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Reaction of Atomically Clean Aluminum and Chemically Modified Aluminum with Alkyl Halides

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Abstract: The interaction of methyl halides with an atomically clean Al(111) surface has been investigated using high-resolution electron energy loss spectroscopy (EELS), Auger electron spectroscopy (AES), and temperature programmed desorption (TPD). CH$_3$I adsorbs on Al(111) both molecularly and dissociatively at 150 K; adsorbed CH$_3$I decomposes to CH$_{(a)}$ and I$_{(a)}$ in the temperature range of 250–450 K. No surface reaction of CH$_3$Cl or CH$_3$Br with clean or chemically modified Al(111) was observed, and a reactive sticking coefficient of $<10^{-5}$ was estimated in the temperature range of 135–500 K (CH$_3$Cl) or at 150 K (CH$_3$Br). Reasons for the reactivity differences of the methyl halides toward the Al(111) surface are discussed. These findings on Al, and their implication in Grignard reaction mechanisms, are compared with recent studies by another group on a Mg surface.

1. Introduction

The chemical reactivity of atomically clean Al surfaces with organic molecules is almost completely unstudied using the methods of surface science now available. Thus, only methanol[1] and two carboxylic acids[2–4] have been characterized in their reaction with clean Al surfaces. In an attempt to broaden our understanding of the surface chemistry of clean Al, we have examined the chemistry of three alkyl halides (methyl chloride, methyl bromide, and methyl iodide) as they interact with an atomically clean Al(111) surface.

It is well known from the classic work of Grosse and Mavity[5] and Adkins and Scanley[6] that the reaction of Al metal with liquid alkyl and aryl halides will occur. The general form of the complete reaction is

$$3RX + 2Al \rightarrow R_2AlX + RAlX_2 \qquad (1)$$

where the mixture of the aluminum alkyl halides is given the general designation "sesquihalides". The reaction falls into the Grignard classification employed for similar Mg-based chemistry.

In almost all experiments, reaction 1 is reported to be sluggish initially, and it is common to add an initiator, either aluminum chloride or elemental iodine. The initial slowness of the reaction has been ascribed to the presence of an oxide layer on the Al surface. In the work to be reported here with atomically clean Al, the possible influence of the oxide overlayer on the reaction rate can be eliminated, and the basic reactivity pattern with the clean metal surface can be discerned.

Recently, a study of the methyl bromide/Mg(0001) surface reaction has been carried out using several surface spectroscopies.[7] Evidence was found for the facile production of a surface bromide accompanied by the formation of ethane gas. No evidence for the formation of a surface Mg–C bond was obtained, and the analogy of these results to the formation of the Grignard reagent, CH$_3$–Mg–Br, could not be made.[7]

In the work to be described here, the interaction of CH$_3$Cl, CH$_3$Br, CH$_3$I, and CD$_3$I with the clean Al(111) surface and with chemically modified Al(111) has been investigated using EELS (high-resolution electron energy loss spectroscopy), AES (Auger electron spectroscopy), and TPD (temperature programmed desorption) methods. Methyl halide adsorption was examined at surface temperatures ranging from 135 to 500 K.

2. Experimental Methods

The ultrahigh vacuum system (base pressure $< 1 \times 10^{-10}$ mbar), containing facilities for EELS, AES, and TPD measurements has been described previously.[8] The Al(111) crystal was oriented to within 0.5° of the (111) direction by Laue back reflection and was ground and polished to the 0.5-μ level using diamond abrasive. Extensive sputter cleaning, accompanied by annealing at 700 K, was required to produce the atomically clean surface, as described previously.[8] Using standard Auger sensitivity factors,[9] we estimate that the impurity levels in the surface region sampled by AES are: C <0.2 atom %; O <0.2 atom %. Slots in the edge of the crystal permitted support by a pair of 0.025-cm diameter W wires which were used for heating the crystal using a temperature controller of our own design.[10] A chromel–alumel thermocouple was employed for temperature measurement, and its junction was wedged into a slot cut into the crystal.

The methyl halides were admitted to the vacuum chamber via a molecular beam doser arrangement which consists of a calibrated conductance in series with either a tubular doser or a glass microchannel plate collimator doser.[11] The gases, CH$_3$Cl and CH$_3$Br (99.5% purity), were obtained from Matheson in gas cylinders and transferred to glass and metal ampoules. CH$_3$I (99% purity), purchased from Chemalog, and CD$_3$I (99+ atom % D), obtained from Aldrich Chemical Co., were transferred under a high-purity nitrogen atmosphere to ampoules through an Al$_2$O$_3$ liquid chromatography column; such procedures were necessary to remove small levels of impurities (e.g., methanol) from the reagent. The CH$_3$I and CD$_3$I were further purified by four freeze–pump–thaw cycles, followed by a single vacuum distillation. Gas purity in the case of CH$_3$Cl and CH$_3$I was checked by gas-phase IR spectroscopy. For adsorption measurements on Al(111) the ampoules were attached to the stainless steel, bakeable gas-handling system, and the backing pressure was adjusted to produce the desired incident molecular beam flux to the crystal (fluences ranged from 1.5×10^{13} to 3.5×10^{13} molecules·cm^{-2}·s^{-1}).

The EEL spectra in this work were collected in the specular direction with a total scattering angle of 120° and an incident beam energy of 2.5–3.5 eV. Typical resolution (fwhm) from the adsorbed layer was 60–90 cm^{-1} with an elastic peak intensity of 1×10^5 counts/s. Auger spectra were recorded in a d$N(E)$/dE mode at a primary beam energy of 3.0 keV, a modulation voltage of 3.0 V$_{pp}$, and a total crystal electron current of 3.0 μA.

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(1) Rogers, J. W., Jr.; Hance, R. L.; White, J. M. *Surf. Sci.* **1980**, *100*, 388. Tindall, I. F.; Vickerman, J. C. *Ibid.* **1985**, *149*, 577.

(2) Crowell, J. E.; Chen, J. G.; Yates, J. T., Jr. *J. Electron Spectrosc. Relat. Phenom.* **1986**, *39*, 97.

(3) Chen, J. G.; Crowell, J. E.; Yates, J. T., Jr. *Surf. Sci.* **1986**, *172*, 733.

(4) Crowell, J. E.; Chen, J. G.; Yates, J. T., Jr. *J. Chem. Phys.* **1986**, *85*, 3111.

(5) Grosse, A. V.; Mavity, J. M. *J. Org. Chem.* **1940**, *5*, 106.

(6) Adkins, H.; Scanley, C. *J. Am. Chem. Soc.* **1951**, *73*, 2854.

(7) Nuzzo, R. G.; Dubois, L. H. *J. Am. Chem. Soc.* **1986**, *108*, 2881.

(8) Crowell, J. E.; Chen, J. G.; Yates, J. T., Jr. *Surf. Sci.* **1986**, *165*, 37.

(9) Estimates of the atomic concentration in the Auger sampling depth were made using the sensitivity factors given in the *Handbook of Auger Electron Spectroscopy*; Davis, L. E., MacDonald, N. C., Palmberg, P. W., Riach, G. E., Weber, R. E.; Eds.; Physical Electronics Div., Perkin-Elmer Corp.: Eden Prairie, MN, **1976**; p 13.

(10) Muha, R. J.; Gates, S. M.; Yates, J. T., Jr.; Basu, P. *Rev. Sci. Instrum.* **1985**, *56*, 613.

(11) Gates, S. M.; Russell, J. N., Jr.; Yates, J. T., Jr. *Surf. Sci.* **1984**, *146*, 199. Bozack, M. J.; Muehlhoff, L.; Russell, J. N., Jr.; Choyke, W. J.; Yates, J. T., Jr. *J. Vac. Sci. Technol.* **1987**, *A5*, 1.

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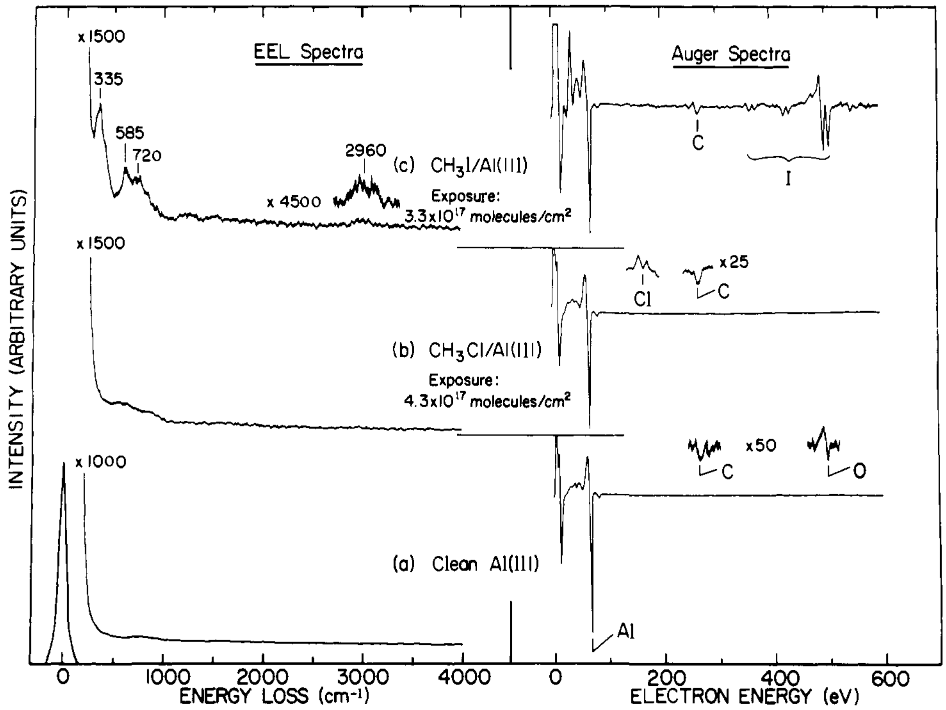

Figure 1. EELS and AES measurements of (a) a clean Al(111) surface, and the same surface exposed to (b) CH_3Cl and (c) CH_3I and 150 K.

Table I. Reactivity Summary for CH_3Cl and CH_3Br Adsorption and Decomposition on Al(111) and Chemically Modified Al(111)

chemical system	crystal temp (K)	alkyl halide exposure (molecules/cm²)	result
$CH_3Cl/Al(111)$	135	4.3×10^{17}	no reaction
	155	4.9×10^{17}	no reaction
	300	1.3×10^{17}	no reaction
	500	1.3×10^{17}	no reaction
CH_3Cl/disordered Al(111)	150	2.0×10^{17}	no reaction
	300	2.0×10^{17}	no reaction
$CH_3Cl/O/Al(111)$ O_2 exposure = 1.4×10^{16} molecules/cm² at 140 K	150	7.0×10^{17}	no reaction
$CH_3Cl/Al_2O_3/Al(111)$ O_2 exposure = 2.6×10^{17} molecules/cm² at 350 K followed by heating to 700 K	145	3.8×10^{17}	no reaction
$CH_3Cl/OH/Al(111)$ (hydroxylated aluminum)	155	3.8×10^{17}	no reaction
$CH_3Br/Al(111)$	152	5.0×10^{17}	no reaction
$CH_3Br/O/Al(111)$ O_2 exposure = 2.1×10^{17} molecules/cm² at 165 K	149	5.0×10^{17}	no reaction

Table II. Observed Frequencies[a,b] for Molecularly Adsorbed $CH_3I(CD_3I)$ and Comparison with Gas-Phase Frequencies

mode	CH_3I (CD_3I) 150 K, Al(111)[c]	CH_3I (CD_3I) gas phase[d]
$\nu_{as}(CH_3)$	*e*	3060 (2298)
$\nu_s(CH_3)$	2960 (2170)	2970 (2155)
$\delta_{as}(CH_3)$	*e*	1436 (1049)
$\delta_s(CH_3)$	not seen[f]	1252 (951)
$\rho(CH_3)$	*e*	882 (656)
ν(CI)	585	553 (501)
ν(Al-I)	335 (360)	

[a] Frequencies are given in wavenumbers, cm⁻¹. [b] Frequencies given in parentheses refer to the fully deuterated species. [c] This work. [d] Reference 12. [e] These entries are not observed, and are indeed not expected to be observed in the specular direction if the symmetry of the molecularly adsorbed species is higher than C_1, due to the surface dipole selection rule. [f] Although expected to be observed, these are not. See section 4.B for discussion of this result.

3. Experimental Results

Quite surprisingly, it was found that the reactivity of both CH_3Cl and CH_3Br with clean Al(111) was undetectable using either EELS or AES methods over a wide range of crystal temperatures for exposures as great as $\sim 5 \times 10^{17}$ molecules·cm⁻². In order to determine the influence of purposely introduced defects, experiments with CH_3Cl were also conducted on the Al(111) crystal roughened by 3.0-kV Ar^+ ion bombardment; there was no observed adsorption or surface chemistry on the roughened Al surface for exposures as great as $\sim 2 \times 10^{17}$ molecules·cm⁻². In order to determine whether reactivity was induced by chemical modification of the surface, experiments were conducted with both CH_3Cl and CH_3Br on the (chemisorbed) oxygen-predosed Al(111) surface, and with CH_3Cl on the oxidized and hydroxylated Al(111) surfaces. No adsorption or surface chemistry was observed for these chemically modified surfaces. A summary of these negative results is given in Table I.

A typical set of EELS and AES results for unsuccessful CH_3Cl adsorption on the Al(111) surface is compared in Figure 1 with the successful adsorpton of CH_3I on the same surface. Using the known fluence of the methyl halides, we estimate, based on the sensitivity of our Auger spectrometer, that the reactive sticking coefficient for either CH_3Cl or CH_3Br is below 10^{-5} on Al(111) or chemically modified Al(111) at 150 K. In the case of CH_3Cl, it has been shown that the low reactivity with the clean Al(111) surface persists up to 500 K.

In Figure 1 it is clear from both the EELS and AES measurements that CH_3I will adsorb at 150 K. The observed vibrational features are readily assigned by comparison with the gas-phase spectrum of CH_3I,[12] which is shown in Table II. Evidence for the presence of a ν(C–I) motion for the adsorbed CH_3I is seen at 585 cm⁻¹, along with a broad carbon–hydrogen stretching mode in the range 2825–3095 cm⁻¹, centered at about 2960 cm⁻¹. In addition, an Al–I mode at 335 cm⁻¹ and an Al–C mode at 720 cm⁻¹ are also seen. The observation of an Al–C mode along with those mentioned above suggests that both the undissociated CH_3I and the fragments from C–I bond cleavage coexist under these conditions.

The thermal decomposition of CH_3I was studied by programmed (2 K/s) heating of the overlayer from 150 to 650 K in steps

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(12) Shimanouchi, R. *Tables of Molecular Vibrational Frequencies*; U. S. Government Printing Office: Washington, D.C., 1972; Consolidated Vol. I.

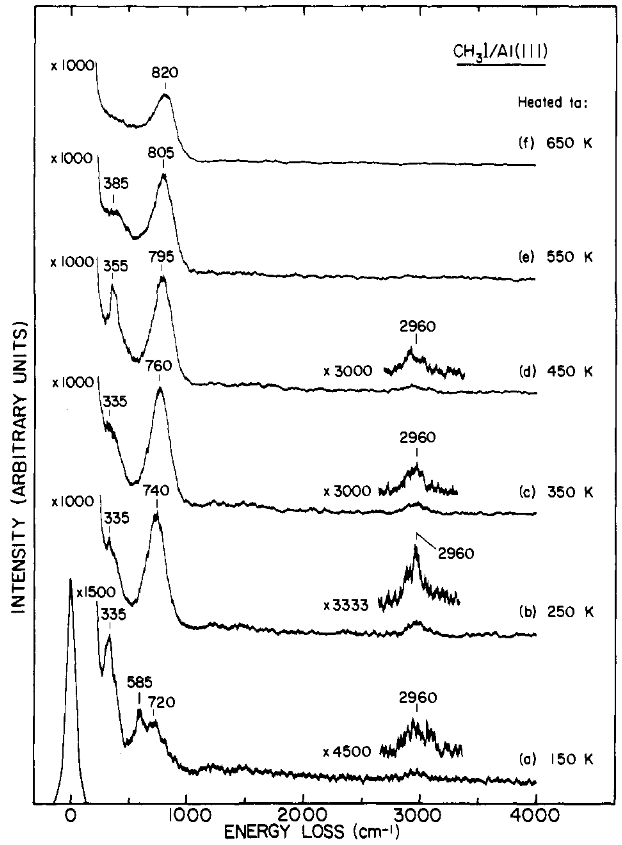

Figure 2. EEL spectra of $CH_3I/Al(111)$ recorded as a function of crystal temperature. The crystal containing the adsorbed layer was resistively heated to the indicated temperatures, then allowed to cool; the spectra were collected between 150 and 170 K.

followed by cooling as shown in Figure 2. It is observed that between 150 and 250 K (spectra 2a and 2b) the 585-cm^{-1} ν(C–I) feature disappears as the C–I bond fragments to produce surface species exhibiting a strong 740-cm^{-1} band due to an Al–C stretching mode, a 355-cm^{-1} band due to an Al–I stretching mode, and a relatively sharp carbon–hydrogen stretching mode near 2960 cm^{-1}. The production of new surface species upon heating the surface to 250 K is indicated by the large intensity increase and slight frequency shifts that occur; these vibrational changes are accompanied by desorption of molecular CH_3I at ~200 K. By 550 K (Figure 2e), the C–H stretching mode has disappeared and the Al–I mode has almost disappeared. By 650 K, only the Al–C mode at 820 cm^{-1} remains.

To check the mode assignments, Figure 3 shows a comparison between CH_3I and CD_3I (spectra 3a and 3b). Two main spectral changes are apparent upon deuteration. The assignment of the 2960-cm^{-1} feature as ν(CH) is verified by the expected shift to 2170 cm^{-1} (due to ν(CD)) for CD_3I decomposition. One also observes that the intense feature in Figure 3a at 760 cm^{-1}, assigned above to ν(Al–C), splits into two features at 590 and 760 cm^{-1} upon CD_3I adsorption (see Figure 3b). The presence of features at ~335 and 760 cm^{-1} in *both* spectra 3a and 3b suggests that these features do not involve hydrogen motions, supporting their assignment as ν(Al–I) and ν(Al–C) motions, respectively.

However, the presence of a new feature at 590 cm^{-1} upon CD_3I decomposition indicates that the 760-cm^{-1} feature contains two overlapping modes in the case of CH_3I adsorption. By comparison with the several studies of hydrocarbon fragments on clusters and metal surfaces,[13] we assign the band at 760 (590) cm^{-1} (numbers in parentheses refer to frequencies for the fully deuterated species) as δ(CH) of a methylidyne species; the bands at 2960 (2170) and 760 (760) cm^{-1} are the ν(CH) and ν(Al–C) modes corresponding to this same species.

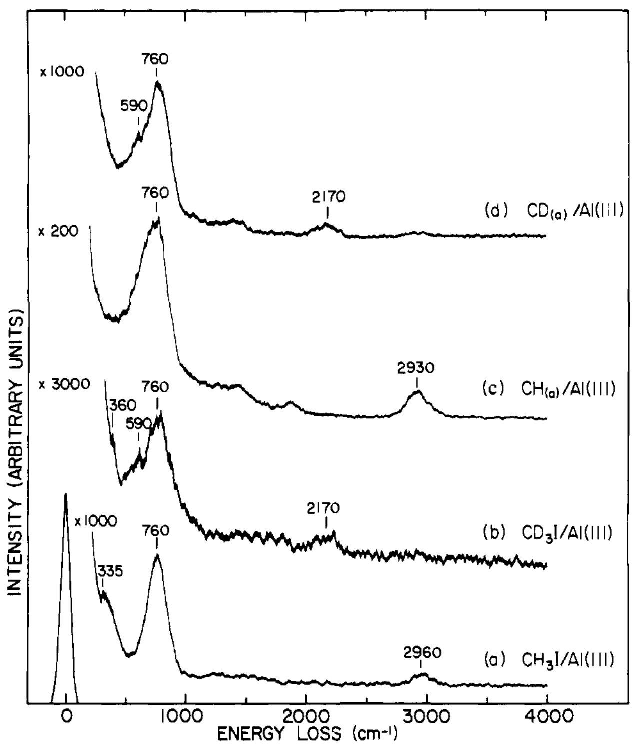

Figure 3. Comparison of EEL spectra of (a) $CH_3I/Al(111)$, (b) $CD_3I/Al(111)$, (c) $CH_{(a)}/Al(111)$, and (d) $CD_{(a)}/Al(111)$ after heating to 350 K. The adsorbed layers were prepared at low temperatures (150 to 170 K for CH_3I and CD_3I, 200 K for $CH_{(a)}$ and $CD_{(a)}$ followed by heating to 350 K, as specified in the text (section 3). Vibrational assignments for $CH_{(a)}$ ($CD_{(a)}$) are: ν(CH), 2930 cm^{-1} (2170 cm^{-1}); δ(CH), 760 cm^{-1} (590 cm^{-1}); ν(Al–C), 760 cm^{-1} (760 cm^{-1}).

The assignment of spectra 3a and 3b is supported by comparison with the $CH_{(a)}$ spectrum produced from acetylene decomposition, shown in Figure 3c. The decomposition of acetylene was achieved by electron bombardment of gas-phase C_2H_2. A broad, uniform 300-eV electron distribution was employed in the vicinity of the Al(111) surface to decompose C_2H_2 at system pressures of 5×10^{-7} mbar. The surface temperature was maintained at 200 K, since, at this temperature, acetylene does not molecularly adsorb on Al(111). The $CH_{(a)}/Al(111)$ layer thus produced was then heated to 350 K and allowed to cool; the EEL spectra were recorded. An intense broad feature at 760 cm^{-1} is observed, along with a 2930-cm^{-1} band in Figure 3c. This spectrum is very similar to spectrum 3a, with the noted absence of a 335-cm^{-1} band, confirming that this feature is due to ν(Al–I) motions. It is noted that this assignment is partially based on the overlap in frequency of two motions at 760 cm^{-1}, namely the ν(Al–C) mode and the δ(CH) mode associated with adsorbed CH. To verify this assignment, a similar experiment with $C_2D_{2\,(g)}$ to produce $CD_{(a)}/Al(111)$ was performed, and the result is shown in Figure 3d. It is seen that a 760-cm^{-1} mode is observed, along with a 590-cm^{-1} mode due to ν(Al–C) and δ(CD), respectively, in agreement with the assignment and with the decomposition spectrum shown in Figure 3b for the process $CD_3I \rightarrow CD_{(a)}$.

4. Discussion

A. Comparison of Alkyl Halide Reactivities on Al(111). It is quite clear that the reactivity of the alkyl halides with Al(111) cannot be kinetically efficient at temperatures between 135 and 500 K. Both methyl chloride and methyl bromide display very low kinetic efficiencies for reaction ($<10^{-5}$/collision). Neither the production of surface defects nor the presence of chemisorbed oxygen causes measurable enhancement of the reaction rate. Similarly, oxidation or hydroxylation of the Al(111) surface does not enhance the reactivity of CH_3Cl at 155 K.[14] In the case of

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[13] See, for example, the following publications and references therein: (a) Koel, B. E.; Crowell, J. E.; Bent, B. E.; Mate, C. M.; Somorjai, G. A. *J. Phys. Chem.* **1986**, *90*, 2949. (b) Crowell, J. E.; Bent, B. E.; Mate, C. M.; Somorjai, G. A.; Koel, B. E., submitted for publication in *J. Am. Chem. Soc.*. (c) Parmeter, J. E.; Hills, M. M.; Weinberg, W. H. *Ibid.* **1986**, *108*, 3563. Seip, U.; Tsai, M.-C.; Küppers, J.; Ertl, G. *Surf. Sci.* **1984**, *147*, 65.

methyl iodide, a higher rate of reaction is observed with the Al(111) surface, and this dissociative adsorption is accompanied at 150 K with the adsorption of the undecomposed CH_3I molecule. We estimate that the reactive sticking coefficient for CH_3I at 150 K is of the order of $10^{-4} - 10^{-3}$, using AES intensities for both C and I.[9]

There are probably two factors which cause the surface reaction of CH_3I to occur on Al, whereas methyl bromide and methyl chloride are very slow to react.

(1) The polarizability of CH_3I is large compared to the lower molecular weight methyl halides. Thus, stronger van der Waals' forces between the molecule and the surface are expected, and the adsorption lifetime of the methyl iodide molecule on the surface will be longer than for the other two halides. Dissociative reaction is thus facilitated.

(2) The C–X bond of methyl iodide is less stable than those of the lower molecular weight methyl halides as indicated by the low CH_3–I bond energy (234 kJ/mol) compared to CH_3–Br (293 kJ/mol) and to CH_3–Cl (349 kJ/mol).

B. Adsorption and Thermal Decomposition of Methyl Iodide on Al(111). The presence of molecular CH_3I on Al(111) at 150 K is indicated by the presence of a ν(C–I) mode at 585 cm^{-1} in the vibrational spectrum and a 142-amu thermal desorption state at ~200 K (due to molecular desorption of CH_3I). However, the simultaneous observation of vibrational features due to both ν(Al–I) and ν(Al–C) in Figure 2a suggests that decomposition of some of the adsorbed CH_3I has already occurred at 150 K.[16] The simplicity of the vibrational spectrum observed at 150 K and the changes observed with heating indicate that a mixture of molecular CH_3I and the decomposition products $I_{(a)}$ and $CH_{(a)}$ exists on the surface at 150 K. The absence of any $\delta(CH_3)$ modes for $CH_3I_{(a)}$ is likely due to the extremely low concentration of $CH_3I_{(a)}$ in Figure 2a.

Assignment of the 150 K spectrum is made possible by the changes observed on heating this layer and by comparison with the adsorption and decomposition spectra of CD_3I. The decomposition fragments obtained after the CH_3I/Al(111) layer was heated to above 250 K (Figure 2b–d) are likely the $CH_{(a)}$ and $I_{(a)}$ species. The presence of the $I_{(a)}$ is verified by the observation of a ν(Al–I) mode at 335–385 cm^{-1} in the temperature range of 250 to 550 K in Figure 2. The presence of an adsorbed methylidyne species is confirmed by the observation of the δ(CH) mode at 760 cm^{-1} and the δ(CD) mode at 590 cm^{-1} (Figure 3a,b), which are the characteristic vibrational features for $CH_{(a)}$ and $CD_{(a)}$ species, as well as by the similarity between the decomposition spectra for CH_3I and CD_3I (Figure 3a,b) and those for C_2H_2 and C_2D_2 (Figure 3c,d). Acetylene typically decomposes to CH or CCH species on late transition metal surfaces;[13] spectrum 3c is consistent with the production of either of these hydrocarbon fragments, but we are not able to distinguish between these species for the C_2H_2 case. Nevertheless, specific isotopic shifts are seen for $CH_{(a)}$ vs. $CD_{(a)}$ in Figure 3c,d. The comparison in Figure 3 clearly shows that $I_{(a)}$ and $CH_{(a)}$ are the only observable surface species produced from CH_3I decomposition on Al(111), suggesting that $CH_{(a)}$ species are more stable than CH_2 or CH_3 groups on Al(111).

Both AES and EELS verify that the adsorbed CH and I species remain on the Al(111) surface at temperatures as high as 450 K. At higher temperatures, $I_{(a)}$ is depleted from the surface,[17] and the methylidyne species decompose to produce a carbon-containing surface displaying no ν(C–H) feature (see Figure 2f). The latter decomposition sequence is similar to observations made for C–H bond scission in carboxylic acids on Al(111).[2-4]

C. Comparison of the Grignard Surface Chemistry of Al and Mg. This study, when compared to similar study[7] of the reactivity of Mg(0001) with CH_3Br, provides useful insight into the factors influencing the Grignard process on the two metals. In comparing Mg and Al reactivity with CH_3Br, we find that atomically clean Mg is much more reactive than atomically clean Al at temperatures of about 120–150 K. The reaction on the Mg surface leads to the production of a surface bromide moiety, with no evidence for the presence of a surface methyl group. The possibility of the facile liberation of ethane gas by the recombination of surface CH_3 groups is envisioned on Mg.[7]

For the less reactive Al surface, CH_3Br does not react at all under conditions of exposure and surface temperature which are comparable to the Mg experiments. This tendency toward low rates of reaction is seen also in similar results for CH_3Cl. However, CH_3I does react slowly on Al(111), and in the temperature range of 150–450 K evidence is seen for the stabilization of a surface CH group, along with a surface iodide moiety.

It would seem then, on the basis of the comparison now available to us, that while Al is kinetically less reactive generally to the alkyl halides, it is more easily able to stabilize a metal–carbon bond than is Mg. Thus, *under high surface concentration conditions* for the alkyl halide reactant, the formation of the aluminum alkyl halides (reaction 1) may occur via corrosive processes involving multiple species attack at the metal center, ultimately resulting in the formation of the volatile products in reaction 1. However, reaction 1 occurs in the presence of surface CH species which exhibit thermodynamic stability below 450 K. At temperatures above about 450 K, final cracking of the surface CH species occurs with the formation of a carbon layer on the Al surface; this may lead to the formation of the surface compound Al_4C_3, although no evidence of this particular stoichiometry has been found in the present study. The presence of a carbonaceous layer could inhibit the sustained reaction of the Al surface with the alkyl halide.

5. Summary

The following results have been obtained in the study of the reactivity of three methyl halides with an atomically clean Al(111) surface.

A. The reactivity of CH_3Cl (135–500 K) or CH_3Br (150 K) per surface collision is very low (<10^{-5} reaction events/collision); only CH_3I shows evidence of a surface reaction at 150 K.

B. CH_3I adsorbs at 150 K as a mixture of the undecomposed molecule and also as $CH_{(a)}$ and $I_{(a)}$. Complete decomposition to these fragment species occurs by 250 K. The reactive sticking coefficient for CH_3I at 150 K is estimated to be 10^{-4}–10^{-3}.

C. The methylidyne group (CH) is stable to about 450 K as is the surface iodide species. Above this temperature, only a carbon residue remains.

D. In contrast to Mg, we have found that Al surfaces have the ability to stabilize surface CH groups in the temperature range of 150 to 450 K. Mg tends to promote loss of surface methyl groups in the same temperature range, possibly by C_2H_6 formation.[7]

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(14) A recent study of high-area alumina containing hydroxyl groups[15] has shown that physical adsorption of CH_3Cl occurs on hydroxyl groups at T ~150 K. This behavior is not seen here because of the low equilibrium vapor pressure of CH_3Cl in the present experiment (<5×10^{-10} mbar). Equilibrium pressures of ~1 torr were necessary to achieve sufficient population of the physisorbed state.[15]

(15) Crowell, J. E.; Beebe, T. P., Jr.; Yates, J. T., Jr. *J. Chem. Phys.*, submitted for publication.

(16) Molecular CH_3I is expected to bond to the surface through the iodine atom, resulting in an Al–I stretching vibration. It is unlikely that molecular CH_3I would bond through the carbon or hydrogen atoms; hence any Al–C mode must indicate at least partial dissociation of CH_3I.

(17) The depletion of $I_{(a)}$ from the surface by 650 K is verified by AES. We suspect $I_{(a)}$ desorbs from the surface as I_2, although iodine has not been detected using mass spectrometry (TPD).