

Formation of H₂SO₄ from SO₃ and H₂O, catalysed in water clusters

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Computer simulations predict the facile conversion of SO₃ to H₂SO₄ in small water clusters having in excess of about twelve solvent molecules, in line with experiment.

The gas-phase reaction of SO₃ with water vapour is considered to be the final stage in the tropospheric oxidation of SO₂ to form acid rain and sulfuric acid aerosols. These are important in heterogeneous stratospheric chemistry and ozone depletion, and also in climatology through the nucleation of cloud droplets in the lower troposphere which can scatter both incoming solar radiation and IR radiation from the Earth's surface.

Recent *ab initio* calculations¹ have shown that the barrier for the 1:1 reaction of H₂O + SO₃ is quite high (32 kcal mol⁻¹, cal = 4.184 J), and is considerably lowered (to 11.5 kcal mol⁻¹) by the catalytic effect of a second water molecule, enabling a six-membered transition state to be achieved. It is of interest from the point of view of atmospheric chemistry to know the minimum number of water molecules, in a water cluster containing SO₃, needed to allow for the facile formation of sulfuric acid.

Studies of reactions using aqueous clusters are a convenient way to study the transition from the gas phase to the condensed liquid phase and thereby investigate the effect of solvation on the dynamics of a reaction in a controlled and systematic manner. Hofmann-Sievert and Castleman² have studied the gas-phase reaction of SO₃ with small water clusters ($n = 2-10$) and we first report here an experimental study of the reactivity of SO₃ attached to larger water clusters ($n \approx 200$). The details

of the experiment have been fully described previously.^{3,4} Briefly, a single SO₃ molecule is deposited using the pick-up method onto a large water cluster formed by a supersonic molecular beam expansion of pure water vapour at *ca* 1.2 bar. Downstream from the expansion region the beam is detected by an electron-impact ionisation quadrupole mass spectrometer after a flight time of *ca*. 0.5 ms. The mass spectrum (Fig. 1) of pure gas-phase SO₃ and of the SO₃(H₂O)₂₀₀ cluster, clearly show the SO₃ to be converted into H₂SO₄ by reaction with the cluster. A similar behaviour was found by Hofmann-Sievert and Castleman² for the smaller clusters and the identity of the reaction product confirmed with electric deflection studies.

Thus the cluster beam studies show that the conversion to sulfuric acid is a facile process, although the theoretical study with just two water molecules suggests a considerable barrier for the reaction in the SO₃(H₂O)₂ cluster. To understand the extent to which further solvation of the SO₃(H₂O)₂ cluster may affect the barrier height we have carried out Monte Carlo simulations of the SO₃(H₂O)_{2+n} cluster, in which the calculated ground- and transition-states of the SO₃(H₂O)₂ cluster are solvated by a further n water molecules described by a molecular mechanical potential. In brief, the structures of the SO₃(H₂O)₂ moiety, predicted from the *ab initio* calculations are kept fixed, the appropriate atomic charges for them are obtained by the usual CHELPG method,⁵ using a 6-311 + G(d,p) basis, and the n solvating water molecules are described by a TIP3P potential.

The calculated charge distribution of the SO₃(H₂O)₂ entities predicts a greater polarity for the transition state, leading to a correspondingly greater average intermolecular interaction in the SO₃(H₂O)₂(H₂O) _{n} cluster containing the transition state compared to reactant. With ten additional water molecules we find this differential transition-state stabilisation to be 10.0 kcal mol⁻¹, from the Monte Carlo simulation. This quantity will essentially counterbalance the internal energy difference (11.5 kcal mol⁻¹) identified by the *ab initio* calculations on SO₃(H₂O)₂. Thus we predict that SO₃, solvated by approximately twelve water molecules will be converted to sulfuric acid with little or no energy barrier.

Thus, although it has long been recognised that bulk solvent can have profound effects on the rate of chemical reactions, we here show that in fact large catalytic effects can be achieved in quite small solvent clusters.

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Footnote

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References

- 1 K. Morokuma and C. Muguruma, *J. Am. Chem. Soc.*, 1994, **116**, 10316.
- 2 R. Hofmann-Sievert and A. W. Castleman, *J. Phys. Chem. A*, 1984, **88**, 3329.
- 3 M. Ahmed, C. J. Apps, C. Hughes, N. E. Watt and J. C. Whitehead, *J. Phys. Chem. A*, 1977, **101**, 1250.
- 4 M. Ahmed, C. J. Apps, R. Buesnel, C. Hughes, I. H. Hillier, N. E. Watt and J. C. Whitehead, *J. Phys. Chem. A*, 1997, **101**, 1254.
- 5 C. M. Breneman and K. B. Wiberg, *J. Comput. Chem.*, 1990, **11**, 361.

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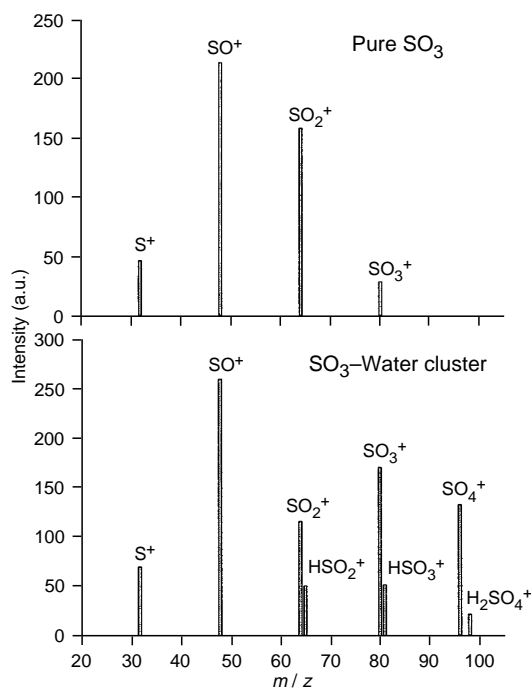


Fig. 1 Comparison of the mass spectrum for gas-phase SO₃ (upper panel) with SO₃ attached to a water cluster. The pick-up source pressure was 7 mbar and the water clusters were formed at a stagnation pressure of *ca*. 1.2 bar.