Spontaneous Intramolecular Hydrogen Migration in Ionized Ethane-1,2-diol

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Ionized ethane-1,2-diol ($HOCH_2CH_2OH^{+\bullet}$) is predicted by *ab initio* calculations to rearrange *via* a barrier-free 1,4-hydrogen shift to give $\dot{O}CH_2CH_2\overset{+}{O}H_2$; this result is consistent with mass spectrometric observations.

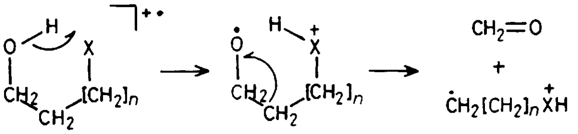
There has been considerable recent theoretical and experimental interest[1] in the chemistry of distonic[2] radical cations, $\dot{Y}[CH_2]_n\overset{+}{X}H$. Such species, in which the charge and radical sites are formally separated, do not generally have stable, neutral counterparts and cannot therefore be prepared in the mass spectrometer by direct ionization of a parent neutral. Rather, they are generally produced through a rearrangement–fragmentation process,[3] *e.g.* reaction (1). In this communication, we describe theoretical and experimental results for the ionization of a prototype system involved in reaction (1), namely ethane-1,2-diol (ethylene glycol, X = OH, $n = 0$).

Our *ab initio* calculations† predict that the preferred structure of ethane-1,2-diol (**1**) contains a strong intramolecular hydrogen bond, in agreement with previous work.[4] Vertical ionization to give the radical cation ($\mathbf{1}^{+\bullet}$) is calculated to require 10.5 eV which compares well with the experimental 10.57 eV.[5]

The ethane-1,2-diol radical cation produced after relaxation of ($\mathbf{1}^{+\bullet}$)[($\mathbf{3}^{+\bullet}$)] is found to lie in a shallow potential well on the HF/6-316G* potential surface. However, the energy of the transition structure ($\mathbf{4}^{+\bullet}$) for rearrangement [to ($\mathbf{2}^{+\bullet}$)] lies lower than that of ($\mathbf{1}^{+\bullet}$), and at the improved MP2/6-31G* level, even drops below that of the local HF/6-31G* minimum ($\mathbf{3}^{+\bullet}$) (see Figure 1). The striking prediction is then that the ethane-1,2-diol radical cation produced by vertical ionization of ethane-1,2-diol is not stable but can undergo a barrier-free intramolecular hydrogen migration to produce the distonic radical cation, $\dot{O}CH_2CH_2\overset{+}{O}H_2$ ($\mathbf{2}^{+\bullet}$).

The distonic radical cation ($\mathbf{2}^{+\bullet}$) is calculated to lie 69 kJ mol^{-1} below ($\mathbf{1}^{+\bullet}$) and 114, 115, and 18 kJ mol^{-1}, respectively, below fragmentation products $CH_2OH_2^{+\bullet}$ + CH_2O, CH_2OH^+ + $CH_2OH^\bullet$, and $CH_3OH_2^+$ + $HCO^\bullet$. Barriers for such dissociation processes are currently under investigation and will be reported in due course. Also under investigation is the rearrangement of ($\mathbf{1}^{+\bullet}$) to a *trans* isomer. This has been characterized recently[1c,6] as having a long C · · · C bond (2.023 Å) and therefore would be the natural precursor for fragmentation to CH_2OH^+ + $CH_2OH^\bullet$.

The calculated energy difference between ($\mathbf{1}^{+\bullet}$) [formed by vertical ionization of (**1**)] and ($\mathbf{2}^{+\bullet}$) [produced from ($\mathbf{1}^{+\bullet}$) without a barrier after geometric relaxation] of 69 kJ mol^{-1} is reasonably close to the experimental estimate[5] (0.5 eV = 48 kJ mol^{-1}) of the difference between the vertical ionization energy (I.E.$_v$) and adiabatic ionization energy (I.E.$_a$) for (**1**). The somewhat smaller experimental value could mean that the true adiabatic ionization is not observed in the photoelectron experiment due to unfavourable Franck–Condon factors associated with the major change in geometry.



(1)

Experimental support for the intermediacy of the distonic molecular ion ($\mathbf{2}^{+\bullet}$) comes from the presence of specific fragment ions ($\dot{C}H_2\overset{+}{O}H_2$, $CH_3\overset{+}{O}H_2$) in the mass spectrum of ethane-1,2,diol.‡ The methyleneoxonium radical cation[3] $\dot{C}H_2\overset{+}{O}H_2$ (*m/z* 32, 8%; base peak CH_2OH^+, *m/z* 31) can be formed either from C–C bond cleavage of ($\mathbf{2}^{+\bullet}$), or in a concerted rearrangement–fragmentation process from ($\mathbf{1}^{+\bullet}$). However, in the case of the more intense ion at *m/z* 33 ($CH_3OH_2^+$, 33%), its formation directly from ($\mathbf{1}^{+\bullet}$) would involve a double hydrogen transfer accompanied by C–C bond cleavage. More reasonably, the intermediacy of ($\mathbf{2}^{+\bullet}$) would

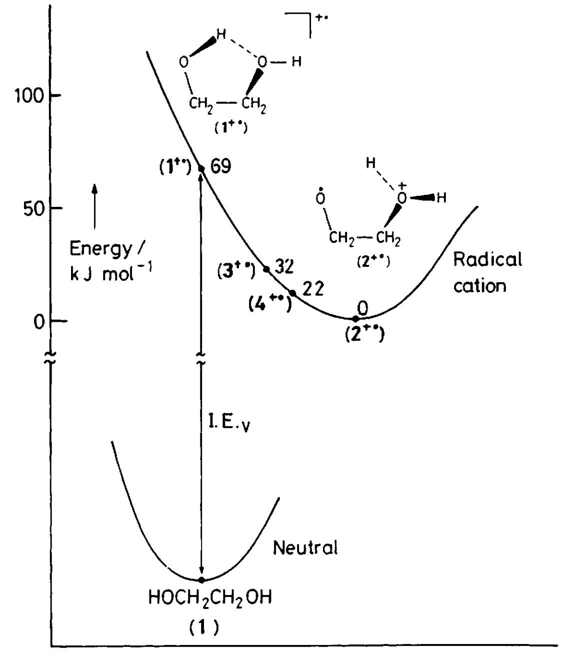


Figure 1. Schematic potential energy profile (MP2/6-31G*//6-31G*) describing ionization and subsequent hydrogen migration in ethane-1,2-diol.

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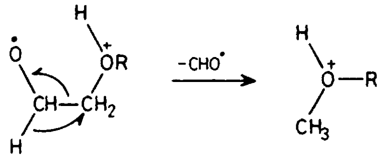
† Carried out with a modified version (J. Baker, R. H. Nobes, and D. Poppinger, unpublished) of the Gaussian 82 series of programs (J. S. Binkley, M. J. Frisch, D. J. DeFrees, K. Raghavachari, R. A. Whiteside, H. B. Schlegel, E. M. Fluder, and J. A. Pople, Carnegie–Mellon University, Pittsburgh, PA 15213, U.S.A.). Geometries were optimized at the Hartree–Fock (HF) level with the 6-31G* basis set (P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213) and improved relative energies obtained at the MP2/6-31G* level (J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem.*, 1976, **10S**, 1).

‡ Measured on a VG7070F mass spectrometer at 70 eV. Compounds were introduced into the ion source *via* an all-glass heated inlet system. First field-free metastable transitions were recorded on a VG7070E spectrometer using a *B/E* scan.

§ We note that in the spectrum of [1,1,2,2-$^2H_4$]ethane-1,2-diol, the *m/z* 33 ion shifts exclusively to *m/z* 36, indicating that there is no interchange of the methylene and hydroxy hydrogen atoms in the molecular ions ($\mathbf{1}^{+\bullet}$) or ($\mathbf{2}^{+\bullet}$).



(2)

allow production of $CH_3OH_2{}^+$ by a single 1,2-hydrogen shift with concomitant C–C bond cleavage [reaction (2), R = H].§ In both the first and second field-free regions, intense metastable signals are present for the unimolecular fragmentation process m/z 62 → m/z 33 but not for m/z 62 → m/z 32. This is consistent[7] with production of the former *via* a rearrangement process and the latter by means of simple homolytic cleavage of (**2**$^{+\bullet}$).

Finally, considerations similar to the above suggest an explanation [reaction (2), R = CH_3] for the existence of an ion corresponding to protonated dimethyl ether $(CH_3)_2\overset{+}{O}H$ in the mass spectrum of 2-methoxyethanol.[8]

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