

## CH<sub>3</sub>O<sup>+</sup> and C<sub>2</sub>H<sub>5</sub>O<sup>+</sup>: High Barriers to Isomerisation and Low Barriers to Symmetry-allowed 1,1-Elimination

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**Summary** Experimental and theoretical evidence is presented to show that the alkoxy cations CH<sub>3</sub>O<sup>+</sup> and C<sub>2</sub>H<sub>5</sub>O<sup>+</sup> have surprisingly high barriers to 1,2-hydride shifts to the oxygen atom, but have very low barriers to 1,1-elimination of H<sub>2</sub> from the α-carbon atom.

IN earlier work,<sup>1</sup> we have shown that CH<sub>2</sub>=OH<sup>+</sup> undergoes symmetry-forbidden 1,2-elimination of H<sub>2</sub> in a reaction requiring *ca.* 330 kJ mol<sup>-1</sup>. The high internal energy required to dissociate CH<sub>2</sub>=OH<sup>+</sup> was shown by deuterium

labelling<sup>1,2</sup> to be insufficient to cause any prior isomerisation of the ion. Yet the reported heat of formation of the methoxy cation (CH<sub>3</sub>O<sup>+</sup>, 850 kJ mol<sup>-1</sup>),<sup>3</sup> is only 140 kJ mol<sup>-1</sup> higher than that of CH<sub>2</sub>=OH<sup>+</sup> (710 kJ mol<sup>-1</sup>).<sup>4</sup> These data imply that the barrier to the CH<sub>2</sub>=OH<sup>+</sup> → CH<sub>3</sub>O<sup>+</sup> isomerisation is >330 kJ mol<sup>-1</sup>, and that the barrier for the reverse reaction CH<sub>3</sub>O<sup>+</sup> → CH<sub>2</sub>=OH<sup>+</sup> (occurring through the same channel) is >190 kJ mol<sup>-1</sup>. The latter barrier appears, at first sight, to be a remarkably high one to a symmetry-allowed 1,2-hydride shift which can lead to a

thermodynamically more stable product. In contrast, in the gas phase a primary carbonium ion appears to rearrange to a secondary carbonium ion *via* a 1,2-hydride shift essentially without activation energy.<sup>5,6</sup>

However, unambiguous experimental evidence for a barrier to the reaction  $\text{CH}_3\text{O}^+ \rightarrow \text{CH}_2=\text{OH}^+$  is available from the work of Hiraoka and Kobarle.<sup>7</sup> Using a pulsed, high-pressure mass spectrometer source, these workers were able to show that in a thermally equilibrated system,  $\text{H}_2$  will add to the formyl cation in a reaction which is exothermic by  $16 \text{ kJ mol}^{-1}$ . This exothermicity is calculated from the temperature variation of the equilibrium constant for the reaction, *i.e.* the reaction is readily reversible. The adduct is formulated as  $\text{CH}_3\text{O}^+$ ,<sup>7</sup> as it clearly must be since 1,2-addition of  $\text{H}_2$  to  $\text{HC}=\text{O}$  would require an activation energy of *ca.*  $220 \text{ kJ mol}^{-1}$ , if occurring by microscopic reversal of 1,2-elimination of  $\text{H}_2$  from  $\text{CH}_2=\text{OH}^+$ . Moreover, the reaction  $\text{CH}_2=\text{OH}^+ \rightarrow \text{HC}=\text{O} + \text{H}_2$  could not occur in a system in thermal equilibrium at the temperatures employed ( $-100$  to  $-165^\circ\text{C}$ ).<sup>7</sup> Thus,  $\text{H}_2$  adds 1,1 to the formyl ion, and dissociation of the adduct requires less energy than isomerisation to  $\text{CH}_2=\text{OH}^+$ .

The product  $\text{CH}_3\text{O}^+$  from the above  $\text{H}_2 + \text{HC}=\text{O}$  reaction has  $\Delta H_f^\circ$   $810 \text{ kJ mol}^{-1}$ , and this should be an accurate value.<sup>7</sup> If it is indeed a more accurate value than the appearance potential value ( $850 \text{ kJ mol}^{-1}$ ) quoted earlier, then the barrier ( $\geq 230 \text{ kJ mol}^{-1}$ ) derived for the  $\text{CH}_3\text{O}^+ \rightarrow \text{CH}_2=\text{OH}^+$  reaction is even higher than the one quoted at the outset of this paper.

We have sought confirmation of the above deductions by generating  $\text{CH}_3\text{O}^+$  and  $\text{CH}_2=\text{OH}^+$  in the mass spectrometer by ionisation and fragmentation of selected compounds. Since it appears that  $\text{RCH}_2\text{O}^+$  ions lose  $\text{H}_2$  through 1,1-elimination with a very small activation energy, precursors of these ions should give very low abundance  $\text{RCH}_2\text{O}^+$  ions and high abundance  $\text{RC}=\text{O}^+$  ions. In contrast,  $\text{CH}_2=\text{OH}^+$  ions generated from  $\text{RCH}_2\text{OH}$  compounds should give large *m/e* 31:29 ratios since the *m/e* 31  $\rightarrow$  29 reaction has a very large activation energy. The experimental results are given in the Table.

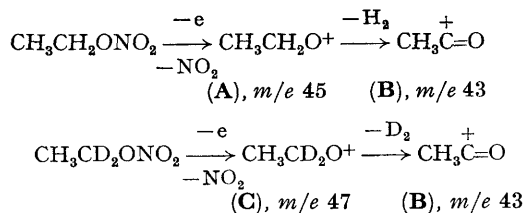
TABLE  
*M/e* 31:29 ratios in the mass spectra (70 eV) of selected compounds

Compound	Anticipated ion at threshold	<i>m/e</i> 31:29
$\text{CH}_3\text{CH}_2\text{OH}$	$\text{CH}_2=\text{OH}^+$	11:1
$\text{CF}_3\text{CH}_2\text{OH}$	$\text{CH}_2=\text{OH}^+$	11:1
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	$\text{CH}_2=\text{OH}^+$	15:1
$\text{CH}_3\text{ONO}_2$	$\text{CH}_3\text{O}^+$	0.08:1
$\text{CH}_3\text{OCH}_3$	$\text{CH}_3\text{O}^+$	0.08:1

The results strikingly confirm expectations, both  $\text{CH}_3\text{ONO}_2$  and  $\text{CH}_3\text{OCH}_3$  producing extremely abundant  $\text{HC}=\text{O}^+$  ions. Furthermore, while  $\text{CH}_2=\text{OH}^+$  loses  $\text{H}_2$  in slow reactions (metastable transitions) with a large kinetic energy release<sup>2</sup> ( $140 \text{ kJ mol}^{-1}$ ) since the reaction is symmetry-forbidden,<sup>1</sup> the  $\text{CH}_3\text{O}^+ \rightarrow \text{HC}=\text{O}$  reaction does not give a discernible metastable peak. Presumably this is because

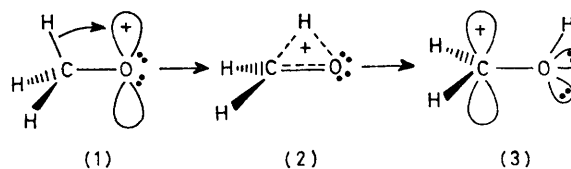
the symmetry-allowed reaction (see below) has a small activation energy and a relatively fast rise of the rate constant with energy, such that almost all the dissociations are relatively fast.

Finally, we wished to establish that an acyl ion  $\text{RC}=\text{O}^+$ , when formed from a compound  $\text{RCH}_2\text{OX}$ , does arise specifically by 1,1-elimination of  $\text{H}_2$  from the oxygen-bound carbon even where other processes are possible. Ethyl nitrate produces in its 70 eV mass spectrum peaks at *m/e* 43 (B) and 45 (A) in the ratio 20:1 (Scheme 1).  $[1,1\text{-}^2\text{H}_2]$ -Ethyl nitrate produces under similar conditions peaks at *m/e* 43 (B) and 47 (C) in the ratio 12:1, with peaks at *m/e* 44 and 45 being of negligible abundance relative to that at *m/e* 43. The  $\text{CH}_3\text{C}=\text{O}^+$  ion is therefore produced by a specific 1,1-elimination.



SCHEME 1

The extremely small barrier to the reaction  $\text{CH}_3\text{O}^+ \rightarrow \text{HC}=\text{O} + \text{H}_2$  is supported by earlier orbital symmetry arguments.<sup>8</sup> 1,1-Elimination from an  $sp^3$  carbon adjacent to a vacant  $p$ -orbital is a symmetry-allowed process.



SCHEME 2

It remains to explain the high barrier ( $\geq 230 \text{ kJ mol}^{-1}$ ) to the reaction  $\text{CH}_3\text{O}^+ \rightarrow \text{CH}_2=\text{OH}^+$ . The hydride shift should occur so that bonding on to the vacant  $p$ -orbital on oxygen is possible in the transition state (1)  $\rightarrow$  (2) (Scheme 2). However, this results in the formation of  $\text{CH}_2\text{OH}^+$  in which the lone-pairs of electrons on the oxygen atom are orthogonal to the vacant  $\pi$ -orbital on the carbon atom (3). Thus (3), formed in this manner, lacks all the  $\pi$ -stabilisation of  $\text{CH}_2=\text{OH}^+$ , but suffers all the destabilisation of the  $\text{CH}_2\text{OH}^+$  cation which exists through  $\sigma$ -electron withdrawal by the electronegative oxygen atom; it may plausibly represent the highest point on the potential surface of the  $\text{CH}_3\text{O}^+ \rightarrow \text{CH}_2=\text{OH}^+$  isomerisation. The heat of formation of (3) may be estimated in the following manner. The difference in heats of formation of  $\text{CH}_4$  and  $\text{CH}_3^+$  is  $1155 \text{ kJ mol}^{-1}$ ,<sup>9</sup> the analogous change performed on methanol [ $\text{CH}_3\text{OH} \rightarrow$  (3)] should require a similar energy difference if  $\pi$  back-donation to the cationic centre did not occur, nor did

inductive destabilisation by oxygen. Lack of  $\pi$ -donation is precisely the situation which we wish to examine in (3). Inductive destabilisation will however be present in (3); calculations by Pople and his co-workers<sup>10</sup> give an inductive destabilisation of a carbocation of 42 kJ mol<sup>-1</sup> when the oxygen atom is separated by one carbon atom from the cationic centre, and 13 kJ mol<sup>-1</sup> when it is separated by two carbon atoms. In view of the rapid decrease of inductive effects due to an increase in the number of intervening  $\sigma$ -bonds, it seems probable that the inductive destabilisation due to a directly bonded oxygen will not be

less than 100 kJ mol<sup>-1</sup>. We therefore conclude that  $\Delta H_f$  (3) is  $\geq 1055$  kJ mol<sup>-1</sup>. Thus, a plausible transition state for the reversible reaction  $\text{CH}_2=\text{OH}^+ \rightleftharpoons \text{CH}_3-\text{O}^+$  appears to be energetically inaccessible at the high internal energies necessary to induce the reaction  $\text{CH}_2=\text{OH}^+ \rightarrow \text{HC}=\text{O}^+ + \text{H}_2$ ; this is in accord with the experimental facts.

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