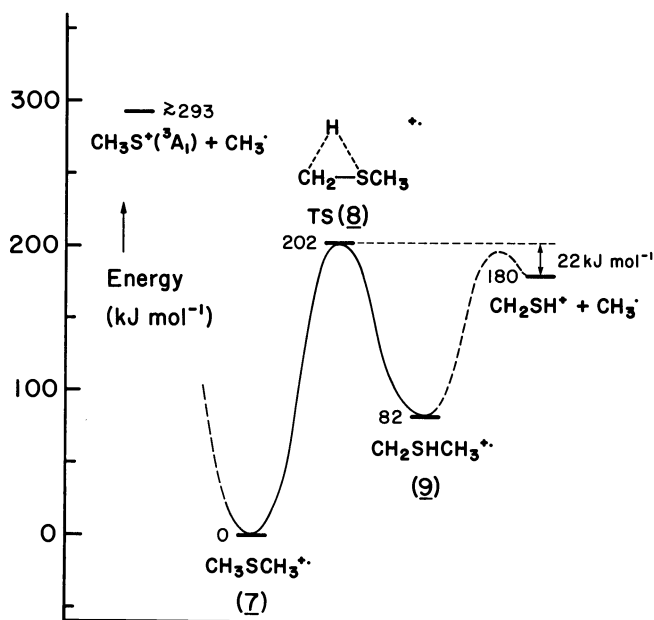


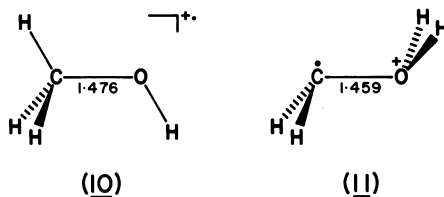
Fig. 2. Schematic potential energy profile for the generation of CH_2SH^+ ions from dimethyl sulfide radical cation (7).

There are two differences between the sulfur (Fig. 2) and oxygen (Fig. 1) systems which are particularly noteworthy. The first is that, whereas the oxonium ion isomer (6) was lower than the dimethyl ether radical cation (4) (by 3 kJ mol^{-1}), the sulfonium ion (9) is higher in energy than dimethyl sulfide radical cation (7) (by 82 kJ mol^{-1}). Nevertheless, the sulfonium ion resides in a respectable potential well and should be observable. The second point is that CH_2SH^+ is formed in this manner with very little excess energy: -22 kJ mol^{-1} . This is precisely in line with the thermochemical data noted above and contrasts with the theoretical and experimental results for CH_2OH^+ . Thus theory is able to reproduce this rather striking difference between the oxygen and sulfur systems.

A POSSIBLE LOW-ENERGY ISOMER OF CH_3OH^+

We saw above that the oxonium ion $\text{CH}_2\text{OHCH}_3^+$ is slightly lower in energy than the dimethyl ether radical cation, $\text{CH}_3\text{OCH}_3^+$. A logical question is to examine the lower homologues and ask: is CH_2OH_2^+ a stable gas-phase isomer of CH_3OH^+ (Ref. 24)?

One of the more interesting features of our calculated (6-31G*) structures for these two species concerns the C-O bond length (Ref. 25).



The C-O length in the methanol radical cation (10) (1.476Å) is somewhat longer than that in neutral methanol (1.400Å) at the same level of theory. On the other hand, the C-O length in the methyleneoxonium radical cation (11) (1.459Å) is dramatically shorter than that calculated for neutral CH_2OH_2 (1.805Å), reflecting the stability and strong bonding in the ion.

Information concerning the relative stabilities of $\text{CH}_3\text{OH}^{\cdot+}$ and $\text{CH}_2\text{OH}_2^{\cdot+}$ is encompassed in the potential energy diagram of Fig. 3. It may be seen that not only is $\text{CH}_2\text{OH}_2^{\cdot+}$ (11) a stable isomer but it lies significantly lower in energy (by 45 kJ mol^{-1}) than $\text{CH}_3\text{OH}^{\cdot+}$ (10). The barrier separating these two isomers (112 kJ mol^{-1} at transition structure 12) is sufficiently large to allow each to be separately observable.

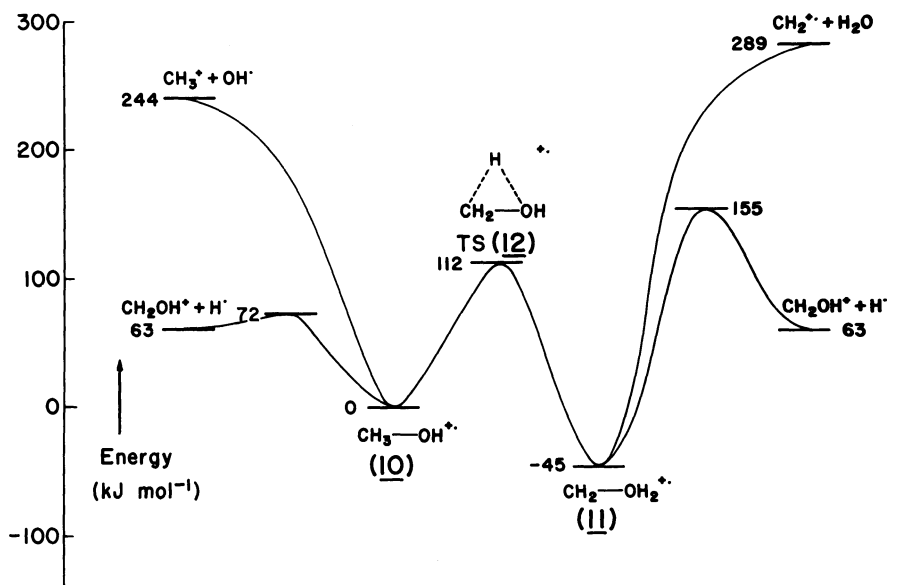
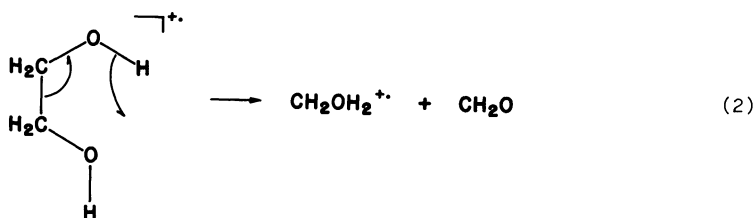


Fig. 3. Schematic potential energy profile connecting the methanol ($\text{CH}_3\text{OH}^{\cdot+}$, 10) and methyleneoxonium ($\text{CH}_2\text{OH}_2^{\cdot+}$, 11) radical cations.

Our conclusion then is that the methyleneoxonium radical cation $\text{CH}_2\text{OH}_2^{\cdot+}$ is a stable CH_4O^+ isomer, lying -45 kJ mol^{-1} lower in energy than $\text{CH}_3\text{OH}^{\cdot+}$. This theoretical prediction has been confirmed by collisional activation experiments carried out independently in Canberra (Ref. 26) and Ottawa (Ref. 27). In these experiments, $\text{CH}_2\text{OH}_2^{\cdot+}$ was generated indirectly from ionization of ethylene glycol (reaction (2)):



The CA spectrum of the $\text{CH}_2\text{OH}_2^{\cdot+}$ formed in this manner was shown to be quite distinct from that of $\text{CH}_3\text{OH}^{\cdot+}$, generated simply by the ionization of methanol. The Ottawa group (Ref. 27) also confirmed that $\text{CH}_2\text{OH}_2^{\cdot+}$ is more stable than $\text{CH}_3\text{OH}^{\cdot+}$, finding an energy difference of 29 kJ mol^{-1} , somewhat smaller than the theoretical 45 kJ mol^{-1} .

GENERALIZATION: YLIDIONS AS A NEW CLASS OF REACTIVE INTERMEDIATES

The observation that $\text{CH}_2\text{OH}_2^{+\cdot}$ is a stable isomer of $\text{CH}_3\text{OH}^{+\cdot}$ may be generalized. Thus, fluoromethane radical cation ($\text{CH}_3\text{F}^{+\cdot}$) has a stable isomer, the methylenefluoronium ion ($\text{CH}_2\text{FH}^{+\cdot}$) lying 46 kJ mol^{-1} lower in energy (Ref. 28). Similarly, the radical cations of methylamine, chloromethane, methanethiol and methylphosphine all have stable isomers with calculated relative energies as shown in Table 1 (Ref. 28-32).

TABLE 1. Calculated (MP3/6-31G^{**}) relative energies (kJ mol^{-1}) of classical and ylidion isomers

Classical	Ylidion	E(Classical)-E(Ylidion)	
$\text{CH}_3\text{F}^{+\cdot}$	$\dot{\text{C}}\text{H}_2\overset{\dagger}{\text{F}}\text{H}$	46	(Ref. 28)
$\text{CH}_3\text{OH}^{+\cdot}$	$\dot{\text{C}}\text{H}_2\overset{\dagger}{\text{O}}\text{H}_2$	45	(Ref. 24)
$\text{CH}_3\text{NH}_2^{+\cdot}$	$\dot{\text{C}}\text{H}_2\overset{\dagger}{\text{N}}\text{H}_3$	8	(Ref. 29)
$\text{CH}_3\text{Cl}^{+\cdot}$	$\dot{\text{C}}\text{H}_2\overset{\dagger}{\text{C}}\text{lH}$	-40	(Ref. 32)
$\text{CH}_3\text{SH}^{+\cdot}$	$\dot{\text{C}}\text{H}_2\overset{\dagger}{\text{S}}\text{H}_2$	-86	(Ref. 32)
$\text{CH}_3\text{PH}_2^{+\cdot}$	$\dot{\text{C}}\text{H}_2\overset{\dagger}{\text{P}}\text{H}_3$	-40	(Ref. 32)

Many of these and related species have also been observed experimentally in the gas phase during the last couple of years (Ref. 26,27,33-35).

What should we call this new class of reactive intermediates? The neutral parents such as CH_2OH_2 and CH_2PH_3 formally belong to the ylide family. The species we are talking about correspond formally to ionized ylides and for that reason we have proposed (Ref. 32) the name ylidion to describe this class of ions:



The carbanionic nature of the ylide carbon facilitates ionization to give the ylidion, compared with ionization of the classical isomer.

YLIDIONS AS A PROBE FOR STUDYING YLIDES

We noted above that the simplest ylides $\bar{\text{C}}\text{H}_2\overset{\dagger}{\text{X}}\text{H}$ are not very stable species but, that in contrast, the ylidions $\dot{\text{C}}\text{H}_2\overset{\dagger}{\text{X}}\text{H}$ display much greater (relative) stability. The ylidions can be used to probe the stability of ylides using neutralization-reionization mass spectrometry.

Neutralization-reionization mass spectrometry (NRMS) is a technique developed recently by McLafferty and co-workers (Ref. 36) which is particularly attractive for studying reactive neutrals which have a stable parent molecular ion. The ylides and ylidions represent precisely such a situation.

The experiment begins by generating, necessarily indirectly, the ion ($\text{AB}^{+\cdot}$) of the neutral (AB) in which we are interested. The ion is then neutralized (to give AB) by charge exchange with a metal vapor of appropriate ionization potential. Finally, the neutral is reionized and characterized using collisionally activated dissociation (CAD). If the CAD spectrum which is observed coincides with that of the parent ion ($\text{AB}^{+\cdot}$), this demonstrates the stability of the neutral (AB) within the timescale ($\sim 10^{-6}$ sec.) of the NRMS experiment. If, on the other hand, AB is unstable and, for example, breaks up into A+B or rearranges, then the CAD spectrum that emerges will clearly not be characteristic of AB.

The questions we sought to answer (Ref. 32) were which simple ylides should be detectable in the NRMS experiment and which should not.

Figure 4 shows what happens in the case of CH_2PH_3 . The ylidion $\text{CH}_2\text{PH}_3^{+\cdot}$ (12) is quite a stable species and can be readily generated from an appropriate precursor. Vertical neutralization leads to the ylide CH_2PH_3 (15) with about 50 kJ mol^{-1} of excess energy.

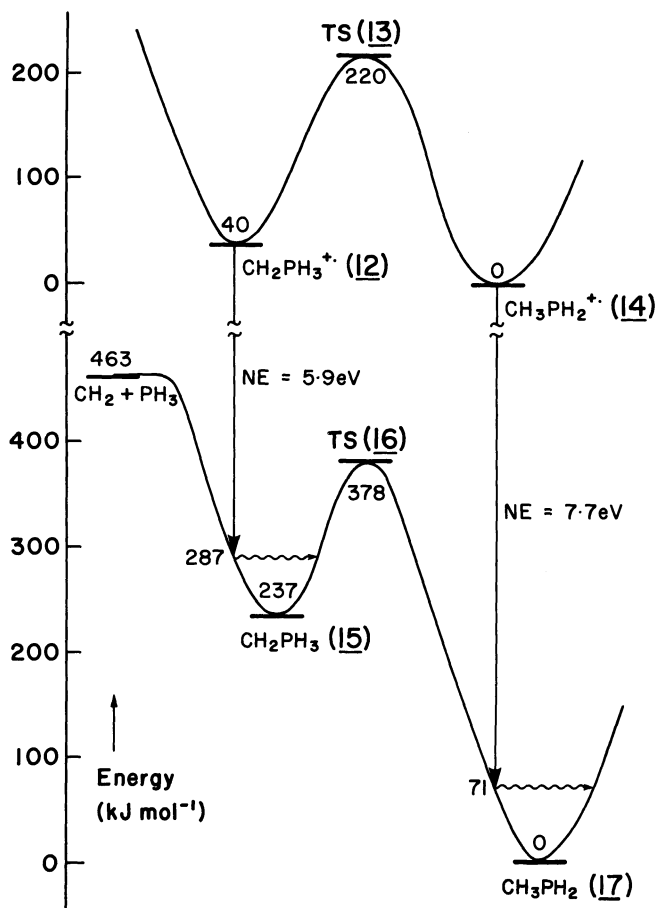


Fig. 4. Schematic potential energy profile showing the production of CH_2PH_3 (15) by vertical neutralization of CH_2PH_3^+ (12).

This is considerably below the barrier (141 kJ mol^{-1} at 16) to rearrangement to the classical isomer CH_3PH_2 (17) and so we would expect CH_2PH_3 to survive the NRMS experiment.

For CH_2SH_2 , the potential energy diagram (Ref. 32) shows that vertical neutralization of the methylenesulfonium radical cation (CH_2SH_2^+) yields CH_2SH_2 with an energy only a small amount below the barrier to rearrangement to methanethiol. In this case, we might expect that the CAD spectrum will contain contributions not only from CH_2SH_2 but from the rearrangement and perhaps dissociation products as well.

Finally, CH_2ClH is extremely weakly bound indeed. There is a binding energy of only $\sim 1 \text{ kJ mol}^{-1}$ with respect to $\text{CH}_2 + \text{HCl}$. It is predicted (Ref. 32) to fly apart when produced by vertical neutralization of CH_2ClH^+ and should not therefore be detectable by NRMS.

FURTHER GENERALIZATION: DISTONIC RADICAL CATIONS

A further extension of the ylidion concept arises from an examination of larger systems, for example $\text{C}_2\text{H}_6\text{O}^+$ (Ref. 37). Possible structural isomers and their calculated relative energies are displayed in Fig. 5.

The $\text{C}_2\text{H}_6\text{O}^+$ potential surface includes the experimentally well-known radical cations of ethanol (20) and dimethyl ether (22). Other isomers ($\text{CH}_2\text{CH}_2\text{OH}_2^+$ (18) and $\text{CH}_3\text{OHCH}_2^+$ (21)) have been experimentally observed more recently (Ref. 27,38). The calculations indicate that ethanol and dimethyl ether radical cations lie higher in energy than their ylidion isomers. Thus $\text{CH}_3\text{CH}_2\text{OH}^+$ (20) is higher in energy than $\text{CH}_3\text{CHOH}_2^+$ (19) by 26 kJ mol^{-1} while $\text{CH}_3\text{OCH}_3^+$ (22) is marginally higher than $\text{CH}_3\text{OHCH}_2^+$ (21), as we noted previously.

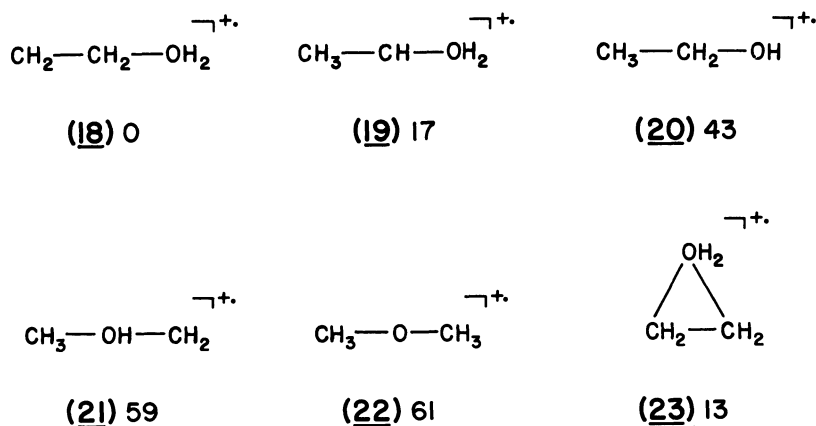


Fig. 5. Possible $\text{C}_2\text{H}_6\text{O}^+$ structural isomers (18-23) with calculated relative energies (kJ mol^{-1}).

The lowest energy isomer on the $\text{C}_2\text{H}_6\text{O}^+$ surface, namely $\dot{\text{C}}\text{H}_2\text{CH}_2\overset{\cdot}{\text{O}}\text{H}_2$ (18) (Ref. 39) is not an ylidion, i.e. it is not an ionized ylide. It corresponds to a species in which the charge and radical sites are on the oxygen and terminal carbon, not on adjacent sites as is required in an ylidion.

We have introduced (Ref. 32) the term distonic radical cation to describe the general class of radical cations in which the charge and radical centers are separated. Distonic comes from the Greek diestós ($\delta\iota\epsilon\sigma\tau\acute{\omega}\varsigma$) or the Latin distans meaning separate. Ylidions, such as $\text{CH}_2\overset{\cdot}{\text{O}}\text{H}_2$, are special cases of distonic radical cations in which the charge and radical centers are on adjacent atoms. The lowest energy $\text{C}_2\text{H}_6\text{O}^+$ isomer, the ethyleneoxonium ion ($\text{CH}_2\text{CH}_2\overset{\cdot}{\text{O}}\text{H}_2$) is an example of a more general distonic radical cation in which the charge and radical sites are on non-adjacent centers.

Many radical cations have several valence structures, one of which might have separated charge and radical sites. For example, formaldehyde radical cation can be written $\dot{\text{C}}\text{H}_2\text{---}\overset{\cdot}{\text{O}}$. Should this ion be regarded as distonic? We propose as a general rule that the term distonic be reserved for those radical cations which arise formally from ionization of neutral systems which are best written as zwitterions (or ylides in the case of adjacent charges). On this basis $\text{CH}_2\overset{\cdot}{\text{O}}$ (arising from $\text{CH}_2=\text{O}$) and $\text{CH}_2\text{CH}_2\overset{\cdot}{\text{O}}$ (arising from $\text{CH}_2=\text{CH}_2$) are not distonic radical cations whereas $\text{CH}_2\text{---}\overset{\cdot}{\text{O}}\text{H}_2$ (arising from $\text{CH}_2\text{---}\overset{\cdot}{\text{O}}\text{H}_2$) is.

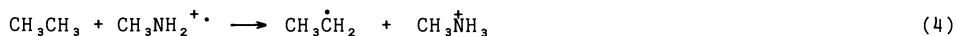
It is of interest to ask what is the effect of further separation of the charge and radical sites in distonic radical cations. We have approached this question (Ref. 40) by examining the series of ions $\text{CH}_2(\text{CH}_2)_n\overset{\cdot}{\text{O}}\text{H}_2$ (compared with the classical isomers $\text{CH}_3(\text{CH}_2)_n\overset{\cdot}{\text{O}}\text{H}_2^+$) and $\text{CH}_2(\text{CH}_2)_n\overset{\cdot}{\text{N}}\text{H}_3$ (compared with the classical isomers $\text{CH}_3(\text{CH}_2)_n\overset{\cdot}{\text{N}}\text{H}_2^+$). Relevant experimental observations among the larger distonic radical cations have been reported for $\text{CH}_2\text{CH}_2\text{CH}_2\overset{\cdot}{\text{O}}\text{H}_2$ (Ref. 41) and for $\text{CH}_2\text{CH}_2\text{CH}_2\overset{\cdot}{\text{N}}\text{H}_3$ (Ref. 35).

Some preliminary results of our calculations (MP2/6-31G* assuming additivity (Ref. 42) of basis set enhancement and electron correlation effects) for all trans conformations of the nitrogen series are displayed in Table 2.

It may be seen that the distonic radical cations ($\text{CH}_2(\text{CH}_2)_n\overset{\cdot}{\text{N}}\text{H}_3$) are consistently more stable than their classical isomers ($\text{CH}_3(\text{CH}_2)_n\overset{\cdot}{\text{N}}\text{H}_2^+$). The energy difference between the two forms appears to converge with increasing n towards a value which is related roughly to the energy of reaction (3):



or, rather better, to the energy of reaction (4):



Calculated values for these two reactions are respectively -76 and -42 kJ mol^{-1} .

TABLE 2. Calculated (MP2/6-31G*) relative energies (kJ mol⁻¹) for distonic radical cations and their classical isomers

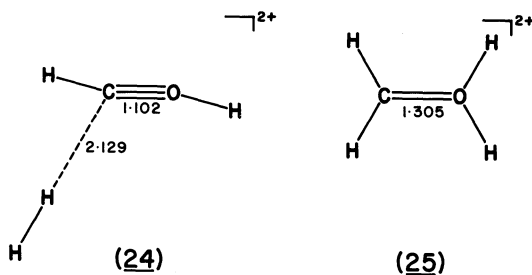
Classical	Distonic	E(classical)-E(distonic)
CH ₃ NH ₂ ^{+•}	$\dot{\text{C}}\text{H}_2\dot{\text{N}}\text{H}_3$	-13
CH ₃ CH ₂ NH ₂ ^{+•}	$\dot{\text{C}}\text{H}_2\text{CH}_2\dot{\text{N}}\text{H}_3$	-36
CH ₃ CH ₂ CH ₂ NH ₂ ^{+•}	$\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}_2\dot{\text{N}}\text{H}_3$	-32
CH ₃ CH ₂ CH ₂ CH ₂ NH ₂ ^{+•}	$\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}_2\text{CH}_2\dot{\text{N}}\text{H}_3$	-31

Recognition of this limiting behaviour provides a ready rationalization for the somewhat surprising stability of distonic radical cations. The stabilities of distonic (relative to classical) radical cations are dependent on the relative proton affinities and ionization potentials of the appropriate species (NH₃ or CH₃NH₂ in the above case). We would propose, as a general (and remarkably simple) rule that a distonic radical cation $\dot{\text{Y}}(\text{CH}_2)_n\dot{\text{X}}\text{H}$ will normally be more stable than its classical isomer $\text{HY}(\text{CH}_2)_n\text{X}^{\bullet+}$ if the pair $\text{CH}_3\dot{\text{Y}} + \text{CH}_3\dot{\text{X}}\text{H}$ (or, more approximately, $\text{HY} + \text{H}_2\dot{\text{X}}$) lie lower in energy than the pair $\text{CH}_3\text{YH} + \text{CH}_3\text{X}^{\bullet+}$ (more approximately $\text{H}_2\text{Y} + \text{HX}^{\bullet+}$). The rule will hold most faithfully when n is large. When n=0, there may be exceptions to the rule due to the superposition of a large short range interaction between the now adjacent groups. The very broad implications of such considerations will be discussed elsewhere.

THE EFFECT OF FURTHER IONIZATION: YLIDE DICATIONS

The final question which we wish to address concerns the effect of further ionization in ylide systems. We have just seen that single ionization reverses the stability of methanol and its ylide isomer, i.e. the methyleneoxonium radical cation is ~45 kJ mol⁻¹ lower in energy than methanol radical cation. What is the effect of an additional ionization? How do the methanol dication and the methyleneoxonium dication compare?

Our calculations (Ref. 43) do not reveal any stable structure for the (classical) methanol dication. Optimization yields a structure (24) which resembles a weak complex of HCOH^{2+} plus H₂. The methyleneoxonium dication (25), on the other hand, is perfectly well behaved. It is planar with a C-O bond length similar to the C=C double bond of ethylene. This is not really surprising since $\text{CH}_2\text{OH}_2^{2+}$ is isoelectronic with ethylene.



The calculated potential energy diagram displaying possible fragmentation reactions of $\text{CH}_2\text{OH}_2^{2+}$ (25) is shown in Fig. 6. Although fragmentation to $\text{CH}_2^{\bullet+} + \text{OH}_2^{\bullet+}$ or to $\text{CH}_2\text{OH}^+ + \text{H}^+$ is exothermic, there are large barriers (375 and 252 kJ mol⁻¹, respectively) for both of these processes, suggesting that $\text{CH}_2\text{OH}_2^{2+}$ should be an observable species.

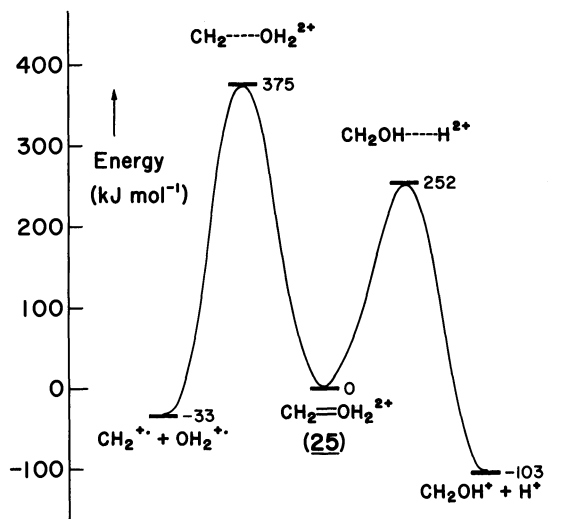


Fig. 6. Schematic potential energy profile for dissociative processes in the methylenexonium dication (25).

Indeed, $\text{CH}_2\text{OH}_2^{2+}$ has been recently observed (Ref. 44,45) in charge-stripping mass spectrometry experiments. Our calculations (Fig. 7) indicate that vertical ionization from

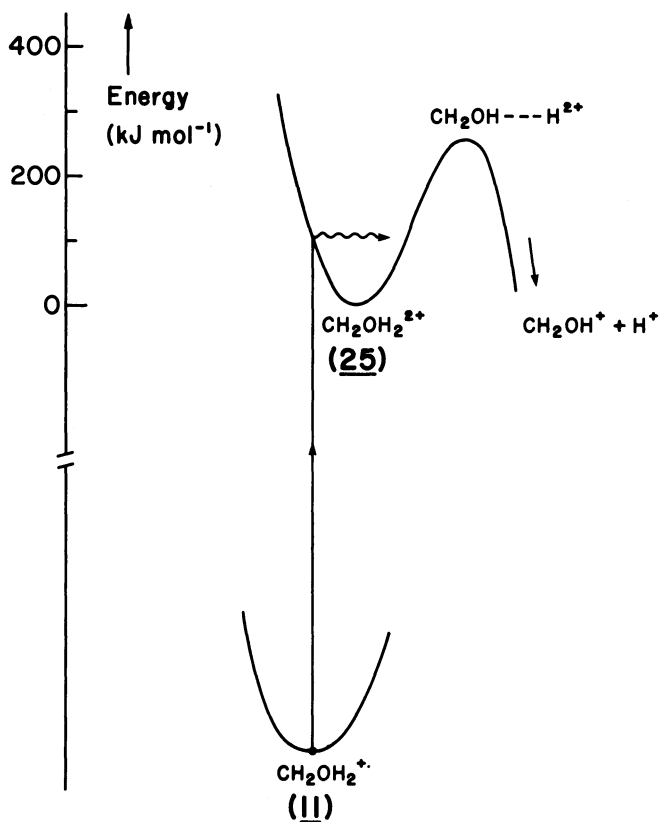


Fig. 7. Generation of methylenexonium dication (25) by charge stripping.

$\text{CH}_2\text{OH}_2^{+\cdot}$ radical cation (11) produces $\text{CH}_2\text{OH}_2^{2+}$ (25) with about 108 kJ mol^{-1} of excess energy. This is insufficient to surmount the barrier ($\sim 250 \text{ kJ mol}^{-1}$) to dissociation to $\text{CH}_2\text{OH}^+ + \text{H}^+$, and the observation of $\text{CH}_2\text{OH}_2^{2+}$ in the charge-stripping experiments is thus consistent with the theoretical data. As expected on the basis of the calculations, the charge-stripping experiments (Ref. 44,45) do not reveal any evidence for a methanol dication.

Similar calculations have been carried out for a variety of other ylide dications and their classical isomers (Ref. 46). The conclusions regarding the stability or instability of these species are summarized in Table 3.

TABLE 3. Characterization of stabilities of ylide dications and their classical isomers

Classical		Ylide Dication	
CH_3F^{2+}	unstable	$\text{CH}_2\text{FH}^{2+}$	stable
$\text{CH}_3\text{OH}^{2+}$	unstable	$\text{CH}_2\text{OH}_2^{2+}$	stable
$\text{CH}_3\text{NH}_2^{2+}$	unstable	$\text{CH}_2\text{NH}_3^{2+}$	stable
$\text{CH}_3\text{Cl}^{2+}$	unstable	$\text{CH}_2\text{ClH}^{2+}$	stable
$\text{CH}_3\text{SH}^{2+}$	marginal stability	$\text{CH}_2\text{SH}_2^{2+}$	stable
$\text{CH}_3\text{PH}_2^{2+}$	marginal stability	$\text{CH}_2\text{PH}_3^{2+}$	stable

The ylide dications are all stable with respect to dissociation and/or rearrangement processes. On the other hand, the classical dications are generally unstable, or at best marginally stable, i.e. show zero or near-zero barriers to decomposition.

Our calculations reveal a smooth progression in the relative stabilities of classical and ylide isomers with successive ionization. For example, in the case of neutral methanol and its ylide, the CH_3OH isomer is considerably lower in energy than CH_2OH_2 which exists only as a very weak complex. This stability ordering is reversed in the radical cations where nevertheless both isomers ($\text{CH}_3\text{OH}^{+\cdot}$ and $\text{CH}_2\text{OH}_2^{+\cdot}$) are reasonably stable and observable. Finally, for the dications the trend continues with $\text{CH}_2\text{OH}_2^{2+}$ being much more stable than $\text{CH}_3\text{OH}^{2+}$.

CONCLUDING REMARKS

Gas-phase ion chemistry is an area where the experiments and/or the interpretation of the experimental results are not always straightforward. Theory provides a powerful complementary approach and at times can guide and direct experimental research.

Theoretical calculations and mass spectrometric studies have shown that distonic radical cations, species in which the charge and radical sites are separated, often display special stability. The situation is exemplified by ylidyons (in which the charge and radical sites are on adjacent centers) which are often more stable than their classical isomers in contrast to the general instability of their neutral ylide parents.

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