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HeI Photoelectron Spectroscopy of Trialkylaluminum and Dialkylaluminum Hydride Compounds and Their Oligomers

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The HeI photoelectron spectra of trimethylaluminum, triethylaluminum, dimethylaluminum, and diethylaluminum hydrides were recorded as a function of temperature. From the spectra observed at different temperatures the spectra of the pure monomers and the trimethylaluminum, dimethylaluminum, and diethylaluminum hydride dimers and some of the bands related to the dimethylaluminum hydride trimer have been obtained. The spectra were interpreted with the aid of ab initio quantum chemical calculations, including Hartree−Fock/Koopmans, outer valence Green's function, and equation of motion coupled-cluster ionization energy calculations. The vertical ionization energies predicted by the latter two methods are in excellent agreement with the experimental values. Furthermore, the association capability of these compounds, the effects of the substituents, and the degree of association on the electronic structure are also discussed.

Introduction

The structure, bonding, and dissociation dynamics of trialkylaluminum and dialkylaluminum hydride oligomers (dimers and trimers), considered as simple model systems of the electron-deficient, multicentered bond, have received great and continuous attention since the end of the 19th century. The investigations were based on a great variety of methods, including vapor density,[1,2] vapor pressure depression,[3,4] and freezing point depression[5−7] measurements, electron,[3,8−12] neutron,[13] and X-ray[14−17] diffraction, mass spectrometric,[3,18−20] IR,[3,21−24] Raman,[25,26] NMR,[3,27−29] and UV photoelectron spectroscopic (UPS) techniques,[30] and quantum chemical calculations.[3,31,32]

Among the trialkylaluminum compounds trimethylaluminum (TMA) has been studied most extensively and for the longest time. According to X-ray[14−17] and recent neutron diffraction[13] measurements, as well as freezing point depression measurements,[5−7] TMA forms dimers in the solid state and in solutions of benzene and cyclopentane. Beyond the structure (Figure 1), ^{1}H NMR investigations[27−29] have additionally confirmed that in hydrocarbon solvents the interchange between the methyl groups in terminal and in bridge position is fast, comparable with the NMR time scale at −75 °C. In contrast to the condensed phase experiments the favored structure of TMA in the vapor phase has not been proved unambiguously. In 1941 Laubengayer and Gilliam[1] have demonstrated by vapor density measurements that TMA forms dimers at 70 °C in the vapor

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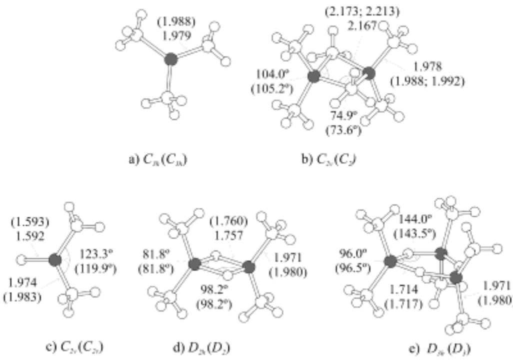

Figure 1. Geometry and the most important structural parameters (as obtained at the HF/6-31G** level of theory) of the (a) monomer and (b) dimer of trimethylaluminum (TMA) and the (c) monomer, (d) dimer, and (e) trimer of dimethylaluminum hydride (DMA). The corresponding values of the ethyl analogues are given in parentheses.

phase, and by increasing the temperature the degree of association decreases rapidly. In good agreement with the age-old experiments of Quincke,[2] they found the average degree of association to be 1.6 at 140 °C. Although there was no agreement concerning the molecular geometry of the TMA dimer for a long time, dimers have been found by gas phase electron diffraction measurements[8−11] and by Raman[25,26] and infrared spectroscopy[21] as well. Contrary to the above observations, Winters and Kiser[18] as well as Tanaka and Smith,[19] evaporating the sample at 190 °C and 60−100 °C, respectively, observed the dimers only in a negligible ratio, <1%, by mass spectrometry. Concurrently Chambers et al.[20] performed a mass spectrometric investigation, in which the sample was evaporated at 44−50 °C. Even in this experiment a monomer/dimer ratio of only 90:3.5 was found. In the case of the mass spectrometric investigation, the low dimer abundance can be the consequence of dissociation caused by the low vapor pressure and/or by the electron impact ionization. Nevertheless, at higher sample pressure, used in HeI photoelectron spectroscopy, Barker et al.[30] could not observe the dimer either.

Although the dissociation energy of triethylaluminum (TEA) dimer is significantly lower than that of TMA dimer, similarly to TMA, TEA forms dimers in benzene solutions.[6,7] Vapor density measurements showed[1] that the abundance of TEA dimer in the gas phase is only 12% at 150 °C. Using mass spectrometry no dimer could be observed at all.[20]

Considering the analogues with bulkier substituents, the equilibrium between the dimers and monomers is shifted to the monomers (even in solutions) in the case of tripropyl- and tributylaluminum, while tri(isopropyl)-, tri(isobutyl)-, and tri(*tert*-butyl)aluminum do not dimerize.[5,6,33,34]

According to the vapor pressure depression measurements of Wartik and Schlesinger,[3] the degree of association of dimethylaluminum hydride (DMA) in isopentane at room temperature is between 3.55 and 3.13 depending on the concentration, while they found it to be 2.04 by vapor density measurements at 167 °C. The gas phase electron diffraction investigations[12] also supported the DMA dimer formation around this temperature. At 83 °C the measured degree of association is 2.44. On the basis of these facts the DMA has to be considered as a mixture of dimers and trimers at lower temperatures. Raman and infrared spectroscopy[22−24] also supported this observation. Downs et al.[4] published recently a comprehensive work of combined infrared spectroscopic, NMR, mass spectrometric, gas phase electron diffraction investigations together with vapor pressure measurements, and ab initio calculations. According to this work DMA exists in the form of dimers and higher oligomers (e.g., tetramers) in hydrocarbon solutions, while it is present as a mixture of dimers and trimers (7:3) at 60 °C. At 200 °C the vapor phase consists of dimers. It should also be noted that in contrast to former mass spectrometric investigations[19,20] they have observed the trimer ions with relatively high intensity in the mass spectrum as well.

The association capability of dialkylaluminum hydrides is higher than that of trialkylaluminum compounds. This is due to two reasons. First, it is originated from the smaller steric demand of the hydrogen atoms in the bridge position. Second, the pyramidalization around the Al atom, taking place during dimerization, requires less energy in the case of dialkylaluminum hydrides.

Diethylaluminum hydride (DEA) exists in the form of trimers in inert solvents,[33,35] while trimers in the gas phase have been observed only in a very low ratio, among dimers and monomers measured by mass spectrometry.[19,20]

Among the higher analogues di(*tert*-butyl)aluminum hydride was investigated, which forms trimers both in solution[33] and in the solid phase.[36]

The purpose of this paper was to study the electronic structure of some trialkylaluminum and dialkylaluminum hydride compounds, namely, TMA, TEA, DMA, and DEA, in the gas phase by HeI photoelectron spectroscopy. An effort was made to observe not only the monomers but the above-mentioned oligomers (dimers, trimers) as well. The association capability of the investigated compounds was studied by recording the spectra as a function of temperature. Similarly to our recent study on alkyllithium clusters,[37] the effects of substituents and degree of association on the electronic structure have also been analyzed.

Experimental Section

A. Sample Preparation. TMA (97%) and TEA (93%) were obtained from Aldrich and were used without further purification. Dialkylaluminum hydrides were prepared by the method of Wartik and Schlesinger,[3] applying the modification by Grady et al.,[24] namely, by the solvent-free heterogeneous reaction of excess $LiAlH_4$ and the corresponding trialkylaluminum at 90 °C. The products were purified by trap-to-trap distillation under vacuum and were collected at −19 °C (DMA) and 0 °C (DEA), while the traces of the unreacted more volatile trialkylaluminum compounds were entrapped by liquid nitrogen. All operations were carried out in an inert atmosphere.

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Table 1. Calculated and Experimental Vertical Ionization Energies (in eV) of the Monomer and Dimer of Trimethylaluminum (TMA)[a]

state[c]	assignment[b]	calculated HF/Koopmans	calculated OVGF	calculated EOM-CCSD	experimental
		Monomer (C_{3h})			
E′	$\sigma_{\text{Al-C}}$	10.47	9.54	9.57	9.85
A′	$\sigma_{\text{Al-C}}$	13.78	12.83	12.81	12.6
	$\sigma_{\text{C-H}}$	14.1−14.6	13.2−13.7	13.2−13.7	13.3−14.0
		Dimer (C_{2v})			
B_2	$\sigma_{\text{Al-C}}$	10.49	9.39	9.42	9.75
A_1	$\sigma_{\text{Al-C}}$	10.51	9.44	9.46	
B_1	$\sigma_{\text{Al-}\mu\text{C-Al}}$	11.08	9.94	9.98	10.45
A_1	$\sigma_{\text{Al-C}} + \sigma_{\mu\text{C-}\mu\text{C}}$	11.22	10.09		
B_2	$\sigma_{\text{Al-C}}$	12.05	10.96	10.96	11.2
	$\sigma_{\text{C-H}}$	14.1−16.3	13.1−15.0	13.0−15.0	12.0−16.2

[a] The calculations have been performed for the HF/6-31G** optimized geometries, using the 6-31G** basis set for HF/Koopmans, OVGF, and EOM calculations. [b] Assignments are based on the population analysis of the HF orbitals. [c] Given for the lowest, experimentally separable states only.

B. HeI Photoelectron Spectroscopic Measurements. HeI photoelectron (PE) spectra were recorded on an ATOMKI ESA-32 spectrometer[38] using a pyrolizer inlet system heatable up to 350 °C. The accuracy of the temperature measurement is estimated to be ±10 °C. The sample pressure at the ionization chamber was kept between 8×10^{-6} and 4×10^{-5} mbar in each experiment. The full width at half-maximum of the $^2P_{3/2}$ peak of argon was 20−50 meV during the measurements of TMA and DMA and 50−100 meV in the case of TEA and DEA. The maximum error in ionization energies is estimated to be less than 0.05−0.1 eV. All spectra were calibrated against argon or nitrogen as internal standards; the background corrections were made by Shirley-type functions. The spectra of the dimers have been obtained by subtracting the spectra recorded at high temperatures from the low-temperature ones.

C. Ab Initio Calculations. Ab initio geometry optimizations were carried out by the PQS 2.1 program system.[39] Outer-valence Green's function (OVGF)[40] ionization energies have been obtained by Gaussian98,[41] while the ACESII program package[42] was used to compute ionization energies in the framework of the equation of motion (EOM) CCSD method.[43]

Geometry optimizations have been performed for the experimentally found[4,12] and theoretically confirmed[4,31] global minimum structures (Figure 1) only. The optimizations were followed by second derivative calculations to determine whether the obtained stationary points correspond to minima. The dependence of the calculated ionization energies on the geometry and on the basis set was verified by OVGF calculations for the monomer and the dimer of TMA. These exploratory calculations were performed using 6-31G**, cc-pVDZ, and aug-cc-pVDZ basis sets and the HF/6-31G** and MP2/6-31G** optimized structures. Since the maximum difference between these results does not exceed 0.3 eV, calculations for all other species were performed for the HF/6-31G** optimized structures only. For the ionization energy calculations the 6-31G** basis set was used.

(As Supporting Information HOMO and LUMO energies, which can be useful in order to estimate the gas phase Lewis-acid character of the investigated compounds, are also presented.)

Results and Discussion

A. Trimethylaluminum. Berthomieu et al.[31] have recently calculated the first vertical and adiabatic ionization energy of the TMA monomer and dimer by ΔHF, ΔMP2, and ΔDFT methods. Despite the small difference (<0.1 eV) between the first vertical ionization energies obtained by ΔHF and ΔMP2 methods, they have concluded on the basis of ΔDFT calculations that "the [first] ionization energy of the dimer is lower than that of the monomer, by about 1 eV, which indicates that TMA^+ and $TMA_2{}^+$ could be separated by ionization techniques". Our ionization energy calculations (Table 1) do not support their conclusion, but they are in good agreement with their ΔHF and ΔMP2 results. Although the first ionization energy of the monomer and the dimer might not be significantly different, our calculations also predict regions in the photoelectron spectrum where the dimer could be distinguished from the monomer unambiguously. These characteristic bands of the dimer are expected to appear at about 10.0, 11.0, and above 14.0 eV, and they are separated from the closest bands of the monomer by about 0.5, 1.5, and 0.5−0.9 eV, respectively.

The experimental photoelectron spectra of TMA recorded at different temperatures are shown in Figure 2. In the low-temperature spectra the above-mentioned bands, characteristic for the dimer, can be observed at only slightly higher ionization energies than predicted by our calculations. Furthermore, the intensity of these bands decreases rapidly with the increase of temperature, indicating the dissociation of the dimers. At about 75 °C the dissociation of the dimers is completed (i.e., the dimer bands are not recognizable in the spectrum, which means that the dimer concentration is below a few percent). Above this temperature, up to 200 °C, the

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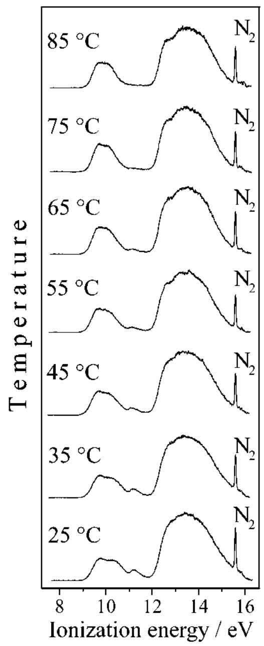

Figure 2. Temperature-dependent HeI photoelectron spectrum of trimethylaluminum (TMA).

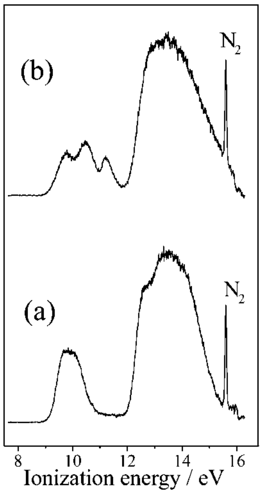

Figure 3. HeI photoelectron spectrum of the (a) monomer and (b) dimer of trimethylaluminum (TMA).

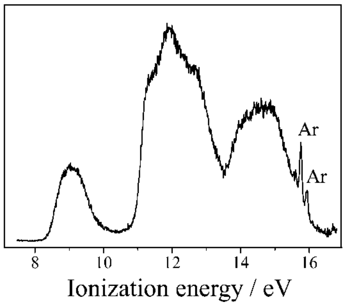

Figure 4. HeI photoelectron spectrum of the monomer of triethylaluminum (TEA).

spectrum does not change any more; consequently at higher temperatures the spectrum of the pure monomer was obtained. This spectrum is in good agreement with the previously published photoelectron spectrum of TMA monomer.[30] The spectra recorded below 75 °C can be related to a mixture of monomers and dimers.

The pure dimer spectrum was obtained by subtracting a high-temperature spectrum from a low-temperature one. This dimer spectrum together with the spectrum of the monomer is presented in Figure 3; the experimental vertical ionization energies are collected in Table 1. The spectrum of the monomer consists of three bands. The first two bands correspond to the ionization of the Al–C bonds, while the third band, which overlaps with the second one, is originated from the ionization of the C–H bonds. As can be seen from Table 1, the first band of the monomer corresponds to the ionization from a degenerate orbital. As a consequence, this band is slightly asymmetrical due to Jahn–Teller splitting. The same structure is evident in the spectra of trimethyl compounds of group 13 elements (B, Al, Ga).[30] In the C_{2v} symmetry dimer two of the degenerate orbitals of the monomer units form four nondegenerate orbitals. Three of these are well recognizable in the low-energy region of the dimer spectrum. The fourth band is faded into the higher energy broad band assigned to the ionization of C–H bonds, which is wider by about 1–2 eV than the corresponding band of the monomer.

As it can be seen from Table 1, the HF/Koopmans calculations predict correctly the main spectral features. Furthermore, as far as absolute values are concerned, both the OVGF and the EOM-CCSD calculations are in very good agreement with the experimental data; the maximum deviation from the measured ionization energies is less than 0.4 eV. The difference between the first vertical ionization energy of the monomer and dimer is only about 0.1 eV. This experimental result clearly shows that the performance of the ΔDFT method to predict this energy difference is much worse than that of any other methods, including ΔHF, ΔMP2, OVGF, EOM-CCSD, and even HF/Koopmans theories. Therefore, the above-mentioned conclusion of Berthomieu et al.[31] based on ΔDFT method is essentially erroneous.

B. Triethylaluminum. To obtain reasonable signal-to-noise ratio, the sample has to be heated at least to 50–60 °C. By heating the path between the sample and the ionization chamber up to 200 °C no change of the photoelectron spectrum was experienced. This observation confirms that already at 50–60 °C the pure monomer spectrum was recorded (Figure 4). This is also supported by the fact that the calculations predict a band at 10.1 eV for the dimer, which cannot be observed in the experimental spectrum. Furthermore, the calculated ionization energies obtained by the OVGF and the EOM-CCSD methods for the monomer are in excellent accordance with the experimental spectrum (Table 2). Similarly to TMA, the maximum error in calculated ionization energies is no more than 0.4 eV.

The main difference between the spectrum of TMA and TEA monomers is that the first ionization energy of TEA is lower almost by 1 eV, which is a consequence of the larger electron-releasing effect of the ethyl group. Furthermore, the broad band in the higher energy region of the spectrum of TMA, corresponding to the ionization of CH_3 groups, is split into two parts in the case of TEA. At the higher energy region, the structureless part between 13.8 and 16.0 eV belongs to the ionization of the CH_3 groups (C–H bonds). In the lower energy part, between 11.0 and 13.5 eV, three bands can be identified at 11.4, 11.9, and 12.65 eV (see Table 2). The first of these (11.4 eV), together with the first band

Table 2. Calculated and Experimental Vertical Ionization Energies (in eV) of the Monomer and Dimer of Triethylaluminum (TEA)[a]

state	assignment	calculated			experimental
		HF/Koopmans	OVGF	EOM-CCSD	
		Monomer (C_{3h})			
E′	$\sigma_{\mathrm{Al-C}}$	9.82	8.82	8.82	9.05
A′	$\sigma_{\mathrm{Al-C}}$	12.49	11.58		11.4
A″	$\sigma_{\mathrm{C-H}}$	12.93	12.07	12.12	11.9
E″	$\sigma_{\mathrm{C-H}}$	12.95	12.07	12.12	
E′	$\sigma_{\mathrm{C-C}}$	13.47	12.26	12.28	12.65
A′	$\sigma_{\mathrm{C-C}} + \sigma_{\mathrm{Al-C}}$	13.42	12.27	12.28	
	$\sigma_{\mathrm{C-H}}$	15.3−16.1	14.2−14.9	14.1−14.9	13.8−16.0
		Dimer (C_2)			
B	$\sigma_{\mathrm{Al-C}}$	9.76	8.58		not
A	$\sigma_{\mathrm{Al-C}}$	9.88	8.72		
B	$\sigma_{\mathrm{Al-\mu C-Al}}$	10.33	9.11		observed
A	$\sigma_{\mathrm{Al-C}} + \sigma_{\mathrm{Al-\mu C-Al}}$	10.52	9.31		
B	$\sigma_{\mathrm{Al-C}}$	11.29	10.14		
	$\sigma_{\mathrm{C-H}}, \sigma_{\mathrm{C-C}}$	12.7−17.3	11.7−15.7		

[a] See footnotes of Table 1.

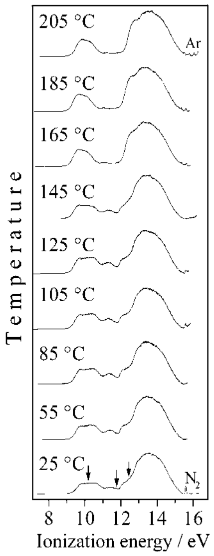

Figure 5. Temperature-dependent HeI photoelectron spectrum of dimethylaluminum hydride (DMA). Arrows on the spectrum recorded at 25 °C indicate the change as compared to higher temperature spectra due to the decomposition of the trimers.

of the spectrum, corresponds to the ionization of the Al−C bonds, while the second two belong to the ionization of the ethyl groups (C−C and C−H bonds).

C. Dimethylaluminum Hydride. The photoelectron spectra of dimethylaluminum hydride recorded at different temperatures are presented in Figure 5. There are two temperature regions where spectrum changes are visible. The first one is between 25 and 55 °C. This change is not dramatic; it can be imperceptibly seen on the side of some bands (see arrows on spectrum recorded at 25 °C). Since the calculations (Table 3) predict only marginal differences between the spectrum of the dimer and trimer of DMA, this change is most likely due to the decomposition of the trimers. This is also in agreement with experiments available from literature,[3,4] which indicate the dissociation of the trimers around this temperature.

The second, much more pronounced change in the spectrum starts at about 125 °C, and it lasts out even to 180−200 °C. This change includes the vanishing of the bands at about 10.5, 11.3, and 12.1 eV. Since all these bands, within reasonable accuracy, are predicted for the dimer by our calculations, consequently this change is due to the dissociation of the dimers. Although, this is in contrast to the observation of Downs et al.,[4] who, as it was mentioned above, found predominantly dimers in the vapor phase at 200 °C. This is probably due to the different conditions (e.g., lower pressure) applied in our experiment.

The photoelectron spectra of the monomer and the dimer of DMA, obtained from the temperature-dependent spectra, are shown in Figure 6. (Due to the complexity of the low-temperature spectra, it was not possible to get the trimer spectrum.) The spectrum of the monomer looks very similar to the TMA monomer spectrum; all of the bands are shifted only by 0.1−0.3 eV to higher energy. A minor difference is observed for the first band, which is less symmetrical in the case of DMA. This is due to the Al−H bond and the lower symmetry of the DMA monomer as compared to TMA. This results in a splitting (predicted to be 0.4−0.5 eV by the calculations) of the ionic states corresponding to the ionization of Al−C bonds, which were degenerate in the case of TMA.

The difference is appreciably larger in the case of the dimers, which is a result of the much stronger interaction between the two monomer units in the DMA dimer. The splitting of the first band corresponding to the ionization of the Al−C (and Al−H) bonds is larger by more than 0.5 eV in the DMA dimer spectrum compared to that of TMA dimer.

The OVGF and EOM-CCSD ionization energies agree very well with the experimental values. The only exception is the value obtained for the ionization of the Al−H bond, which is higher by 0.6 eV than the experimental value.

D. Diethylaluminum Hydride. The calculated and experimental ionization energies of DEA are presented in Table 4. (The photoelectron spectrum of DEA as a function of temperature can be found in the Supporting Information. Due to the low volatility of DEA, the sample holder had to be heated at least to 40 °C.)

Similarly to the observations made in the case of TMA and DMA, the theoretically predicted bands characteristic for the dimers can be identified in the spectra

Table 3. Calculated and Experimental Vertical Ionization Energies (in eV) of the Monomer, Dimer, and Trimer of Dimethylaluminum Hydride (DMA)[a]

		calculated			
state	assignment	HF/Koopmans	OVGF	EOM-CCSD	experimental
		Monomer (C_{2v})			
B_2	σ_{Al-C}	10.67	9.80	9.83	9.9
A_1	σ_{Al-C}	10.94	10.30	10.23	10.2
A_1	$\sigma_{Al-H} + \sigma_{Al-C}$	14.28	13.50	13.41	12.9
	σ_{C-H}	14.4−14.8	13.5−13.9	13.5−13.9	12.2−15.0
		Dimer (D_{2h})			
B_{1g}	σ_{Al-C}	10.63	9.62	9.64	9.7
B_{2u}	σ_{Al-C}	10.89	9.92	9.93	10.1
A_g	$\sigma_{Al-C} + \sigma_{Al-\mu H-Al}$	11.34	10.36	10.35	10.5
B_{1u}	$\sigma_{Al-\mu H-Al}$	12.20	11.40	11.28	11.3
B_{3u}	σ_{Al-C}	13.01	12.02	12.00	12.05
	σ_{C-H} ($\sigma_{Al-\mu H-Al}$)	14.3−17.6	13.3−16.2	13.3−16.1	12.6−15.3
		Trimer (D_{3h})			
E''	σ_{Al-C}	10.74	9.67		
A_2''	σ_{Al-C}	10.91	9.86		
A_1'	$\sigma_{Al-C} + \sigma_{Al-\mu H-Al}$	11.34	10.28		[10.3]
E'	$\sigma_{Al-\mu H-Al} + \sigma_{Al-C}$	11.75	10.73		
E'	$\sigma_{Al-\mu H-Al} + \sigma_{C-H}$	14.31	13.29		
	σ_{C-H} ($\sigma_{Al-\mu H-Al}$)	14.4−17.9	13.9−16.5		
	σ_{C-H}	14.44	13.46		

[a] See footnotes of Table 1.

Table 4. Calculated and Experimental Vertical Ionization Energies (in eV) of the Monomer and Dimer of Diethylaluminum Hydride (DEA)[a]

		calculated			
state	assignment	HF/Koopmans	OVGF	EOM-CCSD	experimental
		Monomer (C_{2v})			
B_2	σ_{Al-C}	9.97	9.04	9.05	9.0
A_1	σ_{Al-C}	10.63	9.88	9.82	9.6
	σ_{C-C}, σ_{Al-H}	12.9−13.8	12.1−12.7	12.1−12.7	11.8−12.8
	σ_{C-H}	15.3−16.0	14.3−15.0	14.3−14.8	14.3−15.0
		Dimer (D_2)			
B_1	σ_{Al-C}	9.93	8.88		9.0
B_3	σ_{Al-C}	10.18	9.16		9.5
A	$\sigma_{Al-C} + \sigma_{\mu H-\mu H}$	10.70	9.65		10.0
B_2	σ_{Al-C}	11.98	11.00		10.7
B_1	$\sigma_{Al-\mu H-Al}$	12.17	11.24		
	σ_{C-C}, σ_{C-H}	13.0−13.6	12.1−12.5		11.8−12.6
	σ_{C-H} ($\sigma_{Al-\mu H-Al}$)	15.3−17.6	14.2−16.1		14.1−15.0

[a] See footnotes of Table 1.

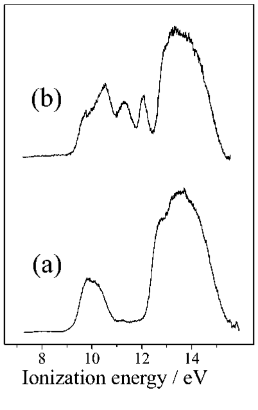

Figure 6. HeI photoelectron spectrum of the (a) monomer and (b) dimer of dimethylaluminum hydride (DMA).

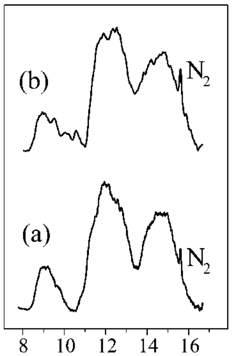

Figure 7. HeI photoelectron spectrum of the (a) monomer and (b) dimer of diethylaluminum hydride (DEA).

recorded at lower temperatures. Changes in the spectrum can be tracked up to 60−70 °C; at this temperature the dissociation seems to be complete. The photoelectron spectrum of the DEA monomer and dimer, obtained from the temperature-dependent spectrum, is presented in Figure 7. The two-band structure at higher energies (11.8−12.8 and 14.3−15 eV) corresponding to the ethyl groups and the splitting of the first band of the monomer are well recognizable in the monomer spectrum. Due to the larger difference in the inductive effect of hydrogen and the ethyl group, this splitting is larger in this case than the case of DMA; it is about 0.6−0.8 eV. Comparing the spectrum of DEA to that of DMA, the shift of the bands (about 1 eV) due to the larger inductive effect of the ethyl groups is also conspicuous.

Similarly to the observations made in the case of the TEA and DMA monomer, and in line with the theoretical predictions, the first ionization energy of the DEA dimer is lower only by about 0.2 eV than that of the DEA monomer. In this case too, the difference between experimental data and calculated ionization energies resulting from OVGF as well as EOM-CCSD methods is less than 0.4 eV. Similarly to DMA, the largest disagreement is found in the case of the Al−H bond.

Conclusions

In this study we have presented the HeI photoelectron spectrum of trimethylaluminum, triethylaluminum, dimethylaluminum, and diethylaluminum hydride monomers and trimethylaluminum, dimethylaluminum, and diethylaluminum hydride dimers, all of which, except the spectrum of the trimethylaluminum, have not been published before. On the basis of these experimental results the following conclusions can be drawn concerning the behavior of the title compounds in the gas phase under high-vacuum conditions.

The complete dissociation of the trimethylaluminum dimer was observed at about 75 °C, while the dissociation of the triethylaluminum dimer takes place below 50−60 °C. In the case of dimethylaluminum hydride even some signal due to the trimer was observable at room temperature. The dissociation of its dimer is completed above 180−200 °C only, while the dissociation of diethylaluminum hydride dimer already occurs at about 70 °C. From these observations, in accordance with the previous experimental and theoretical results available from the literature, the following order of the association capability of alkylaluminum compounds can be established: dimethylaluminum hydride > trimethylaluminum ∼ diethylaluminum hydride > triethylaluminum.

The dimerization of the compounds results in a splitting of the bands corresponding to the ionization of the Al−C bonds. This splitting is larger in the case of dialkylaluminum hydrides than in the case of trialkylaluminum compounds.

Both the experimental observations and theoretical calculations indicate only marginal difference between the ionization energies of the dialkylaluminum hydride dimers and trimers. This is due to the fact that both molecules are closely related as far as chemical bonds and structure are concerned (see geometry parameters in Figure 1).

The substitution of one alkyl group of trialkylaluminum compounds with hydrogen does not result in a remarkable change in the photoelectron spectrum of the monomer. In contrast to this, the change is much more significant in the dimer spectrum. This is a consequence of the increased interaction between the monomer units due to the change of methyl bridges for hydrogen bridges.

The substitution of the methyl groups for ethyl groups results in a decrease of the ionization energies corresponding to the Al−C bonds by about 1 eV.

Calculations related to the ionization energies of trimethylaluminum monomer and dimer clearly demonstrate that the performance of the ΔDFT method is much worse than that of any other methods, including ΔHF, ΔMP2, OVGF, EOM-CCSD, and even HF/Koopmans theories.

As far as the relative order and absolute values of ionization energies are concerned, HF/Koopmans theory predicts correct order of the ionization energies. The OVGF and EOM-CCSD results are even better; the absolute ionization energies obtained by these methods agree mostly with the experimental values within 0.3−0.4 eV even using a medium-quality basis set (6-31G**). The only exceptions are the values obtained for the ionization of the Al−H bond of the dialkylaluminum hydride monomers, which are higher by 0.6 eV than the experimental values.

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Note Added in Proof. After the submission of the corrected manuscript we have realized that some additional papers were formerly published on the HeI photoelectron spectrum of the TMA monomer (Wang, D.; Li, S.; Li, Y.; Zheng, S.; Chen, B.; Ding, C.; Gao, Y. *Chem. Phys. Lett.* **1996**, *260*, 95) and the spectrum of the TMA dimer (Wang, D.; Qian, X.; Zheng, S.; Shi, Y. *Chem. Phys. Lett.* **1997**, *277*, 502). The monomer spectrum recorded by this group is in good agreement with our measurements. Nevertheless, the dimer spectra recorded by the two groups show significant discrepancies, including the value of the first vertical ionization energy. Since our measurements are supported by the sophisticated EOM-CCSD and OVGF calculations (also consistent with our results obtained for the dialkylaluminum hydrides), we believe that the spectrum recorded by us is more reliable. This statement will be elaborated in a follow-up paper or communication after further theoretical investigations.

Supporting Information Available: Table of HOMO and LUMO energies and figure of HeI photoelectron spectrum of DEA. This material is available free of charge via the Internet at http://pubs.acs.org.

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