8334

J. Am. Chem. Soc. **1990,** *112,* 8334-8337

Evidence for the Existence of Unsaturated Organoaluminum Molecules in the Gas Phase: $AlCH_2$, $Al(CH_3)_x$ ($x = 1, 2$), and AlC_2H_4

Ragampeta Srinivas, Detlev Sülzle, and Helmut Schwarz*

Contribution from the Institut für Organische Chemie der Technischen Universität Berlin, Strasse des 17, Juni 135, D-1000 Berlin 12, West Germany. Received April 16, 1990

Abstract: Neutralization–reionization mass spectrometry (NRMS) has been successfully applied to generate for the first time several solitary organoaluminum molecules in the gas phase. It is demonstrated that neutralization of the structurally characterized ions $AlCH_2^+$, $AlCH_3^{\cdot+}$, $Al(CH_3)_2^+$, and $AlC_2H_4^+$ gives rise to recovery signals. Two further points emerge from this study: (i) Isomerization of $AlCH_2$ and $AlCH_3$ (both in their ionic and neutral forms) to the isomeric hydridoaluminum species $HAlCH_x$ ($x = 1, 2$) is negligible, if operative at all. (ii) For the $AlC_2H_4^+$ system, in addition to the isomer corresponding to a π-complex, a second isomer is observed, which, according to its collisional activation mass spectrum, is best described as the hitherto unknown $HCAlCH_3^+$ ion. Neutralization of this species, in contrast to $AlC_2H_4^+$, does however not result in the formation of a detectable $HCAlCH_3$ molecule. Similarly, while $HAlC_2H_5^+$ is found to exist as a species distinct from $Al(CH_3)_2^+$, neutralization of the former failed while the latter provides a recovery signal.

Coordinatively unsaturated metal fragments are suggested to play a pivotal role as intermediates in homogeneous and/or heterogeneous catalysis or in organometallic chemistry in general.[1] Unfortunately, direct evidence for the existence of these species as stable monomeric entities in the condensed phase is often, but not always,[1e] scarce due to facile *inter*molecular reactions. In addition, as recently discussed at great length by Hange, Margrave, and Kafafi,[2] the unambiguous stoichiometric characterization of organometallic species in a matrix can be quite difficult not to mention the effects of the matrix cage which may obscure the intrinsic properties of the solitary molecules in question. Recently, a method of producing isolated neutrals in the dilute gas phase from the cations by first neutralizing a beam of ions followed by reionization (NRMS)[3] has provided direct evidence for the existence of many formerly unobtainable neutral molecules. In this respect it was particularly encouraging that, by using NRMS, several otherwise elusive *organometallic* molecules were generated and characterized as genuine, chemically bound molecules with lifetimes > 1 μs. Typical examples include the following species: $FeCH_x$ ($x = 0-3$),[4] NiL_n complexes ($n = 1, 2$; $L = CO, D_2O, ND_3$),[5] "end-on" $Cu^{(0)}$ complexes of HCN and HNC,[6] the half-sandwiches MC_5H_5 ($M = Fe, Co, Ni$),[7] and the long-sought-after metal acetylides MCCH ($M = Fe, Co, Ni$).[8] In this paper we describe NRMS experiments aimed at generating and characterizing the following aluminum hydrocarbon complexes, e.g. $AlCH_2$, $AlCH_3$, $Al(CH_3)_2$, and AlC_2H_4. While

$AlCH_2$ and $AlCH_3$ are theoretically well characterized by Schaefer's nonempirical quantum mechanical calculations as stable species with dissociation energies of 77 ($AlCH_2$) and 68 kcal/mol ($AlCH_3$),[9a] no experimental studies seem to exist in the literature which would lend direct support to this prediction.[10] We shall demonstrate that (i) either species is indeed viable in the gas phase and (ii) isomerization to an aluminum hydride fragment $AlCH_x$ → $HAlCH_{x-1}$ does *not* take place. Evidence is also presented that $Al(CH_3)_2$ is a stable molecule; the tendency of this fragment to isomerize is quite minor, if prevailing at all. For aluminum complexes of the general composition (Al,C_2,H_4) there already exists a rich literature commencing with the seminal paper of Kasai and McLeod,[11] in which for the first time an aluminum atom-ethylene adduct generated in a neon matrix was characterized by ESR. Later ESR work, conducted in different matrices at varying temperatures,[12-14] as well as an IR study of the AlC_2H_4 molecule in solid argon[15] clearly pointed to the formation of a symmetrical π-complex of the aluminum atom with the CC double bond, rendering both CH_2 groups of C_2H_4 equivalent. Recent laser studies[15] provided binding energies of the aluminum atom to olefins, and for AlC_2H_4 a lower value of 16 kcal/mol was reported. Until recently[17] theory had not been successful in interpreting the experimental observations for AlC_2H_4, in particular the binding energy. In earlier calculations, using a rigid C_2H_4 geometry, the attraction of atomic Al to C_2H_4 was calculated to be <5 kcal/mol.[18] A similar result was found in a recent

(1) Selected reviews and biographies: (a) Hartley, F. R., Patai, S., Eds. *The Chemistry of the Metal-Carbon Bond*; Wiley: Chichester, 1982. (b) Crabtree, R. H. *Chem. Rev.* **1985,** *85,* 245. (c) Collmann, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Book: Mill Valley, CA, 1987. (d) Russell, D. H., Ed. *Gas Phase Inorganic Chemistry*; Plenum: New York, 1989. (e) Andrews, L.; Moskovits, M., Eds. *Chemistry and Physics of Matrix-Isolated Species*; Elsevier: Amsterdam, 1989.

(2) Hange, R. H.; Margrave, J. L.; Kafafi, Z. H.: in ref 1e, Chapter 10.

(3) Reviews: (a) Terlouw, J. K.; Burgers, P. C.; v. Baar, B. L. M.; Weiske, T.; Schwarz, H. *Chimia* **1986,** *40,* 357. (b) Wesdemiotis, C.; McLafferty, F. W. *Chem. Rev.* **1987,** *87,* 485. (c) Terlouw, J. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1987,** *26,* 805. (d) Schwarz, H. *Pure Appl. Chem.* **1989,** *61,* 685. (e) Holmes, J. L. *Adv. Mass Spectrom.* **1989,** *11,* 53. (f) Terlouw, J. K. *Ibid.* **1989,** *11,* 984. (g) Holmes, J. L. *Mass. Spectrom. Rev.* **1989,** *8,* 513. (h) McLafferty, F. W. *Science* **1990,** *247,* 925.

(4) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Organometallics* **1987,** *6,* 2268.

(5) Hudgins, D. M.; Porter, R. F. *Rap. Commun. Mass Spectrom.* **1988,** *2,* 197.

(6) Eller, K.; Sülzle, D.; Schwarz, H. *Chem. Phys. Lett.* **1989,** *154,* 443.

(7) Drewello, T.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1989,** *93,* 177.

(8) Drewello, T.; Schwarz, H. *Chem. Phys. Lett.* **1990,** *171,* 5.

(9) (a) Fox, D. J.; Ray, D.; Rubesin, P. C.; Schaefer, H. F., III *J. Chem. Phys.* **1980,** *73,* 3246. (b) For calculations on $AlCH_2$ see also: Cook, C. M.; Allen, L. C. *Organometallics* **1982,** *1,* 246.

(10) For studies on the laser-induced dissociations of aluminum alkyls in the gas phase and at aluminum alkyl–substrate interfaces, see: (a) Zhang, Y.; Stuke, M. *Jpn. J. Appl. Phys.* **1988,** *27,* L1349. (b) Beuermann, Th.; Stuke, M. *Appl. Phys. B* **1989,** *49,* 145. (c) Zhang, Y.; Stuke, M. *J. Phys. Chem.* **1989,** *93,* 4503. For an earlier review, see: Eisch, J. J. *Comprehensive Organometallic Chemistry*; Pergamon, Oxford, 1982; Vol. 1, pp 555–682.

(11) Kasai, P. H.; McLeod, D., Jr. *J. Am. Chem. Soc.* **1975,** *97,* 5609.

(12) Kasai, P. H. *J. Am. Chem. Soc.* **1982,** *104,* 1165.

(13) Chenier, J. H. B.; Howard, J. A.; Mile, B. *J. Am. Chem. Soc.* **1987,** *109,* 4109.

(14) Howard, J. A.; Mile, B.; Tse, J. S.; Morris, H. *J. Chem. Soc., Faraday Trans.* **1987,** *83,* 3701.

(15) (a) Manceron, L.; Andrews, L. *J. Phys. Chem.* **1989,** *93,* 296. (b) Manceron, L.; Andrews, L. *J. Phys. Chem.* **1990,** *94,* 3513.

(16) Mitchell, S. A.; Simard, B.; Rayner, D. M.; Hachett, P. A. *J. Phys. Chem.* **1988,** *92,* 1655.

(17) (a) Xie, Y.; Yates, B. E.; Yamaguchi, Y.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1989,** *111,* 6163. (b) Also see: Tse, J. S.; Morris, H. *J. Chem. Soc., Chem. Commun.* **1989,** 78. (c) Gao, J.; Karplus, M. *Chem. Phys. Lett.* **1990,** *169,* 410.

Unsaturated Organoaluminum Molecules in the Gas Phase

J. Am. Chem. Soc., Vol. 112, No. 23, 1990 8335

Table I. Collisional Activation Mass Spectra of $AlCH_2^+$ (m/z 41), $AlCH_3^{•+}$ (m/z 42), and $Al(CH_3)_2^+$ (m/z 57) Generated from $Al(CH_3)_3$[a,b]

fragment ion m/z	precursor ions		
	$AlCH_2^+$	$AlCH_3^{•+}$	$Al(CH_3)_2^+$
56			2
55			<1
43			<1
42			45
41		10	3
40	12	6	1
39	10	3	4
28	<1	<1	<1
27	77	79	42
15		<1	<1

[a] Intensities are given in % total fragment ions (excluding the precursor ions). [b] $AlCH_2^+$ and $AlCH_3^{•+}$ were also generated from $Al(C_2H_5)_3$ and were found to give rise to the same CA mass spectra, as given in the table. This observation points to the fact that, irrespective of the neutral precursor, the same fragment ion is generated. However, this does not hold true for the m/z 57 species $(Al,C_2H_6)^+$ when generated from $Al(C_2H_5)_3$. For this ion the major CID fragments are m/z 55 (43%), m/z 29 (20%), m/z 28 (6%), and m/z 27 (27%). Also see text.

theoretical paper by Miralles-Sabater et al., using a large-scale double-ζ-plus-polarization basis set for their CI calculations.[19] A satisfactory theoretical description of the π-bonded AlC_2H_4 species could only be arrived at by simultaneous rigorous geometry optimization and proper treatment of the effects of electron correlation.[17] The binding energy of the ground-state π-complex was determined to exceed 11 kcal/mol, and the theoretical treatment predicted the existence of a second minimum, corresponding to Al–methylcarbene; this species is predicted to lie less than 5 kcal/mol above the π-bonded global minimum. Here, we confirm that the AlC_2H_4 π-complex is indeed a perfectly stable gas-phase molecule. A second (Al,C_2,H_4) isomer could not yet be generated in a NRMS experiment, although experimental data clearly support the existence of an *ionic* species having the connectivity $HCAlCH_3^+$.

Experimental Section

The mass spectrometric experiments were performed on our modified ZAB-HF machine which is of BEBE configuration (B stands for magnetic and E for electric sector).[20] Aluminum-containing organometallic ions are generated in a combined EI/CI source by 100-eV electron impact ionization of suitable AlR_3 precursors (R = CH_3, C_2H_5) employing the following conditions: ion source temperature, 200 °C; ion trap current, 500 μA; repeller voltage, 20 V; and accelerating voltage, 8 kV. Depending on their volatility the AlR_3 samples were introduced by using the direct insertion probe (R = C_2H_5) or the gas inlet line (R = CH_3). Collision-induced dissociations (CIDs),[21] used to characterize the primary ions M_1^+, were brought about by mass-selecting a beam of M_1^+ by means of B(1)E(1) and colliding it with helium in a collision chamber located in the third field-free region (90% transmittance, T; this transmittance corresponds, on the average, to 1.1–1.2 collisions[22]). Ionic dissociation products were recorded by scanning B(2). In the NRMS experiments, a beam of BE-mass-selected M_1^+ ions (having 8-keV translational energy) was neutralized in the first cell of a differentially pumped tandem collision cell by colliding it with xenon (75% T). Unreacted ions were deflected away from the beams of neutral species M_1 by putting a voltage on a deflector electrode; subsequent reionization of M_1 occurred in the second collision cell by collision with oxygen (75% T). The mass spectrum of the resulting ions (M_1^+) was recorded by scanning B(2). The minimal lifetime t (identical with the transit time from collision cell I to
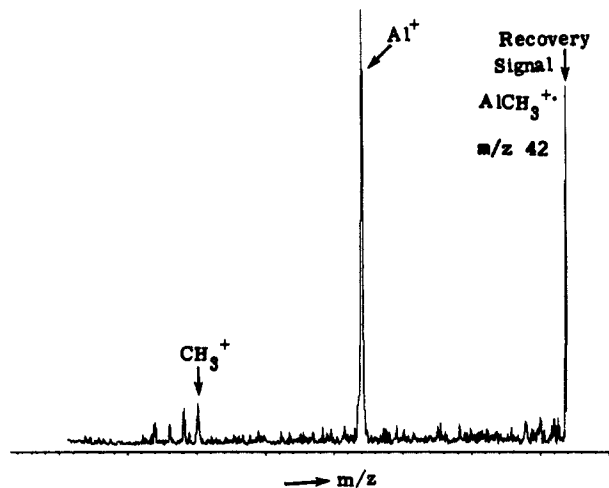
Figure 1. NR mass spectrum (Xe, 75% T; O_2, 75% T) of $AlCH_3^{•+}$.

cell II) in the present experiment is ca. 0.5–1 μs. Sensitivity problems prevented us from performing a CID experiment of reionized M_1^+. Signal-averaging techniques were used to improve the S/N ratio. Twenty to fifty scans were accumulated by on-line processing the data with the VG 11/250 or the AMD-Intectra data system. It should be mentioned that the mass-resolution was always sufficient to unambiguously select $AlC_xH_y^+$ complexes of interest free from any interferences of isobaric hydrocarbon ions.

Results and Discussion

The $AlCH_2^+$ species (m/z 41) is easily accessible by dissociative ionization of $Al(CH_3)_3$ (consecutive losses of $CH_3^•$ and CH_4);[23] its CA mass spectrum gives rise to the reaction products shown, together with the CA mass spectra of $AlCH_3^{•+}$ and $Al(CH_3)_2^+$, in Table I.

The CA mass spectrum is compatible with the connectivity $AlCH_2^+$; in particular, the very weak signal at m/z 28 $(AlH^{•+})$ suggests that the isomeric form $HAlCH^+$ is not likely to be present. A similar situation holds true for the analogous $FeCH_x^+$ system (x = 2, 3), which was also found not to isomerize to the hydrido isomers $HFeCH_{(x-1)}^{+.4}$ Reduction of $AlCH_2^+$ in a NRMS experiment yields an intense recovery signal at m/z 41 (32% total ion current). This may reflect the strength of the $Al–CH_2$ bond (77 kcal/mol[9a]). The fragmentation pattern in the NR spectrum (generation of AlC^+ (6%), $Al^{•+}$ (50%), $CH_2^{•+}$ (4%), and CH^+ (8%)) is also in support of a connectivity $AlCH_2$. We note two important differences in comparison with the CA spectrum: (i) Signals due to loss of $H^•$ (m/z 40) or the formation of $AlH^{•+}$ are absent in the NR mass spectrum; this, again, underlines our conclusion that both $AlCH_2^+$ and $AlCH_2$ do not isomerize to the corresponding hydrido isomers $HAlCH^{+/0}$. (ii) The signals at m/z 14 and 13 are likely to result from reionization of neutral CH_2 generated by collision-induced dissociation of $AlCH_2^+$ ($AlCH_2^{•+}$ → Al^+ + CH_2), followed by dissociation of $CH_2^{•+}$ to CH^+; a second contribution may originate from the neutralization process which yields neutral $AlCH_2$ species having a broad range of internal energies. As a result, the energy-rich fraction of $AlCH_2$ may decompose to AlC + H_2 and Al + CH_2, respectively, followed by reionization and dissociation of the various neutrals formed.

The next organoaluminum fragment to be discussed corresponds to $AlCH_3$. The CA mass spectrum of $AlCH_3^{•+}$, generated by consecutive losses of two methyl radicals from $Al(CH_3)_3^{•+}$,[23b] is given in Table I. As has already been discussed for $AlCH_2^+$, the negligible intensity (<1%) of the signal at m/z 28 $(AlH^{•+})$ suggests that $HAlCH^{•+}$ is quite unlikely to be present; rather the species seems to have retained an intact methyl group attached to the aluminum ion.

(18) Trenary, M.; Casida, M. F.; Brooks, B. R.; Schaefer, H. F. *J. Am. Chem. Soc.* **1979**, *101*, 1638.

(19) Miralles-Sabater, J.; Merchau, M.; Nebot-Gil, I. *Chem. Phys. Lett.* **1987**, *142*, 136.

(20) For a detailed description of the machine and its operation, see: (a) Weiske, T. Ph.D. Thesis, Technische Universität Berlin D 83, 1985, (b) Terlouw, J. K.; Weiske, T.; Schwarz, H.; Holmes, J. L. *Org. Mass Spectrom.* **1986**, *21*, 665.
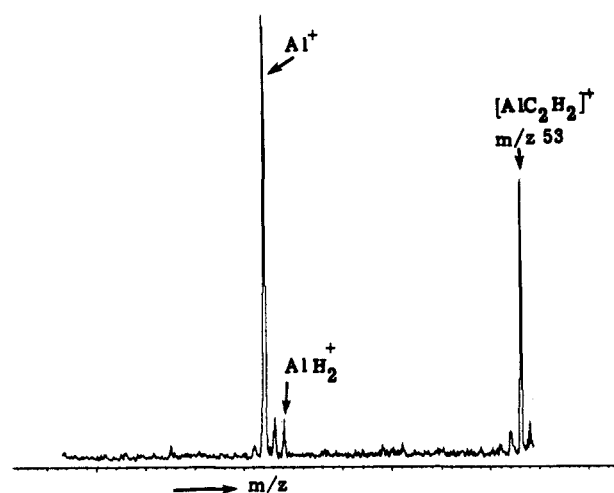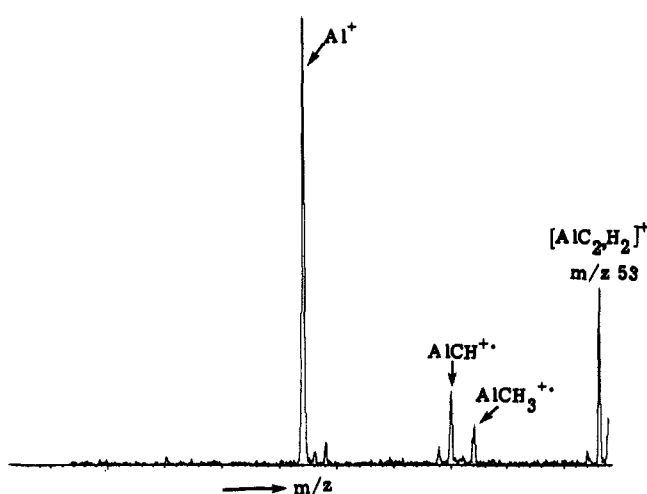
(21) (a) Levsen, K.; Schwarz, H. *Angew Chem., Int. Ed. Engl.* **1976**, *15*, 509. (b) Cooks, R. G., Ed. *Collision Spectroscopy*; Plenum: New York, 1978. (c) Levsen, K.; Schwarz, H. *Mass Spectrom. Rev.* **1985**, *3*, 77.

(22) Holmes, J. L. *Org. Mass Spectrom.* **1985**, *20*, 169.

(23) For a compilation of data and discussion of the electron impact ionization spectra of AlR_3 (R = CH_3, C_2H_5), see: (a) Winters, R. E.; Kiser, R. W. *J. Organomet. Chem.* **1967**, *10*, 7. (b) Chambers, D. B.; Coates, G. E.; Glockling, F.; Weston, M. *J. Chem. Soc. A* **1969**, 1712.

(24) For theoretical studies on $HAlCH_2$, see: (a) ref 9b. (b) Schleyer, P. v. R.; Kost, D. *J. Am. Chem. Soc.* **1988**, *110*, 2105.
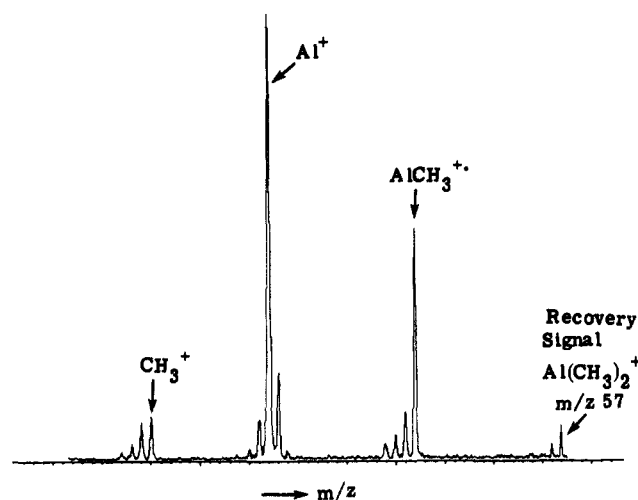
Figure 2. NR mass spectrum (Xe, 75% T; O₂, 75% T) of Al(CH₃)₂⁺.

Figure 3. CA mass spectrum of HCAlCH₃⁺, generated from Al-(CH₃)₃⁺.

Figure 4. CA mass spectrum of AlC₂H₄⁺, generated from Al(C₂H₅)₃⁺.
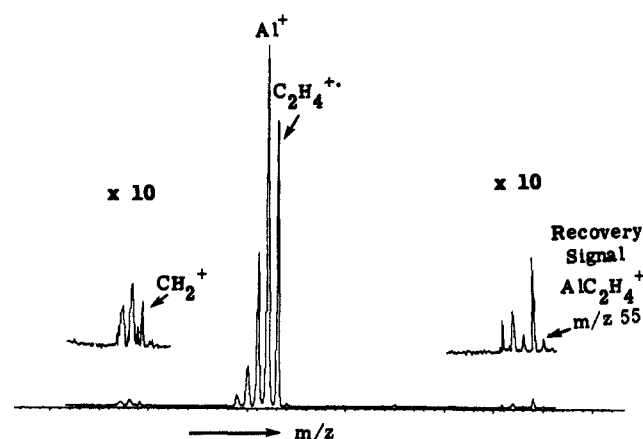
Figure 5. NR mass spectrum (Xe, 75% T; O₂, 75% T) of AlC₂H₄⁺, generated from Al(C₂H₅)₃⁺.

The structural assignment is supported by the NR mass spectrum. This spectrum (Figure 1) is dominated by a quite intense recovery signal, reflecting the theoretically predicted[9a] strong Al–C bond of AlCH₃ (68 kcal/mol), and a signal at m/z 27 (Al⁺); minor signals show up in the m/z 12–15 region (CH$_x$⁺; x = 0–3). We, again, do not observe a signal at m/z 28 that would be indicative for the presence of an aluminum hydride species HAlCH₂.[24] Thus, we conclude that AlCH₃ is a perfectly stable gas-phase species. This finding also lends support to the conclusions based on the elegant laser studies of Al(CH₃)₃ by Stuke et al.[10]

The base peak in the EI spectrum of Al(CH₃)₃ corresponds to m/z 57, Al(CH₃)₂⁺.[23] The CA spectrum (Table I) is dominated by the consecutive eliminations of CH₃• radicals (m/z 42, 27); minor signals are due to losses of H• and CH₄ and the formation of AlH₂⁺ (m/z 29); this fragmentation pattern is consistent with a dimethylaluminum structure.

If Al(CH₃)₂⁺ is subjected to a NRMS experiment, we observe a recovery signal at m/z 57 (Figure 2). The major reactions are, again, due to the consecutive losses of methyl radicals to generate AlCH₃⁺ and Al⁺. The signal at m/z 28 is due to either C₂H₄⁺ or AlH⁺; due to the limited resolution an unambiguous assignment is not possible. In any case, either species requests an isomerization step in the course of the NRMS experiment. We note that the m/z 28 is much less abundant in the CA spectrum (Table I) of Al(CH₃)₂⁺.

As indicated in Table I (footnote b), in addition to Al(CH₃)₂⁺ there seems to exist a second isomer. On the basis of the CID pattern, this species when formed from Al(C₂H₅)₃ via consecutive losses of C₂H₅/C₂H₄ is likely to have the connectivity HAlC₂H₅⁺.

Attempts to neutralize this hydrido ethyl aluminum fragment did, however, fail in that no recovery signal was detected.

The next system to be discussed concerns the (Al,C₂,H₄)⁺ species, m/z 55. A comparison of the CA spectra reproduced in Figures 3 and 4 leaves no doubt that two distinct ions exist. The (Al,C₂,H₄)⁺ ion generated by dissociative ionization of Al(CH₃)₃ has a CA spectrum (Figure 3) that is best compatible with the connectivity HAlCH₃⁺.[25] This assignment is supported by the presence of the structure-indicative fragments at m/z 42 (AlCH₃⁺, loss of CH•). The base peak of the CA spectrum corresponds to Al⁺. For the generation of this ion several possibilities are conceivable: (i) collision-induced consecutive losses of the CH$_x$ ligands from HAlCH₃⁺ and (ii) partial isomerization of HAlCH₃⁺ to the aluminum–ethylene complex Al(C₂H₄)⁺. This second (Al,C₂H₄)⁺ isomer is also generated by the consecutive elimination of C₂H₄/H₂ from Al(C₂H₅)₃⁺. The CA mass spectrum (Figure 4) of this isomer is dominated by the formation of Al⁺ (loss of C₂H₄); most importantly, signals due to the formation of AlCH⁺ (m/z 40) and AlCH₃⁺ (m/z 42) are not present in the spectrum, thus ruling out that the second isomer communicates with the HCAlCH₃⁺ form. We assign an (aluminum/ethylene)⁺ structure to the second isomer.[26]

The structural distinction of the two (Al,C₂,H₄)⁺ isomers is also born out in the NR experiment. While the NR mass spectrum of HCAlCH₃⁺ does not give rise to a detectable recovery signal,

---

(25) We note that although m/z 55 for Al(CH₃)₃ is of only low abundance in the EI spectrum of Al(CH₃)₃, we were able to obtain a CA spectrum of the "pure" (Al,C₂,H₄)⁺ ion. Possible contributions from isobaric hydrocarbon ions can be ignored.

(26) The metastable ion mass spectra of both isomers AlC₂H₄⁺ and HCAlCH₃⁺ are quite similar exhibiting losses of H₂ (100%) and C₂H₄ (20% and 11%, respectively).

in the NR mass spectrum of $AlC_2H_4^{\bullet+}$ (Figure 5) we observe a weak but nevertheless clearly detectable signal at m/z 55, having the proper elemental composition (this is based on the exact elemental composition of the precursor ion which does not contain contribution from isobaric $C_4H_7^+$ species). The major decomposition pathways correspond to the formation of Al^+ (loss of C_2H_4) and $C_2H_4^{\bullet+}$ (loss of Al). As already discussed above, there exist several variants for the formation of these ions. In view of the largely different energy requirements for the formation of the pairs Al^+/C_2H_4 versus $C_2H_4^{\bullet+}/Al^\bullet$, we presume that the $C_2H_4^{\bullet+}$ signal originates from reionization of C_2H_4 generated from xenon-induced dissociation of $AlC_2H_4^+$ (note that the reaction $AlC_2H_4^+ \rightarrow Al^+ + C_2H_4$ gives rise to the base peak in the CA spectrum). We stress, however, that the NR spectrum shown in Figure 5 is compatible with the theoretically predicted[17] existence of a solitary aluminum-ethylene complex. The relatively weak recovery signal observed in the NR of $AlC_2H_4^{\bullet+}$ may be due to two factors: (i) The bond energy of the Al/C_2H_4 π-complex is, undoubtedly, significantly smaller[16,17] than the bond energies of the $AlCH_x$ species ($x = 2, 3$);[9] relatively facile dissociation is expected to occur thus attenuating the flux of intact (Al,C_2,H_4) species. (ii) In the case where the geometries of $AlC_2H_4^+$ and AlC_2H_4 differ, due to the vertical nature[3] of the electron transfer in the NR experiment, the Franck-Condon factors will be small resulting in a smaller abundance of the survivor ions.[27] As the latter argument also applies to the $HCAlCH_3^+/HCAlCH_3$ system, the absence of a recovery signal in the NR spectrum of $HCAlCH_3^+$ does not necessarily imply that neutral $HCAlCH_3$ is not a minimum on the (Al,C_2,H_4) potential energy surface.

Unfortunately, as this species is not included in the otherwise quite exhaustive theoretical study of Schaefer et al.,[17a] no definitive conclusion is permitted for the time being.

Concluding Remarks

The present study provides experimental evidence that the neutral and ionic forms of $AlCH_2$, $AlCH_3$, $Al(CH_3)_2$, and AlC_2H_4 are stable species in the gas phase.[28] Quite remarkable is the finding that isomerization of $AlCH_2$ and $AlCH_3$ to their corresponding hydridoaluminum isomers $HAlCH_x$ ($x = 1, 2$) is negligible, if it takes place at all in gas-phase experiments. For the (Al,C_2,H_4) system evidence for the existence of two non-interconverting ionic isomers is presented. One corresponds to the (aluminum/ethylene)$^+$ complex $AlC_2H_4^+$, which upon neutralization gives rise to a detectable recovery signal. The second isomer is assigned to the hitherto unknown $HCAlCH_3^+$ ion; this isomer, however, could not be successfully neutralized to $HCAlCH_3$.

(27) For further examples and a more detailed discussion of this aspect, see: Sülzle, D.; Terlouw, J. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 404.

(28) For a recent, high-level ab initio MO study of AlCH, AlCH₂, and AlCH₃, see: Jin, S. Q.; Xie, Y.; Schaefer, H. F., III *Chem. Phys. Lett.* **1990**, *170*, 301.

Absolute Rate Constants for the Gas-Phase Si-H Insertion Reactions of Dimethylsilylene with Silane and the Methylsilanes in the Temperature Range 300-600 K

J. E. Baggott, M. A. Blitz, H. M. Frey, and R. Walsh*

Contribution from the Department of Chemistry, University of Reading, Whiteknights, P.O. Box 224, Reading, RG6 2AD, U.K. Received May 3, 1990

Abstract: The title reactions have been investigated by means of laser flash photolysis. Dimethylsilylene, $SiMe_2$, was produced by 193-nm photolysis of pentamethyldisilane and detected via its visible absorption at 457.9 nm. Second-order rate constants were obtained for reactions of $SiMe_2$ with SiH_4, $MeSiH_3$, Me_2SiH_2, and Me_3SiH. With the exception of SiH_4, all the other rate constants decrease with increasing temperature. They represent a classic set of examples of reactions with negative activation energies, increasing to -11.2 ± 1.0 kJ mol^{-1} for reaction with Me_3SiH. The substrate methyl substituent effect suggests the importance of the nucleophilic interaction in the rate-determining step. The measured A factors indicate tight structures for the activated complexes, consistent with kinetic measurements of the reverse reactions. A mechanism proceeding via an intermediate complex is shown to be consistent with the data, with entropy factors dominating the dynamics of the reaction pathway. A variational transition-state model (without an intermediate) is not thought to provide such a satisfactory explanation, although it cannot be ruled out.

Introduction

Grev and Schaeffer[1] have likened the role of the methyl substituent in silicon chemistry to that of hydrogen in traditional organic chemistry. Since silylenes, SiR_2, are ubiquitous intermediates in organosilicon chemistry,[2-4] playing the same central role as free radicals in organic chemistry, one may legitimately claim that in terms of its importance dimethylsilylene, $SiMe_2$, is the "methyl radical" of silicon chemistry.

A great deal about the reactions and pattern of reactivity of $SiMe_2$ has been learned by careful pyrolytic and photolytic studies with end-product analysis. Experimental investigations in both

(1) Grev, R. S.; Schaeffer, H. F., III *J. Am. Chem. Soc.* **1986**, *108*, 5808.

(2) Gaspar, P. P. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley-Interscience: New York, 1978; Vol. 1, p 229; *Ibid.* 1981; Vol. 2, p 335; *Ibid.*, 1985; Vol. 3, p 333.

(3) Tang, Y.-N. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1982; Vol. 2, p 297.

(4) Davidson, I. M. T. *Annu. Rep. Prog. Chem., Sect. C* **1985**, *81*, 47.