

The Hydroalumination of Acetylene. A Self Consistent Field Molecular Orbital Study

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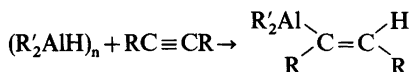
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Self consistent field molecular orbital calculations have been carried out on the reactants and product of the reaction $\text{H}_2\text{AlH}^* + \text{HC}\equiv\text{CH} \rightarrow \text{H}_2\text{Al}-\text{CH}=\text{CHH}^*$, on a symmetric π -complex formed from the reactants, and on the system at various points along the reaction path.

The reaction is best described as one in which bonds are broken and formed in a concerted manner. In the transition state the four reacting atoms (Al, H*, C, C) are joined by fractional bonds. The calculated energy of activation, $E^\ddagger = 14 \text{ kcal mol}^{-1}$, is about 10 kcal mol^{-1} above the experimental estimate.* The calculated activation energy is not improved by configuration interaction calculations involving all single and double excitations from valence orbitals to virtual orbitals.

A symmetric π -complex is found to represent a shallow local minimum on the potential energy surface, and therefore represents a possible intermediate in the reaction rather than the transition state.

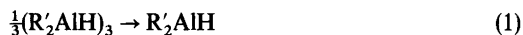
In the hydroalumination of an alkyne a dialkylaluminium hydride adds across the triple bond to give the *cis* product:¹



The most extensively studied reaction of this kind is the reaction of 4-octyne ($\text{R}' = \text{n-propyl}$) with diisobutylaluminium hydride in *n*-hexane.² *i*-Bu₂AlH is trimeric in hydrocarbon solution at room temperature.³ Eisch and Rhee² have shown

* $1 \text{ kcal} = 4.184 \text{ kJ}$.

that the kinetic true order of the reaction is 1.00 in octyne and 0.37 in $(i\text{-Bu})_2\text{AlH}$: $d[\text{product}]/dt = k[\text{RC}\equiv\text{CR}][(\text{R}'_2\text{AlH})_3]^{0.37}$. This rate expression is consistent with the two step mechanism, eqns. (1) and (2), where the second step is rate-determining.



The overall activation energy was found to be $E^\ddagger = 20.84 \pm 0.05 \text{ kcal mol}^{-1}$. Since the enthalpy of (1) ($\text{R}' = i\text{-Bu}$) has been estimated⁴ to $\Delta H_1 = 16.5 \pm 2 \text{ kcal mol}^{-1}$, it follows that the activation energy of the second step is $E_2^\ddagger = E^\ddagger - \Delta H_1 = 4 \pm 2 \text{ kcal mol}^{-1}$.

Eisch and Rhee have also studied the relative rates and the regiospecificity of the hydroalumination reactions of more than a dozen alkynes with diisobutylaluminium hydride.⁵ They considered three possible transition states for the reaction; a symmetric π -complex (as shown in Fig. 1 b), a four center transition state (as shown in Fig. 1 c) and σ -bonded complex in which the Al–C(1) bond has been formed before the Al–H*–C(2) bridge is established. After considering the experimental information, and assuming a concerted reaction proceeding *via* a fourcenter transition state to be forbidden by symmetry,⁶ Eisch and Rhee concluded that the transition state is best described as a π -complex.^{2,5}

We have investigated the model reaction (2') by



ab initio molecular orbital calculation in the hope of obtaining information about the reaction

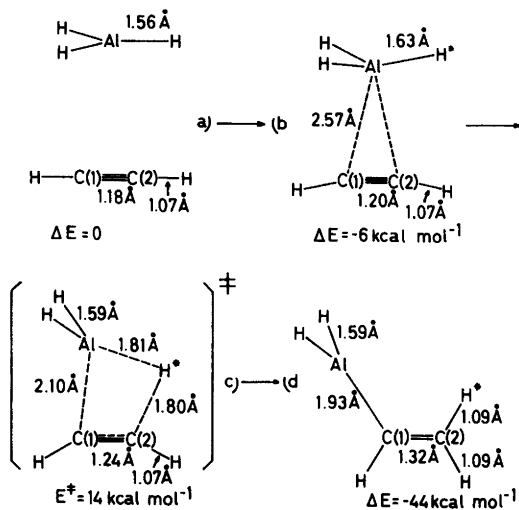


Fig. 1. Bond distances and relative energies of the reactants (a), the π -complex (b), the transition state (c) and the product (d)

mechanism and about the structure and bonding in the activated complex. A similar study of the hydroalumination of ethylene has been initiated.

COMPUTATIONS

The calculations were performed under the LCAO-MO-SCF approximation using the program MOLPRO written by Pulay and Meyer. The basis set consisted of (10,6) GTO functions on Al contracted to $\langle 5,3 \rangle$, (7,3) GTO functions on C contracted to $\langle 3,2 \rangle$,⁷ and four GTO s-functions on H contracted to $\langle 2 \rangle$.⁸ This set was augmented by a set of d-functions on Al. The orbital exponent of the d-functions, 0.35, was determined by optimization on the symmetric π -complex of H_3Al with acetylene.

The geometries of the two reactants, of the π -complex and the product, and of intermediate species with fixed reaction coordinate, were optimized using the force relaxation method of Pulay⁹ in which the forces acting on all atoms are calculated analytically. Population analyses were performed with the program MOMPOS.¹⁰

Finally configuration interaction calculations were carried out on the reactants, the π -complex, the activated complex and on the product using the program system MOLEULE.¹¹

RESULTS AND DISCUSSION

Reactants and product. The optimal $\text{C}\equiv\text{C}$ and $\text{C}-\text{H}$ bond distances obtained for acetylene, 1.184 and 1.076 Å, respectively, may be compared to the experimental values,¹² 1.203 and 1.061 Å. The optimal Al-H bond distance in monomeric AlH_3 , (symmetry D_{3h}) is 1.56 Å, equal to the Al-H bond distance in $\text{H}_3\text{AlN}(\text{CH}_3)_3$,¹³ 1.56(1) Å.

The geometry of the product was optimized under the assumption that the AlH_2 plane is perpendicular to the symmetry plane containing the Al and C atoms. See Fig. 1. The optimal bond distances and valence angles are listed in Table 2. The optimal C=C and C-H bond distances may be compared to the experimental values for ethylene,¹⁴ 1.339(1) and 1.085(2) Å, respectively, the Al-C bond distance to the corresponding bond distance in monomeric $(\text{CH}_3)_3\text{Al}$,¹⁵ 1.957(3) Å.

The energy of the reaction (2') calculated from the electronic energies of the product and reactants is $\Delta E = -44$ kcal. Using Smith's values for Al-H and Al-C bond energies,⁴ 69 and 67 kcal, respectively, in conjunction with standard values for C-H, C=C and C≡C bond energies,¹⁶ we calculate an energy of reaction equal to -46 kcal.

We conclude that our calculations are reasonably successful in predicting both geometries and relative energies of reactants and product.

The π -complex. A nearly symmetric π -complex, the two Al-C bond distances being 2.57 and 2.58 Å, is found to represent a local *minimum* on the potential energy surface. It must therefore be considered a possible intermediate rather than the transition state of the reaction. The minimum is however wide and shallow; the energy of formation of the complex from AlH_3 and acetylene is calculated as -6 kcal mol^{-1} . The barrier to internal rotation of the AlH_3 group is less than 0.1 kcal mol^{-1} .

The reaction coordinate. At the outset of our calculations there appeared to be two possible choices for reaction coordinate: While keeping the midpoint and orientation of the CC bond fixed, we could move either the Al or the H^* atom from its position in the π -complex to its position in the product.

We first chose the former approach: The H_3Al group was translated stepwise in such a way that the Al atom moved from its position in the π -complex to its position in the product: After each step the geometry and orientation of the group, and

Table 1. SCF energies (in atomic units) and energy differences relative to reactants, (in kcal mol⁻¹), along the reaction path. The reaction coordinate, z^* , is defined as the perpendicular distance from H* to the CC bond axis.

| | $z^*(\text{Å})$ | E_{SCF} | ΔE_{SCF} |
|-------------------|-----------------|------------------|-------------------------|
| Reactants | ∞ | -320.0029 | 0 |
| π -complex | 2.68 | -320.0115 | -5.4 |
| | 2.00 | -320.0021 | +0.5 |
| | 1.80 | -319.9938 | +5.7 |
| | 1.70 | -319.9882 | +9.2 |
| | 1.60 | -319.9818 | +13.2 |
| Activated complex | 1.50 | -319.9809 | +13.9 |
| | 1.40 | -319.9929 | +6.3 |
| | 1.20 | -320.0181 | -9.5 |
| Product | 0.92 | -320.0734 | -44.2 |

the geometry of the C₂H₂ substrate were reoptimized. We found, however, that the energy of the system increased monotonically, and that there at no point were forces acting on H* directing it towards its position in the product. This atoms is clearly separated from its position in the product by a potential ridge running approximately parallel to the CC bond, and an additional energy of activation is necessary to move it across the ridge. The model for the transition state in which the Al-C(1) bond has been formed before the Al-H* is broken can therefore be ruled out.

We then selected the perpendicular distance from H* to the CC bond axis as our reaction coordinate. This distance was denoted by z^* and

varied in steps from its value in the π -complex, 2.68 Å, to its value in the product, 0.92 Å. After each step all other structure parameters were reoptimized. The resulting energies are listed in Table 1.

It is seen that the highest energies are obtained for $z^*=1.6$ and 1.5 Å. The saddle point, corresponding to the transition state, is obviously found between these two values, and much closer to the latter than the former.

Comparison of the values calculated for the Al-H*, Al-C and C-H* distances for $z^*=1.6$ and 1.5 Å show that these distances change very rapidly near the saddle point. See Table 2. This prompts us to describe the mechanism as one in which these bonds are broken and formed in a concerted manner.

The concerted addition of an Al-H σ bond across a CC π bond is often assumed to be (partly) symmetry forbidden.^{5,6} In the present case, the Al-H bond is obviously sufficiently asymmetric to make the reaction allowed.

The activated complex. The calculated activation energy, $E^\ddagger = 14$ kcal mol⁻¹, is about 10 kcal mol⁻¹ above the experimental estimate, 4 ± 2 kcal mol⁻¹.

The structure parameters of the activated complex should be close to those obtained with $z^*=1.5$ Å. The bond distances indicated in Fig. 1 have been obtained as the weighted mean of the bond distances obtained with $z^*=1.5$ Å (weight=0.75) and $z^*=1.6$ Å (weight=0.25). The magnitude of the Al-H*, Al-C, C-C and C-H* bond distances is consistent with a description of the transition state as one in which the four reacting atoms are joined by fractional bonds as indicated in Fig. 1c. This description is also in

Table 2. Selected bond distances (in Å) and valence angles (in degrees) for different points on the reaction path.

| $z^*(\text{Å})$ | Reactants | π -complex | | | | | Activated complex | | | Product |
|---------------------|-----------|----------------|------|------|------|------|-------------------|------|------|---------|
| | ∞ | 2.68 | 2.00 | 1.80 | 1.70 | 1.60 | 1.50 | 1.40 | 1.20 | 0.92 |
| Al-H | 1.56 | 1.61 | 1.61 | 1.61 | 1.59 | 1.59 | 1.59 | 1.56 | 1.59 | 1.59 |
| Al-H* | 1.56 | 1.63 | 1.62 | 1.62 | 1.61 | 1.69 | 1.84 | 2.00 | 2.38 | 3.08 |
| Al-C(1) | - | 2.57 | 2.39 | 2.40 | 2.30 | 2.19 | 2.07 | 2.06 | 1.88 | 1.93 |
| C(1)-C(2) | 1.18 | 1.20 | 1.20 | 1.21 | 1.20 | 1.22 | 1.25 | 1.28 | 1.31 | 1.32 |
| C(2)-H* | - | 2.95 | 2.27 | 2.06 | 1.98 | 1.87 | 1.78 | 1.65 | 1.47 | 1.09 |
| C(2)-H | 1.07 | 1.07 | 1.07 | 1.07 | 1.07 | 1.07 | 1.07 | 1.07 | 1.07 | 1.09 |
| \angle HAIH | 120 | 117 | 112 | 112 | 119 | 119 | 125 | 141 | 137 | 125 |
| \angle AlC(1)C(2) | - | 77 | 79 | 79 | 79 | 80 | 84 | 89 | 100 | 125 |
| \angle C(1)C(2)H* | - | 109 | 112 | 113 | 114 | 114 | 115 | 114 | 116 | 122 |
| \angle C(1)C(2)H | 180 | 170 | 170 | 170 | 169 | 160 | 150 | 140 | 130 | 122 |

Table 3. Selected overlap populations and gross atomic populations.

| | Reactants | π -complex | Activated complex ($z^* = 1.5 \text{ \AA}$) | Product |
|--------------------------|-----------|----------------|--|---------|
| Overlap populations | | | | |
| Al-H* | 0.80 | 0.79 | 0.45 | -0.02 |
| Al-C(1) | - | 0.07 | 0.21 | 0.59 |
| C(1)-C(2) | 1.90 | 1.73 | 0.96 | 1.08 |
| C(2)-H* | - | -0.01 | 0.36 | 0.82 |
| C(2)-H | 0.78 | 0.77 | 0.76 | 0.81 |
| Gross atomic populations | | | | |
| Al | 12.50 | 12.54 | 12.36 | 12.15 |
| C(1) | 6.22 | 6.22 | 6.53 | 6.74 |
| C(2) | 6.22 | 6.22 | 6.16 | 6.25 |
| H* | 1.17 | 1.19 | 1.13 | 0.87 |
| H(Al) | 1.17 | 1.18 | 1.15 | 1.15 |
| H(C(1)) | 0.78 | 0.73 | 0.76 | 0.84 |
| H(C(2)) | 0.78 | 0.73 | 0.76 | 0.85 |

accord with the overlap populations listed in Table 3.

The geometry of the transition state is also reasonably consistent with the observed isotope effect for the hydroalumination of 4-octyne with (i-Bu₂AlH)₃,² $k_H/k_D = 1.68$, which indicates that the hydrogen atom is more loosely bonded in the activated complex than in (i-Bu₂AlH)₃. In ((CH₃)₂AlH)₂ the Al-H (bridge) bond distance is 1.68(2) Å.¹⁷

The gross atomic populations listed in Table 3 indicate that the net charges on the Al and C atoms in the activated complex are intermediate between the net charges in the reactants and the product.

Correlation corrections. Finally we have carried out configuration interaction calculations on the reactants, the π -complex, the transition state and the product. All single and double excitations from valence orbitals to virtual orbitals were included

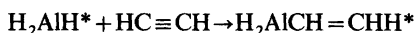
Table 4. Configuration interaction energies (in atomic units), and energy differences including CI, $\Delta E_{\text{SCF+CI}}$ (in kcal mol⁻¹).

| | E_{CI} | $\Delta E_{\text{SCF+CI}}$ |
|-------------------|-----------------|----------------------------|
| Reactants | -0.2460 | 0 |
| π -Complex | -0.2386 | -0.2 |
| Activated complex | -0.2416 | +17.0 |
| Product | -0.2300 | -33.6 |

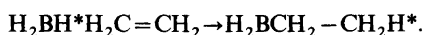
for each species. The results are presented in Table 4.

It was found that these calculations preferentially stabilized the reactants. The energy of the reaction was increased from -44 to -34 kcal mol⁻¹, and we believe the latter to be the more reliable estimate. The activation energy increased from 14 to 17 kcal mol⁻¹, while the experimental estimate is 4 ± 2 kcal mol⁻¹. The limited CI calculations are apparently less effective for the loosely bonded transition state than for the reactants.

Concluding remarks. The results of our calculations indicate that the reaction



is a concerted reaction proceeding *via* a four center transition state. A symmetric π -complex represents a local minimum on the energy surface and must therefore be considered a possible intermediate. Similar conclusions have been reached in recent SCFMO studies of the reaction¹⁸⁻²⁰



At the present time we feel that it would be premature to speculate about the effect of replacing H-atoms on Al or acetylene by other substituents, but wish to return to the question after having made calculations on methyl derivatives.

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