O_2 and CO_2. For each of these neutral species only the higher energy isomer, CCN^+, was found to react (as was observed by Bohme et al.[24]), with the major product in each case being C_2NO^+. If $OCCN^+$ is the most stable structure of C_2NO^+,[26] then considerable rearrangement will be required to produce it from CNC^+ even though the reaction channel leading to this product is probably exothermic for both O_2 and CO_2. The absence of any observed reactivity with CO_2 in the earlier ICR study is also suggestive that CNC^+ was the major isomer present in that study, as we have discussed above on the basis of the density of states calculations.

Conclusions

In their initial paper exploring possible differences in the reactivity of CCN^+ and CNC^+, Haese and Woods[1] suggested that the reactivities of the two isomers might be substantially different and that any differences could have important implications for the astrochemical environment. Kraemer et al.[10] also suggested the possibility of CCN^+ undergoing reaction with H_2, with CNC^+ being unreactive. We have demonstrated experimentally that, in several reactions, viz. those with H_2, CH_4, H_2O, O_2, and CO_2, there is indeed a large difference in reactivity, with the CCN^+ isomer being the more reactive in all cases. However, with the reactant neutrals NH_3, C_2H_2, HCN, and N_2O, the difference in reactivity between CCN^+ and CNC^+ is small or not detectable.

The most significant of these reactions to the interstellar medium is the reaction with hydrogen. We have observed experimentally that reaction 1 can produce *only* CNC^+ (if only ground-state C^+ is present) and that CCN^+ reacts rapidly with hydrogen. This ensures that CNC^+ is the only isomer of C_2N^+ likely to be present in appreciable amounts in dense interstellar clouds. As CNC^+ is unreactive with the major constituents of these clouds, its reactions with minor constituents need to be considered. We should also point out that our ab initio calculations show the reaction of C^+ with HNC (reaction 5), which is also

$$C^+ + HNC \rightarrow CCN^+ + H \qquad (5)$$

present in measurable densities, is exothermic to CCN^+ formation by ~65 kJ mol^{-1}. Assuming that CCN^+ is indeed a significant product in reaction 5, the ensuing reaction of CCN^+ with H_2 to produce H_2CN^+ + C (reaction 6) has sufficient energy to form

$$CCN^+ + H_2 \xrightarrow{0.90} H_2CN^+ + C \qquad (6)$$
$$\xrightarrow{0.10} H_2C_2N^+$$

only the $HCNH^+$ isomer of H_2CN^+. Subsequent dissociative recombination should therefore re-form HCN and HNC (eq 7);

$$H_2CN^+ + e^- \rightarrow HCN \textit{ or } HNC + H \qquad (7)$$

hence, reaction 5, if it occurs, only serves to recycle HNC. Thus, in spite of the undoubted presence of C_2N^+ in the interstellar medium, we would not expect the ion to be accessible to radioastronomical observation as the major isomeric form, CNC^+, is nonpolar.

Further, even though CNC^+ has a relatively large heat of formation (ΔH_f = 1620 kJ mol^{-1}), it does not react as rapidly as one might expect with species such as CH_4, H_2O, O_2, and CO_2 even when exothermic channels are available. If these reactions proceed at substantially less than the collision rate because of barriers in the exit channels, then the rate coefficients should decrease markedly at low temperatures. One avenue that may also present an important loss process for CNC^+ at low temperatures and pressures is the replacement of collisional stabilization of the association adduct of CNC^+ + HCN by the alternative mechanism of radiative stabilization.

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Registry No. CNC^+, 78271-45-1; CCN^+, 76619-90-4; C_2N_2, 460-19-5; CH_3CN, 75-05-8; HC_3N, 1070-71-9; C^+, 14067-05-1; H_2, 1333-74-0; CH_4, 74-82-8; NH_3, 7664-41-7; H_2O, 7732-18-5; C_2H_2, 74-86-2; HCN, 74-90-8; N_2, 7727-37-9; O_2, 7782-44-7; N_2O, 10024-97-2; CO_2, 124-38-9.

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Reaction of Ground-State Aluminum Atoms with Propene: Electron Paramagnetic Resonance Spectroscopic Evidence for a π-Allylmetal Hydride[1]

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Abstract: Reaction of ground-state Al atoms (^2P) with propene on solid inert hydrocarbon surfaces at 77 K gives, in addition to allyl- and a dimethyl-substituted aluminocyclopentane, π-allylaluminum hydride. The magnetic parameters of this species are a_{Al} = 336 G, a_H(Al–H) = 57.4 G, a_H(2-endo) = 13.45 G, a_H(1) = 5.2 G, and g = 2.0023. This is the first direct electron spin resonance spectroscopic evidence for a π-allylmetal hydride, intermediates that are believed to be involved in the isomerization of alkenes.

We have previously shown by electron paramagnetic resonance spectroscopy (EPR) that Al atoms react with ethylene on a solid inert hydrocarbon surface at 77 K in a rotating cryostat to give aluminocyclopentane[3] and aluminum monoethylene.[4-6] The formation of an aluminocyclopentane substantiates Skell and McGlinchey's suggestion[7] that reaction of Al atoms with propene involves the intermediacy of an aluminocyclopentane. A related aluminocyclopentene is also formed by cheleotropic addition of

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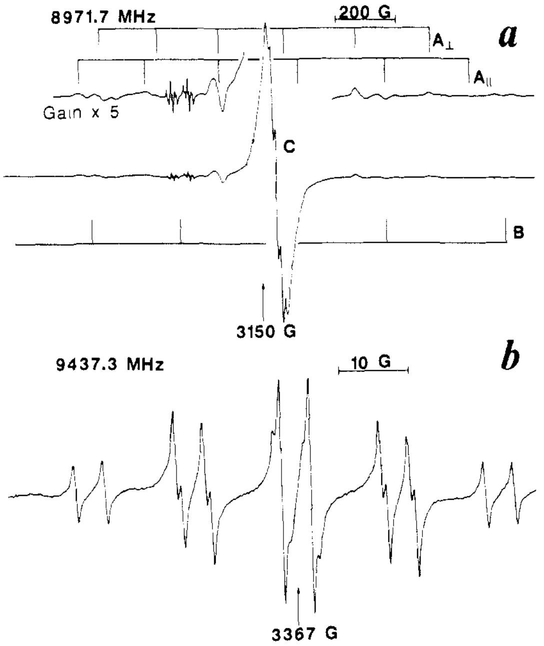


Figure 1. EPR spectrum: (a) Al atoms and propene in adamanatane at ~4 K; (b) central part of the spectrum C at 173 K.

Al atoms to buta-1,3-diene.[8] These cyclic 7-electron organoaluminum compounds are characterized by a singly occupied molecular orbital (SOMO) that has about 30% Al s character and a correspondingly large Al hyperfine interaction. The structure and bonding of aluminum monoethylene in which there is equivalent hyperfine interaction with four protons is still in some doubt. Kasai[5,6] favors a π complex with electron donation from the ligand into an sp-hydrized orbital on the metal and some back-donation of the unpaired electron from the Al ^3p_x orbital into the π^* orbital of the ligand. We were not entirely happy with this bonding scheme and suggested the possibility of σ bonding with the Al atom undergoing a rapid 1,2-shift; i.e., Al[C_2H_4] may be fluxional.[4] Preliminary ab initio molecular orbital calculations[9] using triple-ζ basis sets and polarization on all atoms suggest that β-aluminoethyl is more stable than the π complex by several kilocalories/mole.

In an attempt to confirm the MO prediction we have studied the reaction of Al atoms with propene, an alkene expected to give a more stable secondary β-aluminoalkyl than ethylene. In this preliminary communication we show that β-aluminopropyl is not detected by EPR, but we do find yet another unexpected reaction of ground-state Al atoms, π-allylaluminum hydride formation. This molecule is formed by an intramolecular hydrogen atom transfer reaction, and we believe that this is the first report of this reaction for a coordinatively unsaturated non-transition-metal atom.

The rotating cryostat was used to react ground-state (^2P) Al atoms, produced from aluminum metal in a resistively heated tungsten-coil furnace[10] with newly deposited propene molecules trapped on the cold surface (77 K) of a continuously renewed matrix of adamantane or cyclohexane on the spinning drum containing liquid nitrogen. The resulting deposits were examined by EPR after transfer from the drum still at 77 K and under high vacuum.

The EPR spectrum of the deposit from reaction of Al atoms with CH_3CHCH_2 on adamantane is shown in Figure 1a and has superimposed spectra from one major (C) and two other paramagnetic species (A and B). Spectrum C is shown in expanded scale and at higher temperature (173 K) in Figure 1b and is readily assigned to allyl with the magnetic parameters $a_H(2) = 14.3$ G, $a_H(2) = 15$ G, $a_H(1) = 4.1$ G, and $g = 2.0026$. Spectrum A consists of six absorptive and six derivative lines from a species with axially symmetric g and A tensors with the parameters $a_{\parallel}(\mathrm{Al}) = 273.4$ G, $a_{\perp}(\mathrm{Al}) = 227$ G, $g_{\parallel} = 1.9799$, and $g_{\perp} = 2.0132$. These parameters are similar to those for aluminocyclopentane[3] and are assigned to a dimethyl-substituted aluminocyclopentane, which will be discussed in detail in a full publication.

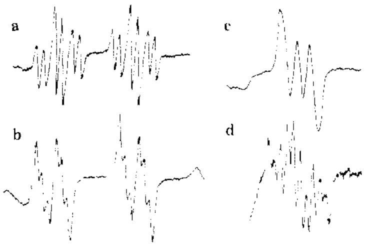


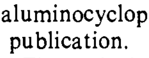
Figure 2. Aluminum $M_I = +^1/_2$ lines of species B from Al atoms and CH_3CHCH_2 (a), CH_3CHCD_2 (b), CD_3CDCD_2 (c), and CD_3CHCH_2 (d).

The most interesting spectrum in Figure 1a is, however, the sextet of multiplets labeled B centered at $g = 2.0023$ with an isotropic Al hyperfine interaction of 336 G (from an exact solution of the spin Hamiltonian), which is much larger than that for unsubstituted[3] and dimethyl aluminocyclopentanes. As with many organoaluminum radicals, the aluminum $M_I = +^1/_2$ lines were sharper and better resolved than the other lines in the spectrum. These lines, which were centered at 2866.7 G at a frequency of 9318 MHz, are shown in Figure 2a and are clearly a doublet of triplets of doublets. The major doublet splitting is 57.4 G, which is similar to the unique hydrogen of methylaluminum hydride CH_3AlH ($a_H = 56, 52, 55$ G; $a_{Al} = 317, 258, 254$ G; and $g = 2.000, 2.002, 2.002$), which is formed by reaction of photoexcited Al atoms (^2S) with methane at cryogenic temperatures.[11]

The triplet splitting of 13.45 G suggests two equivalent hydrogens, and the small doublet splitting of 5.2 G suggests a second unique hydrogen. The two most likely structures for B are the acyclic propenylaluminum hydride (**1**) analogous to the insertion product CH_3AlH[11] and the cyclic π-allylaluminum hydride (**2**), produced by an intramolecular H-transfer reaction from the methyl group to aluminum.

$CH_2{=}CHCH_2AlH$

1



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Reaction of Al atoms with the series of deuteriated propenes CH_3CHCD_2, CD_3CDCD_2, and CD_3CHCH_2 gave the aluminum $M_I = +^1/_2$ lines shown in Figure 2b–d. The lines from CH_3CHCD_2 show a large doublet spacing of 58.6 G, proving that the hydrogen attached to the aluminum nucleus is transferred from the methyl group. Furthermore, the doublet of triplets $a_H(1) = 13.4$ G and $a_D(1) = 2$ G demonstrates that the two equivalent hydrogens with $a = 13.4$ G from CH_3CHCH_2 are not bound to the same carbon nucleus. Thus, species B has structure **2** and not structure **1**. The EPR evidence from CH_3CHCH_2 and CH_3CHCD_2 does, however, indicate that the four hydrogens on carbons 1 and 3 are not magnetically equivalent but are equivalent in pairs as they are in allyl itself. The structure of **2** should therefore be written as **3**, with the endo hydrogens exhibiting a 13.4-G hyperfine interaction and the exo hydrogens having a hyperfine interaction less than the line width of 0.5 G.

This was confirmed by reaction of Al atoms with CD_3CDCD_2 and CD_3CHCH_2, the former giving a triplet (Figure 2c) with $a_D = 9$ G and the latter giving a multiplet (Figure 2d) with $a_H(1) = 5.2$ G, $a_D(1) = 1.9$ G, $a_H(1) = 13.8$ G, and $a_D(1) = 8.7$ G.

The isotropic hyperfine interaction of 336 G divided by the estimated value of $\mathbf{A} = 1395$ G for an electron in the 3s orbital

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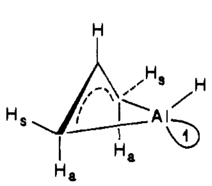
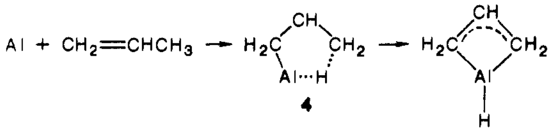


3

aluminum[12] gives an unpaired s spin population, $\rho_{3s}(\mathrm{Al}) = 0.24$, indicating considerable hybridization of the Al 3s and 3p orbitals as found for aluminocyclopentane[3] and aluminocyclopentene.[8] The marked difference between the endo and exo hydrogens is reasonble if the SOMO at Al has sp^x character with $x > 1$ and with a lobe directed downward in the same direction as the endo C–H bonds. The driving force for the reactions is the formation of two strong C–Al and one Al–H bonds with bond strengths of ~65 and ~68 kcal mol^{-1}, respectively.[13],[14]

All of the deuteriated propenes gave the appropriate deuteriated allyl upon warmup while only CD_3CDCD_2 gave a strong signal from the monoligand complex $\mathrm{Al[CD_3CDCD_2]}$ with $a_{\parallel}(\mathrm{Al}) = 44.4$ G, $a_{\perp}(\mathrm{Al}) \sim 5$ G, and $g_{\parallel} = g_{\perp} = 2.0024$, indicating a primary deuterium isotope effect on the formation of π-allylaluminum hydride and allyl.

It would appear from this work that ground-state Al atoms react with propene at 77 K to give π-allylaluminum hydride and not the primary product $HAlCH_2CHCH_2$ analogous to the aluminomethyl hydride formed from photoexcited Al atoms and methane at 12 K.[11] The most likely route to π-allylaluminum hydride is by addition to give β-aluminopropyl, which then undergoes an intramolecular hydrogen-transfer reaction through a five-membered transition state.



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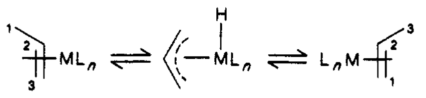
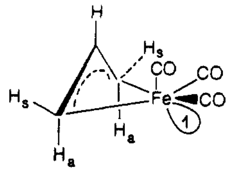
5

Analogous reactions involving a π-allylmetal hydride have been proposed to explain the double-bond isomerization of alkenes by coordinatively unsaturated transition-metal complexes,[15-18] the so-called Bönnemann mechanism.[19] The alkene forms a π complex with the transition-metal center, which rapidly equilibrates with the π-allylmetal hydride, which can give either the original alkene or the isomerized alkene π complex. Such π-allyl complexes are also considered to be important in other surface-catalyzed alkene reactions, e.g. alkene oxidation.[20]



Interestingly, the EPR spectrum of the 17-electron species π-allyltricarbonyliron



produced by photolysis of pentacarbonyliron in the presence of propene in pentane solution at 163 K[21] consists of an isotropic triplet centered at $g = 2.0433$. In this molecule the unpaired electron interacts with the two endo protons (6.1 G), and the hyperfine interaction from the exo protons is also less than the line width. Similar species are also formed from photolysis of $Fe(CO)_5$ in the presence of tetramethylethylene,[22] and in both cases an unstable π-allyltricarbonyliron hydride is invoked as an unobserved intermediate. It appears that under our reaction conditions we have been able to observe the hitherto elusive π-allylmetal hydride complex for the first time. Since we find that a range of alkenes react with Al atoms to give the corresponding π-allylaluminum hydride, the reaction appears to be quite general and has important implications for homogeneous and heterogeneous catalysts where there is a notorious lack of evidence and information about such intermediates.

We are not yet sure of the origin of the allyl spectrum from reaction of Al atoms (^2P) with propene at 77 K. Parnis and Ozin[11] in their experiments observed an intense spectrum of methyl and attributed its formation to H atom abstraction from CH_4 by an Al-containing species formed from traces of O_2 impurity present on deposition. Under our conditions Al atoms react with O_2 to give AlO_2, which can be isolated at 77 K in cyclohexane with no detectable cyclohexyl formation. Furthermore, AlO, formed from Al atoms and N_2O, is reactive enough to abstract a H atom from adamantane. Reactions of Al atoms with other more reactive alkenes suggest that substituted allyls are not formed by H-atom abstraction by an oxygenated Al impurity while thermochemical calculations show the formation of allyl and AlH from CH_3CHCH_2 and Al is too endothermic ($\Delta H \sim 14$ kcal mol^{-1})[14] to occur at any significant rate at 77 K.

There was no evidence for the formation of aluminum hydrides or allyl from a product study of the reaction of Al atoms and propene at 77 K[23] although the latter species may have been a precursor to the production of hexanes.

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