Available online at www.sciencedirect.com

SCIENCE DIRECT®

International Journal of Mass Spectrometry 230 (2003) 77–83

www.elsevier.com/locate/ijms

Does the radical $Me_3O^{\bullet}$ exist in the gas phase? A joint experimental and theoretical study

Suresh Dua, Andrew M. McAnoy, Tom Blumenthal, John H. Bowie*

Department of Chemistry, The University of Adelaide, Adelaide, SA 5005, Australia

Received 3 February 2003; accepted 29 July 2003

Dedicated to Professor John H. Beynon FRS on the occasion of his 80th birthday. John Beynon is a highly respected colleague who has been an inspiration for almost half a century to the many scientists who use mass spectrometry in their particular disciplines, whether that be the chemical, physical, geological, environmental, biological or medical sciences

---

Abstract

A combination of experiment and theory indicate that when Me_3O^+ undergoes vertical Franck–Condon one-electron reduction, it does not produce a stable $Me_3O^{\bullet}$ species, but decomposes to give MeOMe and $Me^{\bullet}$. Theoretical calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-311G(d) level of theory indicate that the symmetrical radical $Me_3O^{\bullet}$ is not a stable species. However, there is a stable doublet neutral corresponding to a van der Waals complex MeOMe · · · Me, a species which requires only 4.5 kJ mol^{-1} of excess energy to cause decomposition to MeOMe and $Me^{\bullet}$.

Keywords: Complex; Decomposition; Energy

---

1. Prologue

The first time I met John Beynon was when I spent a period of sabbatical leave with him in 1979. Apart from John's excellence as a host and a scientist, and the presentation of both a Swansea Mass Spectrometry Research Unit tie and a Swansea Rugby Football Club pullover (my daughter wore the pullover throughout her teens), this stay raised two major matters, both of which have had a lasting influence on my career. The first was that there was more to ion chemistry than the 'organic' mass spectrometry that I had been involved with exclusively in the previous decade. There were senior scientists both part of the Mass Spectrometry Research Unit and also visiting, who had backgrounds ranging from medical and biological chemistry on the one hand right through the discipline spectrum to pure physics, and the interplay between those people and their various experiences, showed the direction in which mass spectrometry was to move i.e., development of new types of ionisation methods, together with the applied application of mass spectrometry across many scientific disciplines backed up by a knowledge of the fundamental chemistry and physics of ion processes. The second matter was that I needed to obtain funds to purchase a VG ZAB 2HF mass spectrometer. Our much modified VG ZAB 2HF is still functioning in 2003, maintained by my friend and colleague Tom Blumenthal. This following report follows on from some work reported by the Beynon group in 1987: it involves an experimental approach using the ZAB 2HF instrument together with theoretical potential surface calculations.

2. Introduction

Following a first year lecture (in mid-2002) on acids and bases, a lecture which involved a discussion of the structure of the hydronium cation, a student asked me whether the hydronium radical was stable, because she had difficulty in using the valence bond theory to rationalise the structure of this molecule. First year lectures often present interesting ideas which initiate research projects, and I immediately thought of John Beynon's work in 1987 where he and his colleagues had used neutralisation/reionisation of H_3O^+ to report the detection of $H_3O^{\bullet}$ with a lifetime of at least a

---

* Corresponding author. Tel.: +61-8-8303-5767; fax: +61-8-8303-4358.
E-mail address: john.bowie@adelaide.edu.au (J.H. Bowie).

1387-3806/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2003.07.003

$$\begin{aligned} H_3O^+ + e &\rightarrow H_2O + H \quad &&(\text{branching ratio, } 0.33)\\ &\rightarrow HO\cdot + H + H &&(0.48)\\ &\rightarrow HO\cdot + H_2 &&(0.18)\\ &\rightarrow O + H_2 + H &&(0.01)\end{aligned}$$

Scheme 1.

microsecond [1]. It was subsequently claimed that the interpretation of the results of this experiment was in error, and the neutral species formed in such low yield corresponding to *m*/*z* 19 was, in fact, the natural isotope HOD rather than $H_3O^\bullet$ [2]. My response to the student was that the hydronium radical is, at best, a transient species which could decompose to yield H_2O and $H^\bullet$. I left the lecture with the intention of finding out what the current knowledge is concerning the hydronium radical and associated systems.

Water is a molecule widely distributed amongst interstellar dust clouds, circumstellar envelopes and interstellar ice (including comets). It is intimately involved in the rate with which interstellar clouds compact to form star systems [3]. One of the ways in which water may be formed in interstellar clouds has long been considered to involve the reaction between H_3O^+ and an electron [4,5]. This reaction has recently been identified as one of four which occur in dissociation recombination of H_3O^+ [6,7]. The reactions are shown above in Scheme 1.

The Franck–Condon vertical one-electron reduction of H_3O^+ initially gives a neutral $H_3O^\bullet$ with precisely the same geometry as the cation, but is a species corresponding to $H_3O^\bullet$ a reactive intermediate in the reactions shown in Scheme 1? For example, in the reaction $H_3O^+ + e \rightarrow H_3O^\bullet \rightarrow H_2O + H$. The stability of the hydronium radical has engendered controversy for more than 30 years, with early work reported from the 1960s to the 1980s [8–14]. There have been many experimental [1,2,9–11,13,15–19] and theoretical studies [20–24] devoted to this system. There is still debate as to whether (i) a species $H_3O^\bullet$ has been observed experimentally, and (ii) if it is stable, what is its structure [1,2,9,10,15,16]. Following the report of the experimental detection of $H_3O^\bullet$ by Beynon and co-workers [1] (a result questioned by March and Young [2]), it was reported that $H_3O^\bullet$ cannot be detected when a fast beam of H_3O^+ ions is neutralised by charge transfer with Na, but the isotopic species $D_3O^\bullet$ is detectable under the same experimental conditions [16–18]. This means that the lifetime of $D_3O^\bullet$ is at least several microseconds. Further, a “solvated” species $D_3O^\bullet(D_2O)$ (structure not determined unequivocally) was also detected, whereas the lighter isotopic species $H_3O^\bullet(H_2O)$ was not detected under the same experimental conditions [19].

In a theoretical study, Ketvirtis and Simons [22] propose, (i) $H_3O^\bullet$ is an intermediate in the process $H_3O^+ + e \rightarrow H_2O + H$, (ii) $H_3O^\bullet$ is a species of C_{3v} geometry with an HO bond length of 1.018 Å [at the MP2(full)/6-311G(d,p) level of theory], and (iii) $H_3O^\bullet$ is formed from H_3O^+ with sufficient excess energy to effect dissociation to give H_2O and H (barrier 22.3 kJ mol^{-1} [22]; more recent reports [23,24] predict this barrier to be as low as 0.2 kJ mol^{-1}). In addition, Ketvirtis and Simons [22] suggest that the products of this reaction may recombine to give an intermediate which is the precursor of the $HO^\bullet$ radical (see sequences 2–3, Scheme 1). A weakly bound complex between and $HO^\bullet$ and H_2 may also have a bearing on the last observation [25].

The $H_3O^\bullet$ story is clearly not complete. Although extensive potential surface calculations have already been done for this system, the structure(s), stabilities and lifetimes of $H_3O^\bullet$ (and $D_3O^\bullet$) will need to be determined by further experimentation.

Similar deuterium isotope effects (to those reported for $H_3O^\bullet$ and $D_3O^\bullet$) are observed for analogous hypervalent radicals derived from methanol and dimethyl ether [26,27]. For example, the deuterated forms of the methyl and dimethyl oxonium radicals ($MeOD_2$ and Me_2OD) are readily detectable in $^+NR^+$ experiments, whereas $MeOH_2$ and Me_2OH are not [26,27]. Holmes and Sirois [27] and Turecek and Reid [28] (published after the submission of this paper) propose that the observation of the deuterated radical (at least in the case of Me_2OD) in preference to the H analogue, is a function of the occupancy of excited states of the metastable and hypervalent radical.

In this paper, we report the results of an investigation, both experimental and theoretical, to determine whether $Me_3O^\bullet$ is a detectable entity under similar neutralisation/reionisation conditions as those used initially for $H_3O^\bullet$ by Beynon and co-workers [1]. We have chosen this species because, (i) it is the carbon analogue of the system studied by Beynon and co-workers, and (ii) it does not have the problem of the primary deuterium isotope effects associated with analogous systems containing OH bonds (e.g., H_3O, $MeOH_2$ and Me_2OH).

3. Experimental

3.1. Mass spectrometric experiments

All experiments were performed with a VG ZAB 2HF two-sector mass spectrometer of BE configuration (B stands for magnetic and E for electric sector), which has been described previously [29]. In summary, Me_3O^+ was formed from $[(MeO)_3(MeOH)C]^+$ in the chemical ionisation (CI) source of the mass spectrometer by a known method [30–33]. The ions were accelerated to 7 keV translational energy and mass selected by means of the magnet. For collisional activation experiments [34], the ions were collided in the field-free regions between B and E with helium at 80% transmission (T) of the incident beam; these conditions approximate single-collision conditions [35].

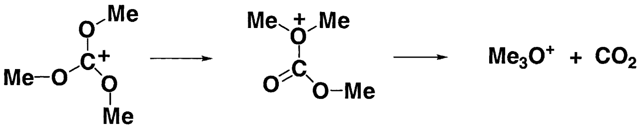
In neutralisation–reionisation experiments ($^+NR^+$) [36], the radical cations were neutralised by high-energy collisions with a mixture of benzene and molecular oxygen (ca. 1:1; 80% transmission of the ion beam) in the first of the two collision cells located in the field-free region between B and E. Unreacted ions were deflected away from the beam of neutral species by applying a voltage of 300 V on a deflector electrode located between the two collision chambers. Reionisation of the neutrals to cations occurred in the second cell by collision with benzene/oxygen (1:1; 80% transmission of main beam). The resulting mass spectra were recorded by scanning E. All spectra were recorded a minimum of three times in order to establish their reproducibility.

3.2. Precursor molecules

Tetramethoxy methane was a commercial sample (Aldrich). $(CD_3O)_4C$ was made by a reported procedure [37].

3.3. Theoretical methods

Geometry optimisations were carried out with the Becke 3LYP method [38,39] using the 6-311G(d) basis set within the GAUSSIAN 98 suite of programs [40]. Stationary points were characterised as minima (no imaginary frequencies) by calculation of the frequencies using analytical gradient procedures. The calculated frequencies were also used to determine zero-point vibrational energies which were then used as a zero-point correction for the electronic energies calculated at this and higher levels of theory. More accurate energies for the B3LYP geometries were determined using the CCSD(T) method [41–46] together with the Dunning aug-cc-pVDZ basis set [47,48]. All calculations were carried out on the Alpha server at the APAC National Facility (Canberra).



Scheme 2.

4. Results and discussion

4.1. The experimental evidence

The first problem was to find a suitable synthesis of the ion $Me_3O^{\bullet+}$. The most obvious way to make this species is by allowing dimethyl ether to react with the methyl cation. This has been achieved in an ion cyclotron resonance instrument [49], but this procedure is not appropriate to form abundant precursor species Me_3O^+ in the CI source of the VG ZAB instrument. The Me_3O^+ cation is a well studied species [30–33,48] which can also be formed by an interesting rearrangement process following dissociation of the MH^+ ion of tetramethoxy methane [30,32], as shown below. Interestingly, the corresponding species $(EtO)_3C^+$ formed from the MH^+ ion of tetraethoxy methane yields $(HO)_3C^+$ by three successive C_2H_4 eliminations: no Et_3O^+ is formed [50].

$$[(MeO)_4C]H^+ \rightarrow (MeO)_3C^+ + MeOH, \text{ then}$$

$$(MeO)_3C^+ \rightarrow Me_3O^+ + CO_2$$

The CID mass spectrum of $(MeO)_3C^+$ is shown in Fig. 1. This spectrum is different in detail from that reported previously [32]. Although Me_3O^+ (*m/z* 61) is a major fragment ion, other ions are also formed. These are identified in Fig. 1. The mechanism proposed for the formation of Me_3O^+ is shown in Scheme 2. This reaction sequence has been investigated by reaction coordinate calculations [32]. The first

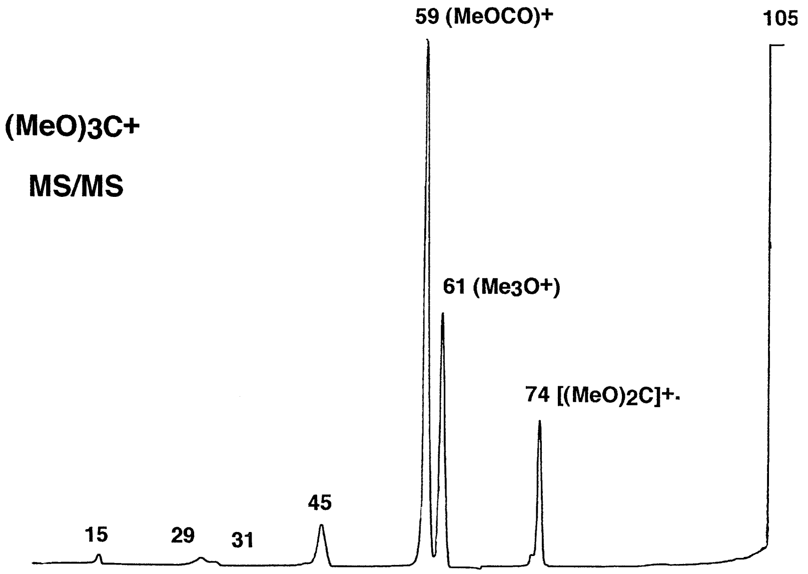


Fig. 1. Collision-induced mass spectrum (MS/MS) of $(MeO)_3C^+$. VG ZAB 2HF instrument. For experimental details see Section 3.

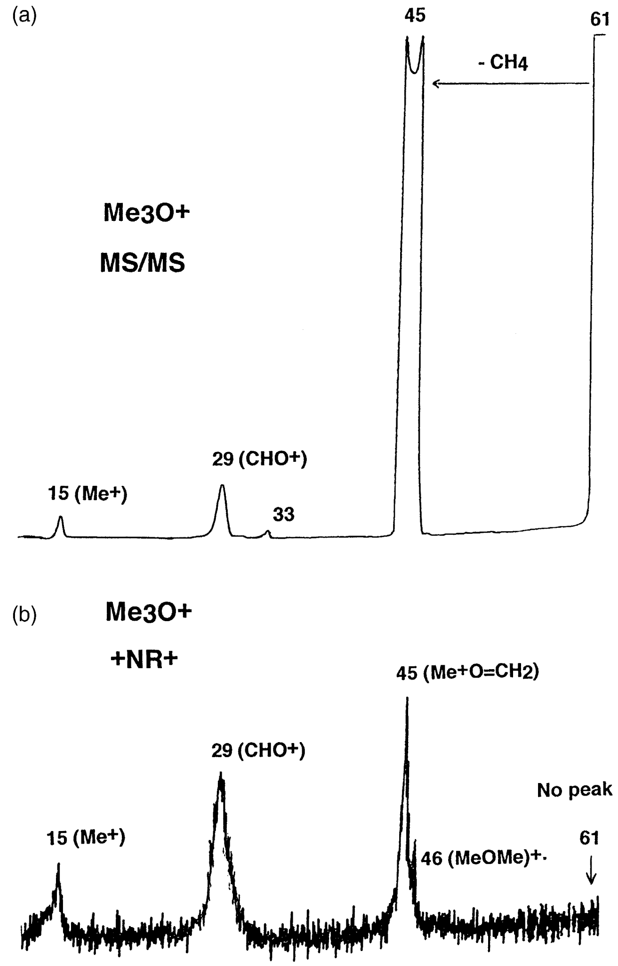


Fig. 2. (A) Collision-induced mass spectrum (MS/MS) of Me_3O^+. (B) $^+NR^+$ spectrum of Me_3O^+. VG ZAB 2HF instrument. For experimental conditions see Section 3.

step has the larger barrier (213 kJ mol^{-1}) with the overall process being endothermic by 109 kJ mol^{-1} (at the modest AM1 level of theory).

The CID mass spectrum (MS/MS) and the $^+NR^+$ spectrum of Me_3O^+ are shown in Fig. 2A and B. The loss of methane is the major decomposition in the CID mass spectrum (Fig. 2A). This four centre reaction has been studied previously [30,31]. The reaction occurs to form $CH_3{-}^+O{=}CH_2$ without hydrogen scrambling to give the broad dish-shaped peak at *m/z* 45. The $^+NR^+$ spectrum (Fig. 2B) is different from the CID mass spectrum. The $^+NR^+$ spectrum of Me_3O^+ is a composite spectrum resulting from ionisation of all neutrals (formed following vertical one-electron reduction of Me_3O^+ in the first collision cell) that have proceeded to, and are ionised in the second collision cell, together with any product cations resulting from the decomposition of these ionised species. We had some difficulty obtaining this spectrum and found the best collision gas system was benzene/oxygen (1:1). Even so, the spectrum is unusually weak and the baseline noisy as a consequence. There is no observable peak at *m/z* 61 corresponding to ionised $Me_3O^\bullet$ in this $^+NR^+$ spectrum. Since the spectrum is noisy, we scanned manually through the *m/z* 61 region on a number of occasions but were unable to detect any peak. We conclude (i) that $Me_3O^\bullet$ is not stable under NR conditions, and (ii) if $Me_3O^\bullet$ is "stable", then it has a lifetime of less than a microsecond.

Table 1
CID mass spectra of $(CD_3O)_3O^+$ and $(CD_3)_3O^+$ and the $^+NR^+$ spectrum of $(CD_3)_3O^+$

CID $(CD_3O)_3O^+$ [from $(CD_3O)_4O^{\bullet+}$]: fragment ions; [*m/z* (loss or formation) relative abundance]; 80 ($CD_3O^\bullet$) 15; 70 (CO_2) 100; 62 (CD_3OCD_3) 86; 50 ($CD_3{-}O^+{=}CD_2$) 8; 34 ($CD_2{=}^+OD$) 1; 30 (CDO^+) 2; 18 (CD_3^+) 2.

CID $(CD_3)_3O^+$ [from $(CD_3O)_3O^+$]: fragment ions; [*m/z* (loss or formation) relative abundance]; 50 (CD_4) 100; 30 (CDO^+) 6; 18 (CD_3^+) 3.

$^+NR^+$ $(CD_3)_3O^+$ (weak spectrum, abundances correct to ±5%): [*m/z* (formation) abundance]; 70 (no peak); 52 ($CD_3OCD_3^{\bullet+}$) 15; 50 ($CD_3O^+{=}CD_2$) 100; 30 (CDO^+) 45; 18 (CD_3^+) 20.

It is likely that the peaks at *m/z* 46 and 15 in the $^+NR^+$ spectrum are due to ionisation of the products of the decomposition $Me_3O^\bullet \rightarrow MeOMe + Me^\bullet$. The major peak at *m/z* 45 ($CH_3{}^+O{=}CH_2$) is almost certainly formed by loss of H from $[MeOMe]^{\bullet+}$ [51], and *m/z* 29 (CHO^+) is likely to be formed by decomposition of *m/z* 45 [1]. We propose that the peaks observed in the $^+NR^+$ spectrum are best explained by ionisation of the neutrals formed following decomposition of $Me_3O^\bullet$ to MeOMe and Me.

We have also measured the CID and $^+NR^+$ spectra of the deuterated species $(CD_3)_3O^+$ (formed by loss of CO_2 from $(CD_3O)_3C^+$ (cf. Scheme 2)). The spectra are listed in Table 1, and are directly analogous to those of Me_3O^+ (Fig. 2). The $^+NR^+$ spectrum is again noisy, but there is no recovery signal. Thus, there is no significant secondary deuterium isotope effect operating during the vertical one-electron reduction $(CD_3)_3O^+ + e \rightarrow CD_3OCD_3 + CD_3^\bullet$.

4.2. The theoretical evidence

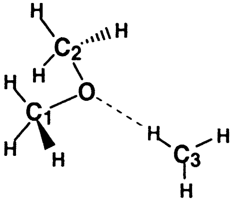
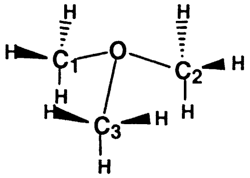
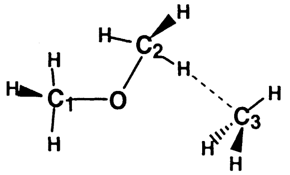
Calculations at the B3LYP/6-311G(d) level of energy indicate that symmetrical $Me_3O^\bullet$ does not occupy a minimum on the doublet radical potential surface. However, there is a neutral species of this atomic composition which occupies a minimum on the surface; this corresponds to H bonded **A** (Scheme 3), where the O···H distance is 2.44 Å at this level of theory. Details of the geometry [B3LYP/6-311G(d)] and energy [CCSD(T)/aug-cc-pVDZ//B3LYP/6-311G(d)] of this species are listed in Table 2.

The situation concerning the cation potential surface is more complex because there are stable singlet and triplet

---

[1] The CID mass spectrum of $Me^+O{=}CH_2$ (a source formed ion from Me_3O^+) was measured with the ZAB 2HF instrument using the same experimental conditions as those used for Me_3O^+. The CID mass spectrum (MS/MS) for $Me^+O{=}CH_2$ is as follows:—*m/z* (relative abundance)—45 (parent, 100%), 44 (75), 43 (18), 42 (5), 41 (1), 40 (0.1), 30 (15), 29 (97, CHO^+), 15 (5), 14 (1), 13 (0.2).

Table 2
Selected properties of optimised B3LYP/6-311G(d) geometries[a,b]

 neutral **A**, 0.0 kJ mol^{-1}		 cation **B**, 583 kJ mol^{-1}		 cation **C**, 933 kJ mol^{-1}	
Neutral (C_s)		Singlet cation (C_{3V})		Triplet cation (C_1)	
C_1O, C_2O (Å)	1.411	C_1O, C_2O, C_3O (Å)	1.483	C_1O (Å)	1.409
OH	2.436	C_1OC_2, C_2OC_3 (°)	114.5	C_2O	1.404
HC_3	1.082	$C_1OC_2C_3$ (°)	−135.2	C_2H	1.116
C_1OC_2 (°)	112.7			HC_3	2.466
C_1OH	113.9			C_1OC_2 (°)	121.9
OHC_3	177.2			OC_2H	104.7
C_1OC_2H	−137.7			C_2HC_3	172.9
C_1OHC_3	65.6			C_1OC_2H	−115.9

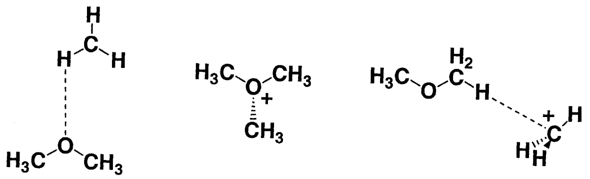
[a] Full geometries are given in the form of standard orientations in Appendix A.

[b] Relative energies (in kJ mol^{-1}) calculated at CCSD(T)/aug-cc-pVDZ//B3LYP/6-311G(d) level of theory and include zero-point correction. A reviewer has indicated that this basis set is not satisfactory for hypervalent radicals of this type as it does not include diffuse functions (cf. [28]). We have, therefore, reoptimised $Me_3O^{\bullet}$ and neutral complex **A** at the B3LYP/6-311++G(d) level of theory and find no significant differences when comparing the results of the two levels of theory. $Me_3O^{\bullet}$ is not stable at either level of theory, while the only difference in the structure of **A** at the two levels (of theory) involves the relative orientation of $Me^{\bullet}$ towards Me_2O. Neutral **A** [B3LYP/6-311++G(d) level of theory]: C_1O, C_2O 1.412 Å; OH 2.436; C_3H 1.082; C_1OC_2 112.9°; C_1OH 123.3; OHC_3 179.5; C_1OC_2H −172.4; C_1OHC_3 85.8.

forms of the even-electron cation. The singlet ground state corresponds to symmetrical **B** (Scheme 3), while the triplet form is a hydrogen bonded complex **C** with a C···H distance of 2.46 Å. Details of the geometries and energies of these species are given in Table 2.

Our interpretation of the $^{+}$NR^{+} spectrum is that one-electron reduction of Me_3O^+ results in the formation of MeOMe and $Me^{\bullet}$. Calculations indicate that the reaction **A** → MeOMe and $Me^{\bullet}$ is endothermic by only 4.5 kJ mol^{-1} at the level of theory used in this study. These data explain why a recovery signal is not observed in the $^{+}$NR^{+} experiment.

Let us now consider the vertical Franck–Condon reductions of the singlet and triplet cations **B** and **C**. The data are summarised in Fig. 3a and b. If the energy of neutral doublet **A** is set as 0 kJ mol^{-1}, the relative energies of the singlet cation **B** and triplet cation **C** are +582 and +933 kJ mol^{-1}, respectively. The energies of the neutrals with the geometries **B** and **C** on the doublet neutral surface are +262 and +44.5 kJ mol^{-1}, respectively. Therefore, we can construct the diagrams shown in Fig. 3. The synthetic procedure by which Me_3O^+ is made is likely to form the singlet cation and the one-electron reduction of that singlet cation will result in decomposition. The likelihood of the formation of any triplet cations is small, but even in such a case, the excess Franck–Condon energy of the neutral (+44.5 kJ mol^{-1}) is sufficient to effect dissociation to MeOMe and Me.



Scheme 3.

We conclude that even though there is a neutral **A** which occupies a minimum on the doublet neutral surface, the excess energy produced as a consequence of the vertical reduction in the NR experiment is sufficient to cause decomposition of this species. Experiment and theory are in accord. No neutral species $Me_3O^{\bullet}$ are detected following vertical one-electron reduction of Me_3O^+.

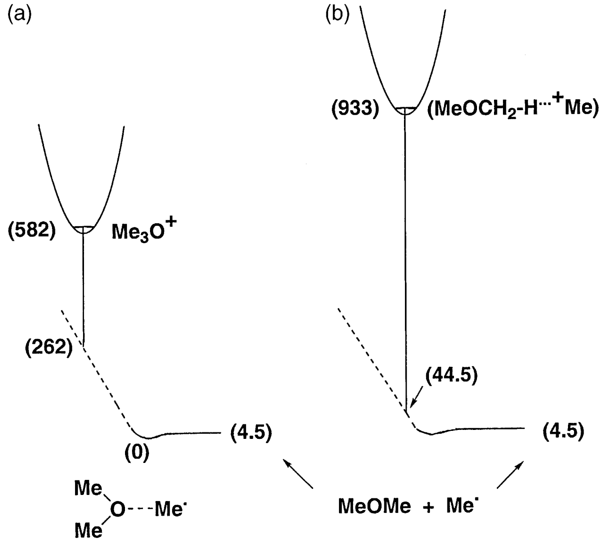


Fig. 3. Pictorial representation of Franck–Condon vertical reduction of (a) singlet Me_3O^+, and (b) triplet MeOMe···$^{+}$Me. Relative energies in kJ mol^{-1}.

Acknowledgements

We thank the Australian Research Council for continuing financial support of our ion chemistry programme. One of us (S.D.) thanks the A.R.C. for a research associateship. We acknowledge a generous allocation of time on the Alpha server of the APAC National Facility (Canberra).

Appendix A. Full details of structures A, B and C

Standard orientations of B3LYP/6-311G(d) stationary points. Energies are calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-311G(d) level of theory and include (scaled) zero-point correction.

$(CH_3)_2O–CH_3$ neutral

State	${}^2A''$
Symmetry	C_s
Energy	−194.261601

Atomic no.	*x*	*y*	*z*
6	1.603543	−2.467369	0.000000
8	0.000000	0.663034	0.000000
6	−0.739824	0.917857	1.174436
6	−0.739824	0.917857	−1.174436
1	2.680775	−2.564393	0.000000
1	0.992570	−3.360090	0.000000
1	1.143270	−1.488246	0.000000
1	−0.092737	0.687797	−2.020856
1	−1.046848	1.971888	−1.235070
1	−1.640405	0.289506	−1.231199
1	−0.092737	0.687797	2.020856
1	−1.046848	1.971888	1.235070
1	−1.640405	0.289506	1.231199

$(CH_3)_2O^+$ singlet cation

State	${}^1A_1$
Symmetry	C_3V
Energy	−194.039678

Atomic no.	*x*	*y*	*z*
8	0.000000	0.000000	−0.288138
6	0.000000	1.440207	0.064657
6	−1.247256	−0.720104	0.064657
6	1.247256	−0.720104	0.064657
1	0.000000	1.539676	1.149599
1	0.893346	1.862996	−0.384587
1	−0.893346	1.862996	−0.384587
1	−1.333399	−0.769838	1.149599
1	−2.060075	−0.157838	−0.384587
1	−1.166729	−1.705158	−0.384587
1	1.333399	−0.769838	1.149599
1	1.166729	−1.705158	−0.384587
1	2.060075	−0.157838	−0.384587

$[CH_3OCH_3–CH_3]^+$ triplet cation

State	–
Symmetry	C_1
Energy	−193.906078

Atomic no.	*x*	*y*	*z*
8	0.964393	0.024527	−0.480456
6	0.222171	1.042641	0.138412
6	1.992685	−0.662602	0.195591
6	−3.047013	−0.402841	0.027406
1	2.903268	−0.488981	−0.403837
1	2.101476	−0.349487	1.231173
1	1.769287	−1.733000	0.073065
1	−3.527073	0.557960	0.165662
1	−2.963794	−0.806932	−0.973592
1	−2.965616	−1.073006	0.873871
1	−0.821118	0.648342	0.176960
1	0.606935	1.316664	1.118070
1	0.174439	1.869036	−0.586175

CH_3OCH_3

State	${}^1A_1$
Symmetry	C_s
Energy	−154.565017

Atomic no.	*x*	*y*	*z*
6	0.000000	1.172040	−0.194918
8	0.000000	0.000000	0.588213
6	0.000000	−1.172040	−0.194918
1	0.000000	−2.020019	0.490538
1	0.891548	−1.232353	−0.836940
1	−0.891548	−1.232353	−0.836940
1	0.000000	2.020019	0.490538
1	−0.891548	1.232353	−0.836940
1	0.891548	1.232353	−0.836940

CH_3

State	${}^2A_2''$
Symmetry	D_3H
Energy	−39.694842

Atomic no.	*x*	*y*	*z*
6	0.000000	0.000011	0.000000
1	0.936000	0.540400	0.000000
1	0.000000	−1.080800	0.000000
1	−0.936000	0.540400	0.000000

References

[1] W.J. Griffiths, F.M. Harris, J.H. Beynon, Int. J. Mass Spectrom. Ion Process. 77 (1987) 77.
[2] R.E. March, A.B. Young, Int. J. Mass Spectrom. Ion Process. 85 (1988) 237.
[3] T.R. Geballe, T. Oka, Nature 384 (1996) 334.
[4] E.F. Van Dishoeck, in: T.W. Hartquist (Ed.), Molecular Astrophysics, Cambridge University Press, Cambridge, UK, 1990, p. 55;
T.J. Miller, in: T.W. Hartquist (Ed.), Molecular Astrophysics, Cambridge University Press, Cambridge, UK, 1990, p. 115;
D.R. Bates, in: T.W. Hartquist (Ed.), Molecular Astrophysics, Cambridge University Press, Cambridge, UK, 1990, p. 211.
[5] D.A. Neufeld, S. Lepp, G.J. Melnick, Astrophys. J. Suppl. Ser. 100 (1995) 132.
[6] L.H. Andersen, O. Heber, D. Kella, H.B. Pedersen, H.T. Schmidt, D. Zajfman, Phys. Rev. Lett. 77 (1996) 4891.
[7] L. Vejby-Christensen, L.H. Andersen, O. Heber, D. Kella, H.B. Pedersen, H.T. Schmidt, D. Zajfman, Astrophys. J. 483 (1997) 531.
[8] H.J. Bernstein, J. Am. Chem. Soc. 85 (1963) 484.
[9] C.E. Melton, H.W. Joy, J. Chem. Phys. 46 (1967) 4275.
[10] C.E. Melton, H.W. Joy, J. Chem. Phys. 48 (1967) 5286.
[11] T.W. Martin, L.L. Swift, J. Am. Chem. Soc. 93 (1971) 2788.
[12] J.A. Wargon, F. Williams, Chem. Phys. Lett. 13 (1972) 579.
[13] S. Noda, H. Yoshida, L. Kevan, Chem. Phys. Lett. 19 (1973) 240.
[14] T.A. Claxton, I.S. Ginns, M.J. Godfrey, K.V.S. Rao, M.C.R. Simons, J. Chem. Soc. Faraday Trans. 2 (69) (1973) 217.
[15] B.W. Williams, R.F. Porter, J. Chem. Phys. 73 (1980) 5598.
[16] G.I. Gellene, R.F. Porter, J. Chem. Phys. 77 (1984) 6680, and references therein.
[17] S.-J. Jeon, A.B. Raksit, G.I. Gellene, R.F. Porter, J. Am. Chem. Soc. 107 (1985) 4129.
[18] A.B. Raksit, R.F. Porter, Int. J. Mass Spectrom. Ion Process. 76 (1987) 299.
[19] D.M. Hudgins, R.F. Porter, Int. J. Mass Spectrom. Ion Process. 130 (1994) 49.
[20] D. Talbi, R.P. Saxon, J. Chem. Phys. 91 (1989) 2376.
[21] P.W. McLoughlin, G.I. Gellene, J. Phys. Chem. 96 (1992) 4396.
[22] A.E. Ketvirtis, J. Simons, J. Phys. Chem. 103 (1999) 6552.
[23] H. Tachikawa, Phys. Chem. Chem. Phys. 2 (2000) 4327, and references therein.
[24] H. Tachikawa, T. Yamano, Chem. Phys. Lett. 335 (2001) 305.
[25] R.A. Loomis, M.I. Lester, J. Chem. Phys. 103 (1995) 4371.
[26] J.L. Holmes, Mass Spectrom. Rev. 8 (1989) 513, and references therein.
[27] J.L. Holmes, M. Sirois, Org. Mass Spectrom. 25 (1990) 481.
[28] F. Turecek, P.H. Reid, Int. J. Mass Spectrom. 222 (2003) 49, and references therein.
[29] M.B. Stringer, J.H. Bowie, J.L. Holmes, J. Am. Chem. Soc. 108 (1986) 3888.
[30] D. Farcasiu, R.C. Pancirov, Int. J. Mass Spectrom. Ion Process. 74 (1986) 207.
[31] D. Wang, R.R. Squires, D. Farcasiu, Int. J. Mass Spectrom. Ion Process. 107 (1991) R7.
[32] V. Nguyen, H.E. Audier, A. Milliet, P. Mourgues, Rapid Commun. Mass Spectrom. 9 (1995) 1185.
[33] M.T. Nguyen, G. Bouchoux, J. Phys. Chem. 100 (1996) 2089.
[34] K.L. Busch, G.L. Glish, S.A. McLuckey, Mass Spectrometry/Mass Spectrometry: Techniques and Applications of Tandem Mass Spectrometry, VCH Publishers, Weinheim, 1988.
[35] J.L. Holmes, Org. Mass Spectrom. 20 (1985) 169.
[36] For a recent review which contains a discussion of NR nomenclature, see C.A. Schalley, G. Hornung, D. Schröder, H. Schwarz, Chem. Soc. Rev. 27 (1998) 91.
[37] S. Sakai, M. Kominami, K. Chonan, T. Enomoto, T. Fujinami, Synthesis (1984) 233.
[38] A.D. Becke, J. Phys. Chem. 98 (1993) 5648.
[39] P.J. Stevens, F.J. Devlin, C.F. Chablowski, M.J. Frisch, J. Phys. Chem. 98 (1994) 11623.
[40] M.J. Frisch, G.M. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennuchi, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Pedersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B. Stefanov, G. Liu, M.A. Al-Latam, C.Y. Peng, A. Nanayakkara, M. Chalacombe, P.M.W. Gill, B. Johnson, W. Chem, M.W. Wong, J.L. Andres, C. Gonzales, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98, Revision A.9 ed., Gaussian Inc., Pittsburgh, PA, 1998.
[41] J. Cizek, Adv. Chem. Phys. 14 (1969) 35.
[42] K. Raghavachari, G.W. Trucks, J.A. Pople, M. Head-Gordon, Chem. Phys. Lett. 157 (1989) 479.
[43] C. Hampel, K. Peterson, H.-J. Werner, J. Chem. Phys. 190 (1992) 1.
[44] J.D. Watts, J. Gauss, R.J. Bartlett, J. Chem. Phys. 98 (1993) 8718.
[45] P.J. Knowles, C. Hampel, H.-J. Werner, J. Chem. Phys. 99 (1993) 5219.
[46] M.J.O. Deegan, P.J. Knowles, J. Chem. Phys. Lett. 227 (1994) 321.
[47] T.H. Dunning, J. Chem. Phys. 90 (1989) 1007.
[48] D.E. Woon, T.H. Dunning, J. Chem. Phys. 98 (1993) 1358.
[49] T.D. Fridgen, T.B. McMahon, J. Am. Chem. Soc. 123 (2001) 3980.
[50] P. Gerbaux, F. Turecek, J. Phys. Chem. 106 (2002) 5938.
[51] A.G. Harrison, A. Ivko, D. VanRaalte, Can. J. Chem. 44 (1966) 1625.