Ab initio and molecular-mechanics studies of aluminosilicate fragments, and the origin of Lowenstein's rule

C. R. A. Catlow,[a] A. R. George[a] and C. M. Freeman[b]

[a] Davy Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London, UK W1X 4BS
[b] MSI, 9685 Scranton Road, Suite A, San Diego, CA 92121-2777, USA

We present results of the energies of formation and hydration of small clusters and rings containing Si and Al; the results provide a rationalisation of Lowenstein's rule in terms of the energetics of species containing Al–O–Al bridges.

There has been long debate and controversy about the factors controlling the Al distribution in zeolites.[1,2] In particular the fundamental factors controlling 'Lowenstein's rule'[3] which forbids Al–O–Al bridges in zeolitic and related solids remain uncertain. Recent computer simulation studies of Bell et al.[4] found evidence for a small energy penalty for 'non-Lowensteinian' structures in zeolite A. The calculations reported in this letter suggest, however, that it is likely that the energetics of Al–O–Al bridges in small rings and clusters (which provide some of the smaller secondary building units in zeolite structures) are crucial in preventing the formation of structures containing directly linked AlO$_4$ tetrahedra.

Our approach in this communication is based on a combination of ab initio and molecular mechanics techniques which we use to calculate the formation and condensation energies of a range of relevant aluminate, aluminosilicate and silicate clusters. More extensive detail of the methods will be provided in a detailed survey of the energetics of silica clusters.[5] We are also able, for the first time in these systems, to include explicit representations of the effects of hydration. We find that, in the gas phase, clusters show a strong energetic preference for the formation of Si–O–Al bridges, although the energy differences are smaller when the effects of hydration are included.

Ab initio methods based on both Hartree–Fock and local density functional (LDF) methodology have been used in several previous studies of silica fragments.[6–12] In the present study we employed the LDF DMOL code[13] for the ab initio calculations and DISCOVER[15] for our molecular mechanics studies. We used 'DN' basis sets[14] in the ab initio studies and the combined valence forcefield[15] was employed in the molecular-mechanics calculations. Our more detailed studies on silicate clusters[5] demonstrate the reliability of these methods for this type of study. Hydration of the clusters was studied using the 'soak' procedure in the INSIGHT II package of BIOSYM Technologies.[16] This allows us to hydrate species explicitly; in the present calculations, therefore, all clusters were surrounded by a sphere of water of diameter 15 Å, centred on the zeolite fragment. The energy of the cluster–water system was calculated after minimisation, from which the hydration energy was calculated after subtraction of the energy of the minimised hydration sheath. The clusters investigated are illustrated in Fig. 1; these graphical representations were taken from the geometry optimised ab initio configurations.

The calculated total energies obtained for the geometry optimised clusters investigated by the LDF techniques are reported in Table 1. Table 2 gives the calculated condensation energies for key reactions. We immediately note results of considerable significance for the origin of Lowenstein's rule. We find that Si–O–Al bridge formation in dimers is energetically favourable (by 27 kcal mol^{-1}; cal = 4.184 J) unlike the formation of Al–O–Al bridges for which there is a substantial
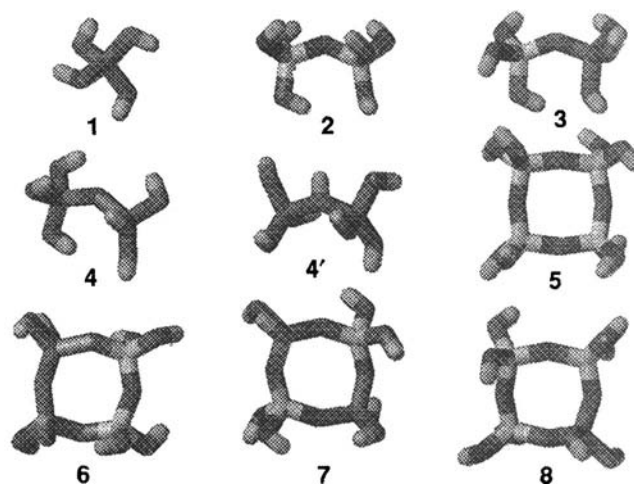

Fig. 1 Cluster structures investigated in this study; the numbering scheme is that in Table 1

Table 1 Total energies for ab initio calculations on Al-containing clusters[a]

Cluster		Energy (a.u.)
1	[Al(OH)$_4$]$^-$	−542.886792
2	[Si$_2$O(OH)$_6$]	−1103.553365
3	[SiAlO(OH)$_6$]$^-$	−1056.761091
4	[Al$_2$O(OH)$_6$]$^{2-}$	−1009.806140
4′	[Al$_2$OH(OH)$_6$]$^-$ [b]	−1010.456306
5	[Si$_4$O$_4$(OH)$_8$]	−2055.345439
6	[Si$_2$Al$_2$O$_4$(OH)$_8$]$^{2-}$ [c]	−1961.638161
7	[Si$_2$Al$_2$O$_4$(OH)$_8$]$^{2-}$ [d]	−1961.666805
8	[Si$_3$AlO$_4$(OH)$_8$]$^-$	−2008.566598

[a] Energies calculated for H$_2$O and OH$^-$ with same basis sets are respectively −75.882892 a.u. and −75.251442 a.u. Energy for [Si(OH)$_4$] cluster is calculated as −589.714178 a.u. For labelling of clusters see Fig. 1. [b] In this cluster, the bridging oxygen has been protonated. [c] Non-Lowensteinian distribution. [d] Lowensteinian distribution.

Table 2 Calculated energies (E) of condensation reactions

	Reaction		E/kcal mol^{-1}
1	Si(OH)$_4$ + [Al(OH)$_4$]$^-$	→ [SiOAl(OH)$_6$]$^-$ + H$_2$O	−27.0
2	2Si(OH)$_4$	→ [Si$_2$O(OH)$_6$] + H$_2$O	−4.9
3	2[Al(OH)$_4$]$^-$	→ [Al$_2$OH(OH)$_6$]$^-$ + OH$^-$	41.1
4	2[Al(OH)$_4$]$^-$	→ [Al$_2$O(OH)$_6$]$^{2-}$ + H$_2$O	53.0
5	2[SiAlO(OH)$_6$]$^-$	→ [Si$_2$Al$_2$O$_4$(OH)$_8$]$^{2-}$ + 2H$_2$O	56.0[a]
6	2[Si$_2$O(OH)$_6$]	→ [Si$_4$O$_4$(OH)$_8$] + 2H$_2$O	−2.8
7	[Si$_2$Al$_2$O$_4$(OH)$_8$]$^{2-}$	→ [Si$_2$Al$_2$O$_4$(OH)$_8$]$^{2-}$	18.0[b]
8	[Si$_2$O(OH)$_6$] + [SiOAl(OH)$_6$]$^-$	→ [Si$_3$AlO$_4$(OH)$_8$]$^-$ + 2H$_2$O	−11.3

[a] Assumes formation of Lowensteinian cluster. [b] Lowensteinian to non-Lowensteinian reaction.

energy penalty of 40 or 50 kcal mol^{-1} for formation of both singly and doubly charged species. We may be confident in the qualitative conclusions drawn from these results. As noted by Delley,[14] basis set superposition errors will be small with the numerical basis sets employed in this study. In addition, earlier calculations[17] using much simpler procedures obtained qualitatively similar results.

Interestingly, the subsequent condensation of Si–O–Al dimers to form ring tetramers is energetically unfavourable, which contrasts with the case of the purely siliceous ring tetramer, although we note that of the two ring structures studied, the Lowensteinian model is of lower energy. We find, however, that condensation to form clusters containing *one* Al is energetically favoured.

The most significant aspects of the molecular-mechanics studies (in which we minimise the energy of the cluster with respect to bond lengths and angles using an effective interatomic potential) concerns the differences between the calculated energies of Lowensteinian and non-Lowensteinian four or six-rings. We found that the Lowensteinian structure has the lower energy, but that the difference of 6 kcal mol^{-1} calculated for both sizes of ring is substantially smaller than in the case of the *ab initio* calculations. Both molecular mechanics and *ab initio* methods thus concur in predicting that the formation of Al–O–Al bridges is energetically unfavourable in small clusters, and the larger value calculated by the *ab initio* techniques is almost certainly more reliable.

Calculated hydration energies are reported in Table 3, while in Table 4 we summarise the effects of solvation on the energetics of the condensation reactions. We find again that formation of the non-Lowensteinian ring structures is

unfavourable energetically. Formation of a four-ring containing two Al species in a 'Lowensteinian' configuration is only just exothermic, while condensation reactions resulting in the formation of structures with one Al in the four-ring are more strongly favoured. Interestingly, the formation of an Al–O–Al dimer does seem to be accompanied by a large hydration term, although further condensation of this species does not appear to be likely. The main implications of these calculations are, however, clear. Both *in vacuo* and in solution, formation of small rings involving Al–O–Al bridges is energetically unfavourable, and the magnitude of the calculated energies for such structures is such that the effect is unlikely to be outweighed by any entropic terms.

If we now compare our energy penalty calculated for the small clusters considered here with that obtained by Bell *et al.*[4] for the full periodic crystal structure using lattice-energy minimisation techniques, we find that the former values are substantially larger than the latter, which were calculated as ca. 10 kcal mol^{-1} per Al–O–Al bridge. Thus although thermodynamic factors, as suggested by the calculations of Bell *et al.* favour Lowensteinian distributions, the origin of the rule is almost certainly to be found in the unfavourable energetics of the small clusters and rings which form during the syntheses of zeolitic structures. Lowenstein's rule would appear to have predominantly a kinetic basis in the energetics of the structures involved in the hydrothermal synthesis of zeolites.

The calculations described in this communication show, moreover, that the techniques of computational chemistry are able to contribute to our understanding of the complex factors controlling the synthesis of silicate and aluminosilicate systems.

We would like to thank Dr J. M. Newsam for several useful discussions. We are grateful to BIOSYM/MSI for supporting this work.

Table 3 Estimated hydration energies (E_{hydr})

Cluster	$E_{hydr}/$ kcal mol^{-1}
[Si(OH)$_4$]	−11.1
[Al(OH)$_4$]$^-$	−50.2
[Si$_2$O(OH)$_6$]	−16.0
[SiAlO(OH)$_6$]$^-$	−68.6
[Al$_2$O(OH)$_6$]$^{2-}$	−196.2
[Si$_4$O$_4$(OH)$_8$]	−10.5
[Si$_2$Al$_2$O$_4$(OH)$_8$]$^{2-}$ [a]	−150.4
[Si$_2$Al$_2$O$_4$(OH)$_8$]$^{2-}$ [b]	−171.0
[Si$_3$AlO$_4$(OH)$_8$]$^-$	−68.5

[a] Non-Lowensteinian distribution. [b] Lowensteinian distribution.

Table 4 Effects of solvation energies on condensation reactions

Reaction[a]	$E_{condens}$[b]/ kcal mol^{-1}
1	−45.6
2	−10.0
4	−54.1
5	−0.3
6	−3.8
7	+38.6
8	−17.7

[a] For numbering, see Table 2. [b] Calculated condensation energy in hydration environment; the energy is obtained by adding the hydration energies (Table 3) to the *ab initio* energies (Table 2); also added is the latent heat of vapourisation of water per H$_2$O eliminated (which is calculated as 11.26 kcal in our model).

References

1 G. Engelhardt, D. Zeigen, E. Lippmaa and M. Z. Magi, *Z. Anorg. Allg. Chem.*, 1980, **468**, 35.
2 A. K. Cheetham, C. A. Fyfe, J. V. Smith and J. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 1982, 823.
3 W. Lowenstein, *Am. Mineral.*, 1954, **39**, 92.
4 R. G. Bell, R. A. Jackson and C. R. A. Catlow, *Zeolites*, 1992, **12**, 870.
5 C. R. A. Catlow, A. R. George, C. M. Freeman and J. C. Pereira, in preparation.
6 J. R. Hill, and J. Sauer, *J. Phys. Chem.*, 1994, **98**, 1238.
7 J. Sauer, P. Ugliengo, E. Garrone, and V. R. Saunders, *Chem. Rev.*, 1994, **94**, 2095.
8 S. P. Greatbanks, P. Herwood and I. H. Hillier, *J. Phys. Chem.*, 1994, **98**, 8134.
9 G. J. Kramer, A. J. M. de Man and R. A. van Santen, *J. Am. Chem. Soc.*, 1991, **113**, 6435.
10 M. S. Stave and J. B. Nicholas, *J. Phys. Chem.*, 1993, **97**, 9630.
11 J. D. Gale, C. R. A. Catlow and R. Carruthers, *Chem. Phys. Lett.*, 1993, **216**, 155.
12 K.-P. Schroder and J. Sauer, *J. Phys. Chem.*, 1993, **97**, 6579.
13 DMOL, MSI, 9658 Scranton Road, San Diego, CA 92121-2777, USA.
14 B. Delley, *J. Chem. Phys.*, 1990, **92**, 508.
15 DISCOVER, MSI, 9658 Scranton Road, San Diego, CA 92121-2777, USA.
16 INSIGHT II, MSI, 9658 Scranton Road, San Diego, CA 92121-2777, USA.
17 P. Mezey, *ACS Symp. Ser.*, 1984, **248**, 145.