

Electron states of 1:1 addition compounds of AlCl_3 and GaCl_3 with electron donor molecules: a HeI photoelectron spectroscopic study*, **

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Abstract

HeI photoelectron spectra of the 1:1 adducts of AlCl_3 and GaCl_3 with $(\text{C}_2\text{H}_5)_2\text{O}$ in the vapour phase are presented and the bands assigned to orbital ionizations based on MO calculations. Spectra of the adducts with $(\text{C}_2\text{H}_5)_2\text{S}$ are reported with tentative assignments.

INTRODUCTION

Electron states of donor-acceptor complexes have been effectively studied by means of UV photoelectron spectroscopy in the vapour phase [1]. We have been interested in investigating the electron states of 1:1 addition compounds formed between Lewis acids and Lewis bases and have recently reported the results of our studies of the addition compounds formed by BF_3 in the vapour phase [2]. One of the main results of this study was that the ionization energies of the fluorine orbitals of BF_3 are shifted substantially on the formation of addition compounds with oxygen-donor molecules and that the magnitude of the shift increases in the same direction as the dissociation energy of the adduct. We considered it instructive to investigate the electron states of the strong 1:1 addition compounds formed by AlCl_3 and GaCl_3 with donors such as diethylether, since their dissociation energies [3] are considerably larger ($\approx 125 \text{ kJ mol}^{-1}$) than those of BF_3 ($\approx 50 \text{ kJ mol}^{-1}$). In this communication, we report the results of the first photoelectron spectroscopic investigation of the 1:1 addition compounds of AlCl_3 and GaCl_3 in the vapour phase. The donor molecules studied are diethylether and diethylsulphide.

*Dedicated to the memory of Professor George Wilkinson.

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EXPERIMENTAL AND METHODS OF CALCULATION

Ultraviolet photoelectron spectroscopic measurements were carried out employing a spectrometer fabricated in the laboratory with a conventional sample inlet system [4]. The 1:1 addition compounds were prepared by mixing the individual components under vacuum. Vapours of the addition compounds were admitted to the spectrometer through a needle valve. In all the addition compounds studied here, external heating of the sample was necessary to obtain a sufficient vapour pressure. Samples were taken in a glass ampoule and heated to ≈ 420 K by means of a heating tape. The temperature of the ampoule was maintained constant throughout the experiment. Absence of water vapour in the collision chamber was certain since no trace of HCl formed by the hydrolysis of the acceptor halides was present in the HeI spectra.

Hartree-Fock energies of the complexes were computed in the framework of the SCF-LCAO-MO method using the GAUSSIAN 86 [5] system of programs. Monomer geometries were fully optimized and used as initial inputs for the calculations on the adducts.

RESULTS AND DISCUSSION

The HeI photoelectron spectrum of AlCl_3 shows features at 12.01, 12.47, 12.73, 13.33, 14.04 and 15.97 due to $a'_2(n_{\text{Cl}})$, $e'(n_{\text{Cl}})$, $e''(n_{\text{Cl}})$, $a''_2(\pi_{\text{Al-Cl}})$, $e'(\pi_{\text{Al-Cl}})$ and $a'_1(\sigma_{\text{Al-Cl}})$ orbital ionizations respectively [6]. The first ionization energy of diethylether at 9.6 eV is due to the oxygen lone pair [7]. In Fig. 1 we show the HeI photoelectron spectrum of $(\text{C}_2\text{H}_5)_2\text{O}$ and $\text{AlCl}_3 + (\text{C}_2\text{H}_5)_2\text{O}$. We

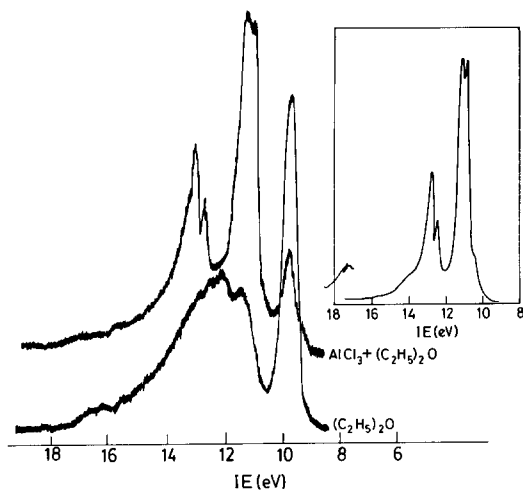


Fig. 1. HeI photoelectron spectra of $(\text{C}_2\text{H}_5)_2\text{O}$ and a mixture of AlCl_3 and $(\text{C}_2\text{H}_5)_2\text{O}$. The spectrum of the 1:1 adduct obtained after stripping is shown in the inset.

see that many of the features in the spectrum of the latter are not present in the spectrum of either $(\text{C}_2\text{H}_5)_2\text{O}$ or AlCl_3 and these are ascribed to the 1:1 addition compound. The spectrum of the pure 1:1 addition compound was obtained by subtracting any features due to the donor or the acceptor molecule. The spectrum of $(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{AlCl}_3$ thus obtained is shown in the inset of Fig. 1.

In order to assign the various bands in the HeI spectrum of $(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{AlCl}_3$, we have carried out ab initio calculations on the model compound $\text{H}_2\text{O} \cdot \text{AlCl}_3$, wherein the b_1 orbital of H_2O is involved in bonding with AlCl_3 . Our earlier studies on the complexes of BF_3 and BH_3 [1,2] with H_2O and H_2S have shown that the b_1 donor orbital participates in bonding with the acceptor orbital. Furthermore, it is expected that the ordering of the first few valence orbitals would not significantly differ between the adducts of H_2O and $(\text{C}_2\text{H}_5)_2\text{O}$ with AlCl_3 . Calculations with the 3-21G basis set gave a binding energy of 255 kJ mol^{-1} which is much higher than the experimental dissociation energy of 155 kJ mol^{-1} [3]. The $\text{Al} \cdots \text{O}$ distance was 2.58 \AA while the magnitude of charge transfer was $0.2 e$ giving a dipole moment of 7.8 D. Single point calculations with 3-21G* and 6-31G* basis sets were carried out with the 3-21G optimized geometry. These calculations show that the first few features in the HeI spectrum are all due to the lone pair orbitals of chlorine followed by $\pi_{\text{Al-Cl}}$ and $\sigma_{\text{Al-Cl}}$ orbitals. We could assign the HeI spectra of the $(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{AlCl}_3$ adduct based on the orbital ordering suggested by the calculations as shown in Table 1. It is difficult to assign any feature in the spectrum to the oxygen lone pair of the ether in the addition compound. It is expected to be shifted to a very high IE, possibly by as much as 6 eV.

The ionization energies of GaCl_3 obtained from the HeI photoelectron spectrum are at 11.96, 12.30, 12.44, 13.20, 13.96 and 16.44 eV due to a'_2 (n_{Cl}), e' (n_{Cl}), e'' (n_{Cl}), a''_2 ($\pi_{\text{Ga-Cl}}$), e' ($\pi_{\text{Ga-Cl}}$) and a'_1 ($\sigma_{\text{Ga-Cl}}$) orbitals respectively [6]. The HeI spectrum of $(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{GaCl}_3$ (Fig. 2) is similar to that of

TABLE 1

Occupied orbital energies and assignments of the addition compounds of $(\text{C}_2\text{H}_5)_2\text{O}$ with AlCl_3 and GaCl_3

Observed IE (eV)		Scaled 3.21G* energies of $\text{H}_2\text{O} \cdot \text{AlCl}_3$ (eV)*	MO character
$(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{AlCl}_3$	$(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{GaCl}_3$		
10.5	10.1	10.6	$n_{(\text{Cl})}$
10.9		10.9	$n_{(\text{Cl})}$
11.2	11.2	11.0-11.4	$n_{(\text{Cl})}$
12.5		12.2	$\pi_{(\text{Al/Ga-Cl})}$
12.9	12.9	12.4	$\sigma_{(\text{Al/Ga-Cl})}$
13.9	14.3	13.7	$\sigma_{(\text{Al/Ga-Cl})}$

*0.9 ϵ .

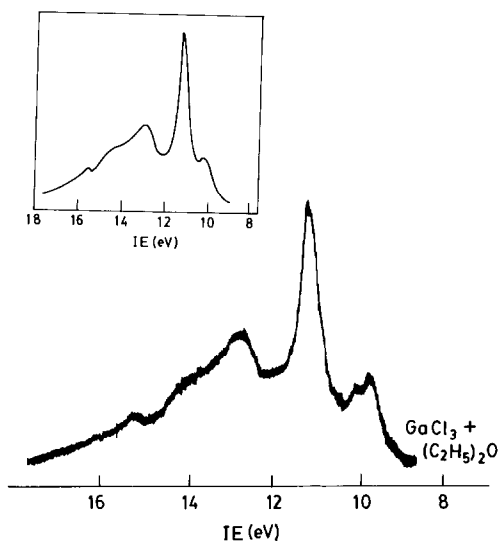


Fig. 2. HeI photoelectron spectrum of a mixture of GaCl_3 and $(\text{C}_2\text{H}_5)_2\text{O}$. The spectrum of the complex obtained after stripping is shown in the inset.

$(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{AlCl}_3$, but shows fewer features. By analogy, we have assigned the bands in the spectrum of $(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{GaCl}_3$ as shown in Table 1. The most striking feature in the spectra of the addition compounds of diethylether with AlCl_3 and GaCl_3 is the shift of the ionization energies of the chlorine lone pair orbitals to lower values compared to those of the parent acceptor molecules. The observed shift is 1.5 eV in $(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{AlCl}_3$ and 1.8 eV in $(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{GaCl}_3$. In strong donor-acceptor complexes, the lowest unoccupied molecular orbital (LUMO) of the acceptor molecule receives considerable electron density from the lone pair orbital of the donor molecule. Although there are many factors determining the magnitude of the shift in the ionization energy [8], the most important factor in such complexes appears to be charge transfer.

We have obtained the HeI spectrum of the addition compound of diethylsulphide with AlCl_3 (Fig. 3). Diethylsulphide itself shows bands in the HeI spectrum at 8.4, 10.7, 11.6 and 12.6 eV due to n_{S} , \bar{n}_{S} , $\sigma_{\text{C-S}}$ and π_{CH_3} ionizations. A unique feature in the spectrum of $(\text{C}_2\text{H}_5)_2\text{S} \cdot \text{AlCl}_3$ is the intense band at 8.9 eV which can only be ascribed to the sulphur lone pair orbital. The HOMO in $\text{H}_2\text{S} \cdot \text{BF}_3$ was earlier found to be the sulphur lone pair followed by the lone pair orbitals of fluorine [8]. MO calculations on the model compound $\text{H}_2\text{S} \cdot \text{AlCl}_3$ in the 3-21G, 3-21G* and 6-31G* basis sets show the first few ionizations to be due to chlorine lone pairs followed by $\pi_{\text{Al-Cl}}$ and $\sigma_{\text{Al-Cl}}$ orbitals with the n_{S} and \bar{n}_{S} falling in between. However, this is not in conformity with the experimental data. Situations where the orbital ordering predicted by MO calculations are not in accord with the experiment are not uncommon [1]. Thus, in their study

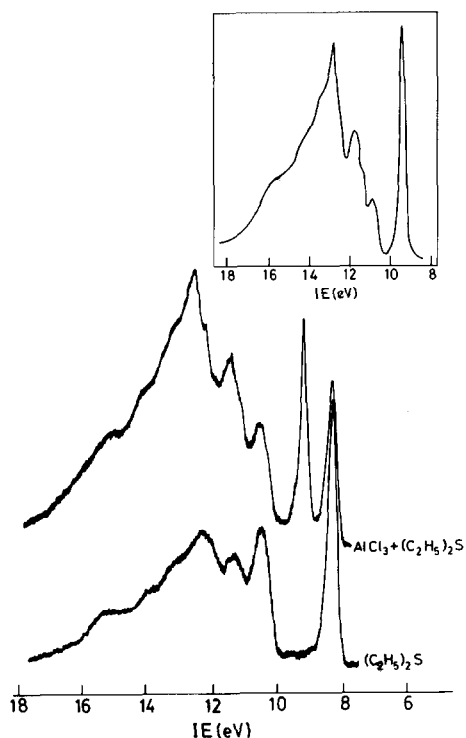


Fig. 3. HeI photoelectron spectrum of $(\text{C}_2\text{H}_5)_2\text{S}$ and a mixture of AlCl_3 and $(\text{C}_2\text{H}_5)_2\text{S}$. The spectrum of the 1:1 adduct is shown in the inset.

TABLE 2

Occupied orbital energies and tentative assignments of $(\text{C}_2\text{H}_5)_2\text{S} \cdot \text{AlCl}_3$

IE (eV)	Assignment
8.9	n_{S}
9.9	n_{Cl}
11.4	\bar{n}_{S}
11.7	n_{Cl}
12.4	$\pi_{\text{Al-Cl}}$
12.7	$\pi_{\text{Al-Cl}}$
13.4	$\sigma_{\text{C-S}}$
14.4	$\sigma_{\text{Al-Cl}}$

of $(\text{CH}_3)_2\text{O} \cdot \text{HCl}$, Carnovale et al. [9] found that at the optimized geometry, the calculated highest occupied molecular orbital (HOMO) was one of the chlorine lone pair orbitals, although the experiment showed it to be the oxygen lone pair. A similar situation was encountered in the case of $\text{H}_2\text{S} \cdot \text{BH}_3$ as well.

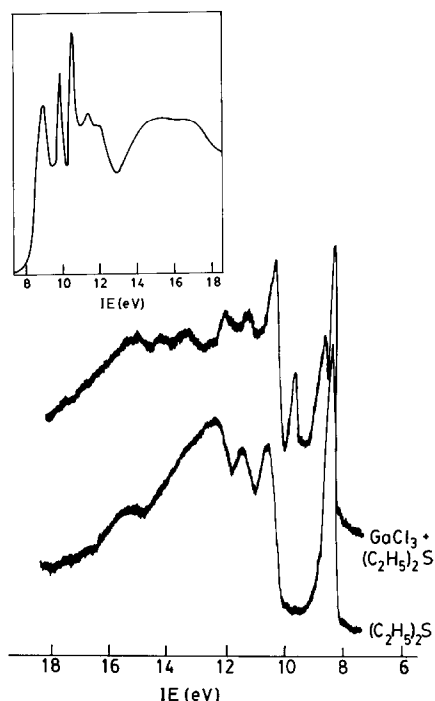


Fig. 4. HeI spectrum of $(\text{C}_2\text{H}_5)_2\text{S}$ and GaCl_3 . The spectrum of the 1:1 adduct is shown in the inset.

MO calculations showed $\text{H}_2\text{S} \cdot \text{AlCl}_3$ to be weaker than $\text{H}_2\text{O} \cdot \text{AlCl}_3$. The experimental values of dissociation energies of the complexes of AlCl_3 with $(\text{C}_2\text{H}_5)_2\text{O}$ and $(\text{C}_2\text{H}_5)_2\text{S}$ are, however, nearly the same [3]. In Table 2, we list the experimentally observed ionization energies and tentative assignments for $(\text{C}_2\text{H}_5)_2\text{S} \cdot \text{AlCl}_3$.

We have also examined the HeI spectrum of $(\text{C}_2\text{H}_5)_2\text{S} \cdot \text{GaCl}_3$ (Fig. 4). Here also, the first band observed at 9.0 eV is due to the sulphur lone pair, followed by features at 9.8, 10.6, 11.4 and 11.9 eV due to chlorine or Ga-Cl derived orbitals just as in the ether adducts discussed earlier.

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