

8065–8078 V. The relative abundances of the reactions corresponding to water and hydrogen atom losses were measured from the areas of the associated metastable peaks in the MIKES<sup>40</sup> spectra of the M<sup>+</sup> ions of the appropriate *n*-propan-1-ol. Kinetic energy release data were computed by means of a one-line formula,<sup>41</sup> from the width at half-height ( $w_{1/2}$ ) of the relevant metastable peak; the usual correction (eq 3) was applied for the width at half-height ( $W_{1/2}$ ) of the main beam.<sup>53</sup> The quoted results were obtained from data accumulated over 50–200 scans.

$$w_{1/2}(\text{corr}) = (w_{1/2}^2 - W_{1/2}^2)^{1/2} \quad (3)$$

(53) Baldwin, M. A.; Morgan, R. P.; Derrick, P. J. *Org. Mass Spectrom.* 1976, 11, 440.

The CID and CS measurements were made with the MIKES<sup>40</sup> technique, after helium had been admitted as the collision gas so as to give 60% attenuation of the original signal due to M<sup>+</sup>. The CID spectra were accumulated over 5–15 scans, and the CS spectra were accumulated over 50–150 scans.

**Acknowledgment.** Financial support from KRATOS and from the SERC (U.K.), including the award of an Advanced Fellowship to R.D.B., is gratefully acknowledged. The assistance of Dr. Steen Hammerum and Professor David McAdoo, who communicated results prior to publication, is acknowledged with thanks. Special thanks are due to Mrs. M. Callaway for her care in preparing the typescript.

## Thermal Decomposition of Alkyl Halides on Aluminum. 1. Carbon–Halogen Bond Cleavage and Surface $\beta$ -Hydride Elimination Reactions

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Received May 29, 1990. Revised Manuscript Received September 6, 1990

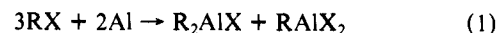
**Abstract:** The thermal decomposition of alkyl iodides adsorbed on Al(100) and Al(111) surfaces has been studied by using temperature-programmed desorption, integrated desorption mass spectrometry, and high-resolution electron energy loss spectroscopy. We find that alkyl iodides with three or more carbons adsorb dissociatively on aluminum at temperatures  $\geq 130$  K. The adsorbed alkyl ligands generated by C–I bond scission are stable on the surface up to  $\sim 450$  K and are not significantly affected by the presence of the coadsorbed halogen atom. The dominant mechanism for thermal decomposition of the alkyl fragment is  $\beta$ -hydride elimination, and the kinetics of this surface reaction are similar to those for  $\beta$ -hydride elimination by aluminum alkyls in both the gas phase and solution.

### 1. Introduction

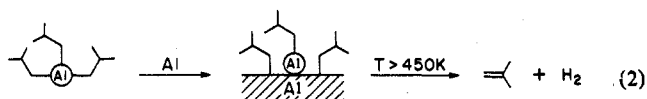
Recent studies have established that adsorbate bonding on metal surfaces is often analogous to the bonding of ligands in metal complexes.<sup>1</sup> An understanding of the extent to which reactivity patterns of discrete molecular complexes are predictive of reaction pathways on surfaces has yet to emerge, however. This failing arises, in part, because many adsorbates decompose on *transition-metal* surfaces rather than desorb intact. Consequently, extensive spectroscopic studies are often required to identify the products of even the simplest surface reactions.

We have recently found that both saturated and unsaturated hydrocarbons bind only weakly to aluminum surfaces.<sup>2</sup> As a result, mass spectrometry can be applied readily to determine both the products<sup>3</sup> and kinetics<sup>2</sup> of hydrocarbon-producing reactions. In the present work, we have exploited this fact and determined the thermal surface reaction pathways followed by a variety of alkyls and metallacycles on aluminum surfaces generated by the dissociative adsorption of alkyl halides. We discuss our results in the context of the extensive literature for the reactivity patterns exhibited in the gas phase and in solution by aluminum–alkyl complexes.

It should be noted that in all of the studies described below, the coadsorbed halogen atom remains on the surface throughout the temperature range where the adsorbed alkyl moiety decomposes (and the products subsequently desorb). This is a particularly striking observation given that the reaction of aluminum with alkyl halides is an industrially important process for the synthesis of aluminum sesquihalides in bulk (eq 1). Although



this metal-consuming reaction is extremely facile in solution, under ultrahigh vacuum (UHV) conditions alkyl decomposition predominates. Thus, for example, previous studies of the decomposition of adsorbed isobutyl groups formed on aluminum by the adsorption of either triisobutylaluminum (TIBA, eq 2) or 1-iodo-2-methylpropane (eq 3) have shown that the adsorbed alkyl ligands (with or without coadsorbed iodine atoms present) decompose thermally by  $\beta$ -hydride elimination to evolve isobutene and hydrogen at  $\sim 500$  K.<sup>2,4,5</sup>



(1) See, for example: Albert, M. R.; Yates, J. T., Jr. *The Surface Scientist's Guide to Organometallic Chemistry*; American Chemical Society: Washington DC, 1987. Muettterties, E. L. *Angew. Chem.* 1978, 17, 545. Muettterties, E. L. *Chem. Soc. Rev.* 1982, 11, 283. Canning, N. D. S.; Madix, R. J. *J. Phys. Chem.* 1984, 88, 2437. Bent, B. E.; Somorjai, G. A. *Adv. Coll. Int. Sci.* 1989, 29, 223.

(2) Bent, B. E.; Nuzzo, R. G.; Dubois, L. H. *J. Am. Chem. Soc.* 1989, 111, 1634.

(3) Dubois, L. H. *Rev. Sci. Instrum.* 1989, 60, 410.

(4) Bent, B. E.; Nuzzo, R. G.; Dubois, L. H. *J. Vac. Sci. Technol. A* 1988, 6, 1920; *Mat. Res. Soc. Symp. Proc.* 1988, 101, 177.

(5) Bent, B. E.; Dubois, L. H.; Nuzzo, R. G. *Mat. Res. Soc. Symp. Proc.* 1989, 131, 327.

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**Table I.** Comparison of the Vibrational Frequencies<sup>a</sup> in the Fingerprint Region (700–1500 cm<sup>-1</sup>) for 1-Iodopropane in Solution and Adsorbed on an Al(100) Surface

1.0 L at 105 K <sup>b</sup>	40 L, warm to 310 K <sup>c</sup>	liquid, trans conformation <sup>d</sup>
		1460
1445	1450	1456
		1428
~1350, sh	1385	1380
~1300, sh	~1300, sh	1328
1195	1160	1185
		1089
1030	1000	1019
~845, br	806, br	895
735		726

<sup>a</sup> Frequencies in cm<sup>-1</sup>; sh = shoulder; br = broad. <sup>b</sup> Frequencies from Figure 1B for a submonolayer coverage of molecularly adsorbed 1-iodopropane. <sup>c</sup> Frequencies from Figure 1D for a monolayer of chemisorbed propyl groups. <sup>d</sup> Frequencies from ref 9; only those for modes of A' symmetry are given.

## 2. Experimental Section

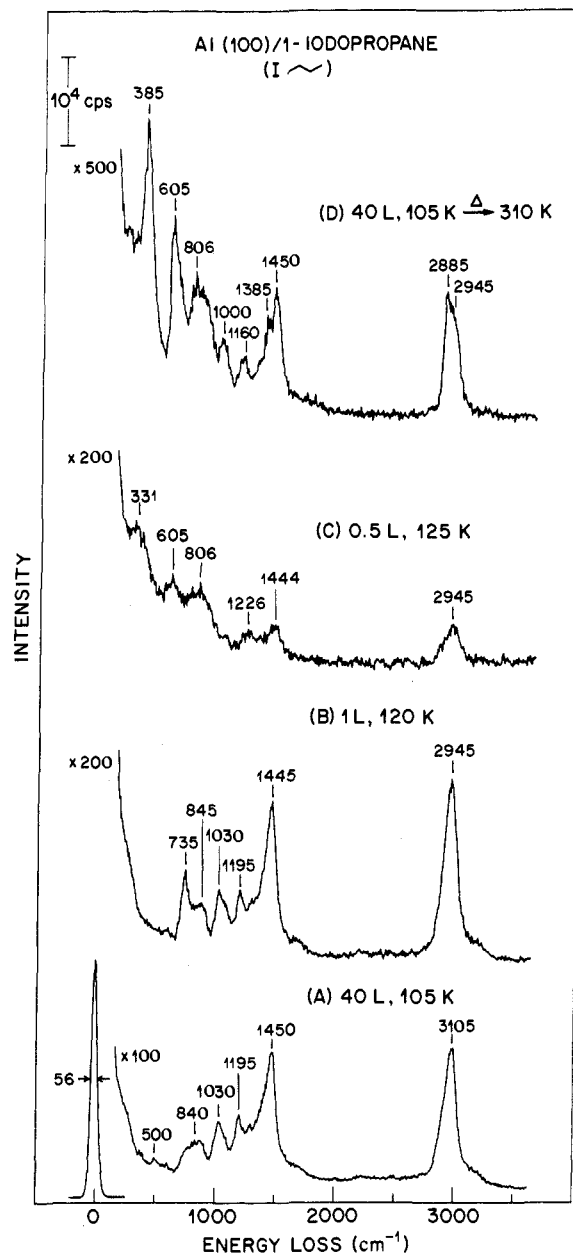
The experimental procedures and apparatus have been described in detail elsewhere;<sup>2</sup> selected aspects will be summarized here. In temperature-programmed desorption (TPD), the alkyl halide was adsorbed onto the aluminum surface at either room temperature or 100 K followed by linearly ramping the crystal temperature at 1–10 K/s while monitoring the intensity of a single desorbing mass. In integrated desorption mass spectrometry (IDMS),<sup>3</sup> entire mass spectra (typically 0–90 amu) were rapidly acquired and summed over the temperature range of a desorption peak determined previously by TPD. As described elsewhere,<sup>3</sup> this technique provides, after background subtraction, an accurate fingerprint of the ionization cracking pattern of the desorbing species. Product identification was made by reference to both published<sup>6</sup> and experimentally determined mass spectral standards.

The alkyl halides used in this work were of >99% purity and were obtained from Aldrich except for 1-iodopropane-2,2-*d*<sub>2</sub> and 1-iodobutane-*d*<sub>9</sub>, which were purchased from Merck. The adsorbate samples (shielded from light) were placed in glass tubes containing high surface area alumina powder and clean, etched copper wire. In most of the experiments reported, a plugged flow column of activated alumina was placed in the line between the liquid sample and the leak valve to remove trace quantities of HI from the dosing gas. Each alkyl halide was thoroughly degassed and checked for purity in situ by mass spectrometry. Gas exposures are given in Langmuirs (L) [1 L = 10<sup>-6</sup> Torr-s] and are uncorrected for differing ion gauge sensitivities.

## 3. Results and Interpretation

**3.1. Carbon–Halogen Bond Cleavage.** The high-resolution electron energy loss (EELS) spectrum in the bottom trace of Figure 1 was obtained from a multilayer (40 L exposure) of propyl iodide condensed on an Al(100) surface at 105 K (molecular desorption temperature ≈ 180 K). Immediately above it are shown two near monolayer spectra (≤1.0 L exposures): the first (B), is a spectrum as dosed at 120 K; the second (C), as dosed at 125 K. The spectrum shown at the top of the figure (D) was taken at 105 K after briefly annealing the adsorbed layer in (A) to 310 K.

Spectra (A) and (B) are quite similar and can be attributed to molecular iodopropane, and the peak frequencies in the 700–1500-cm<sup>-1</sup> fingerprint region of these spectra are compared in Table I with the A' mode frequencies measured by infrared spectroscopy for liquid 1-iodopropane in the trans configuration.<sup>7</sup> While the resolution of EELS does not permit a definitive assignment of these spectra, the peaks observed in the fingerprint region are consistent with those of 1-iodopropane, and the mode at 500 cm<sup>-1</sup> is assigned to the carbon–iodine stretch.<sup>9</sup> On the



**Figure 1.** Specular high-resolution EELS spectra for 1-iodopropane adsorbed on an Al(100) surface: (A) 40 L at 105 K to form a multilayer, (B) 1 L at 120 K, (C) 0.5 L at 125 K, and (D) 40 L adsorbed at 105 K followed by briefly annealing to 310 K to induce carbon–iodine bond breaking. All spectra were recorded at 105 K. Peak assignments are summarized in Table I, and interpretations are given in the text.

basis of the similarity of both the peak positions and intensities in the monolayer and multilayer spectra, we conclude that there are no large distortions in the bonding of the adsorbate at submonolayer coverages when  $T \lesssim 120$  K.

In contrast to the low-temperature spectra, two new peaks (at 385 and 605 cm<sup>-1</sup>) are apparent in the spectra taken on samples which had been warmed above 120 K (C and D). We attribute these peaks to Al–I and Al–C stretching modes, respectively. Similar peaks (380 and 590 cm<sup>-1</sup>) are also observed in the spectrum of 1,3-diiodopropane dosed on Al(100) at room temperature.<sup>10</sup> The appearance of such modes strongly implicates carbon–iodine bond dissociation. Despite this C–I bond scission, the peaks in the 700–1500-cm<sup>-1</sup> region remain similar to those

(6) Heller, S. R.; Milne, G. W. A. *EPA/NIH Mass Spectral Data Base*; Washington, DC, Vol. 1.

(7) The major difference between the trans and gauche conformers is the symmetry of the vibrational modes. Trans was chosen for this comparison because in most cases this will be the lowest energy conformer. Only the A' symmetry modes are compared, since these are the ones expected to have the most significant intensity in the specular EELS spectrum.<sup>9</sup>

(8) Ibach, H.; Mills, D. L. *Electron Energy Loss Spectroscopy and Surface Vibrations*; Academic Press: New York, 1982.

(9) Shimanouchi, T.; Matsuura, H.; Ogawa, Y.; Harada, I. Tables of Molecular Vibrational Frequencies, Part 10. *J. Phys. Chem. Ref. Data* **1980**, *9*, 1149.

(10) Bent, B. E.; Nuzzo, R. G.; Zegarski, B. R.; Dubois, L. H., following paper in this issue.

**Table II.** Thermal Decomposition Chemistry of Alkyl Iodides on Al(100) Summarized

adsorbate	major hydrocarbon desorption product <sup>a</sup>	desorption peak temp <sup>b</sup> (K)
iodoethane	ethylene/ethane	580 → 480 <sup>c</sup>
1-iodopropane	propylene	520
1-iodopropane-2,2- <i>d</i> <sub>2</sub>	propylene- <i>d</i> <sub>1</sub>	540
1-iodobutane	butene <sup>d</sup>	535
1-iodobutane- <i>d</i> <sub>3</sub>	butene- <i>d</i> <sub>3</sub> <sup>d</sup>	545
1-iodohexane	hexene <sup>e</sup>	520–535
1-iodo-2-methylpropane	butene <sup>d</sup>	505 <sup>f</sup>

<sup>a</sup>Products identified by integrated desorption mass spectrometry over a temperature interval of about 150 K symmetric about the thermal desorption peak maximum. Both the mass spectral cracking patterns<sup>6</sup> and ionization cross sections<sup>11</sup> for other potential products are well-known, and their presence can therefore be ruled out. <sup>b</sup>Saturation dose of the indicated alkyl halide; temperature ramp = 7 K/s. <sup>c</sup>Peak shift with increasing coverage. <sup>d</sup>Isomer not readily determined by mass spectrometry. <sup>e</sup>The IDMS spectrum of this compound is shown in ref. 3. <sup>f</sup>On Al(111) this peak shifts to 490 K.

of molecularly adsorbed 1-iodopropane, consistent with the formation of adsorbed propyl groups on the surface (see Table I). The slight differences in the intensities of the room-temperature and low-temperature spectra may be due to changes in the orientation of the propyl moiety, for example, from lying approximately flat for 1-iodopropane to standing upright on the surface after breaking the C–I bond.<sup>8</sup> The important points to note, however, are that the EELS spectra indicate low-temperature C–I bond cleavage and that the resulting vibrational spectrum is consistent with an adsorbed propyl species. This latter point is supported by the thermal desorption experiments discussed below.

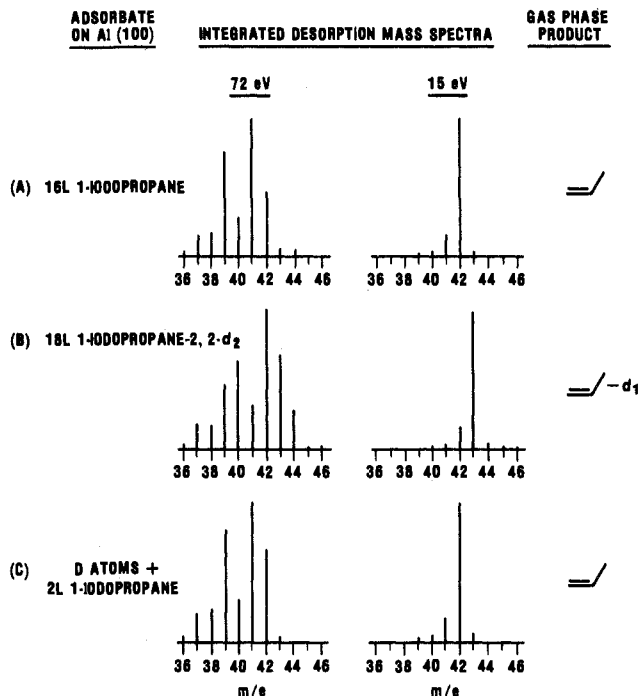
**3.2. Alkyl Decomposition Products and Kinetics.** The decomposition of adsorbed *n*-alkyl iodides proceeds cleanly; Auger electron spectroscopy detected no carbon or iodine on surfaces heated to 700 K. The desorbing hydrocarbon species were identified by mass spectrometry as discussed in the Experimental Section. Examples of IDMS spectra for the thermal decomposition of 1-iodopropane are shown in Figure 2 A. The two partial mass spectra (72- and 15-eV ionizer energies) allow us to identify the desorbing species as propylene. The 15-eV spectrum, which highlights the molecular ion(s), indicates one product with  $m/e = 42$ . The 42:41 ratio of 0.5 in the 72-eV cracking pattern confirms that this product is propylene and not cyclopropane (42:41 = 1.26 at 72 eV).

Table II summarizes the *major* products and the TPD peak temperatures we have found in similar studies of saturation coverages of the indicated alkyl halides. As shown in the table, the decomposition of all the surface alkyl groups studied involves the loss of one hydrogen to evolve an alkene. While the *absolute* amount of each alkene produced is not known, based on tabulated ionization cross sections of hydrocarbons,<sup>11</sup> we conclude that other hydrocarbon products would be detectable at least down to a 5% level. The only other detected desorption product (except in the case of ethyl) is H<sub>2</sub> which desorbs at the same temperature as the alkene (to within experimental uncertainty). Auger electron spectroscopy showed that the iodine atom remains on the surface *throughout the temperature range of the alkyl decomposition* (450–550 K), a result consistent with the earlier findings of Chen et al.<sup>12</sup> The desorption of AlI ( $m/e = 154$ ) was observed at temperatures above ~600 K.<sup>13</sup>

(11) See, for example: Beran, J. A.; Kevan, L. *J. Phys. Chem.* **1969**, *73*, 3866.

(12) Chen, J. G.; Beebe, T. P.; Crowell, J. E.; Yates, J. T., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 1726.

(13) All desorption from Al(111) is observed as a broad peak centered at ~670 K. We cannot rule out the possibility that this feature is due to the cracking of AlI<sub>3</sub> ( $m/e = 408$ , above the range of our mass spectrometer), although we were unable to find an ion corresponding to AlI<sub>2</sub><sup>+</sup> (a result suggesting that AlI may in fact be the primary product). We can also infer from these findings that there are no significant quantities of organoaluminum halides desorbing at lower temperatures; these would crack to give an ion at  $m/e = 154$ .



**Figure 2.** Partial mass spectra (normalized) at 72- and 15-eV electron ionization energies of the propylene which desorbs from an Al(100) surface between 480 and 600 K. The monolayers in (A) and (B) were formed at room temperature, while that in (C) was formed at <150 K. The deuterium atom coverage in (C) corresponds to about half of saturation as determined by thermal desorption. Part of the intensity in the peak at  $m/e = 44$  may be due to a CO<sub>2</sub> background which is always present in our diffusion pumped UHV system. As discussed in the text, these spectra show that the propyl groups are converted to propylene by an irreversible  $\beta$ -hydrogen abstraction. The heating rate was 7 K/s.

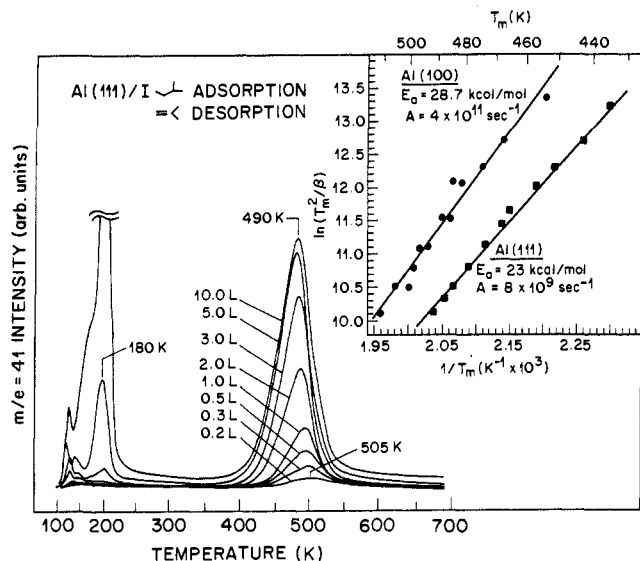
To determine whether the desorption of hydrogen and/or alkene product from the surface is the rate-determining process in the TPD experiments, we adsorbed each separately onto an Al(100) surface. We find that the alkene desorbs intact at about 130 K. Since molecular hydrogen does not adsorb dissociatively on aluminum, experiments in which atomic hydrogen was evaporated from a hot tungsten filament onto Al(100) at 100 K were used to determine that hydrogen recombination and desorption occur at temperatures near 330 K (a result consistent with the literature).<sup>14</sup> On the basis of the facility of both H<sub>2</sub> and olefin desorption, we conclude that product desorption is *not* the rate-determining step in the thermolysis.<sup>15</sup> These results further suggest that any dehydrogenation of the adsorbed alkyl groups at low temperature should produce a hydrogen desorption peak in the 300 K range, a feature which is not observed experimentally.<sup>16</sup> We conclude, therefore, that carbon-iodine bond cleavage at low temperature produces a surface alkyl intermediate which remains intact until alkene is formed and evolved at temperatures  $\geq 450$  K. EELS studies of the thermal stability of these and related surface species<sup>2,10</sup> confirm this interpretation. Thus, for simple *n*-alkyl groups, the alkene thermal desorption spectrum directly reflects the decomposition kinetics of the adsorbed alkyl group.

A rate-determining unimolecular decomposition of the adsorbed alkyls would be expected to show first-order kinetics. This presumption is supported experimentally by the thermal desorption spectra. As a representative example, Figure 3 shows the butene desorption spectra obtained after 1-iodo-2-methylpropane (isobutyl iodide) is adsorbed on an Al(111) surface at <150 K. The

(14) Paul, J. *Phys. Rev. B* **1988**, *37*, 6164.

(15) This point is not necessarily valid for an endothermic process unless the barrier for the reaction of hydrogen with olefin is larger than the barrier for hydrogen desorption. We have examined this point previously and found that hydrogen desorption is not rate-determining.<sup>2</sup>

(16) Although we have found that iodine adsorption perturbs the rate of hydrogen desorption, the effect is not large enough to alter our conclusion.

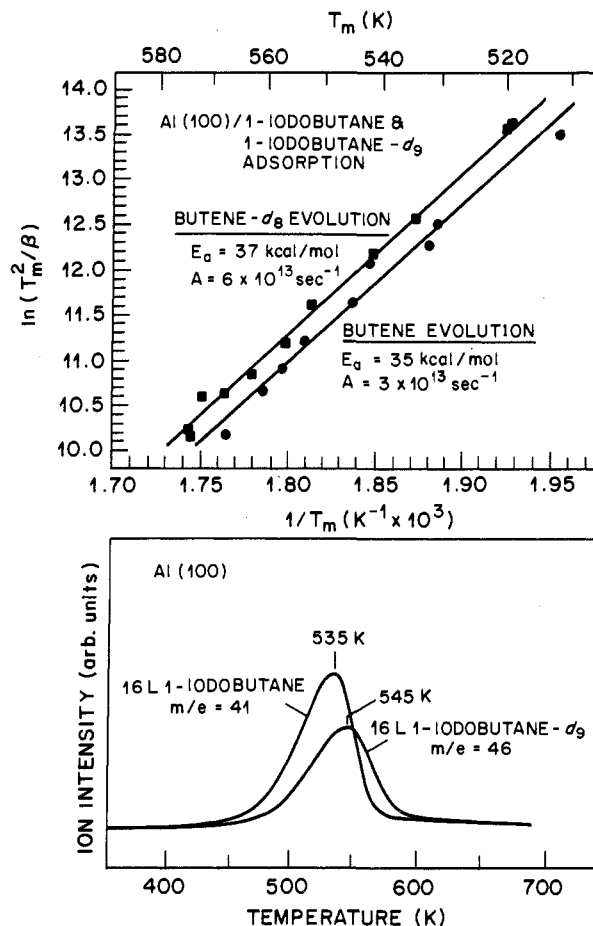


**Figure 3.** Thermal desorption experiments monitoring  $m/e = 41$  as a function of 1-iodo-2-methylpropane (isobutyl iodide) dose on an Al(111) surface. The peak at 490 K is due to butene (presumably isobutene<sup>17</sup>) desorption, while the low-temperature peaks are molecular desorption from a multilayer (the peak at 120 K may be due to the tantalum mounting tabs). The heating rate in these experiments was 7 K/s. The effects of heating rate on the 490 K peak maximum temperature (for saturation coverages on both an Al(111) and an Al(100) surface) are plotted in the upper right.  $T_m$  is the temperature of the peak maximum, while  $\beta$  is the heating rate in K/s.  $\beta$  was varied from 0.35 to 10 K/s in these experiments. The slope of this plot (assuming coverage independence of the kinetic parameters) is the activation energy divided by Boltzmann's constant.<sup>18</sup>

asymmetric peak shape and the approximately constant value of the peak temperature with increasing gas exposure are indicative of first-order desorption kinetics.<sup>18</sup> Assuming that the kinetic parameters are independent of surface coverage, their values can be determined by varying the surface heating rate ( $\beta$ ) and monitoring the peak temperature ( $T_m$ ) shift. An analysis of these results according to the method of Redhead<sup>18</sup> is shown in the inset. The observed linearity of this latter plot confirms that the decomposition reaction obeys a first-order rate law. The slope of this plot is  $E_a/k$ , the activation energy divided by Boltzmann's constant. The measured activation energy is  $\sim 23$  kcal/mol with a preexponential factor,  $A$ , of  $8 \times 10^9$  s<sup>-1</sup>. Similar experiments conducted on an Al(100) surface gave thermal desorption peak temperatures that were uniformly 5–15 K higher in temperature than on Al(111). The kinetic parameters determined on this surface are  $E_a = 28$  kcal/mol and  $A = 4 \times 10^{11}$  s<sup>-1</sup> (see inset). On the basis of a comparison with our previous studies on the decomposition of the isobutyl groups derived from TIBA on both Al(111) and Al(100),<sup>25</sup> it is clear that coadsorbed iodine atoms affect the kinetics of the reaction (while the desorption peak temperatures do not change significantly, both  $E_a$  and  $A$  are lowered in the presence of iodine adatoms); the hydrocarbon products, however, remain unchanged.

### 3.3. Surface Reaction Mechanism and Kinetic Isotope Effects.

On the basis of the precedents established by the reactions of aluminum alkyls in the gas phase<sup>19,20</sup> and solution,<sup>21–23</sup> one would



**Figure 4.** Plot showing the effects of surface heating rate on the temperature of the thermal desorption peak maximum for 1-L doses of 1-iodobutane and 1-iodobutane- $d_9$  on an Al(100) surface. These results show that the isotope effect for  $\beta$ -hydride elimination to evolve butene is small but measurable. The panel at the bottom shows the same trends in TPD spectra taken for saturation (16 L) doses at 300 K.

expect that the conversion of an alkyl group to an olefin involves abstraction of a  $\beta$ -hydrogen atom. To test this hypothesis, we have studied the decomposition of 1-iodopropane-2,2- $d_2$  on Al(100).<sup>24</sup> Figure 2 compares the integrated desorption mass spectra obtained for saturation coverages of 1-iodopropane and 1-iodopropane-2,2- $d_2$ . Also shown is the IDMS data for a layer of D atoms (about half of saturation) coadsorbed with about 20% of a saturation monolayer of 1-iodopropane.

For identifying the molecular weights of a mixture of desorbing species, the 15-eV spectra are most informative. On comparing the 15-eV spectra for 1-iodopropane and the 2,2- $d_2$  isomer, it is evident that they are virtually identical, but shifted by one mass unit. As discussed above, the iodopropane product is propylene.<sup>25</sup> We therefore conclude that the dideuterioiodopropane product is *exclusively* propylene- $d_1$ .<sup>26</sup> This product requires loss of one deuterium from the  $\beta$ -carbon in the starting material and provides conclusive evidence for the involvement of a  $\beta$ -hydride elimination pathway.

(23) Ziegler, K. In *Organoaluminum Compounds*; Zeiss, H., Ed.; ACS Monograph Series 147, Organometallic Chemistry; Reinhold Publishing: New York, 1960.

(24) These results have been reported partially in earlier publications.<sup>2,5</sup>

(25) Mass spectral standards of propylene, cyclopropane, and propadiene were run over a 15–72-eV range of electron impact ionization energies. Propylene and cyclopropane can be distinguished readily by the  $m/e$  42:41 ratios of 0.66 and 1.26, respectively, at 72 eV.

(26) It is not obvious that the 15-eV mass spectrum for propylene- $d_1$  should be exactly the same but shifted by one mass unit from that of propylene. This only holds if the  $m-1$  fragment is due predominantly to hydrogen loss from C<sub>1</sub> or C<sub>2</sub> rather than D loss from C<sub>2</sub>. The data do, however, militate against the concurrent formation of alkane (whose ionization cross section at 15 eV is very similar to olefin<sup>11</sup>).

(17) It is very difficult to distinguish the butene isomers by mass spectrometry. On the basis of the isotope labeling studies for propyl iodide, however, it appears safe to assume that the butene is the product of  $\beta$ -hydride elimination, in this case isobutene.

(18) Redhead, P. A. *Vacuum* **1962**, *12*, 203.

(19) Egger, K. W. *J. Am. Chem. Soc.* **1969**, *91*, 2867.

(20) Egger, K. W. *Int. J. Chem. Kinet.* **1969**, *1*, 459.

(21) Eisch, J. J. Aluminum. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 1, Chapter 6.

(22) Mole, T.; Jeffery, E. A. *Organoaluminum Compounds*; Elsevier: New York, 1972.

The IDMS results in Figure 2C for 1-iodopropane coadsorbed with deuterium atoms provide information about the reversibility of the  $\beta$ -hydride elimination reaction. The 15-eV spectrum shows that virtually all of the desorbing propylene is undeuterated, indicating that exchange is not facile for  $T < 350$  K, the desorption temperature for hydrogen.<sup>16</sup> We conclude from this observation that the  $\beta$ -hydride elimination chemistry for propyl and presumably other simple alkyls on Al(100) is irreversible under ultrahigh vacuum conditions.

Having previously established that the rate of product desorption reflects the rate of the surface  $\beta$ -hydride elimination reaction, we now present results which define the kinetic isotope effect for this C-H (C-D) bond-breaking process on Al(100). Figure 4 shows the heating rate dependence of the butene and butene- $d_3$  desorption kinetics from saturation monolayers of *n*-butyl and *n*-butyl- $d_9$  species, derived from the adsorption of the corresponding iodides. Analysis of the data yields a value of  $A_H/A_D \approx 2$  and a difference in activation energies of  $\sim 2$  kcal/mol. The TPD spectra shown in the bottom panel of Figure 4 are consistent with these results in that the perhydro compound decomposes at a faster rate (as judged by the lower peak temperature) than the perdeuterio compound. A similar conclusion is reached by analyzing TPD data from the decomposition of 1-iodopropane and 1-iodopropane-2,2- $d_2$ .<sup>2</sup> Taken together, our results suggest a value for  $k_H/k_D$  that is in the lower end of the range expected for classical kinetic isotope effects in rate-determining C-H (C-D) bond-breaking processes such as occur in  $\beta$ -hydride elimination reactions.<sup>27</sup>

In general, all the alkyls with  $\beta$ -hydrogens (Table II) behave quite similarly. They decompose to liberate the corresponding alkene in the temperature range of 450–600 K. Ethyl iodide proved to be an exception in that it also produced lesser amounts of ethane over the same temperature range (small peaks at  $m/e = 29, 30$ ; ionization cross section  $\sim 20\%$  more than that of ethylene).<sup>11</sup> Our studies of this compound were limited, however, by its low reactive sticking probability.<sup>28</sup> The low surface coverages obtained lead us to suspect that surface defects may be important in this *specific* case.

#### 4. Discussion

**4.1. Carbon-Halogen Bond Cleavage.** We can use the EELS data presented above to determine the approximate energetics for the dissociation of the C-I bond in propyl iodide. We assume that the molecule is physisorbed on the aluminum surface at 105 K and that the dissociation, as indicated by the appearance of the 385-cm<sup>-1</sup> loss in the EELS spectra of Figure 1C after annealing to 125 K, occurs from this weakly bound state by a process described by a first-order rate law. If we further assume that the preexponential factor for this decomposition is  $1 \times 10^{13} \text{ s}^{-1}$ <sup>18</sup> and that the half-life at 125 K is  $\sim 1$  s (i.e., that the reaction goes to completion during the several seconds required to flash the sample to this temperature), an estimation of the activation energy can be made; this value is  $\sim 7$  kcal/mol. We conclude from this analysis that the cleavage of the carbon-iodine bond on Al(100) is facile and occurs by a low activation energy pathway.

We also have observed that the reactive sticking probabilities ( $S_r$ ) of the alkyl iodides studied here (Table II) span nearly four orders of magnitude, increasing with alkyl chain length as  $S_r(C_1) \leq 10^{-4}$  (in agreement with the findings of Chen et al.<sup>12</sup>)  $< S_r(C_2) \ll S_r(C_3) < S_r(C_4) \approx S_r(C_6) \approx 0.1$ .<sup>28</sup> The reactivity inferred from the kinetic analysis reported above is thus only representative of the longer chain length iodides.

**4.2.  $\beta$ -Hydride Elimination Chemistry.** All the  $\beta$ -hydrogen-containing alkyls we have studied decompose on aluminum surfaces to evolve olefin and hydrogen. The mechanistic features of the surface reactions are summarized for the specific case of

propyl fragments in Figure 5. Our studies of the desorption of propylene and hydrogen from aluminum demonstrate that the rate-determining step on the surface is the  $\beta$ -hydrogen abstraction. This conclusion is further supported by studies of the coadsorption of deuterium with both propylene and iodopropane (Figure 2C), which suggest that all the steps in the decomposition are irreversible under UHV conditions. By contrast, gas-phase, solution, and even surface  $\beta$ -hydride elimination processes at higher pressures are reversible (with olefins rapidly inserting into Al-H bonds<sup>19,20,23</sup>). The lack of reversibility under UHV conditions reflects, we believe, the different conditions under which the reactions are carried out (the alkyl decomposition rate is essentially pressure-independent) rather than a fundamental difference in the available reaction pathways or their energetics.

The asserted correspondence between gas-phase, solution, and surface aluminum alkyl decomposition chemistry is made all the more plausible when one notes that the energetics for these various processes are very similar. For example, the activation energy for the  $\beta$ -elimination of a surface isobutyl group is  $\sim 30$  kcal/mol, while that for the similar  $\beta$ -elimination of 1 equiv of isobutene from triisobutylaluminum in the gas phase is 27.6 kcal/mol.<sup>19</sup> In addition, the  $\beta$ -hydride elimination rate both at aluminum surfaces and in aluminum compounds increases with increasing alkyl substitution at the  $\beta$ -carbon. The magnitude of this effect can be inferred for the surface case from the thermal desorption peak temperatures listed in Table II. The  $\beta$ -hydride elimination rate decreases (the peaks shift to higher temperature) in the order

isobutyl > butyl  $\approx$  hexyl  $\approx$  propyl > ethyl

which is the same sequence observed for similar alkyls in aluminum compounds.<sup>22</sup>

A less direct comparison between surface and solution  $\beta$ -hydride elimination kinetics can also be made with regard to the significantly faster decomposition rate we observed for butyl decomposition on Al(111) versus Al(100). While aluminum compounds do not provide a direct analogue for this metal "surface structure effect", if we *assume* that the major difference between the two aluminum surfaces is electronic in nature, and if we use the work function of the surface as a measure of these electronic properties, then a correlation can be made. It has been reported by others that the work function of the (111) surface is lower than that for the (100).<sup>29</sup> We have noted previously that the difference in the work functions almost exactly matches the difference in  $\beta$ -hydride elimination activation energies.<sup>2</sup> An electronic effect analogous to changing the surface work function can be achieved in aluminum alkyl compounds by substituting halide for one of the alkyls. The chemical effect of such a substitution is to decrease the  $\beta$ -hydride elimination rate<sup>23</sup> analogous to the decrease in rate found for the higher work function Al(100) surface.

As noted above, the activation energies for  $\beta$ -hydride elimination both on the surface (ref 2 and this paper) and in the gas phase<sup>30</sup> fall in the range of 24–37 kcal/mol. These values are actually quite small considering that gas-phase  $\beta$ -hydride elimination reactions are *endothermic* by  $\sim 19$ –26 kcal/mol (see Table III). These enthalpies can partially account for the effects of alkyl structure on the activation energy for the gas-phase  $\beta$ -hydride elimination kinetics, the activation energy tending to be larger for the more endothermic reactions. This thermodynamic/rate correlation is not rigorous (for example, the activation energies for 1-butene formation from *sec*- and *n*-butyl alkyls are inversely related to the  $\Delta H_{rxn}$ ). However, as noted above, the measured gas-phase activation energies do monotonically decrease with increasing alkyl substitution at the  $\beta$ -carbon (i.e., primary vs secondary vs tertiary). This latter rate-structure profile can be rationalized by considering the likely structure of the  $\beta$ -hydride elimination transition state. In particular, for the gas-phase reaction, both the large negative entropy of activation (10–13 kcal/mol K<sup>30</sup>) and the kinetic isotope effect ( $k_H/k_D = 2.5$  at 520

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(28) The variation of  $S_r$  with increasing alkyl chain length will be presented elsewhere. We note that systematic variations in the C-I bond strength contribute only weakly to this effect. Dubois, L. H.; Nuzzo, R. G., to be published.

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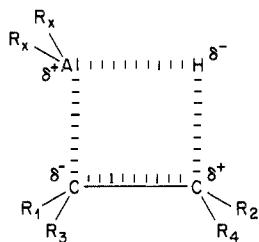
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**Table III.** Thermochemical Data<sup>a</sup> for  $\beta$ -Hydride Elimination by Aliphatic Alkyls Adsorbed on Aluminum

ligand	$\beta$ -carbon <sup>b</sup>	gas-phase $\beta$ -hydride elimination <sup>c</sup>			$\beta$ -hydride elimination on an Al(100) surface: TPD peak temp <sup>g</sup> (K)
		$\Delta H_{rxn}^d$ (kcal/mol)	$\log A^e$ (s <sup>-1</sup> )	$E_a^f$ (kcal/mol)	
ethyl [CH <sub>2</sub> CH <sub>3</sub> ]	1°	25.8		<30, <28	580 <sup>h</sup>
<i>sec</i> -butyl [CH(CH <sub>3</sub> )(CH <sub>2</sub> CH <sub>3</sub> )] <sup>i</sup>	1°	21.6		28.7	
<i>n</i> -butyl [CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	2°	22.6	10.6	27.8	535
<i>sec</i> -butyl [CH(CH <sub>3</sub> )(CH <sub>2</sub> CH <sub>3</sub> )] <sup>j</sup>	2°	19.9		27.5	
<i>i</i> -butyl [CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub> ]	3°	20.5	11.2	26.6	490

<sup>a</sup>Gas-phase data from ref 21, pp 608–609 and citations therein. <sup>b</sup>Type of  $\beta$ -carbon atom from which the hydride elimination occurs: 1° (primary), 2° (secondary), and 3° (tertiary) depending on whether the  $\beta$ -carbon is bonded to one, two, or three carbon atoms, respectively. <sup>c</sup> $\beta$ -hydride elimination of one alkyl from the trialkylaluminum compound in the gas phase to give the dialkylaluminum hydride and olefin. <sup>d</sup>Calculated from heats of formation [ref 21, p 618]. <sup>e</sup>Arrhenius preexponential factor. <sup>f</sup>Activation energy. <sup>g</sup>This work, Table II. <sup>h</sup>Low coverage value. <sup>i</sup>Product olefin is 1-butene. <sup>j</sup>Product olefin is 2-butene.

K<sup>20</sup>) have been used along with transition-state theory and more recent molecular orbital calculations<sup>31</sup> to infer the four-center transition state shown below



The partial charges indicate the expected polarity in the bonds being broken and formed. Studies of olefin insertion/ $\beta$ -hydride elimination in permethylniobocene olefin hydride complexes have implicated an analogous transition state for this early transition-metal system.<sup>32</sup> Our experimental results suggest that a similar four-center transition state *may* also be operative on an Al surface. In particular, the pre-exponential factors ( $10^9$ – $10^{11}$  s<sup>-1</sup>), the structure/rate profiles (Table III), and the kinetic isotope effect (2–3 at  $\sim 500$  K) that we find are in line with those expected for such a four-center transition state.

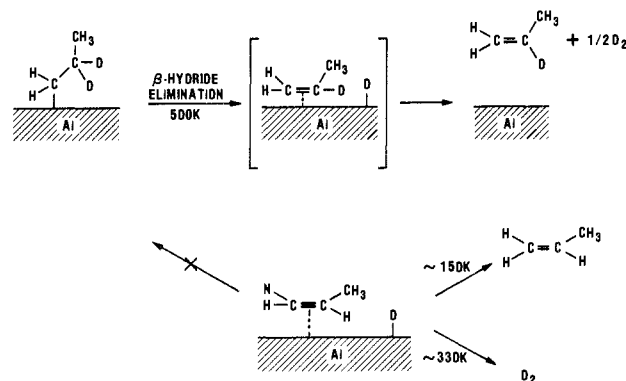
## 5. Conclusions

The results presented above show that alkyl iodides dissociate on the Al(100) surface above  $\sim 125$  K to yield adsorbed alkyl

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## PROPYL CHEMISTRY ON Al (100)



**Figure 5.** Summary of the thermal decomposition chemistry found for propyl species (generated by the adsorption of 1-iodopropane) on Al(100). The irreversible  $\beta$ -hydride elimination chemistry shown is typical for aliphatic alkyls on aluminum surfaces and occurs at a significant (measurable) rate for surface temperatures above 450 K.

groups. The barrier to C–I bond dissociation is small ( $\lesssim 7$  kcal/mol for propyl iodide). The reactive sticking probabilities of a series of *n*-alkyl halides also appear to be very sensitive to the molecular structure of the adsorbate. The thermal decomposition of these adsorbed alkyl fragments proceeds by a  $\beta$ -hydride elimination pathway whose energetics and structure-rate sensitivities closely parallel those exhibited by discrete organoaluminum complexes.