A Theoretical Study of the Ion Structures produced by the Reaction of the s-Propyl Cation with Water

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The structure of the ionic hydrogen-bonded adduct of the s-propyl cation and water, and of protonated propan-2-ol, have been determined at the 3-21G and 6-31G* levels. The relative energies of these species have been determined with the inclusion of electron correlation effects. The predicted greater stability of protonated propan-2-ol is in line with collisional activation mass spectrometric studies of Holmes *et al.*

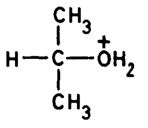
The study of the interaction between ions and water molecules has a central role to play in understanding ion solvation. Studies of the addition of water, and other *n*-donors such as CH_3OH to carbenium ions $[R]^+$ have led to the suggestion that covalently bound products $[ROH_2]^+$ and/or hydrogen-bonded structures involving CH $\cdots$ O interactions could be produced.[1] Indirect information on the structure of such products may be obtained from the technique of collisional activation (CA) mass spectrometry. Meot-Ner *et al.*[1] report that the ions generated by the addition reactions of $[t\text{-}C_4H_9]^+$ and $[s\text{-}C_3H_7]^+$ with water have CA mass spectra that differ from those obtained by direct protonation of the appropriate alcohols. This observation led to the suggestion that a cluster ion, rather than the covalently bound species, is formed in these cases. However, Holmes and co-workers,[2] in contrast to this work, report that the CA mass spectra of protonated propan-2-ol and t-butyl alcohol are indistinguishable from those of the corresponding $[C_3H_7/H_2O]^+$ and $[C_4H_9/H_2O]^+$ ions generated by the addition of $[s\text{-}C_3H_7]^+$ and $[t\text{-}C_4H_9]^+$ with the *n*-donor H_2O. This led to the conclusion that the CA mass spectra do not lend support to the suggestion that condensation of $[t\text{-}C_4H_9]^+$ or $[s\text{-}C_3H_7]^+$ with H_2O gives rise to unconventional clusters.

In view of these conflicting results we here report *ab initio* theoretical studies of the structures and stabilities of the ions produced by the addition of the s-propyl cation to water. We use geometry-optimization methods to obtain the possible ion structures and calculations that include the effect of electron correlation to obtain the stabilities of these structures.

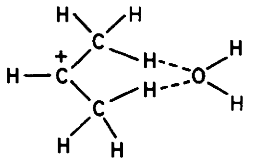
Computational Methods and Results

The calculations have been carried out using the standard 3-21G, 6-31G*, and 6-31G** basis sets of Pople and his co-workers,[3] the polarization functions being those of Ahlrichs and Taylor.[3] Optimized geometries were obtained at the restricted Hartree–Fock (RHF) level using analytic derivatives of the energy as implemented in the program GAMESS.[4] Correlation effects were included by carrying out configuration interaction (CI) calculations by the direct CI method.[5] The CI expansion included all single and double excitations from the filled orbitals to all virtual orbitals using a single reference configuration, the RHF configuration (SDCI). The effects of higher order excitations were included by the use of Davidson's correction.[6]

Geometry-optimization studies of water, the s-propyl cation, and of the two possible structures of the adduct (I) and (II) were carried out in the 3-21G and 6-31G* bases. Structure (I) is the protonated alcohol and structure (II) involves two hydrogen bonds. With the optimized structures obtained with the larger basis (6-31G*), single-point RHF calculations were carried out using the 6-31G** basis, having polarization functions on all atoms, to give the energies denoted 6-31G**//6-31G*. The results of the subsequent CI calculations at this level are denoted SDCI/6-31G**//6-31G*. The results are summarized in the Table and the structures optimized in the 6-31G* basis are shown in the Figure. For use in our following discussions we have also calculated the proton affinity of propan-2-ol at the same levels of approximation. This involved geometry optimization of the alcohol using the 3-21G and 6-31G* basis sets.



(I)



(II)

It is apparent from the data of the Table that the 3-21G values are of little use for a quantitative discussion of the energetics, and that in additon to a larger atomic basis, correlation effects

Table. Relative energies of adducts (I) and (II)[a] and proton affinity of propan-2-ol

	Structure		
	(I)	(II)	Propan-2-ol
3-21G	−198.5 (−192.3880)	−82.0 (−192.3436)	891.7 (−192.0484)
6-31G*	−115.6 (−193.4322)	−50.9 (−193.4076)	838.6 (−193.1128)
6-31G**//6-31G*	−107.7 (−193.4586)	−49.8 (−193.4366)	857.5 (−193.1320)
SDCI/6-31G**//6-31G*	−140.4 (−194.0572)	−54.6 (−194.0246)	854.9 (−193.7316)
+ Davidson's correction	−148.6 (−194.1676)	−56.5 (−194.1326)	852.3 (−193.8430)

[a] The energies (in kJ mol^{-1}) are relative to those of the s-propyl cation and water. The total energies (in a.u.) are given in parentheses.

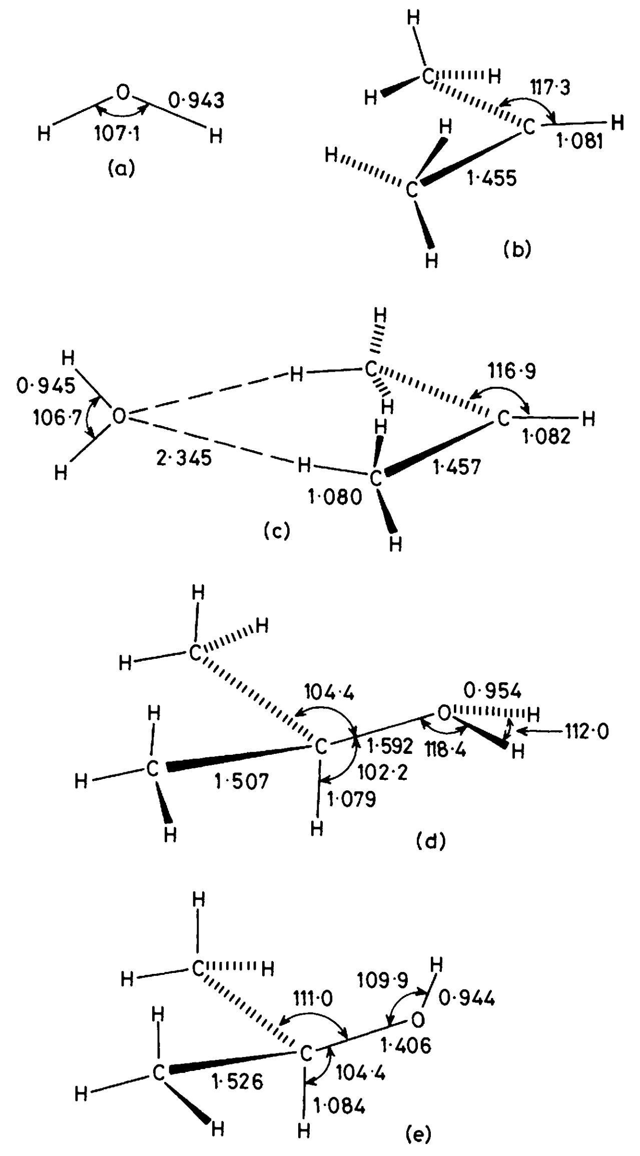


Figure 1. Structures optimized in 6-31G* basis: (a) H_2O, (b) s-propyl cation $(CH_3)_2CH^+$, (c) hydrogen-bonded adduct of (a) and (b), (d) protonated propan-2-ol, (e) propan-2-ol. Bond lengths are given in Å and angles in °

need to be included. These observations are not unexpected since basis set superposition effects will be important at the 3-21G level, but much less so for the extended basis sets. Also, the tendency for a 3-21G basis to overestimate the electrostatic contribution to the strength of hydrogen bonds is well known.[7] As seen from the Table, correlation effects are especially important for structure (I) where a covalent bond is formed between the s-propyl cation and water. It should also be noted that the inclusion of zero-point vibrational energies would reduce the magnitude of the quantities given in the Table, particularly the calculated enthalpy leading to structure (I). The calculation of the vibrational frequencies for the species studied here is, however, prohibitive in terms of computer time.

We turn now to the calculated optimal structures shown in the Figure. The major change in the geometry of propan-2-ol [Figure (e)] upon protonation [Figure (d)] is an increase in the C–O bond length by *ca.* 0.2 Å. The unconventional ionic hydrogen-bonded structure [Figure (c)] reflects the relatively weak interaction between the s-propyl cation and water. Thus, the structure of the s-propyl cation [Figure (b)] is largely unaltered in the adduct. The O • • • H distances in the bifurcated hydrogen bond are also considerably larger than that in a normal, single hydrogen bond. However, the formation of the C–O covalent bond in the protonated propan-2-ol results in the expected considerable lengthening of the C–C bonds, compared with those in the s-propyl cation.

The calculated relative stabilities of the two isomeric $[C_3H_9O]^+$ species (Table) would predict that the protonated alcohol is more stable than the hydrogen-bonded adduct. This order of stabilities is in line with the conclusion of Holmes and co-workers.[2] that his CA mass spectral results are compatible with the proposal that the condensation of $[s\text{-}C_3H_7]^+$ with H_2O results in the formation of the protonated alcohol (I).

We may however estimate an experimental value of ΔH for reaction (1) leading to the formation of the protonated alcohol

$$s\text{-}C_3H_7^+ + H_2O = s\text{-}C_3H_7OH_2^+ \qquad (1)$$

from the following experimental heats of formation [s-$C_3H_7^+$, 799 kJ mol^{-1};[8] H_2O, −241.8 kJ mol^{-1};[9] H^+, 1 536.2 kJ mol^{-1};[9] $(CH_3)_2CHOH$, −272.5 kJ mol^{-1} [10]] together with the experimental proton affinity of $(CH_3)_2CHOH$, 808 ± 21 kJ mol^{-1}.[11] The value obtained (−101 ∓ 21 kJ mol^{-1}) is somewhat smaller than the value (−148.6 kJ mol^{-1}) that we have directly calculated due mainly to the neglect of zero-point effects. Our best calculated value of the proton affinity (852 kJ mol^{-1}; Table) is apparently in error by a similar amount. A previous calculation [12] of the proton affinity of N_2O showed that the zero-point energy reduces the calculated proton affinity by *ca.* 30 kJ mol^{-1}. If our calculated proton affinity of propan-2-ol is reduced by a similar amount, the estimated value, *ca.* 820 kJ mol^{-1}, is now within the experimental uncertainty of this quantity. However, even the smaller estimate of ΔH for reaction (1) (−80 kJ mol^{-1}) is significantly greater than our estimate of ΔH for formation of the hydrogen-bonded adduct (−56.5 kJ mol^{-1}) which is again overestimated due to neglect of zero-point vibrations. We thus consider that our calculations definitely point to the greater stability of the protonated alcohol.

Conclusions.—The results of the large-scale *ab initio* MO calculations described herein show that the energetically preferred adduct of the s-propyl cation and water is protonated propan-2-ol, rather than the bifurcated hydrogen-bonded adduct.

Acknowledgements

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References

1 M. Meot-Ner (Mautner), M. M. Ross, and J. E. Campana, *J. Am. Chem. Soc.*, 1985, **107**, 4839.
2 J. K. Terlouw, T. Weiske, H. Schwarz, and J. L. Holmes, *Org. Mass Spectrom.*, 1986, **21**, 665.
3 J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, 1980, **102**, 939; W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257; P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213; R. Ahlrichs and P. R. Taylor, *J. Chim. Phys.*, 1981, **78**, 315.
4 M. F. Guest and J. Kendrick, GAMESS User Manual, CCP1/86/1. Daresbury Laboratory, 1986.
5 V. R. Saunders and J. H. van Lenthe, *Mol. Phys.*, 1983, **48**, 923; D. Moncrieff and V. R. Saunders, ATMOL Manual, NAT 648, University of Manchester Regional Computer Centre, 1986.
6 E. R. Davidson and D. W. Silver, *Chem. Phys. Lett.*, 1977, **52**, 403.

7 J. E. Del Bene and J. A. Pople, *J. Chem. Phys.*, 1973, **58**, 3605.

8 H. M. Rosenstock, R. Buff, M. A. A. Ferreira, S. G. Lias, A. C. Parr, R. L. Stockbauer, and J. L. Holmes, *J. Am. Chem. Soc.*, 1982, **104**, 2337.

9 D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, F. M. Bailey, K. L. Churney, and R. L. Nuttall, *J. Phys. Chem. Ref. Data*, (*Suppl. 2*), 1982, 11.

10 A. Snelson and H. A. Skinner, *Trans. Faraday Soc.*, 1961, **57**, 2125.

11 J. Long and B. Munson, *J. Am. Chem. Soc.*, 1973, **95**, 2427.

12 M. Vincent and I. H. Hillier, *Chem. Phys. Lett.*, 1986, **130**, 330.

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