# '$CH_3O^{+}$' and $CH_2{=}O^{+}H$: High Barriers to Isomerization

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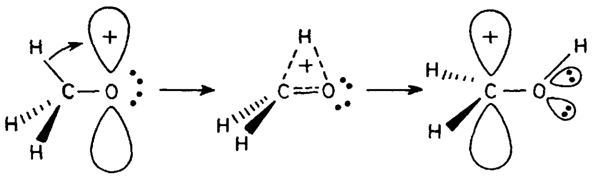
*Summary* Contrary to a recent report, the 'perpendicular' hydroxymethyl cation (**3**) is not responsible for the high isomerization barrier between '$CH_3O^{+}$' (better described as $H_2{\cdot}HCO^{+}$, a loose hydrogen–formyl cation complex) and $CH_2{=}O^{+}H$ (protonated formaldehyde).

BOWEN and WILLIAMS[1] recently called attention to 'the high barrier (> 230 kJ mol$^{-1}$) to the reaction $CH_3O^{+} \rightarrow CH_2{=}O^{+}H$' which they felt was remarkable for 'a symmetry-allowed 1,2-hydride shift which can lead to a thermodynamically more stable (by 140 kJ mol$^{-1}$) product.' Depicting the process as in Scheme 1, they attributed the high barrier to the instability of (**3**), which 'lacks all the $\pi$-stabilization of $CH_2{=}O^{+}H$, but suffers all the destabilization of the $^{+}CH_2OH$ cation which exists through $\sigma$-electron withdrawal by the electronegative oxygen atom.' As this rationalization is inconsistent with other information, both theoretical and experimental, we propose an alternative explanation.

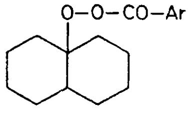


(1) (2) (3)

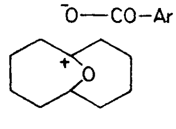
SCHEME 1

1,2-Shifts to 'positive' (electron-deficient) oxygen are known to take place readily: *e.g.*, the Baeyer–Villiger reaction, the acid-catalysed rearrangement of hydroperoxides, and the ionic decomposition of peresters.[2] While all these reactions are likely to be concerted processes, they all must involve pathways similar to that in Scheme 1, and 'destabilized' species with perpendicular geometries similar to (**3**). The Criegee rearrangement (**4**) → (**5**) is especially pertinent, since the intermediate (**5**) is constrained to a more or less perpendicular (**3**)-like geometry.[3]

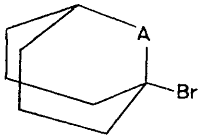
Solvolysis studies also show that such geometries do not produce large destabilizations; *cf.* relative rates of (**6**) and (**7**) (A = O) compared with their carbocyclic analogues.[4–6]



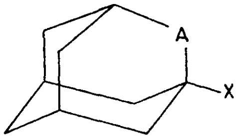
(4)



(5)



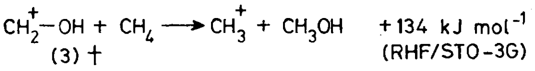
(6)



(7)

| | | |
|---|---|---|
| Relative rates | $A = CH_2$; 1·0 (ref. 4) | $A = CH_2$, $X = Br$; 1·0 (ref. 5) |
| | $A = O$; 0·32 | $A = O$, $X = Br$; 0·14 |
| | | $A = CH_2$, $X = OTs$; 1·0 (ref. 6) |
| | | $A = O$, $X = OTs$; 0·004 |

*Ab initio* MO calculations suggest that a perpendicular hydroxy-group, as in (**3**), actually has a stabilizing influence, relative to hydrogen.[7]†



$$\underset{(3)\,\dagger}{\overset{+}{C}H_2{-}OH} + CH_4 \longrightarrow \overset{+}{C}H_3 + CH_3OH \qquad \underset{(RHF/STO\text{-}3G)}{+134\ \mathrm{kJ\ mol^{-1}}}$$

Scheme 2

It is better to regard the two lone pairs on oxygen as being nonequivalent, occupying $p$ and $sp^2$ orbitals.[8] The former is energetically more favourable for $\pi$-donor interaction with an adjacent vacant orbital of a carbenium ion; planar $H_2C{=}O^+H$ ($C_s$) is the most stable arrangement.[7] However, in the perpendicular geometry (**3**) the $sp^2$-oxygen lone pair orbital can also interact with an adjacent vacant $p$-orbital on carbon and, as Scheme 2 illustrates, stabilization relative to a hydrogen substituent results. Thus, the observed barrier for the interconversion of $CH_3O^+$ is not likely to be due to the alleged instability of (**3**).

To demonstrate this further, we have carried out a series of *ab initio* MO (RHF/STO-3G) calculations to simulate the rearrangement shown in Scheme 1. Starting with a singlet $CH_3O^+$ (**1**) in which one HCO angle was fixed at 100°, rearrangement *via* (**2**) and (**3**) to a $C_{2v}$ structure and from there to the global energy minimum (planar protonated formaldehyde with $C_s$ symmetry) was found to proceed exothermically without a detectable barrier.‡ However, it is significant that the energy difference involved was 369 kJ mol$^{-1}$, consistent in magnitude with the barrier height discussed by Williams and Bowen.[1]

What is the nature of '$CH_3O^+$'? The ground state of the methoxy cation ($C_{3v}$) should be a triplet ($^3A_1$).[9] The conversion of triplet $CH_3O^+$ to a singlet $CH_2{=}O^+H$ would be a spin-forbidden reaction with a low probability. However, the experimentally observed '$CH_3O^+$' species under discussion is probably not the triplet methoxy cation, but is rather 'a loose complex of $H_2$ and $HCO^+$.'[10] Representation as $H_2{\cdot}HCO^+$, rather than as $CH_3O^+$, seems preferable.[10] Our preliminary calculations on $H_2{\cdot}HCO^+$ indicate that bound species exist,[11] but with rather low interaction energies consistent with the experimental findings.[10]

Although we have yet not probed the *ab initio* reaction surface fully, the conversion of $H_2{\cdot}HCO^+$ into $H_2C{=}O^+H$ is indicated to have a high barrier. All geometries of the singlet methoxy cation we have investigated (see above) are high in energy, and no local minimum has yet been found. Dewar has located the transition state for 1,2-hydrogen elimination from $CH_2{=}O^+H$ at the MINDO/3 level of calculation;[12] a barrier of 351 kJ mol$^{-1}$ was indicated in comparison with Williams' experimental value of 335 kJ mol$^{-1}$.[13]

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† As structure (**3**) is an arbitrary point (neither a minimum nor a transition state) on the potential energy surface (ref. 7), the geometry employed in Scheme 2 held ∠HOC at 110°, but otherwise optimized all other parameters within $C_s$ symmetry. The absolute energy corresponding to this structure is −112·65295 a.u. (1 a.u. = 2625 kJ mol$^{-1}$). For other energies used in Scheme 2 see W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Progr. Phys. Org. Chem.*, 1974, **11**, 175. All calculations used the Gaussian 70 series of programs: W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana.

‡ ∠HCO of singlet (**1**) was decreased by 20° increments while otherwise allowing full optimization within $C_s$ symmetry. The energies relative to the 0° structure ($C_{2v}$, the planar inversion transition state) (ref. 7) were (kJ mol$^{-1}$): 245 (100°), 238 (80°), 196 (60°), 69 (40°), and 4 (20°). Total energy of $CH_2O^+H$ ($C_{2v}$) = − 112·65969 a.u.; this structure is less stable than the most stable structure, protonated formaldehyde, (ref. 7) by 124 kJ mol$^{-1}$.

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[11] For example, $H_2$ - - - $HCO^+$ ($C_{2v}$) (total energy −112·62415 a.u.) is bound by 3·6 kJ mol$^{-1}$ at the STO-3G level. The RHF/4-31G value is 7·1 kJ mol$^{-1}$ (exptl. 16·3 kJ mol$^{-1}$) (ref. 10). *Cf.*, J. B. Collins, P. v. R. Schleyer, J. S. Binkley, J. A. Pople, and L. Radom, *J. Amer. Chem. Soc.*, 1976, **98**, 3436.

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