

***Ab Initio* Study on the Stability of Al-C₂H₄ Adducts†**

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Theoretical *ab initio* calculations have confirmed that the π complex is the most stable product for the reaction of aluminium with ethene; the calculated spin distribution and binding energy of the adduct are consistent with experiments.

Aluminium atoms are very reactive towards both saturated and unsaturated hydrocarbons in a variety of reactions.¹ There is abundant evidence showing that the Al atom participates in many modes of chemical bonding. For instance, it can be inserted directly into the C-H bond of CH₄;² the formation of aluminocyclopentene through cheletropic reaction with buta-1,3-diene³ and codimerization of two ethene molecules to form aluminocyclopentene.⁴ The analysis of the e.s.r. spectrum of the reaction product of Al atom with ethyne isolated in a rare gas matrix at liquid helium temperatures⁵ favours a σ bonded structure over the classical Dewar-Chart-Duncanson^{6,7} π co-ordination. This interesting observation is confirmed by theoretical M.O. calculations^{8,9} which predicted a fairly strong Al-C bond of 83.6 kJ/mol. The calculations also

show that the π complex is not a stable molecule but is a stationary point (transition state) on the [1,2]-Al migration potential surface.¹⁰ In contrast, the e.s.r. spectra of the aluminium-ethene adduct obtained from vapour codeposition of the atoms with ethene in neon,^{11,12} cyclopentane, and adamantane¹³ matrices are consistent with a π structure. Warm-up experiments in adamantane matrix revealed a remarkable stability of the adduct.¹³ This observation was later substantiated by a direct determination of the binding energy of the adduct in the gas phase by a time-resolved resonance fluorescence experiment.¹⁴ A recent pseudopotential multi-reference CI calculation on the π bonded symmetric Al-C₂H₄ molecule gave a contradictory conclusion.¹⁵ The calculation indicated that the interactions between the Al and ethene is van der Waal's in nature with a binding energy of only 7.6 kJ/mol. In order to resolve the discrepancy between

† Published as NRCC 29781.

theory and experiments and to understand further the nature of the π bonding we attempted a more thorough theoretical investigation of the reaction products of aluminium with ethene.¹⁶

The M.O.s active in chemical bonding for both the σ and π complexes of Al-C₂H₄ are depicted in Figure 1. These orbitals are derived from the Al 3p and from the π and π^* orbitals of ethene. For the π complex, the relevant molecular orbitals are the 1a₁, 1b₂, and 1b₁ orbitals. Assuming the direct interactions between Al and C_{p π} are stronger than the sideways overlap with the π^* orbital, filling the M.O. with three electrons results in a ²B₂ (1a₁² 1b₂) state. On the other hand, if the π interactions are more favourable, the ordering of the 1b₂ and 1a₁ will be reversed and the ²A₁ (1b₂² 1a₁) becomes the ground state. Finally, although most unlikely on energetic grounds, if all three M.O.s are of similar energies, then the three valence electrons can populate evenly among them and with uncoupled spins to give a ⁴A₂ state or spin coupled to give a ²A₂ state. In this case, the electron distribution at the Al atom would be

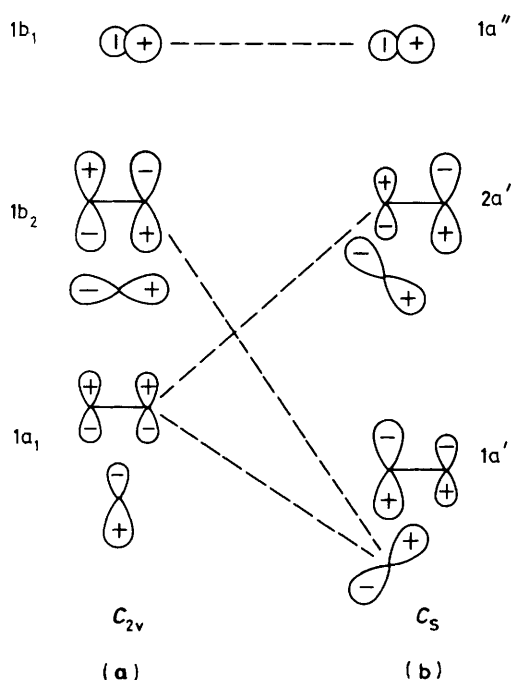


Figure 1. Qualitative M.O. diagram showing the active valence orbitals for (a) symmetric π -bonded and (b) σ -bonded Al-C₂H₄ adducts.

very close to isotropic which contradicts the e.s.r. results. The π complex may be converted into the σ complex by shifting the Al atom to the terminal carbon. Once the axial symmetry is removed, the in plane 1a₁ and 1b₂ orbitals can be mixed, forming the 1a' and 2a' orbitals. Therefore, the ground state symmetry of the σ bonded Al-C₂H₄ complex is ²A'.

Open shell *ab initio* Hartree-Fock (HF) calculations were carried out in the unrestricted formalism.¹⁶ Several basis sets, including the double zeta (DZ), double zeta plus polarization d functions on the heavy atoms (DZ*),¹⁷ and polarized triple zeta (TZ*) basis set (6-311G* for H and C, and MC-311G* for Al) were used in the calculations.¹⁶ A summary of the total energies of the stationary points located on the potential energy surface is tabulated in Table 1. With the exception of molecule I, the spin contaminations of the unrestricted wave functions are insignificant.

Initial DZ-HF calculations show that the ²A₁ state of the symmetric (C_{2v}) π structure is much higher energy than the ²B₂ state. Geometry optimizations at the DZ-HF level predicted the σ -bonded complex (²A') I to be a genuine stable structure whilst the π -complex (²B₂) II is a transition state with one imaginary frequency (229i cm⁻¹) corresponding to the terminal [1,2]-Al shift (Figure 2). Inclusion of d functions on the heavy atoms (DZ*) causes little change in the structures and the energetics. At this level (DZ*) of calculations, the energy difference between the σ and π structures is 28.3 kJ/mol. To test the stability of the wave function of the π complex towards symmetry breaking, we reoptimized the structure in C_s symmetry by removing the mirror plane bisecting the ethene molecule. No change in the structure was observed. At this stage, the effect of electron correlation was then introduced through the Møller-Plesset (MP) perturbation theory¹⁹ and coupled cluster (CC) theory.²⁰ The computational results obtained at various levels of approximation are compared in Table 1. The energy separation between the σ and π adducts reduced significantly once electron correlations were taken into account. In fact the π structure becomes *more* stable by -2.6 kJ/mol at the MP2 level although the original energy order is restored at the highest level of approximation (ST4CCD) in which the energy difference is only 1.8 kJ/mol. At this point, it was decided to reoptimize all the structures incorporating the correction for electron correlation to the second order (MP2). The results are most remarkable. The π complex ceases to be a stationary point and becomes a local minimum. More importantly, attempts to optimize the σ complex converged to the symmetric structure even with tight geometrical constraint. These results clearly indicate that the σ complex is no longer the global minimum on the MP2 potential surface. The symmetric structure is confirmed to be a

Table 1. Total energies (a.u.) and (\hat{S}^2) for the Al-C₂H₄ adducts.

Structure	(\hat{S}^2)	HF	MP2	MP3	MP4(DQ)	CCD	ST4CCD
I ^a	0.887	-319.9055	-320.1972	-320.2092	-320.2139	-320.2160	-320.2278
II ^a	0.760	-319.8947	-320.1802	-320.2079	-320.2120	-320.2136	-320.2271
II ^b	0.764		-320.1908	-320.2185	-320.2226	-320.2240	-320.2368
II ^c	0.766		-320.2383	-320.2664	-320.2853		
III ^a	0.824	-319.8294	-320.1152	-320.1438	-320.1484	-320.1503	-320.1632
IV ^a	0.769	-319.9131	-320.1825	-320.2148	-320.2200	-320.2220	-320.2321
Al ^a	0.750	-241.8561	-241.8790	-241.8864	-241.8890	-241.8904	-241.8909
Al ^c	0.757		-241.9023	-241.9118	-241.9153		
C ₂ H ₄ ^a		-78.0423	-78.2884	-78.3105	-78.3131	-78.3143	-78.3245
C ₂ H ₄ ^b			-78.2894	-78.3114	-78.3141	-78.3154	-78.3260
C ₂ H ₄ ^c			-78.3146	-78.3355	-78.3506		

^a DZ* Basis set. ^b Calculated at DZ*-MP2 optimized geometry. ^c TZ* Basis set. The MP4 energy includes contributions from singles and triples substitutions.

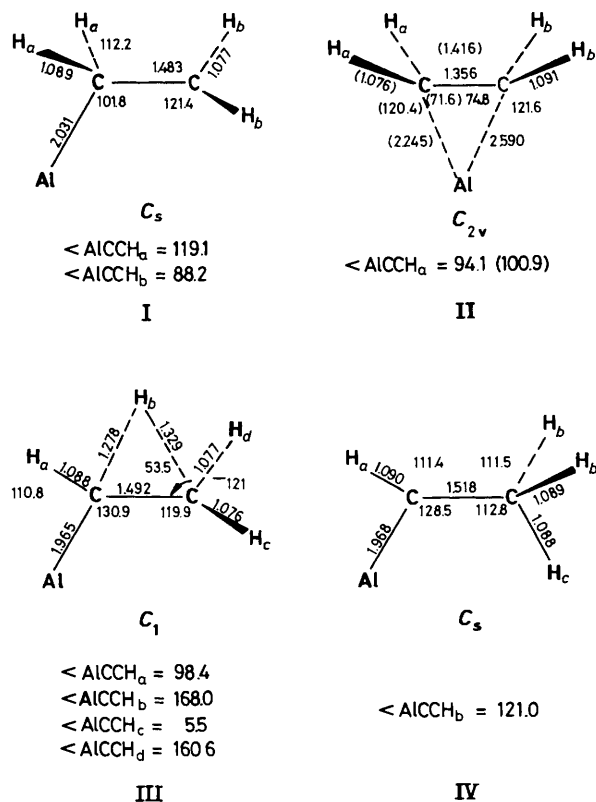


Figure 2. DZ^* Optimized geometries. The numbers in parentheses are the MP2 optimized values.

minimum from vibrational analysis. The calculated spin density is localized mainly in the Al 3p orbital parallel to the C-C bond. This spin distribution is in good accord with the e.s.r. observation^{11,12,13} and corresponds to the structure originally suggested by Kasai.¹¹ It is important to note that both the DZ and DZ^* calculations favour the symmetric over the end-on structure once the electron correlation effects are included in the geometry optimization. To investigate further the effect of basis set on the calculated quantities, the π complex was reoptimized at the MP2 level with the triple zeta plus polarization function basis sets (TZ*). The optimized structural parameters are $r(\text{Al}-\text{C}) = 2.256 \text{ \AA}$, $r(\text{C}-\text{C}) = 1.407 \text{ \AA}$, $\angle(\text{H}-\text{C}-\text{C}) = 120.7^\circ$ and $\angle(\text{Al}-\text{C}-\text{C}-\text{H}) = 99.8^\circ$. The results differ very little from that of the MP2- DZ^* calculations (Figure 2). The MP4-TZ*/MP2-TZ* binding energy of the π complex relative to the free atom and ethene is 51.0 kJ/mol. In comparison, the best estimated binding energy from the ST4CCD- DZ^* /MP2- DZ^* calculations is 51.8 kJ/mol. The predicted binding energies are encouragingly close to the zero point energy corrected experimental value of >67 kJ/mol. In passing, it is noteworthy that preliminary RHF/MCSCF calculations employing the smaller DZ basis sets also produced the same observation. At the RHF level, the σ adduct is found to be a local minimum and the π complex is a saddle point. The RHF optimized structures are very similar to that obtained from the UHF calculations indicating that the spin contaminations in the unrestricted wave functions do not affect the geometries. More significantly, optimization on the end-on structure using the MC(CAS)HF method^{21,22} with the active space (CAS) constructed from the ethene π and π^* , Al 3s and 3p orbitals led to the symmetric structure.

The HF optimized structure for the Al-ethene σ adduct (I) shows the methylene carbon is almost planar with the singly occupied molecular orbital (SOMO) perpendicular to the plane of the methylene group (Figure 2). The effect of electron correlation is to reduce the coulombic repulsion between the electrons by allowing excitations from occupied to unoccupied orbitals. In the MP2 calculations, excitations from the singly occupied π^* in ethene into the empty Al 3p_y orbital help to enhance the lateral Al-C interactions. As a result, the Al atom migrates towards the symmetric position and benefits from bonding to two carbon atoms. The bonding situation in the analogous aluminium-ethyne adduct is quite different. In Al-C₂H₂, the *cis* complex with the Al-C bond pointing away from the singly occupied orbital is slightly more stable than the *trans* complex.^{8,9} This conformation curtails any significant overlaps between the empty Al p orbitals with the singly occupied π^* orbital and there is no substantial energy gain in moving the Al atom to the symmetric position. Consequently, only the σ complex was observed in the e.s.r. spectra.

The conclusions reached in the present study differ from that of a previous calculation. In the earlier calculation,¹⁵ even though elaborate electron correlation treatments were employed, only the C-C and Al-C bond distances were optimized with the hydrogen atoms fixed to be coplanar with the carbon atoms. This does not allow enough flexibility for the carbon atoms to rehybridize and underestimated the interactions between the ethene and Al atom. A weak π donation was suggested as the reason for the small stability of the π adduct.

The difference between the electronic structures of Al-C₂H₂ and Al-C₂H₄ may also be rationalized on simple energetic grounds. The HF structure of I shows a C-C bond of 1.483 Å which is very close to a single C-C bond (~1.54 Å). In contrast, in the π complex II, the C-C bond still retains substantial double bond character. In the π complex the ethene carbons rehybridized from sp² to sp³ to facilitate the overlaps with the Al atom. The relative stability of the σ and π adducts is determined by a competition between the formation of the Al-C bond(s) to that of losing the C-C π interactions. From thermodynamic data, the energy for losing a π bond for ethyne is about 92 kJ/mol less than that of ethene.²³ In the case of Al-C₂H₂, the energy gained from the formation of a strong Al-C σ bond⁸ more than compensates for the loss of a partial π bond. This, however, may not be energetically feasible for ethene and the alternative π complex is thermodynamically more stable. Moreover, the spatially diffuse Al 3p orbital ($\langle r \rangle_{3p} = 1.82 \text{ \AA}^2$) may simply overlap more efficiently with the π orbital in ethene than in ethyne which has a shorter C-C bond.

It was recognized from previous theoretical study of the aluminium-ethyne reaction that the vinyl radical is not the most stable isomer.^{8,9} The vinylidene structure, which can be converted from the vinyl radical *via* a [1,2]-H shift, is the global minimum. A similar isomeric structure is expected to occur in the Al-ethene system. To this end, we have explored the reaction pathway for the [1,2]-H shift from the σ adduct I using the DZ^* basis sets. The structures of the intermediate (III) and the product (IV) are shown in Figure 2. Since suprafacial [1,2]-H shift is symmetry forbidden,²⁵ at the transition state, the methene group has to twist by ~90° relative to the AlCH_aC plane. The transition state (III) possesses no symmetry and the migrating proton is almost halfway between the carbon atoms. When the rearrangement is over, the molecule regains a C_s symmetry with the Al atom eclipsed by one of the methyl proton. The activation energy for the [1,2]-H shift is about 171 kJ/mol and is quite insensitive

to the level of electron correlation treatments. This energy is comparable to the corresponding activation energy for the aluminium vinyl \rightarrow vinylidene isomerization reaction of 163 kJ/mol.⁹ Unlike the aluminium-ethyne reaction, the total energy of **IV** is slightly *higher* than the π complex **II**. The best estimated energy difference between **II** and **IV** from ST4CCD/DZ* calculations is about 12 kJ/mol.

Received, 2nd June 1988; Com. 8/02196A

References

- 1 D. M. Cox, D. J. Trevor, R. L. Whetten, and A. Kaldor, *J. Phys. Chem.*, 1988, **92**, 421.
 - 2 J. M. Parnis and G. A. Ozin, *J. Am. Chem. Soc.*, 1986, **108**, 1699.
 - 3 J. H. B. Chenier, J. A. Howard, J. S. Tse, and B. Mile, *J. Am. Chem. Soc.*, 1985, **107**, 7290.
 - 4 J. H. B. Chenier, J. A. Howard, and B. Mile, *J. Am. Chem. Soc.*, 1987, **109**, 4109.
 - 5 P. H. Kasai, D. McLeod, Jr., and T. Watanabe, *J. Am. Chem. Soc.*, 1977, **99**, 3521.
 - 6 M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, 1951, **C71**, 18.
 - 7 J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 1953, 2939.
 - 8 M. Trenary, M. E. Casida, B. R. Brooks, and H. F. Schaefer, III, *J. Am. Chem. Soc.*, 1979, **101**, 1638.
 - 9 A. C. Scheiner and H. F. Schaefer, III, *J. Am. Chem. Soc.*, 1985, **107**, 4451.
 - 10 S. Sakai and K. Morokuma, *J. Phys. Chem.*, 1987, **91**, 3661.
 - 11 P. H. Kasai and D. McLeod, Jr., *J. Am. Chem. Soc.*, 1975, **97**, 5609.
 - 12 P. H. Kasai, *J. Am. Chem. Soc.*, 1982, **104**, 1165.
 - 13 J. A. Howard, B. Mile, J. S. Tse, and H. Morris, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 3701.
 - 14 S. A. Mitchell, B. Simard, D. M. Rayner, and P. A. Hackett, *J. Phys. Chem.*, 1988, **13**, 3869.
 - 15 J. Miralles-Sabater, M. Merchan, and I. Negbot-Gil, *Chem. Phys. Lett.*, 1987, **142**, 136.
 - 16 The computer program used in this study is Gaussian 86, M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, R. L. Martin, J. P. Stewart, F. W. Bobrowicz, D. J. Defrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fleuder, and J. A. Pople, Carnegie-Mellon Quantum Chemistry Publication Unit, Pittsburgh PA, 1984.
 - 17 T. H. Dunning and P. J. Hay, 'Modern Theoretical Chemistry,' vol. 3, ed. H. F. Schaefer, Plenum Press, New York, 1977.
 - 18 $\alpha_d(\text{Al}) = 0.6$, $\alpha_d(\text{C}) = 0.75$, J. S. Tse, *J. Mol. Struct. (THEOCHEM)*, 1988, **165**, 21.
 - 19 C. Möller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618.
 - 20 K. Raghavachari, *J. Chem. Phys.*, 1985, **82**, 4607.
 - 21 P. E. M. Siegbahn, J. Almlöf, A. Heiberg, and B. Roos, *J. Chem. Phys.*, 1981, **74**, 2384.
 - 22 MC(CAS)HF calculations were performed with program GAMESS. M. Dupius, D. Spangler, and J. J. Wendoloski, National Resource for Computations in Chemistry, Software Catalog, **1**, program QG01 (1980).
 - 23 'Handbook of Chemistry and Physics,' 56th edn., ed. R. C. Weast, CRC Press, 1975.
 - 24 J. B. Mann, 'Los Alamos Scientific Laboratory Report,' LA-3691.
 - 25 R. B. Woodward and R. Hoffmann, 'Conservation of Orbital Symmetry,' Springer-Verlag, Berlin.
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