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Reorganization Energy of AlH_3

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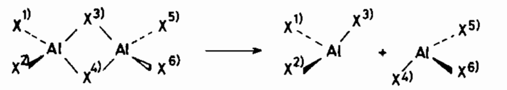
The enthalpy of a dimer Al_2X_6 dissociation into planar monomers AlX_3 does not provide a good estimate of the strength of the AlXAl bridge bonds. It is assumed that the energy needed to separate Al_2X_6 into pyramidal monomers $AlX_3{}^*$



(1)

would be a better approximation of the strength of the bridge [1]. The enthalpy of the reaction

(2)

is called the reorganization energy (ΔE_r). Given the enthalpy of dissociation and the reorganization energy, the bridge bond strength is approximated as their sum.

Some rather unexact estimates of the ΔE_r of process (2) were made [1]. A zero ΔE_r was expected for the AlH_3. It might be thus useful to get more accurate data for AlH_3. Since the reorganization energies cannot be measured directly, the quantum mechanical calculations have been performed.

Computational Details

The existence of Al_2H_6 was observed by Breisacher and Siegel [2], but no structure investigations have been made. The geometry of H^1H^2Al fragment was taken from ab initio molecular orbital calculations for AlH_3($r(Al, H^1) = r(Al, H^2) = 3$ a.u., $\alpha(H^1AlH^2) = 120°$) [3,4]. The geometry of AlH^3 part was transferred from $Me_2AlH_2AlMe_2$ experimental bridge structure [5] ($r(Al, H^3) = 3.16$ a.u., $\alpha(H^3AlH^4) = 77.4°$).

The computations were carried out with the program POLYATOM [6] for a Gaussian-type basis. The basis used was a (10, 6, 1/3, 1) set contracted to double ζ [7, 8]. The value 0.15 was used for the d-orbital exponent for Al [7].

Results and Discussion

The results are collected in Table 1. The reorganization energy of AlH_3, Eq. (2), equals $E^{tot}(AlH_3) - E^{tot}(AlH_3{}^*) = 0.156$ a.u. $= 9.8$ kcal/mol. It is perhaps interesting to note that this is approximately reproduced by the highest occupied MO energy change, which is 11 kcal/mol.

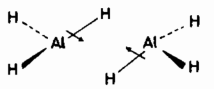
TABLE I. Energy Calculations.

MO Energies:	58.4984	58.5083
(negative in a.u.)	4.9072	4.9155
	3.2160	3.2242
	3.2143	3.2227
	3.2143	3.2224
	0.5740	0.5696
	0.4309	0.4299
	0.4309	0.4133
Total Energy: (negative in a.u.)	243.5726	243.5570
Dipole Moment (in debyes)	0	3

We are now in a position to estimate the strength of the Al–H bridge bond as the sum of the dissociation energy of Al_2H_6(17.9 kcal/mol [1]) and the reorganization energy of AlH_3(9.8 kcal/mol): $17.9 + 9.8 = 27.7$ kcal/mol. This should be compared with Al–X bridge bond strength estimates, X = Cl, Br, I, Me, H, obtained accordingly [1].

The change of dipole moment in the process (2) reflects the change of electron distribution in the AlH_3 unit.

Let us draw two excited monomer units, $AlH_3{}^*$, in the dimer geometry with the dipole moment directions indicated (we use the convention $+q \rightarrow -q$ for the dipole moment direction):



(3)

We realize that in the tetrahedral excited conformation of AlH_3($AlH_3{}^*$) the electron density shifts in the direction of the empty sp^3 hybrid. It should be noted that this is mainly due to the highest occupied MO electron density redistribution in process (2). This picture could suggest a covalent character of the bridge bonds in Al_2H_6.

Acknowledgements

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