Observation of an Alkyl Aluminium Complex formed by Reaction of CH_2I_2 with an Al(111) Surface

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The desorption of an alkyl aluminium complex, a dimer of hydroiodomethylaluminium: $[MeAl(H)I]_2$, from the reaction between an adsorbed species of CH_2I_2 and an Al(111) single crystal surface, was observed at 480 K under ultra-high vacuum.

Many important organometallic compounds such as Grignard reagents are involved in solid surface reactions with alkyl halides. These reaction processes have recently been investigated on well defined solid surfaces by means of surface analytical techniques under ultra-high vacuum (UHV).[1–3] It has been found that methylene and ethylene are formed from the decomposition of CH_2I_2 on a clean polycrystalline Al surface below 200 K.[3] This reaction can be compared with the Simmons–Smith reaction involving the organo-zinc compound formed by the reaction between Zn and CH_2I_2. In the present study, an organo-aluminium compound formed on an Al(111) surface through the reaction of Al and CH_2I_2 was examined under UHV (base pressure $<2 \times 10^{-10}$ Torr).

The Al(111) (7 × 7 × 1 mm) surface was cleaned by Ar^+ bombardment at room temperature and annealed at 723 K. The surface cleanliness and the surface structure were confirmed by Auger electron spectroscopy (AES) and low energy electron diffraction (LEED), respectively. CH_2I_2 was adsorbed at 108 K through a gas doser. For thermal desorption (TD), the temperature of the crystal was raised from 108 to 730 K with a heating rate of 15 K s^{-1}. The desorbed species were detected by a quadrupole mass spectrometer. It was found that in TD experiments CH_2I_2 began to desorb at around 190 K over a certain dosage of CH_2I_2, which we defined as 1 monolayer (1 ML).

Fig. 1 shows the TD spectrum for *m/z* 27 at 2 ML. The peak observed at 150 K was attributed to ethylene, since signals at *m/z* 28 ($C_2H_4^+$) and 26($C_2H_2^+$) and no TD signals with *m/z* $\geqslant 28$ were detected at this temperature. The peak at 190 K, at which the desorption of CH_2I_2 was also observed, was due to the desorbed CH_2I_2. TD signals with *m/z* 27 ($C_2H_3^+$) at 190 K are due to the cracking of CH_2I_2 in the mass spectrometer. Two dominant signals appeared at 416 and 480 K. Very weak signals with *m/z* 28 and 26 were observed above 300 K under the same experimental conditions as in Fig. 1. This result indicates that signals at 416 and 480 K are not due to the cracking of the desorbed hydrocarbons but to Al^+ (*m/z* 27)

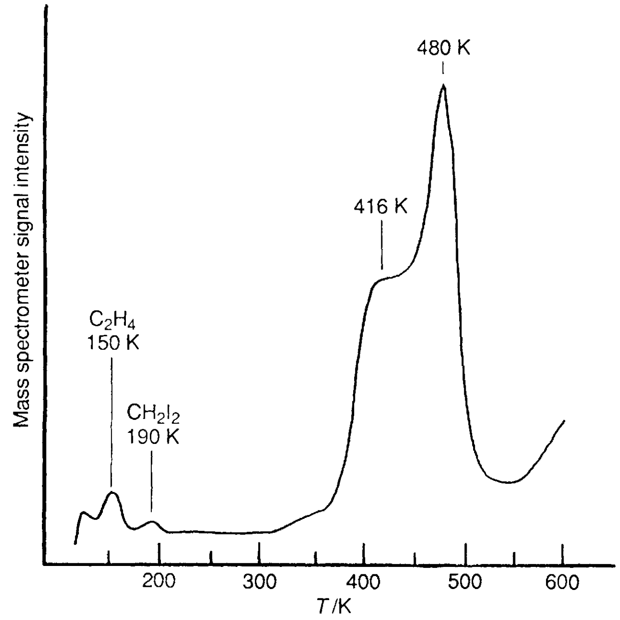

Fig. 1 TD spectrum for *m/z* 27 for CH_2I_2/Al(111) (2 ML); heating rate is 15 K s^{-1}

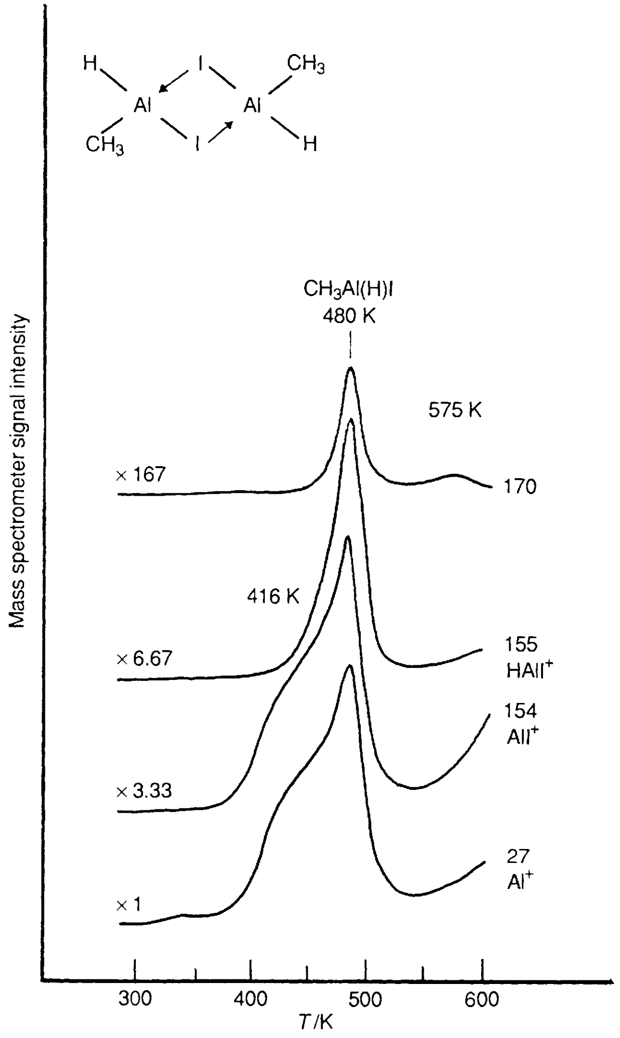

Fig. 2 TD Spectra for *m/z* 27 (Al^+), 154 (AlI^+), 155 ($HAlI^+$) and 170 on CH_2I_2/Al(111) (1 ML) inset dimer of hydroiodomethylaluminium

produced by the fragmentation of desorbed aluminium compounds from the Al surface.

To determine the formulae of the aluminium compounds desorbed from the Al(111) surface, TD spectra for various mass numbers were examined. TD spectra for *m/z* 27 (Al^+), 154, 155, 169 and 170 at 1 ML are shown in Fig. 2. Peaks were observed at 480 K for all TD spectra in Fig 2. Apparently, the mass numbers of 154 and 155 arise from AlI^+ and $HAlI^+$, respectively. Because TD signals with *m/z* 15 (CH_3) and 42 (CH_3Al) were detected at 480 K, the TD peak with *m/z* 169 at 480 K can be attributed to CH_3AlI^+. TD peaks with *m/z* 171–200 were not detected at this temperature. Thus, the mass number of 170 can be assigned to hydroiodomethylaluminium, $CH_3Al(H)I$ (*m/z* 170). In addition, the mass signal with *m/z* 297 corresponding to $CH_3Al(H)I_2^+$ was detected at 480 K. This indicated that $CH_3Al(H)I$ desorbs in dimeric form by bridge bonding *via* I atoms as shown in the inset of Fig. 2, alkylaluminium halides being known to form dimers with the coordination of Al and halogen atoms.[4] This organoaluminium compound involves Al–H and CH_3–Al bonds. It is well known that Al–H bonds form alkyl-Al compounds on addition of the hydrogen to alkenes.[5] In the CH_2I_2/Al(111) reaction, it is expected that the Al–H bond is formed from CH_2I_2 and the reaction between CH_2I_2 and Al–H forms the CH_3–Al bond.

Fig. 2 shows shoulders at 416 K for TD spectra for *m/z* 27 and 154. TD spectra for mass numbers derived from hydrocarbon fragments were not observed. Therefore, the compound observed at 416 K is considered to be composed of only Al and I atoms. In addition, the TD signal with *m/z* 281 due to AlI_2^+ was detected at this temperature. We assigned these peaks to AlI_3. The TD peak of $CH_3Al(H)I$ appeared above 0.05 ML, but desorption of AlI_3 and ethylene was not detected until 1 ML. AlI_3 probably is formed by the resident iodine, which is generated by the formation of ethylene from CH_2I_2. Following a similar discussion, the *m/z* 170 peak at 575 K is attributed to the desorption of an iodopropane, C_3H_7I. Although TD peaks of Al^+ and AlI^+ were detected above 600 K, we could not assign these peaks.

Thus, the reaction between CH_2I_2 and the Al(111) surface is found to lead to the desorption of hydroiodomethylaluminium. To our knowledge, this is the first direct observation of desorption species of organometallic compounds produced from a reaction between an adsorbate and a solid surface. Studies in this direction will provide useful information on the mechanism of formation of organometallic compounds over solid surfaces.

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