Reappraisal of the spin-forbidden unimolecular decay of the methoxy cation†

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The mechanism of the unimolecular loss of H_2 from triplet methoxy cations ($^3CH_3O^+$) is revised.

The mental representation of chemical reactions relies on the paradigm of the potential energy surface (PES): the reactive system moves from the reactant minimum of the PES through a transition state to the product minimum. Reactions which involve a change in total spin appear to violate this paradigm, since they must necessarily occur on two or more PESs. For this reason, they have been difficult to understand, both qualitatively and quantitatively.[1] A typical example which has been the subject of numerous studies[2] is the unimolecular decomposition of triplet methoxy cation ($^3CH_3O^+$) to form H_2 and formyl cation (HCO^+), both singlet species. The present consensus (path A) is that this process occurs in a *stepwise* manner, *i.e.* first

$$^3CH_3O^+ \rightarrow {}^1CH_2OH^+ \rightarrow {}^1HCO^+ + H_2 \qquad \text{Path A}$$

$$^3CH_3O^+ \rightarrow {}^1HCO^+ + {}^1H_2 \qquad \text{Path B}$$
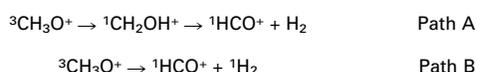
hydrogen shift, concurrent with spin change, to form *singlet* hydroxymethyl cation ($^1CH_2OH^+$), then the well documented[3] [1,2]-elimination to yield HCO^+ and H_2. The main support for this mechanistic scheme is derived from the observation of almost identical kinetic energy releases associated with the losses of molecular hydrogen from both $[C,H_3,O]^+$ cations.[2e] However, neither this experimental nor the computational evidence are conclusive. Indeed, a *concerted* pathway (path B) involving simultaneous spin change and [1,1]-elimination from $^3CH_3O^+$ has been suggested, but not established.[2f] Here we present experimental results[4–6] for the H/D isotope effect on unimolecular hydrogen loss from $[C,H_2,D,O]^+$ isotopomers of the methoxy and hydroxymethyl cations,[7] and discuss the mechanistic implications on the basis of supporting computational results in order to clear up the long-standing questions concerning the unimolecular decay of methoxy cation.

Assuming that only the *stepwise* mechanism occurs, Scheme 1 implies that the observed kinetic isotope effect KIE_{obs} for loss of molecular hydrogen from $^3CH_2DO^+$ is expected to be smaller than the kinetic isotope effect for loss of hydrogen from the intermediate $CHDOH^+$ (KIE_2), *whatever* the actual values of KIE_1 and KIE_2.[8] Assuming that KIE_2 does not depend much on the way in which $CHDOH^+$ is formed,[9] it can be obtained from the decay of independently generated $CHDOH^+$ cations. The relevant metastable ion (MI) spectra[4] (Fig. 1) lead to $KIE_{obs} = 8.0 \pm 1.0$ and $KIE_2 = 1.3 \pm 0.1$, respectively.[10] This value of KIE_{obs} is inconsistent with the above analysis, therefore
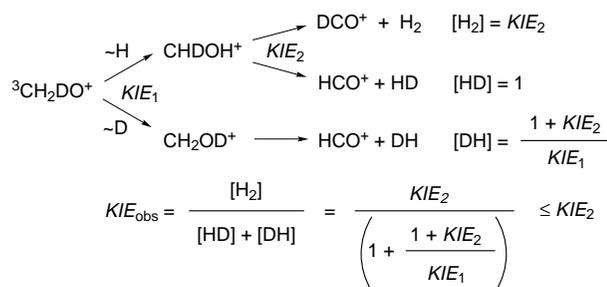
Scheme 1 (diagram):
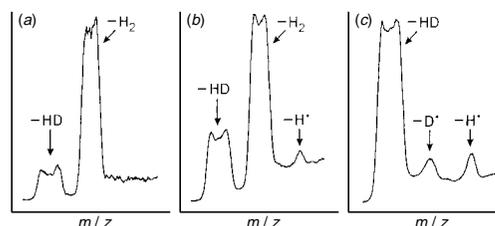
$$^3CH_2DO^+ \xrightarrow[KIE_1]{\sim H} CHDOH^+ \xrightarrow{KIE_2} \begin{array}{l} DCO^+ + H_2 \quad [H_2] = KIE_2 \\ HCO^+ + HD \quad [HD] = 1 \end{array}$$

$$^3CH_2DO^+ \xrightarrow[KIE_1]{\sim D} CH_2OD^+ \rightarrow HCO^+ + DH \quad [DH] = \dfrac{1 + KIE_2}{KIE_1}$$

$$KIE_{obs} = \frac{[H_2]}{[HD] + [DH]} = \frac{KIE_2}{\left(1 + \dfrac{1 + KIE_2}{KIE_1}\right)} \leq KIE_2$$

Scheme 1

the stepwise path A alone cannot account for the experimental findings. Other mechanisms must strongly contribute; an obvious candidate is the *concerted* pathway B which could well have a kinetic isotope effect larger than KIE_2.

Further evidence comes from eqns. (1) and (2) for the relative yields of ideal *stepwise* and *concerted* mechanisms, respectively.[11] The experimental kinetic isotope effect for HD *vs.*

$$[HD] = 0.5 \left([H_2] + [D_2]\right) \qquad (1)$$

$$[HD] = \sqrt{[H_2] \cdot [D_2]} \qquad (2)$$

D_2 loss from $^3CHD_2O^+$ cations[2e] is 10 ± 2, which, together with a kinetic isotope effect of 8.0 for H_2 *vs.* HD loss from $^3CH_2DO^+$, gives a branching ratio of $[H_2]:[HD]:[D_2] = 100:12.5:1.25$. Based on the measured $[H_2]$ and $[D_2]$ abundances, eqns. (1) and (2) predict [HD] values of 51 and 11 for *stepwise* and *concerted* pathways, respectively. Within the error margins, the observed [HD] figure of 12.5 is identical with the latter value, again suggesting that dehydrogenation of methoxy cation occurs in a concerted manner.

The $[C,H_3,O]^+$ hypersurfaces have been the subject of several computational studies.[2,3] The key events in the present reactions are, however, the spin changes, which can be assumed to proceed through surface hopping in the vicinity of the minimum energy crossing points (MECPs) between the PESs of different spin. Any computational description of unimolecular reactivity must therefore also consider the MECPs for paths A and B. This can be done with several methods which use analytical energy gradients.[1,12] The MECP corresponding to the *concerted* pathway (MECP1) has been described in the literature,[2f] but not that for the hydrogen migration in the *stepwise* route (MECP2).

Table 1 and Fig. 2 show the calculated[14] PESs for singlet and triplet $[C,H_3,O]^+$, including both MECPs. The key point is that MECP1 is slightly lower than MECP2 at each of the three levels of theory considered, although the relative energies of the two MECPs compared to $^3CH_3O^+$ vary somewhat. Further, the surface-hopping probability at the MECPs depends strongly on the spin-orbit coupling constant H^{SO} between the two wavefunctions. In fact, if the values of H^{SO} were very different at MECP1 and MECP2, the pathway with the larger H^{SO} could dominate, whatever the energies. To evaluate this possibility, we calculated[16] the value of H^{SO} at both MECPs, and obtained similar results, $50\ \text{cm}^{-1}$ for H^{SO} (MECP1) and $56\ \text{cm}^{-1}$ for H^{SO} (MECP2). With the present energies and H^{SO} values for MECP1 and MECP2, it is thus reasonable to expect that the

Fig. 1 MI spectra of (*a*) $^3CH_2DO^+$, (*b*) $CHDOH^+$ and (*c*) CH_2OD^+. Note that weak H/D atom losses are observed for the hydroxymethyl cations, which can be distinguished from H_2 loss by their peak shapes.

Table 1 Calculated (ref. 14) energies relative to $^3CH_3O^+$ at different points on the $[CH_3O^+]$ PESs, based on total energies[a] with no zero-point energy corrections

Species	UMP2	B3LYP	CCSD(T)	G2[b]
$HCO^+ + H_2$	−65.1	−38.4	−51.8	−54.5
CH_2OH^+	−92.4	−76.5	−85.6	−88.3
TS for H_2 loss	−6.4	11.7	2.5	−0.5
MECP1[c]	11.6	17.6	13.2	—
MECP2[c]	13.7	19.4	14.3	—

[a] Total energies (in Hartrees) for methoxy cation are −114.37456 (UMP2/BSI), −114.70013 (B3LYP/BSI), −114.47930 (CCSD(T)/BSII//B3LYP/BSI) and −114.50621 (G2). [b] G2 total energies are taken for comparison from ref. 13. [c] The calculated geometries for each MECP are very similar at all levels. The results for MECP1 reported in ref. 2(f) are similar to those obtained here.
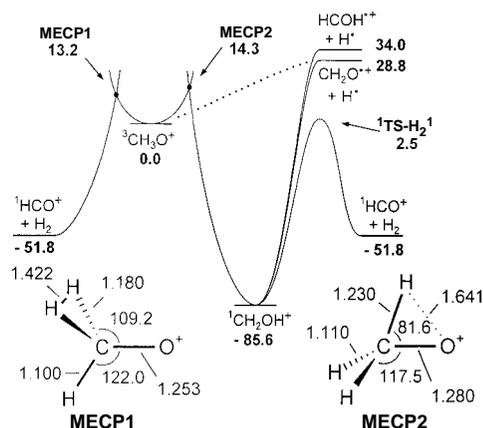
Fig. 2 Relevant parts of the triplet and singlet potential energy surfaces of $[C,H_3,O]^+$ cations calculated at the CCSD(T)/BSII//B:3LYP/BSI level (ref. 14). Bond lengths are given in Å and angles in degrees. Energies relative to the methoxy cation are given in kcal mol^{-1}.

concerted mechanism should at least be favoured over the *stepwise* pathway, although precise quantitative predictions would require a much more thorough analysis.[18]

The observation of nearly identical kinetic energy releases from both $[C,H_3,O]^+$ cations[2e] is an argument in favour of the *stepwise* mechanism. However, if one considers that the height of MECP1 is less than 11 kcal mol^{-1} higher than ^{1}**TS-H$_2^+$** (see Fig. 2), then it can be seen that these identical kinetic energy releases could come from different mechanisms.

In conclusion, the kinetic isotope effect results reported here provide very strong support for a reappraisal of the mechanism of unimolecular decomposition of the triplet methoxy cation and the present results suggest a [1,1]-elimination in which dehydrogenation and spin crossover occur in concert.[19,20]

Notes and References

† This ChemComm is also available in expanded form *via* the World Wide Web: http://www.rsc.org/ccenhanced
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4 The experiments were carried out with a four-sector ZAB-2F-HF/AMD604 mass spectrometer (ref. 5). Methoxy cations were generated by charge reversal (CR) of the corresponding anions [ref. 2(d)]. Hydroxymethyl cations were formed by electron ionization of labelled ethanols. The ions' connectivities were checked by collisional activation (CA) and CR/CA experiments [refs. 2(e), 3(b)]. The metastable ion decomposition products were monitored in MI and CR/MI experiments by scanning the fourth sector.
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6 B. A. Rumpf, C. E. Allison and P. J. Derrick, *Org. Mass Spectrom.*, 1986, **21**, 295.
7 The MI mass spectra of $[C,H_3,O]^+$ and $[C,D_3,O]^+$ were also recorded, and the results are consistent with the present analysis.
8 KIE_1 and KIE_2 are product determining. Intermolecular kinetic isotope effects have not been taken into account, but, of course, would not affect the qualitative conclusions made here.
9 The effect of different internal energies of non-ergodicity on KIE_2 is probably small; an *enormous* change would anyway be needed to modify the conclusions outlined in Scheme 2.
10 For evaluation of the kinetic isotope effects, several experiments were averaged and the intensities were corrected for mass discrimination (see ref. 6) and for the statistical weights of H_2, HD and D_2.
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14 Calculations at the UMP2 and B3LYP levels of theory were performed with GAUSSIAN94 [ref. 15(a)] and the 6-311+G(d,p) (BSI) basis set. The MECPs were located using our recently described method (ref. 12), and the gradients at these points were inspected to verify that they connect to the relevant minima. The CCSD(T) calculations at B3LYP optimized geometries were performed in MOLPRO [ref. 15(b)] with the cc-pVTZ basis set, omitting the *d* functions on hydrogen (BSII). At this level, the MECPs were optimized using the hybrid method of ref. 12 with B3LYP/BSI gradients.
15 (a) GAUSSIAN 94, Revision E.1, Gaussian, Inc., Pittsburgh, PA, 1995; (b) MOLPRO 96.4 is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowles; (c) GAMESS USA (18th March 1997 version), M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347. PC version compiled by A. A. Granovsky, Moscow State University.
16 These calculations were performed using an approximate one-electron Hamiltonian (ref. 17), as implemented in GAMESS [ref. 15(c)]. The GAMESS TZV basis set was used with one heavy atom d-polarisation function; the singlet and triplet states were described by CI wavefunctions expanded within a basis of HF orbitals generated either for the singlet or the triplet; the effective nuclear charges used were those recommended in ref. 17. The CI expansion included all possible determinants formed by allocating the eight valence electrons into five orbitals, and by allowing single excitations into the virtual orbitals. The value reported is the magnitude of the H^{SO} complex matrix element between coupled substates.
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18 The relative slope of the two surfaces at the MECP also affects the surface hopping probability. This factor is very similar at the two MECPs.
19 Spin crossover is also important in transition and metal chemistry. See, for example S. Shaik, M. Filatov, D. Schröder and H. Schwarz, *Chem. Eur. J.*, 1998, **4**, 193.
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