Relative Stability of ⋟Al—O—Al⋞ Linkages in Zeolites. A Nonempirical Molecular Orbital Study

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Nonempirical quantum chemical STO-3G calculations were performed for cluster models of two oxygen-bridged TO_4 tetrahedra ($T = Si$, Al). The models are based on $[(HO)_3TOT(OH)_3]^{n-}$ structures and, in case of Al-containing models ($n = 1,2$), their electric neutrality is ensured by adding positive point charges.

The calculations suggest the occurrence of ⋟Al—O—Al⋞ pairings provided certain electric fields act at the corresponding sites.

New experimental evidence mainly from solid state ^{29}Si NMR and electron and neutron diffraction studies points to the presence of ⋟Al—O—Al⋞ linkages in Linde A [1] and some other natural or synthetic zeolites [2]. Such ⋟Al—O—Al⋞ pairings violate the well-known Loewenstein rule [3] and, though exceptions of this rule are established and its uncritical acceptance has been criticized [4], a lively pro- and contra-Loewenstein discussion is just now going on with special emphasis on the above-mentioned NaA zeolite [5]. If the relative stabilities of ⋟Al—O—Al⋞ and ⋟Si—O—Al⋞ structures can be understood in terms of local binding phenomena, quantum chemical calculations of carefully selected models may throw some light on the general background of Loewenstein's rule.

In what follows we report on nonempirical quantum chemical calculations on the energetics of equilibria

$$2\,M[Al,Si] \rightleftharpoons M'[Al,Al] + M''[Si,Si]\,, \qquad (1)$$

where M, M′, and M″ denote appropriate molecular cluster models for two oxygen-bridged TO_4 tetrahedra ($T = Si$, Al) in aluminosilicates. Previous quantum chemical attempts in this field were based on less reliable semiempirical methods (EHT [6], CNDO/2 [7]). After our calculations were essentially completed the comprehensive STO-3G investigation of Hass et al. [8] has been published which is largely parallel to this study but differs substantially as far as the modelling of charged clusters is concerned (vide infra). Moreover, equilibria of type (1) are not explicitly considered therein. Thus, complementary information may emerge from both studies. For treating homodesmic reactions such as equilibrium (1) the Hartree-Fock level of quantum chemistry is generally accepted. Although the use of a basis set of "double zeta plus polarization" quality would be desirable, the size of the models specified below confines us to minimum or near minimum basis sets. Actually all calculations were made by means of the STO-3G method [9].

As in previous studies [7, 8, 10], the models M, M′, and M″ are primarily represented by the molecular clusters

$(HO)_3SiOSi(OH)_3$ **1**, $[(HO)_3AlOSi(OH)_3]^-$ **2**,

and $[(HO)_3AlOAl(OH)_3]^{2-}$ **3**. The geometries of these systems were found by optimizing all parameters except the tetrahedral O—T—O angles, the T—O—H bond angles, and the TO—H bond distance. The values for the latter two parameters were taken from the optimized geometries of $Si(OH)_4$ and $Al(OH)_4^-$ [11]. The T—O—T angles found are 146°, 141°, and 151° for systems **1**, **2**, and **3**, resp. The Si—O (bridging) distances in systems **1** and **2** are 160 and 158 pm, resp., and the Al—O (bridging) distances in systems **2** and **3** are 169 and 165 pm, resp. These values may be compared with the experimental T—O—T angles in SiO_2 (144° [12]), in zeolite NaA (149° [13]) and in crystalline potassium aluminate containing $[(HO)_3AlOAl(OH)_3]^{2-}$ ions (132° [14]). The mean values of the Si—O and Al—O bond lengths in zeolite NaA are 160 and 173 pm [13] and the average Si—O bond length in SiO_2 is 161 pm [12], whereas for potassium aluminate Al—O (bridging) =

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Table 1. Total energies, E (au), obtained by the STO-3G method for the model systems investigated[a].

Compensating charges included in the model[b]	Molecular Cluster		
	$[(HO)_3SiOAl(OH)_3]^-$ $E + 1045$	$(HO)_3SiOSi(OH)_3$ $E + 1091$	$[(HO)_3AlOAl(OH)_3]^{2-}$ $E + 998$
non	− 0.15338	− 0.78103	− 0.33986
+ 1 (P_c)	− 0.22271	− 0.77968	− 0.47973
+ 1 (P_1)	− 0.30819	− 0.79585	− 0.64528
+ 1 (P_6)	− 0.32414	− 0.79882	− 0.65108
+ 2 (P_c)	− 0.29204	− 0.77833	− 0.61959
+ 2 (P_1)	− 0.47341	− 0.82171	− 0.96152
+ 2 (P_6)	− 0.50825	− 0.82965	− 0.97485

[a] The geometries of the clusters without point charges were found by optimization (see text), and these geometries were used for all other systems including point charges, too.

[b] The meaning of the symbols is explained in the text.

173 pm was found [14]. These results support the validity of molecular cluster models with the solids under study and justify to some extent the method applied. Results for the geometry and the electronic structure of the systems **1**—**3** will be given in detail elsewhere [15].

The total energies of the models **1**—**3** (see Table 1) are the lowest energies reached for these systems so far (cf. Refs. [8, 10]). They may be directly used for calculating the reaction energy of the equilibrium

$$2\,[\text{Al, Si}]^- \rightleftharpoons [\text{Al, Al}]^{2-} + [\text{Si, Si}]\,, \qquad (2)$$

where $[T, T]^{n-}$ stands for $[(HO)_3TOT(OH)_3]^{n-}$ [16].

The models $[\text{Al, Si}]^-$ and $[\text{Al, Al}]^{2-}$ involved in equilibrium (2) are incomplete in a serious way: Cutting off the clusters $[\text{Al, Si}]^-$ and $[\text{Al, Al}]^{2-}$ leaves singly and doubly positively charged surroundings the interaction of which with the cluster may contribute significantly to the stability of structures like $[\text{Al, Si}]^-$ or $[\text{Al, Al}]^{2-}$ in aluminosilicates. Therefore attempts are made to include the positive charge of the surroundings in the models. At first, the charge of the surroundings is uniformly distributed around the molecular cluster. Arbitrarily, six fractional point charges (of $+\frac{1}{6}$ for $[\text{Al, Si}]^-$ and of $+\frac{2}{6}$ for $[\text{Al, Al}]^{2-}$) were placed in a distance of 750 pm from the bridging oxygen atom (situated in the origin of the coordinate system) in the directions $\pm x$, $\pm y$ and $\pm z$ as shown in Figure 1. This kind of field is referred to as P_c. Alternatively, we may put the compensating point charge [17] at positions which are related to typical cation positions in zeolites (denoted by P_1 and P_6 in Figure 1). In these cases strong local fields will operate on the molecular clusters. The experimental distance between the Na^+ ions and oxygen sites in the NaA zeolite (245 pm [13]) was used for fixing the distance of the point charge from the oxygen atoms (see Figure 1). This procedure leads to the equilibrium

$$\begin{aligned}&2\,[\text{Al, Si}]^- \ldots (+)\\ &\rightleftharpoons [\text{Al, Al}]^{2-} \ldots (2+) + [\text{Si, Si}]\,, \qquad (3)\end{aligned}$$

which contains electrically neutral models only.

Another approach of making the model equilibrium (2) more realistic considers the influence of a cation or point charge [17] when added to *each of the systems* involved in equilibrium (2). This point of view was adopted in [8] where a Li^+ ion was added to all the systems. The resulting equilibria

$$\begin{aligned}&2\,[\text{Al, Si}]^- \ldots (n+)\\ &\rightleftharpoons [\text{Al, Al}]^{2-} \ldots (n+) + [\text{Si, Si}] \qquad (4)\end{aligned}$$

($n = 1, 2$) are, we feel, less reliable models for investigating the Al—Si-ordering than equilibrium

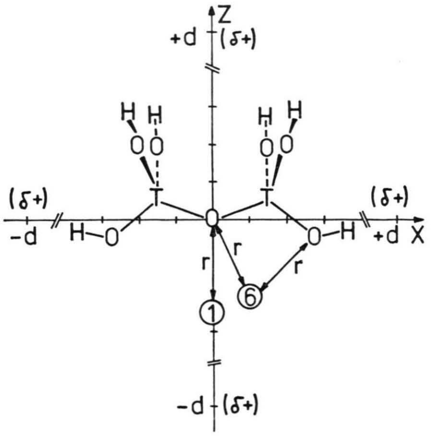

Fig. 1. Position of point charges in the models P_1, P_6 (r = 245 and 275 pm, resp.) and P_c (d = 750 pm). In the latter case two further fractional charges $\delta+$ are placed on the y-axis at $\pm d$.

Table 2. Reaction energies, ΔE (kJ/mol), for the model equilibria.

Equilibrium	Field included in the models[a]	Reaction energy ΔE (kJ/mol)
(2)	non	488[b]
(3)	P_c	118
	P_6	− 282
	P_1	− 331
(4), $n = 1$	P_c	488
	P_6	521
	P_1	460[c]
(4), $n = 2$	P_c	489
	P_6	557
	P_1	429

[a] The meaning of the symbols P_c, P_1, P_6 is explained in the text.

[b] $\Delta E = 483$ kJ/mol was obtained from the total energies given in [8].

[c] For models containing a Li^+ ion $\Delta E = 440$ kJ/mol was obtained from the energies of [8].

(3). Nevertheless, results obtained for the same positions of point charges as mentioned above (P_c, P_1, P_6) are given in Table 2.

In Table 1 all relevant total energies are compiled. Table 2 shows the reaction energies for equilibria (2)—(4) derived from these data. The calculations for model equilibrium (2) — involving clusters with uncompensated negative net charges — and for equilibria (4) involving models with either positive or negative excess charges — are in favour of the Al-avoidance rule. In contrast, for models with properly compensated charges (3) the reaction energy decreases if a more uniform field is applied (P_c) and reaches even negative values if the compensating charges are put at positions P_1 or P_6. As further calculations show the results for models such as P_1 and P_6 depend neither on the actual position nor on the actual distance of the point where the charge is located. The calculations for equilibrium (3) suggest the possibility for $\geqslant$Al—O—Al$\leqslant$ pairings to occur in aluminosilicates provided that certain local fields act at the corresponding sites in the solids.

The most significant conclusion emerging from Table 2 is the strong dependence of the reaction energies on introducing in the models charges that compensate the cluster net charges and on the *distribution in space* selected for these charges (i.e. model P_c compared to models P_1, P_6). Thus, hope is fading to conclude on the implementation of the Al-avoidance principle for a special solid on the basis of local models alone. When performing cluster calculations it seems absolutely necessary to take into account the proper electric field connected with the real structure of the solid. The major role of the overall structure in stabilizing $\geqslant$Al—O—Al$\leqslant$ pairings in aluminosilicate lattices is demonstrated by the striking difference found between the A- and X-type zeolites both having a Si/Al ratio of 1.0: $\geqslant$Al—O—Al$\leqslant$ pairings were observed in the former [1] but not in the latter case [19].

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[11] $R(\mathrm{OH}) = 98$ pm, $\angle$Si—O—H $= 108°$ in $Si(OH)_4$; $R(\mathrm{OH}) = 99$ pm, $\angle$Al—O—H $= 105°$ in $[Al(OH)_4]^-$ [15].

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[16] When doing so, no difference is found to the reaction energy calculated from the total energies of [8] (cf. Table 2).

[17] Due to the large basis set superposition error met in the STO-3G method when adding cations to n-donors the use of point charges should be preferred to real cations [18]. Comparison with the results of [8] however shows that virtually no difference in the reaction energies appears (cf. Table 2).

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