CH_3O^+ and $C_2H_5O^+$: 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_3O^+ and $C_2H_5O^+$ have surprisingly high barriers to 1,2-hydride shifts to the oxygen atom, but have very low barriers to 1,1-elimination of H_2 from the α-carbon atom.

In earlier work,[1] we have shown that $CH_2{=}\overset{+}{O}H$ undergoes symmetry-forbidden 1,2-elimination of H_2 in a reaction requiring *ca.* 330 kJ mol^{-1}. The high internal energy required to dissociate $CH_2{=}\overset{+}{O}H$ was shown by deuterium labelling[1,2] to be insufficient to cause any prior isomerisation of the ion. Yet the reported heat of formation of the methoxy cation (CH_3O^+, 850 kJ mol^{-1}),[3] is only 140 kJ mol^{-1} higher than that of $CH_2{=}\overset{+}{O}H$ (710 kJ mol^{-1}).[4] These data imply that the barrier to the $CH_2{=}\overset{+}{O}H \rightarrow CH_3O^+$ isomerisation is >330 kJ mol^{-1}, and that the barrier for the reverse reaction $CH_3O^+ \rightarrow CH_2{=}\overset{+}{O}H$ (occurring through the same channel) is >190 kJ mol^{-1}. 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.[5,6]

However, unambiguous experimental evidence for a barrier to the reaction $CH_3O^+ \rightarrow CH_2{=}\overset{+}{O}H$ is available from the work of Hiraoka and Kebarle.[7] Using a pulsed, high-pressure mass spectrometer source, these workers were able to show that in a thermally equilibrated system, H_2 will add to the formyl cation in a reaction which is exothermic by 16 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 CH_3O^+,[7] as it clearly must be since 1,2-addition of H_2 to $HC^+{=}O$ would require an activation energy of *ca.* 220 kJ mol^{-1}, if occurring by microscopic reversal of 1,2-elimination of H_2 from $CH_2{=}\overset{+}{O}H$. Moreover, the reaction $CH_2{=}\overset{+}{O}H \rightarrow H\overset{+}{C}{=}O + H_2$ could not occur in a system in thermal equilibrium at the temperatures employed (−100 to −165 °C).[7] Thus, H_2 adds 1,1 to the formyl ion, and dissociation of the adduct requires less energy than isomerisation to $CH_2{=}\overset{+}{O}H$.

The product CH_3O^+ from the above $H_2 + HC^+{=}O$ reaction has ΔH_f 810 kJ mol^{-1}, and this should be an accurate value.[7] If it is indeed a more accurate value than the appearance potential value (850 kJ mol^{-1}) quoted earlier, then the barrier ($\geqslant$230 kJ mol^{-1}) derived for the $CH_3O^+ \rightarrow CH_2{=}\overset{+}{O}H$ reaction is even higher than the one quoted at the outset of this paper.

We have sought confirmation of the above deductions by generating CH_3O^+ and $CH_2{=}\overset{+}{O}H$ in the mass spectrometer by ionisation and fragmentation of selected compounds. Since it appears that RCH_2O^+ ions lose H_2 through 1,1-elimination with a very small activation energy, precursors of these ions should give very low abundance RCH_2O^+ ions and high abundance $R\overset{+}{C}{=}O$ ions. In contrast, $CH_2{=}\overset{+}{O}H$ ions generated from RCH_2OH compounds should give large *m/e* 31 : 29 ratios since the *m/e* 31 → 29 reaction has a very large activation energy. The experimental results are given in the Table.

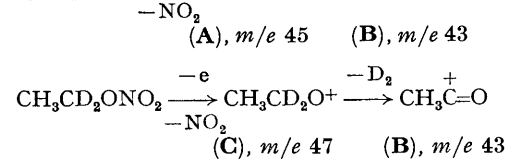
TABLE

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

Compound	Anticipated ion at threshold	*m/e* 31 : 29
CH_3CH_2OH	$CH_2{=}\overset{+}{O}H$	11 : 1
CF_3CH_2OH	$CH_2{=}\overset{+}{O}H$	11 : 1
$CH_3CH_2CH_2OH$	$CH_2{=}\overset{+}{O}H$	15 : 1
CH_3ONO_2	CH_3O^+	0·08 : 1
CH_3OCH_3	CH_3O^+	0·08 : 1

The results strikingly confirm expectations, both CH_3ONO_2 and CH_3OCH_3 producing extremely abundant $H\overset{+}{C}{=}O$ ions. Furthermore, while $CH_2{=}\overset{+}{O}H$ loses H_2 in slow reactions (metastable transitions) with a large kinetic energy release[2] (140 kJ mol^{-1}) since the reaction is symmetry-forbidden,[1] the $CH_3O^+ \rightarrow H\overset{+}{C}{=}O$ 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 $R\overset{+}{C}{=}O$, when formed from a compound RCH_2OX, does arise specifically by 1,1-elimination of 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-$^2H_2$]-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 $CH_3\overset{+}{C}{=}O$ ion is therefore produced by a specific 1,1-elimination.



$$CH_3CH_2ONO_2 \xrightarrow[-NO_2]{-e} CH_3CH_2O^+ \xrightarrow{-H_2} CH_3\overset{+}{C}{=}O$$

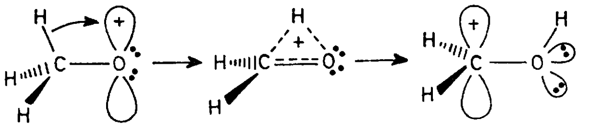
(**A**), *m/e* 45 (**B**), *m/e* 43

$$CH_3CD_2ONO_2 \xrightarrow[-NO_2]{-e} CH_3CD_2O^+ \xrightarrow{-D_2} CH_3\overset{+}{C}{=}O$$

(**C**), *m/e* 47 (**B**), *m/e* 43

SCHEME 1

The extremely small barrier to the reaction $CH_3O^+ \rightarrow H\overset{+}{C}{=}O + H_2$ is supported by earlier orbital symmetry arguments.[8] 1,1-Elimination from an sp^3 carbon adjacent to a vacant *p*-orbital is a symmetry-allowed process.



(1) (2) (3)

SCHEME 2

It remains to explain the high barrier ($\geqslant$ 230 kJ mol^{-1}) to the reaction $CH_3O^+ \rightarrow CH_2{=}\overset{+}{O}H$. The hydride shift should occur so that bonding on to the vacant *p*-orbital on oxygen is possible in the transition state (**1**) → (**2**) (Scheme 2). However, this results in the formation of $\overset{+}{C}H_2OH$ in which the lone-pairs of electrons on the oxygen atom are orthogonal to the vacant π-orbital on the carbon atom (**3**). Thus (**3**), formed in this manner, lacks all the π-stabilisation of $CH_2{=}\overset{+}{O}H$, but suffers all the destabilisation of the $\overset{+}{C}H_2OH$ cation which exists through σ-electron withdrawal by the electronegative oxygen atom; it may plausibly represent the highest point on the potential surface of the $CH_3O^+ \rightarrow CH_2{=}\overset{+}{O}H$ isomerisation. The heat of formation of (**3**) may be estimated in the following manner. The difference in heats of formation of CH_4 and CH_3^+ is 1155 kJ mol^{-1};[9] the analogous change performed on methanol [$CH_3OH \rightarrow$ (**3**)] should require a similar energy difference if π back-donation to the cationic centre did not occur, nor did inductive destabilisation by oxygen. Lack of π-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[10] give an inductive destabilisation of a carbocation of 42 kJ mol^{-1} when the oxygen atom is separated by one carbon atom from the cationic centre, and 13 kJ mol^{-1} 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 σ-bonds, it seems probable that the inductive destabilisation due to a directly bonded oxygen will not be less than 100 kJ mol^{-1}. We therefore conclude that ΔH_f (**3**) is $\geqslant$ 1055 kJ mol^{-1}. Thus, a plausible transition state for the reversible reaction $CH_2{=}\overset{+}{O}H \rightleftharpoons CH_3{-}\overset{+}{O}$ appears to be energetically inaccessible at the high internal energies necessary to induce the reaction $CH_2{=}\overset{+}{O}H \rightarrow H\overset{+}{C}{=}O + H_2$; this is in accord with the experimental facts.

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