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Reactions of Pulsed-Laser-Evaporated Al with C and C_2H_2. Infrared Spectra and CASSCF Calculations for AlC, Al_2C, Al_2C_2, and AlC_2H

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Abstract: Pulsed-laser evaporated Al and C atoms have been reacted in a condensing argon stream to form AlC, Al_2C, and AlCCAl. These molecules were identified from carbon-13 substitution and by comparing observed and CASSCF-calculated frequencies. The analogous Al atom reaction with C_2H_2 gave HCCAl in higher yield than in earlier thermal Al experiments with C_2H_2 following photolysis of the AlC_2H_2 complex. These aluminum acetylide molecules contain $C\equiv C$ bonds that are calculated to be slightly longer than that for C_2H_2.

Introduction

Information about binary group IIIA metal atom carbides is limited. Electronic spin resonance and optical spectra of BC, AlC, and AlC_2 and infrared spectra of BC_2 molecules have been obtained,[1–7] and several theoretical studies have been devoted to these systems.[8,9] In related work pulsed-laser-evaporated B and thermal Al atoms have been reacted with acetylene to form several new addition and insertion product species,[10,11] and pulsed-laser-evaporated Al atoms have been reacted with O_2 and H_2 molecules.[12,13] The related reaction between laser ablated Al atoms and acetylene has been examined for differences between the reaction of thermal and hyperthermal Al atoms; it was found that energized Al atoms prefer the insertion reaction. The new compounds prepared here AlCCAl and HCCAl are of chemical interest as aluminum acetylide molecules, which may have synthetic applications. The reaction of aluminum with acetylene to give first the Al–C_2H_2 π complex, which on photolysis rearranges to the HAlCCH insertion product, is analogous to reactions of several transition-metal species, particularly cationic ruthenium alkyne complexes[14–20] and reactive metal bicarbide complexes.[19] These complexes may involve HMCCR intermediates on the way to the metal–vinylidine complexes employed in organometallic synthesis. In order to complement these studies and to provide other synthetic routes to aluminum acetylides, it was decided to examine infrared spectra of the vapor species from laser-ablated solid Al/C samples.

Experimental Section

The experimental technique for laser ablation of solids for IR matrix spectroscopy has been described in detail previously.[7,12] Briefly the 1064-nm fundamental of the Nd:YAG laser (10-ns pulse width) was focused through a hole in a CsI cryogenic window onto a rotating pellet (13-mm diameter, 3-mm thick). Pellets were pressed (10 tons) from mixtures of aluminum powder (Aldrich) and graphite powder (Aldrich). The typical molar ratio Al/C (graphite) was 2:1, but 5:1, 3:1, and 1:1 mixtures were also examined. Aluminum and amorphous carbon-13 (Isotec) pellets were formed in a hot press at 630 °C (Thermal Technology). Pellets from Al_4C_3 powder (Johnson Matthey) were also pressed, and several experiments were done. FTIR spectra were recorded on a Nicolet-5DXB at 2-cm^{-1} resolution and on Nicolet-60SXR and Nicolet 750 at 0.5-cm^{-1} resolution. Sample annealing and photolysis were also done.

Additional experiments were performed for ultraviolet–visible–near-infrared spectroscopic examination using a Cary 17 spectrometer. A similar pulsed-laser-evaporation apparatus was used with quartz optics. In contrast to the IR experiments, slightly less laser power, lower argon flow rate, and shorter deposition periods were employed.

Results

Infrared spectra for three different aluminum/carbon matrix systems, optical spectra, and theoretical calculations will be presented.

Al/C System. Ablation of Al/C pellets produced strong absorptions in the 2300–1500-cm^{-1} region and weak absorptions in the 1150–970-cm^{-1} region from the well-known carbon cluster bands described previously.[7,21–23] No evidence was found for aluminum hydrides.[13] Bands in the 1200–970-cm^{-1} region were observed for the Al_2O_2, OAlO, and Al_2O molecules.[12,24] Below 900 cm^{-1} new bands were observed at 802.0, 629.8, 605.1, and

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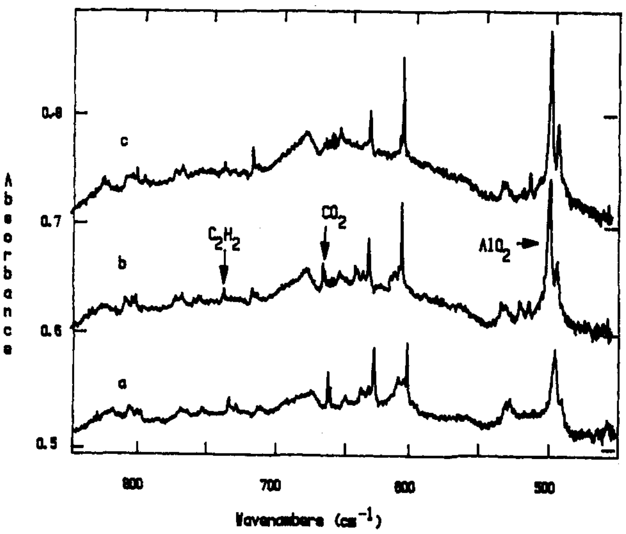

Figure 1. Infrared spectra in the 1050–450-cm^{-1} region for Al/C = 2:1 pellet ablated into argon: (a) sample condensed at 10 K for 3 h; (b) sample after annealing to 25 K; (c) sample after annealing to 35 K.

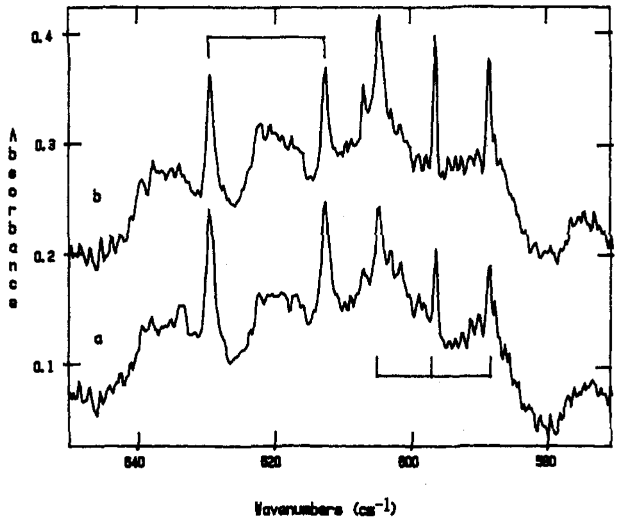

Figure 2. Infrared spectra in the 650–570-cm^{-1} region for Al/^{12}C/^{13}C = 10:1.5:1 pellet ablated into argon: (a) sample condensed at 10 K for 2.5 h; (b) sample after annealing to 29 K.

496 cm^{-1} for all Al/C ratios; a representative spectrum is shown in Figure 1 using a 2:1 pellet.

Bands at 629.8 and 605.1 cm^{-1} were produced by ablation even with low laser power. Matrix splittings for these bands were observed at 640.9 and 613.4 cm^{-1}; increasing laser power increased the latter bands, which were most intense with temperature of deposition around 15 K. Annealing decreased the 629.8-cm^{-1} band and increased the 802.0- and 605.1-cm^{-1} bands. This effect was more dramatic in other experiments than the one shown in Figure 1. The 496-cm^{-1} AlO_2 band also increased on annealing as in previous experiments.[12,24] The 5:1 pellet gave a greater yield of the 802.0 cm^{-1} band relative to those of the 629.8- and 605.1-cm^{-1} bands.

Isotopic substitution was examined with Al/^{12}C/^{13}C = 10:1.5:1 and Al/^{13}C = 4:1 pellets (Figures 2 and 3). For the mixed isotopic pellet 802.0-, 780.1-, 629.8-, 612.8-, 605.1-, 596.8-, and 589.0-cm^{-1} bands were observed. The behavior of these bands was analogous to that of the corresponding bands in the Al/^{12}C system: the doublet 802.0/780.1 cm^{-1} and triplet 605.1/596.8/589.0 cm^{-1} increased, and the doublet 629.8/612.8 cm^{-1} decreased upon annealing. The Al/^{13}C pellet gave only the 780.1-, 612.8-, and 589.0-cm^{-1} bands with matrix site satellites. The results of isotopic substitution (including matrix splitting) are shown in Table 1. The sharp 716.5-cm^{-1} band appeared in natural and isotopic carbon experiments and in earlier Al/H_2 studies[13] and hence does not involve carbon. Absorptions for carbon clusters were less evident with amorphous carbon-13 in the sample, but $^{12,13}C_3$ and $^{13}C_3$ were observed.

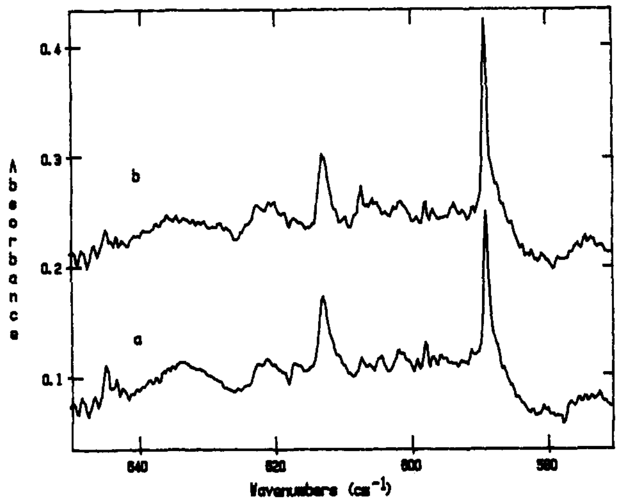

Figure 3. Infrared spectra in the 650–570-cm^{-1} region for Al/^{13}C = 4:1 pellet ablated into argon: (a) sample condensed at 10 K for 3 h; (b) sample after annealing to 30 K.

Table 1. Observed Frequencies (cm^{-1}) and Assignment in the Al/C System

^{12}C	^{12}C^{13}C	^{13}C	assignment
802.0	802.0, 780.1	780.1	Al_2C
640.1	640.1, 622.8	622.8	AlC site
629.8	629.8, 612.8	612.8	AlC
613.4	613.4, (607), 596.7	596.7	Al_2C_2 site
605.1	605.1, 596.8, 589.0	589.0	Al_2C_2

Al/C_2H_2 System. The Al + C_2H_2/Ar system has been investigated previously using thermal evaporation of aluminum.[11] It was decided to repeat these experiments first for differences between thermal and pulsed-evaporated atom reactions and second to produce carbon for the synthesis of aluminum acetylides. Two sets of experiments were done: ordinary deposition of ablated Al atoms with C_2H_2 /Ar mixtures and a flowing C_2H_2/Ar (1:5) mixture over the Al surface during ablation with subsequent codeposition with pure argon. No differences were observed between the two methods using pulsed-laser ablation.

The reaction of pulsed-laser-ablated Al atoms with C_2H_2 produced bands observed in the thermal codeposition work[11] at 579.3, 569.5, and 425 cm^{-1}, assigned to the AlC_2H_2 π complex, and at 609 cm^{-1}, assigned to cyclic AlC_2H_2. In addition the strong bands at 1976.7, 683.5, and 512.8 cm^{-1}, assigned to HCCAl, and weak bands at 2000.8 (with a 1996.9-cm^{-1} site) and 1803.9 cm^{-1}, assigned to HAlCCH, observed here were photolysis products in the thermal experiments. Figure 4 shows the 2050–1750-cm^{-1} region for experiments with low laser power, and Figure 5 illustrates spectra recorded using higher laser power. Notice the increased yield of the 1976.7-cm^{-1} band (labeled 6) with higher laser power and the more extensive photochemical growth of the 1976.7-cm^{-1} band in the experiment with lower laser power (Figure 4b). In both experiments the 2000.8- and 1803.9-cm^{-1} bands (labeled 7) were destroyed by photolysis (Figures 4b and 5b).

In addition to the bands obtained in previous work,[11] several new bands were observed. In the 2000–1500-cm^{-1} region, 1591.4-, 1668-, and 1846.1-cm^{-1} bands were detected. In the middle region, 1128.7-, 629.9-, and 605.1-cm^{-1} bands were detected. The behavior of the 1591.4-, 1668-, and 1128.7-cm^{-1} bands under annealing and photolysis was similar to that of the corresponding bands in the Al + H_2 system (AlH and HAlHAl molecules).[13] The 1846.1-cm^{-1} band due to the HC_2 radical[20] was more intense

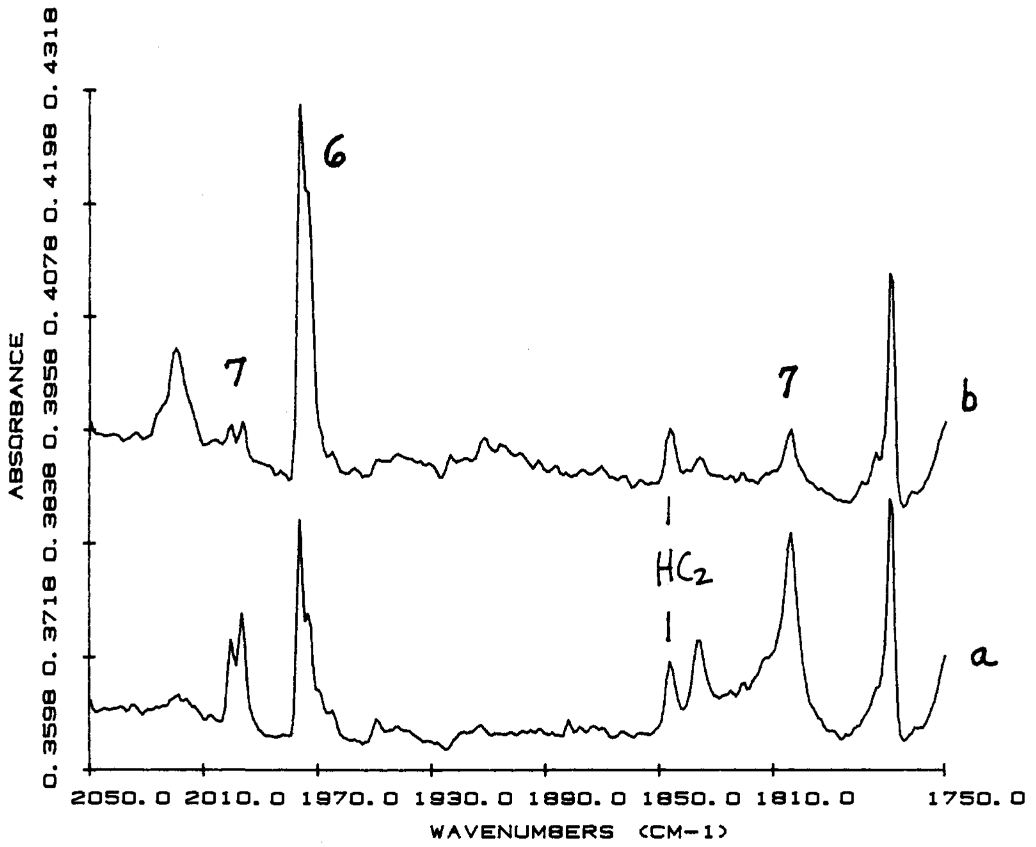

Figure 4. Infrared spectra in the 2050–1750-cm^{-1} region for pulsed-laser-ablated Al atoms codeposited with Ar/C_2H_2 = 200:1 mixture: (a) sample condensed using low laser power for 6 h; (b) sample after ultraviolet photolysis for 30 min. The 1770-cm^{-1} band is probably due to an $Al_x(CO)_4$ species; see: Xu, C.; Manceron, L.; Perchard, J. P. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1291.

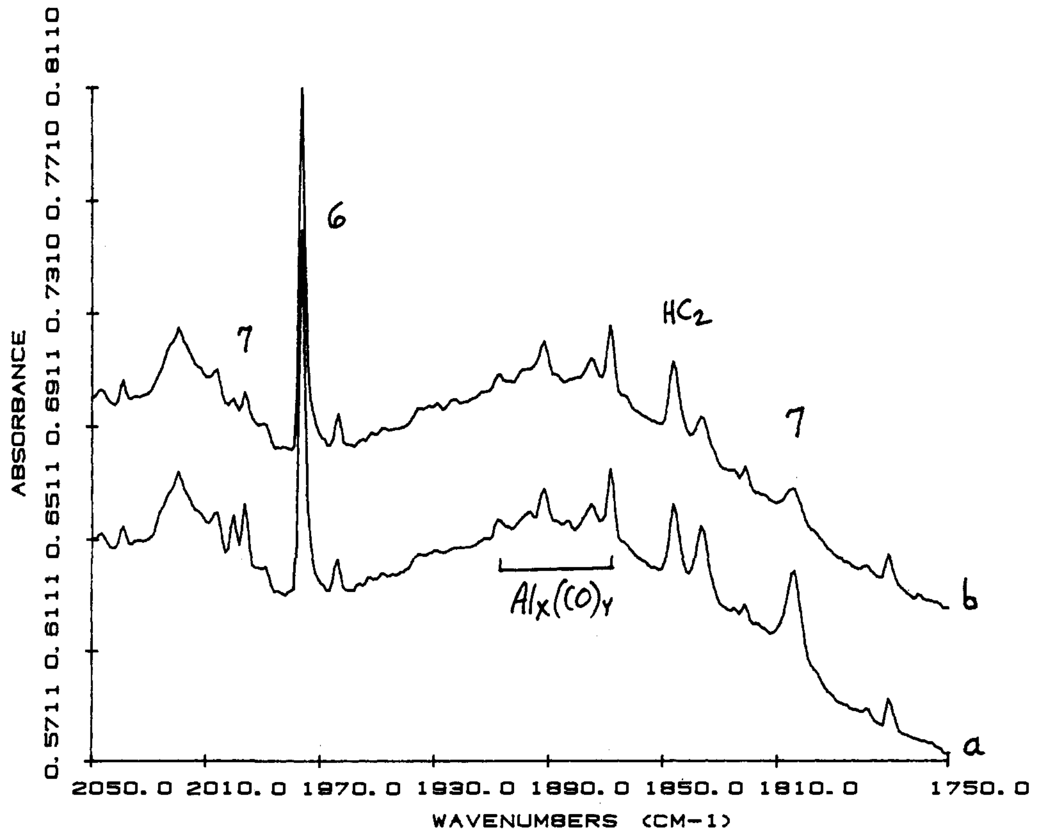

Figure 5. Infrared spectra in 2050–1750-cm^{-1} region for pulsed-laser-ablated Al atoms codeposited with Ar/C_2H_2 = 200:1 mixture: (a) sample condensed with higher laser power for 4 h; (b) sample after ultraviolet photolysis for 60 min.

in pulsed-laser experiments. The behavior of the 629.9- and 605.1-cm^{-1} bands was similar to that of the corresponding bands in the above-described Al/C system; the 629.8-cm^{-1} band decreased, and the 605.1-cm^{-1} band increased on annealing.

Al_4C_3 System. Ablating the Al_4C_3 pellet and codepositing with an argon stream produced only one strong band in the 700–600-cm^{-1} region at 605.1 cm^{-1} and weak aluminum oxide impurity bands.

UV–Visible–Near-Infrared Experiments. Several experiments were performed for examination of electronic spectra. First a pellet of pure carbon was investigated and numerous carbon cluster bands were detected. Among the most important are C_2 clusters, which cannot be observed in the IR but should be one of the major products of ablation. Bands at 1203, 1004, and 868 nm were assigned to the 0–0, 1–0, and 2–0 vibronic transitions of the $A^1\pi_u \leftarrow X^1\Sigma_g^+$ system of C_2 on the basis of comparison with gas-phase data.[26] The intensities of these bands decreased after annealing, which is in good correlation with previous results where aggregation takes place for carbon clusters.[23] Higher carbon cluster bands were also observed including C_3 at 409, 407, and 405 nm.[21-23]

New sharp bands in the Al/C system at 427.5 and 441.5 nm are due to 0–0 and 1–0 vibronic transition of the $B^4\Sigma \leftarrow X^4\Sigma$ system of AlC, in agreement with recent works.[5,6] New bands were also observed at 918/909 nm. The carbon cluster bands were much weaker, and C_2 was not observed. Similar experiments with Al + C_2H_2 gave a very strong Al band at 339 nm, a strong Al_2 absorption at 398 nm, and a sharp weak C_2^- absorption at 520 nm.[13,27,28]

Calculations. Geometry optimizations and harmonic frequency calculations were performed for aluminum/carbon species at the complete active space self-consistent field (CASSCF) level. Full valence active spaces were used for AlC_2 and Al_2C. For isomers of AlCCH and Al_2C_2, the lowest lying occupied valence orbital and the highest lying unoccupied valence orbitals were excluded from the active space. These orbitals are almost entirely C–C σ bonding and antibonding, respectively. The result of this reduction in the active space is that the CC stretching frequency will be predicted somewhat too high in these molecules. For C and H Dunning's correlation-consistent valence double-ζ plus polarization (VDZ) set[29] was used, while for Al a [6s 4p] contraction of Huzinaga's (11s 7p) primitive basis[30] was augmented with a single d function (exponent 0.311).[31] This Al basis should be of similar quality to the VDZ basis sets for first-row atoms.

In order to obtain more accurate energy differences between the various species, a series of coupled-cluster calculations was undertaken. The coupled-cluster method with single and double excitations and a perturbational estimate of triple excitations (CCSD (T)) was used, together with larger basis sets. The valence triple-ζ (VTZ) set of Dunning[29] was used for C and H, while the McLean–Chandler sp basis,[32] augmented with a 2d1f set, was used for Al. The geometries were taken from the CASSCF/VDZ optimizations.

The CASSCF geometry optimizations and harmonic frequency calculations were performed using the SIRIUS/ABACUS program.[33] The CCSD (T) calculations were performed using ACES II.[34] Calculations were run on an IBM RS/6000 Model 350 workstation or a CRAY Y-MP/864 computer at the San Diego Supercomputer Center.

Table 2. Ab Initio Frequencies (cm^{-1}), Intensities (km/mol), and Structures for AlC_2 and Al_2C Calculated at the CASSCF Level with the VDZ Basis Set

	$\nu(a_1)$	$\nu(a_1)$	$\nu(b_2)$	comments
$^2A_1{}^a$	1733.1	680.2	442.0	$Al^{12}C_2$
	(0.05)	(11.8)	(12.3)	
	1699.3	673.4	433.9	$Al^{12}C^{13}C$
	1664.9	666.1	426.2	$Al^{13}C_2$
$^2B_2{}^b$	1547.6	487.7	430.0	$Al^{12}C_2$
	(142)	(143)	(36)	
$^2A_1{}^c$	715.1	164.6	855.3	$Al_2{}^{12}C$
	(0.07)	(3)	(23)	
	697.6	163.3	831.2	$Al_2{}^{13}C$

[a] R(Al–C) = 1.922 Å, ∠CAlC = 39.4°, infrared intensities in parentheses. [b] R(Al–C) = 2.031 Å, ∠CAlC = 37.9°. [c] R(Al–C) = 1.84 Å, *R*(Al–Al) = 2.79 A, ∠AlCAl = 98.6°.

Our previous experience with the boron analogs[7] of these Al-containing molecules suggests that the CASSCF vibrational frequencies should be in rather close agreement with experiment (errors of a few percent). More importantly, the isotopic shifts are given very accurately at this level of calculation: to better than one part in a thousand. The CASSCF/VDZ bond lengths can be expected to be too long by about 0.03 A. The total atomization energies ($\sum D_e$) calculated at the CCSD (T)/VTZ level can be in error by as much as 12 kcal/mol, although other thermochemical quantities of interest here, such as energy differences between isomers or different electronic states, should be accurate to within 3–4 kcal/mol or better. By using a correction formula developed by Martin,[35] the error in the $\sum D_e$ values can be reduced to some 3 kcal/mol. Energy differences should then be accurate to 1–2 kcal/mol.

Discussion

The new aluminum/carbon species produced here will be identified with the help of ab initio calculations, and reaction mechanisms will be discussed.

AlC. The bands at 640.1 and 629.8 cm^{-1} exhibited 12/13 isotopic ratios of 1.027 74 and 1.027 78, which are very close to the harmonic ratio 1.027 74 for the diatomic AlC molecule. An earlier ESR study[4] identified AlC as the main product of the Al + C reaction. For the ground state of AlC, ω_e = 639.3 and $\omega_e x_e$ = 4.5 cm^{-1} were found from analysis of fluorescence spectra in solid argon.[6] Gas-phase values of these constants[5] are 654.8 and 4.29 cm^{-1}. High-level theoretical calculations (CASSCF and MRCI) predict 629 cm^{-1} for the AlC fundamental.[8] On the basis of these results, bands 640.1 and 629.8 cm^{-1} are assigned to the AlC molecule in two different matrix environments. The first one is very close to the gas-phase value, and the second indicates a red matrix shift due to perturbation. The 640.1-cm^{-1} band may be due to the AlC molecule on a grain surface, and the 629.8-cm^{-1} band may be due to AlC surrounded by argon. Agreement between the 630.3-cm^{-1} fundamental deduced from the fluorescence spectrum and that observed here at 629.8 cm^{-1} in solid argon is excellent.

Al_2C_2. The 605.1-cm^{-1} band gave a triplet structure in Al/$^{12}C/^{13}C$ experiments. This molecule therefore contains two equivalent carbon atoms. Possible structures are AlC_2 and isomeric forms of symmetric Al_2C_2 molecules. It was proposed earlier[9] that the most stable structure of AlC_2 is a triangle with CAlC angle around 32°. A similar conclusion was made from the ESR spectrum of this molecule.[4] The MCSCF level of theory predicts a $^2A_1$ ground state and $^2B_2$ exited state lying 62.3 kcal/mol above for this molecule. The structure and frequencies for both states are presented in Table 2. For Al_2C_2 only one minimum corresponding to linear symmetric AlCCAl was found on the

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Table 3. Ab Initio Frequencies (cm^{-1}) and Intensities (km/mol) for the Linear AlCCAl, AlCCH, and HAlCC Molecules Calculated at the CASSCF Level with the VDZ Basis Set

$Al^{12}C^{12}CAl$;[a] $Al^{13}C^{13}CAl$	HCCAl;[b] $H^{13}C^{13}CAl$	HAlCC;[c] $HAl^{13}C^{13}C$
2032.7(0)(σ_g); 1952.9	3571.3(20)(σ); 3554.8	1997.6(323)(σ); 1991.7
604.9(469)(σ_u); 588.5	1983.4(66)(σ); 1920.7	1958.1(191)(σ); 1887.2
350.9(0)(σ_g); 350.9	716.2(46)(π); 709.8	732.3(18)(σ); 716.7
193.2(0)(π_g); 185.8	511.3(134)(σ); 501.4	428.8(206)(π); 428.0
69.8(67)(π_u); 67.9	157.2(10)(π); 151.2	34.9i( )(π); 33.6i

[a] R(Al—C) = 2.002 Å, R(C≡C) = 1.258 Å; C_2H_2 for comparison R(C—H) = 1.084 Å, R(C≡C) = 1.217 Å. [b] R(Al—C) = 1.987 Å, R(C—C) = 1.245 Å, R(C—H) = 1.068 Å. [c] R(H—Al) = 1.585 Å, R(Al—C) = 1.775 Å, R(C≡C) = 1.283 Å.

potential surface (see Table 3). The theoretical isotopic 12/13 ratio for the strongest AlC_2 band is 1.0211, and for AlCCAl the ratio is 1.027 89. The experimental 605.1/589.0 isotopic ratio (1.027 31) is very close to the last value. On the basis of these results, the band at 605.1 cm^{-1} is assigned to the linear symmetrical AlCCAl molecule. Support for this assignment is found in observation of the 605.1-cm^{-1} band in the Al + C_2H_2 system where HCCAl was also a product. The 613.4-cm^{-1} band is a component of matrix splitting. The counterparts of its isotopic structure overlap with isotopic structure from the 605.1-cm^{-1} band. In experiments with Al/^{13}C pellets when the 613.4-cm^{-1} band was strong, a 596.7-cm^{-1} band was also observed. The isotopic ratio 613.4/596.7 = 1.027 82 is very close to the ratio for the 605.1-cm^{-1} band.

Al_2C. The 802.0-cm^{-1} band grew on annealing in all experiments and is assigned to the Al_2C molecule for several reasons. This band indicated only two components of isotopic structure in experiments with Al/^{12}C/^{13}C and belongs to a molecule with one carbon atom. This band increased relative to that of AlC with increasing Al concentration, suggesting a more Al-rich product. The experimental isotopic shift (1.0281) is almost equal to the theoretical prediction for the Al_2C molecule (see Table 2). Theoretical calculations predicted that this molecule should have only one strong band (b_2) in the IR and that this band should occur above Al–C vibrations for the AlC, AlC_2, and Al_2C_2 molecules.

AlC_2. The AlC_2 molecule is predicted to absorb in the 650–680- and 420–440-cm^{-1} regions, where no distinct bands were found. It must be concluded that the AlC_2 molecule was not prepared in infrared observable quantity although AlC_2 was observed in comparable ESR experiments.[4]

Cyclic and linear AlC_2 have been studied previously by Flores and Largo.[9] These workers performed geometry optimization at the Hartree–Fock level, obtaining two different solutions for each of the cyclic and linear structures. The CASSCF method used here allows all important electron configurations to mix properly, and we find only one minimum for each structure. The CASSCF method also correctly predicts a cyclic ground state. Our cyclic structure is closer to the "Structure 2" of Flores and Largo, although the vibrational frequencies computed here are quite different. In addition, the configuration interaction calculations of these authors somewhat overestimate the cyclic/linear energy separation in AlC_2: 11 kcal/mol compared to the present estimate of 8 kcal/mol.

HCCAl. The bands at 1976.7, 683.5, and 512.8 cm^{-1} in the Al/C_2H_2 system are assigned to the C≡C stretching, HCC deformation, and Al—C stretching vibrations of the HCCAl molecule. The experimental isotopic 12/13 ratios for each vibration (1.0370, 1.0102, and 1.0217) were measured earlier;[11] these ratios are very close to ratios from the calculated frequencies (1.0379, 1.0090, and 1.0197; see Table 3). The isomeric linear molecule HAlCC is calculated to be less stable than HCCAl by 60 kcal/mol. The present ab initio calculations verify that the 1976.7-, 683.5-, and 512.8-cm^{-1} bands are due to the more stable HCCAl molecule. Although the 1983.4- and 1958.1-cm^{-1} values calculated for the C≡C stretching mode bracket the observed value, the 511.3-cm^{-1} value calculated for the Al–C stretching mode in HCCAl is in much better agreement with the 512.8-cm^{-1} observed value than the 732.3-cm^{-1} value calculated for HAlCC. As noted in the Calculations section, the CASSCF calculation gives a C≡C stretching frequency that is too high, which is also more consistent with HCCAl than HAlCC. Finally, the relative intensities calculated for the three strongest bands of HCCAl are in very good agreement with the observed (6, 4, and 9, respectively) relative band absorbances.

Reaction Mechanisms. It is interesting to consider possible reaction mechanisms required to produce the above-described new molecules. In the Al/C system the main channel is reaction between Al and C atoms in the condensing argon matrix to form the AlC molecule, reaction 1.

$$\mathrm{Al + C \rightarrow AlC} \qquad (1)$$

Several ways to form AlCCAl come to mind.

$$\mathrm{2AlC \rightarrow Al_2C_2} \qquad (2a)$$

$$\mathrm{Al + C_2 \rightarrow AlC_2;\ AlC_2 + Al \rightarrow Al_2C_2} \qquad (2b)$$

$$\mathrm{Al + AlC \rightarrow Al_2C;\ Al_2C + C \rightarrow Al_2C_2} \qquad (2c)$$

The first channel (2a) is preferred over the second and the third channels, as the AlC band decreased and the Al_2C_2 band increased after annealing.

In the Al + C_2H_2 system the stepwise mechanism takes place:

$$\mathrm{Al + C_2H_2 \rightarrow (HAlCCH)^* \rightarrow HAlCCH} \qquad (3a)$$

$$\mathrm{\rightarrow H + AlCCH} \qquad (3b)$$

$$\mathrm{\rightarrow HAl + C_2H} \qquad (3c)$$

The matrix relaxes and stabilizes some of the insertion product HAlCCH, reaction 3a, which has been identified from the observed 2000.8- and 1803.9-cm^{-1} bands.[11] Recall that HAlCCH is photosensitive and that AlCCH is one of the photolysis products.[11] In the pulsed-laser experiments, a major fraction of the insertion product formed decomposes to give AlCCH, reaction 3b, and HAl and C_2H, reaction 3c, which are observed in the product spectrum.

The observation of C_2^- in the Al + C_2H_2 experiments shows that C_2 is produced from C_2H_2 and suggests that reaction 2b is involved in the formation of Al_2C_2 from C_2H_2. Alternatively, a second hyperthermal Al atom can react with the HCCAl product of (3b) to give AlCCAl, reaction 3d.

$$\mathrm{Al + HCCAl \rightarrow (HAlCCAl)^* \rightarrow H + AlCCAl} \qquad (3d)$$

The above reaction (3a) requires hyperthermal Al atoms, which can produce vibrationally exited insertion product molecules that lead to rapid dissociation. Also in this system ordinary π complex AlC_2H_2 and cyclic AlC_2H_2 molecules were observed, but only at low laser power.

It is known that laser ablation produces Al atoms with a wide distribution of kinetic energies; under similar conditions average kinetic energies near 5eV have been measured.[36] Hence two types of processes are occurring in the matrix. First interaction between thermal or near thermal Al atoms (low energy tail of distribution and collisionally relaxed atoms) and C_2H_2 forms AlC_2H_2 complexes. Under photolysis, which always accompanies ablation, these complexes convert to HAlCCH and then to AlCCH molecules. Second is interaction between hyperthermal Al atoms (maxima and high-energy tail of distribution) with acetylene

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(36) Wang, H.; Salzberg, A. P.; Weiner, B. R. *Appl. Phys. Lett.* **1991**, *59*, 935.

molecules to form the exited insertion products, which decompose to AlCCH. Support for this conclusion is that bands of the former molecules were most intense in spectra after deposition and the bands of AlCCAl were not observed in thermal experiments even after prolonged photolysis. Finally, the reaction of Al and C_2H_2 is analogous to the reaction of Al and O_2 where thermal aluminum atoms add to give cyclic AlO_2 without activation energy and hyperthermal aluminum atoms insert to give the linear OAlO molecule.[12]

It is necessary to emphasize that the relative intensities of carbon cluster bands depended significantly on the pellet ablated. For Al/C experiments (as in UV–visible–near-infrared and IR regions) the intensities of C_x bands were less than those in experiments with pure carbon pellets. In infrared experiments the strongest band after Al/C ablation was 2039.2 cm^{-1} (C_3). Increasing the Al/C ratio led to decreasing C_3 intensity (also to decreasing intensities of all other carbon cluster bands). Moreover, during the work with isotopically enriched pellets, this band, its isotopic counterparts, and other cluster bands were much weaker than that in the Al/C case. The same situation was found with boron/carbon experiments.[7] If formation of clusters occurs on the surface, then the presence of Al terminates cluster formation. According to Vala et al.[23] and the present optical experiments, the major ablation products are C, C_2, C_3, C_5, C_6 and C_9. The dominant aggregation process should be $C + C_x$, as the relative concentration of carbon atoms is much larger than that of clusters and $C_x + C_y$ aggregation is less probable. If the formation of clusters occurs on a matrix surface, then competition between the Al + C reaction and aggregation takes place and leads to decreasing intensities of carbon cluster bands. Indeed in the optical spectra for Al/C pellets, bands of C_2 were not observed and bands of C_x molecules were weaker than those in experiments with pure carbon.

Thermochemistry. Total atomization energies for the various systems considered here have been computed at the CCSD (T)/VTZ level and are listed in Table 4. We also list results corrected using the scheme suggested by Martin.[35] The latter should be considerably more reliable than the directly computed numbers.

Table 4. Total Atomization Energies for Various Al/C/H Systems (kcal/mol)

	Al_2C	Al_2C_2	AlCCH	AlC_2 (lin)	AlC_2 ($2A_1$)	AlC_2 ($2B_2$)
ΣD_e	166.0	352.2	378.6	245.8	255.7	196.3
corrected[a]	172.1	363.3	389.7	253.8	261.7	202.3

[a] Results corrected as in ref 35, see text.

From Table 4 it can be seen that the energy of the reaction AlCCH → AlCC + H is 135 kcal/mol, which is about 20 kcal/mol larger than that for the boron analog. Cyclic AlC_2 is more stable than the linear isomer by almost 8 kcal/mol. This estimate should be accurate to at least 2 kcal/mol, so it appears definite that the AlC_2 ground state is cyclic. The separation between the $2A_1$ and $2B_2$ states of the cyclic structure is almost 60 kcal/mol.

Conclusions

Two important conclusions are reached from the present studies. First, the reaction of aluminum and carbon atoms and the reaction of energized aluminum atoms and acetylene lead to the formation of dialuminum acetylide (AlCCAl) and in the latter case to aluminum acetylide (HCCAl). These linear molecules are analogous to acetylene and contain similar $C\equiv C$ bonds; however, the $C\equiv C$ bond length increases slightly with each Al substituent, suggesting increasing ionicity in the aluminum acetylides. Second, thermal Al atoms add to C_2H_2 to make a π complex; on photoexcitation this π complex rearranges to the organometallic insertion product HAlCCH, which decomposes to the acetylide HCCAl. These reactions with Al and C_2H_2 may provide a model for the reaction of other metal atoms with C_2H_2.

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