

Thermal Decomposition of Alkyl Halides on Aluminum. 2. The Formation and Thermal Decomposition of Surface Metallacycles Derived from the Dissociative Chemisorption of Dihaloalkanes

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

Abstract: Surface metallacycles are formed on aluminum single-crystal substrates when dihaloalkanes of the general structure $RCHX(CH_2)_nCH_2X$ ($R = Me, H; n = 1, 2; X = Br, I$) are dissociatively adsorbed in ultrahigh vacuum. All members of this class thermally decompose to evolve hydrocarbon products between 450 and 550 K. The energetics of the reaction pathways are similar to those reported in the preceding paper for β -carbon-hydrogen bond activation on Al surfaces. The C_3 metallacycles derived from 1,3-dihaloalkanes yield propylene, while the C_4 species derived from the corresponding 1,4-dihaloalkanes yield predominantly butadiene. The metallacycle derived from 1,3-dibromobutane partitions selectively along the olefin yielding reaction channel. A unified mechanism consistent with isotopic labeling experiments and surface vibrational spectroscopy studies is presented along with a discussion of the nature and structure of the intermediates involved.

1. Introduction

In the preceding paper in this issue,¹ we demonstrated that many simple aliphatic alkyl iodides dissociate on Al(100) and Al(111) single-crystal surfaces at temperatures above 130 K. These reactions generate surface alkyl groups and coadsorbed halogen atoms. The structurally simple materials examined there all decomposed by the familiar β -hydride elimination pathway with energetics similar to those of the mechanistically related decompositions of organoaluminum compounds. The coadsorbed halogen atom does not participate in a direct manner in the decomposition, rather it remains bound to the surface during the alkyl decomposition process and then subsequently desorbs as an inorganic aluminum iodide (AlI or AlI_3).

In the present paper we focus on the formation and thermal chemistries of surface metallacycles derived from the dissociative adsorption of halides of the general structure $RCHX(CH_2)_nCH_2X$, where $R = H$ or CH_3 and $n = 1$ or 2 . The thermal decomposition of these surface metallacycles shows both similarities to and differences from the β -hydride elimination reactions observed for simple alkyls on aluminum. We show that the character of these decompositions, both in terms of products and rates, depends strongly on the carbon chain length of the metallacycle. A simple mechanistic scheme is presented which accounts for the structure-reactivity trends seen.

2. Experimental Section

The materials used (see Table 1) were obtained from Aldrich with the exception of 1,3-dibromopropane- d_6 which was purchased from Merck. The experimental techniques are described in the preceding paper in this issue.¹

3. Results and Interpretation

3.1. C-X Bond Dissociation of Dihaloalkanes. We first consider the reactivity of an aluminum surface toward a series of dihalides of the general structure $I(CH_2)_nI$. Previous studies by others have discussed the reaction of diiodomethane ($n = 1$) with aluminum in ultrahigh vacuum (UHV).² The significant point for our studies is that these authors report C-I bond cleavage on Al films at temperatures of 105-110 K. Studies performed with the next member of this series, 1,2-diiodoethane, are complicated by the lability of this compound toward the elimination of HI. We have studied therefore 1,2-dibromopropane, a 1,2-dihaloalkane of significantly higher thermal stability. At low exposures (≤ 2 L), the evolution of propylene ($m/e = 41$) was observed at ~ 135 K by temperature-programmed desorption (TPD). The identity of

Table I. Thermal Decomposition Chemistry of Alkyl Halides on Al(100) Summarized

adsorbate	major hydrocarbon desorption product ^a	desorption peak temp ^b (K)
1,2-dibromopropane	propylene	135 ^c
1,3-diiodopropane	propylene	510
1,3-dibromopropane	propylene	515
1,3-dibromopropane- d_6	propylene- d_6	525
3-iodo-1-propene + H	propylene	505
3-bromo-1-propene + H	propylene	520
1,4-diiodobutane	1,3-butadiene	490
4-bromo-1-butene	1,3-butadiene	465 ^d
1,3-dibromobutane	butene	465

^a 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 patterns⁸ and ionization cross sections⁹ for other potential products are well-known and their presence, except where indicated in the text, can be ruled out. ^b Saturation dose of the indicated alkyl halide; temperature ramp = 7 K/s. ^c A small amount ($\sim 10\%$ the amount in the 135-K peak) of propylene also desorbs at ~ 240 K. ^d Temperature ramp = 1 K/s; when corrected for this difference in heating rate, the peak shifts to 495 K.

the product was confirmed by integrated desorption mass spectrometry (IDMS).³ Control studies revealed that surfaces dosed directly with propylene give rise to a similar desorption feature. These observations establish two important features of the reactivity of 1,2-dihaloalkanes. First, halogen cleavage is facile and, at low temperature, yields a weakly bound olefin. Second, aluminum surfaces exhibit very high reactivity toward the C-X bonds in dibromoalkanes. This result contrasts with the reactivity of methyl halides⁴ where the bromides are found to be significantly less reactive than the corresponding iodides.

The reaction of either an Al(100) or Al(111) surface with 1,3-diiodopropane yields a surface phase of decidedly different character than that obtained with the lower molecular weight homologs. High-resolution electron energy loss spectroscopy (EELS) studies show that, like the 1,1- and 1,2-dihalides, both

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

(2) Domen, K.; Chuang, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 5288. M6dl. A.; Domen, K.; Chuang, T. J. *Chem. Phys. Lett.* **1989**, *154*, 187.

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

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

[†] Present address: Department of Chemistry, Columbia University, New York, NY 10027.

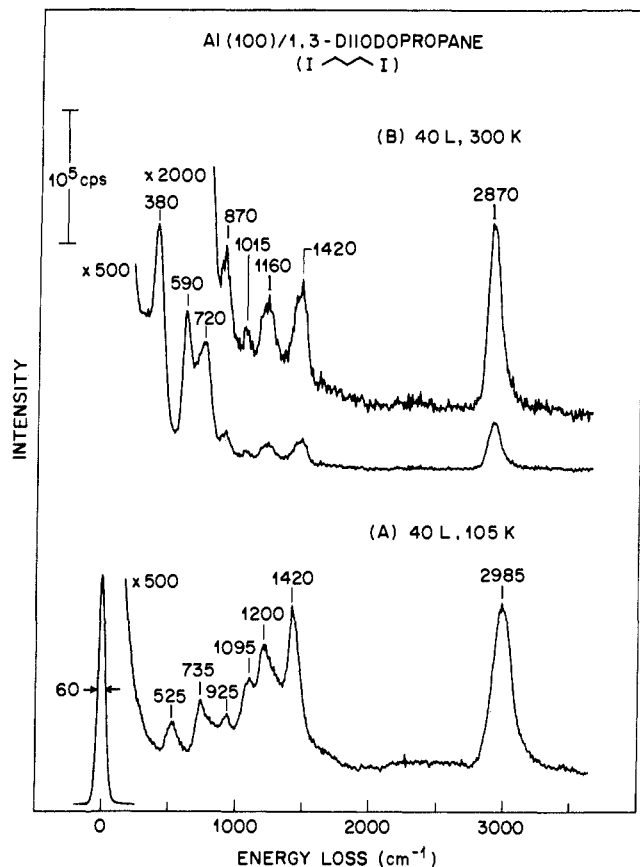


Figure 1. Specular high-resolution electron energy loss surface vibrational spectra for 1,3-diiiodopropane adsorbed on an Al(100) surface: (A) 40 L at 105 K to form a multilayer and (B) 40 L adsorbed at 300 K to form a monolayer of a three-carbon metallacycle species. Peak assignments are summarized in Table II.

Table II. Comparison of the Vibrational Frequencies^a in the Fingerprint Region (700–1500 cm⁻¹) for 1,3-Diiiodopropane in Solution and Adsorbed on an Al(100) surface

40 L/Al(100) 105 K ^b	40 L/Al(100) 300 K ^c	liquid, gauche, gauche conformation ^d
1420	1420	1456
		1418
1300, sh	1280, sh	1275
1200	1160	1195
1095	1015	1101
925		938
	870	
		824
735	720	

^a Frequencies in cm⁻¹; sh = shoulder. ^b Frequencies from Figure 1A, the spectrum for multilayers of 1,3-diiiodopropane on Al(100). ^c Frequencies from Figure 1B. The surface species at this temperature consists of a three-carbon metallacycle and adsorbed iodine atoms. ^d Frequencies from ref 5; only those for modes of A symmetry are given.

C–I bonds cleave on aluminum at temperatures ≤ 300 K; the resulting hydrocarbon species is much more stable, however, remaining intact to temperatures well above 400 K. Representative data obtained on an Al(100) surface are shown in Figure 1. Figure 1A is the spectrum obtained from a multilayer of the adsorbate as dosed at 105 K, while Figure 1B is of the monolayer retained on the surface after warming to 300 K. The significant differences between the two spectra are the disappearance of the 525-cm⁻¹ peak (C–I stretch^b) and the appearance of the 380- and 590-cm⁻¹ peaks (Al–I and Al–C stretches,¹ respectively) in the spectrum taken at room temperature. Inspection of the compilation of frequencies in Table II reveals that the fingerprint region has modes similar to those found in *gauche, gauche*-1,3-diiiodopropane.⁵ These data strongly suggest that the C₃ fragment is

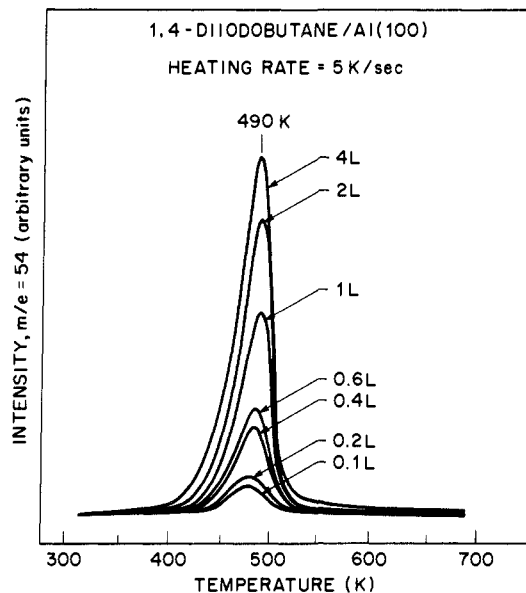


Figure 2. Butene evolution from an Al(100) surface after adsorbing between 0.1 and 4 L of 1,4-diiiodobutane at room temperature and heating the surface at 5 K/s. The asymmetric peak shape and the nearly constant value of the peak temperature are characteristic of first-order desorption.⁷

retained on the surface and is bonded at *both* ends of the carbon chain (i.e., a three-carbon metallacycle is formed). We also know that the hydrocarbon chain is not dehydrogenated on the surface based on the absence of an H₂ recombination peak at 350 K in the thermal desorption spectra.

We conclude this section by noting that higher molecular weight diiodoalkanes are also very reactive toward Al(100). Thus, for example, we find that 2–4-L exposures of 1,4-diiiodobutane or 1,6-diiiodohexane saturate the surface with strongly adsorbed species, presumably iodine atoms and surface metallacycles. Substitution of bromide for iodide in this adsorbate class does not greatly diminish the observed reactivity, and, as inferred from their spectroscopic and thermolytic behaviors, the bromides decompose to form stable surface metallacycles and bromine atoms.

3.2. The Thermal Chemistry of Surface Metallacycles. Heating the monolayer derived from the dissociation of 1,4-diiiodobutane on Al(100) yields the TPD profiles shown in Figure 2. The ion monitored ($m/e = 54$) is one common to most C₄ fragments. The temperature range in which this decomposition occurs is similar to that in which β -hydride elimination reactions are observed.¹⁶ The asymmetric line shapes in Figure 2 as well as the insensitivity of the peak temperature to coverage suggest first-order reaction kinetics.⁷ The IDMS data shown in Figure 3A for a 2-L dose of 1,4-diiiodobutane were acquired by using a 15-eV ionizer energy. These conditions, which accentuate the molecular ions, show that there are two products formed in the decomposition with molecular ions of $m/e = 54$ and 56. The 72-eV IDMS data for a similar exposure of 1,4-diiiodobutane (not shown) identify these products as 1,3-butadiene and a butene (presumably 1-butene), respectively. The intensity ratio of the ions $m/e = 54$ and 39 (0.65) mitigates against 1,2-butadiene and the butynes as a significant source of the $m/e = 54$ peak.⁸ On the basis of experimentally determined and literature ionization cross sections,⁹ we can conclude that the *predominant* hydrocarbon produced is butadiene. There is no evidence that other volatile organic and organometallic species

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

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

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

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

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

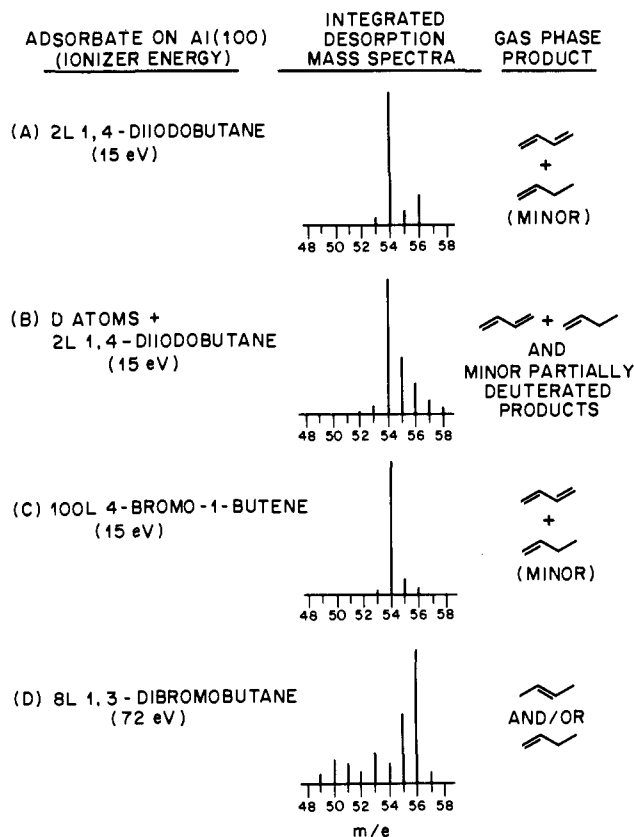


Figure 3. Partial mass spectra at either 72 or 15 eV ionizer energy of the hydrocarbons desorbing from the indicated monolayers on Al(100). All but the monolayer in (B), which was dosed at <150 K, were formed by adsorption at room temperature. Product desorption in these experiments was monitored over about a 150-K temperature range centered around the peak temperatures given in Table 1. The deuterium atom coverage in (B) is about half of saturation as determined by temperature-programmed desorption.

are produced, and Auger electron spectroscopy (AES) studies confirm that the iodine atom remains on the surface to temperatures in excess of 600 K, a finding consistent with the results of studies of other alkyl iodide decomposition reactions on aluminum.^{1,4}

A series of experiments was conducted in which the 1,4-diiodide adsorbate was dosed onto a surface covered with ca. one-half monolayer of deuterium atoms. As shown in Figure 3B, TPD and IDMS indicate that small quantities of deuterium can be exchanged into the hydrocarbon products. The appearance of an ion at $m/e = 55$ in the 15-eV IDMS data establishes that a few percent of the butadiene formed is in fact the d_1 isomer. In an independent control experiment shown in Figure 3C, we determined that the adsorbed species derived from 4-bromo-1-butene also yields butadiene on heating. The mechanistic interpretation of these findings is deferred to the Discussion section.

Figure 4 shows TPD spectra ($m/e = 42$) of the products evolved from an Al(100) surface after exposure to 1,3-diiodopropane. The asymmetric peak shape suggests a first-order desorption process (albeit one exhibiting small coverage dependences of the relevant Arrhenius parameters). Similar kinetic profiles were also obtained from a (100) surface dosed with 1,3-dibromopropane. The IDMS data in Figure 5A shows that the molecular ion of the predominant product (~95% of the hydrocarbons formed) is $m/e = 42$. Ionization energy dependent mass spectral studies by IDMS established that this product is propylene.¹⁰ If cyclopropane is

(10) To differentiate propylene from propadiene and cyclopropane, calibrations were made at ionizer energies between 10 and 70 eV at 5-eV increments. Specifically, the 70-eV IDMS spectrum for 1,3-diiodopropane has a $m/e = 42:41$ ratio of 0.66, quite consistent with propylene (0.70) but not cyclopropane (1.26).

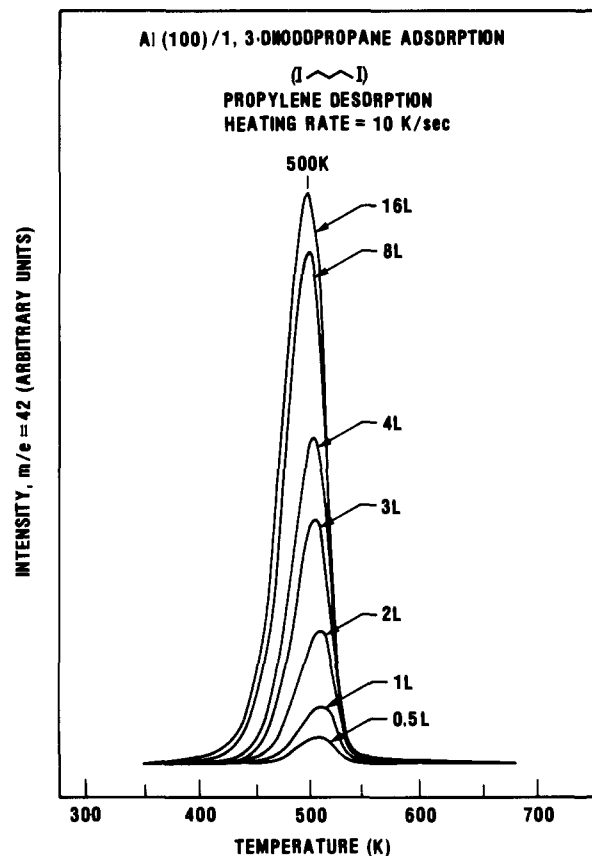


Figure 4. Propylene evolution from an Al(100) surface after adsorbing between 0.5 and 16 L of 1,3-diiodopropane at room temperature and heating the surface at 10 K/s. The peak shape and the temperature for the peak maximum are similar to that shown in Figure 2 for the decomposition of 1,4-diiodobutane.

present in the desorbing molecules, it must be a minor component. The most significant point to note is that although the number of C-H bonds during the surface metallacycle and the product propylene are the same, they have been rearranged during the surface reaction.

Also shown in Figure 5 are IDMS spectra obtained from a sample dosed with a 1:1 mixture of 1,3-dibromopropane and 1,3-dibromopropane- d_6 (see also ref 3). Since the data acquired at 15 eV are dominated by the molecular ions, the ions detected at $m/e = 43-47$ in addition to $m/e = 42$ (C_3H_6) and $m/e = 48$ (C_3D_6) indicate significant cross-exchange of the isotopic label in this system. H-D exchange is also observed when a surface pre-dosed with deuterium atoms ($\theta \approx 0.5\theta_{sat}$) is exposed to 2 L of 1,3-diiodopropane (Figure 5C). In this case, the predominant products are propylene- d_0 , $-d_1$, and $-d_2$. The relative intensities suggest a near statistical incorporation of H and D (from a 1:1 mixture) into the product propylene. These results implicate a potential preequilibrium involving a surface allyl intermediate.

As a test of this hypothesis, allyl iodide and allyl bromide (3-iodo-1-propene and 3-bromo-1-propene) were exposed to an Al(100) surface onto which hydrogen atoms ($\theta \approx 0.5\theta_{sat}$) had been adsorbed. As shown in Figure 5D, the product formed on thermolysis is predominantly propylene; the TPD spectra are virtually identical with those shown in Figure 4 for 1,3-diiodopropane. Substitution of deuterium atoms in the above experiment yields propylene with isotope contents up to d_2 . Since surface deuterium atoms recombine and desorb from aluminum ~100 K below where the propylene is evolved, it appears that surface allyl moieties are readily hydrogenated to form a saturated C_3 metallacycle.

The structure of the allyl intermediate is suggested by the high-resolution EELS data of Figure 6. Figure 6A is the vibrational spectrum of a 3-bromo-1-propene multilayer produced by a 40-L exposure at 105 K, while Figure 6B shows the spectrum obtained after dosing at room temperature. Because of their

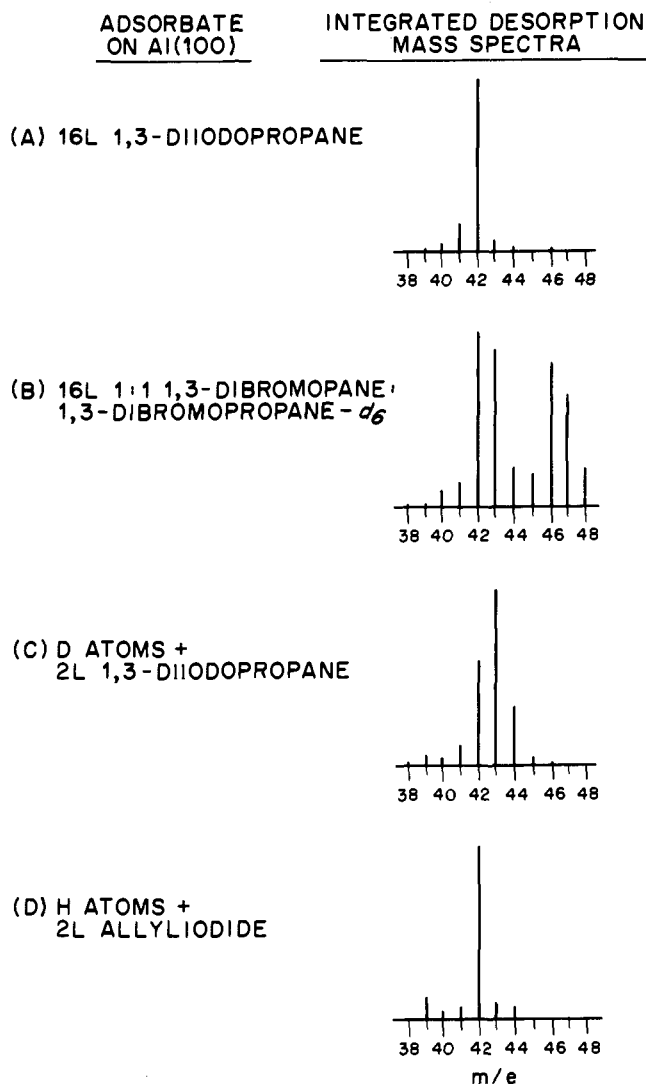


Figure 5. Partial mass spectra at 15 eV ionizer energy of the propylene(s) desorbing from the indicated monolayers on Al(100). The co-adsorbed hydrogen (deuterium) coverage in (C) and (D) was about half of saturation. The adsorption temperature in (A) and (B) was ~ 310 K, while that in (C) and (D) was < 150 K. The heating rate was ~ 7 K/s in all cases.

complexity, these spectra cannot be definitively assigned; it is clear that both spectra are substantially different from those for 1,3-diiiodopropane shown in Figure 1, however. The most important difference is the small peak at 1655 cm^{-1} in the monolayer allyl spectrum. This mode, which is absent in the metallacycle spectra, is outside the region in which C-H bending and stretching frequencies normally occur. We assign this mode to the stretching vibration of a C-C double bond. For comparison, the C-C stretching frequency of ethylene in the gas phase occurs at 1623 cm^{-1} . The presence of this mode in the spectrum shown in Figure 6B is not compatible with a flat-lying, conjugated allyl moiety, since such species do not have vibrational modes in the $1500\text{--}1700\text{ cm}^{-1}$ region.¹¹ The presence of a carbon-carbon double bond is also supported by the broadening of the C-H stretching peak to higher frequency.¹² On the basis of these EELS results, we infer that at least part of the adsorbed allyl groups on Al(100) bond formally as propenyl species, although we cannot determine the specific molecular orientation of this species from the specular EELS data.¹²

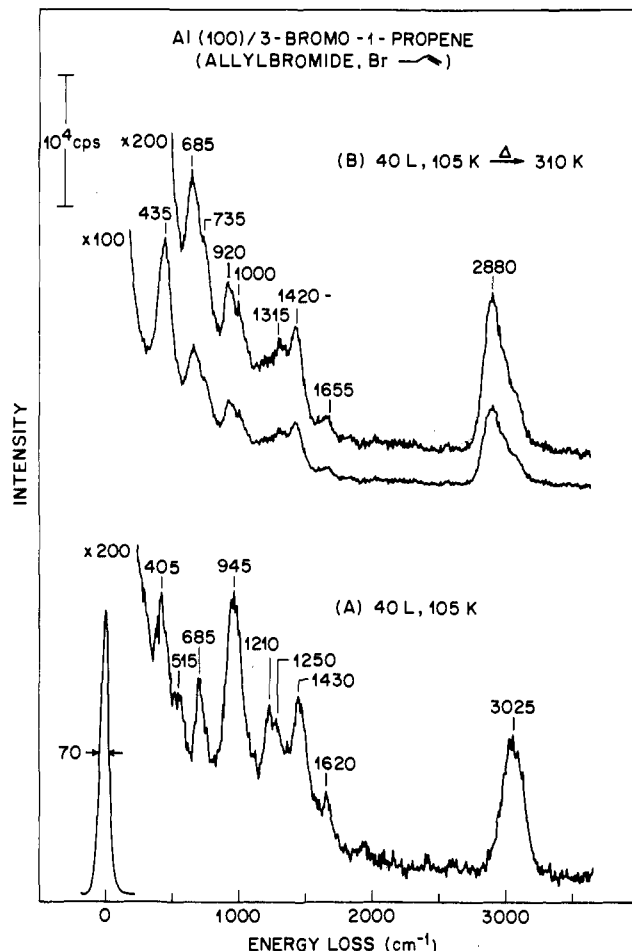


Figure 6. Specular high-resolution electron energy loss spectra of 3-bromo-1-propene (allyl bromide) on an Al(100) surface. The 40-L dose at 105 K in (A) forms multilayers of allyl bromide, while dosing at room temperature gives the monolayer whose spectrum is shown in (B). As discussed in the text, the 1655 cm^{-1} peak in spectrum (B) shows that the resulting propylene species bonds to the surface through one carbon rather than lying flat as a π -allyl species.

The data presented above are summarized in Table I. These results demonstrate that the thermal chemistries of C_3 and C_4 metallacycles on aluminum are quite distinct. The C_4 moiety gives predominantly butadiene as the hydrocarbon product. Since the temperature range in which this occurs is similar to that found for simple β -hydride eliminations, the logical inference is that this process involves sequential β -eliminations at both ends of the metallacycle.¹³ The C_3 chemistry is one which preserves (formally) the oxidation state of the hydrocarbon fragment. The cross-exchange seen suggests, however, that reversible β -eliminations *must* occur and the formation of an allyl intermediate is implied. The TPD data also suggest that the energetics of this process cannot be very different from that of a β -elimination.

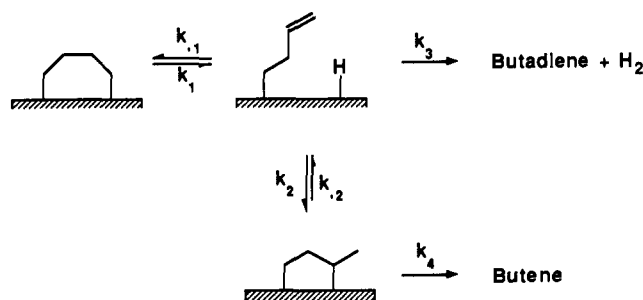
In this regard, studies with 1,3-dibromobutane are of particular interest. The α -methyl-substituted C_3 metallacycle formed when this compound dissociatively adsorbs can either undergo double β -hydride elimination to produce butadiene or transform analogously to the unsubstituted C_3 metallacycle to give butene. The IDMS results in Figure 3D for this compound show that the decomposition product is, in fact, butene (we cannot differentiate between 1- and 2-butene). While these results might appear to conflict with the slower decomposition rate (higher peak temperature) observed for the unsubstituted C_3 vs C_4 metallacycle, one must recall that the β -hydride elimination rate is strongly

(11) Maslowsky, E. *Vibrational Spectra of Organometallic Compounds*; J. Wiley: New York, 1977; p 263.

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

(13) Larger metallacycles (i.e., C_4) also decompose by pathways involving β -eliminations although competitive cyclization reactions complicate the product mixture.

Scheme I



dependent on substituents at the β -carbon, occurring at ~ 50 K higher temperature for unsubstituted vs methyl-substituted β -carbons.¹

4. Discussion

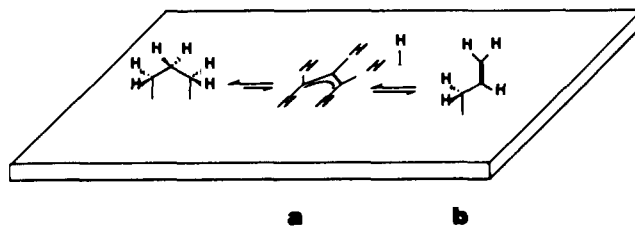
The thermal chemistries described above can be understood in terms of a simple mechanistic picture. For convenience of discussion, we will consider the adsorption chemistries separately from the thermal decomposition processes.

4.1. Carbon-Halogen Bond Cleavage. The data presented above demonstrate that C-X bond cleavage in dihaloalkanes is facile on Al(100) (and Al(111)). It is striking, indeed, that our studies suggest very little kinetic differentiation between the various bromides and iodides studied.¹⁴ There is a natural inclination to view the bond dissociation process as being centrally dependent on the relative bond strengths of the adsorbates. In solution-phase environments, this intuition describes the varying reactivities seen experimentally across a series of halides ($I > Br > Cl$) in, for example, the formation of Grignard reagents.¹⁵ While the homolytic bond strength of the C-I bond is ~ 17 kcal/mol less than that of the C-Br bond,¹⁶ there clearly cannot be a significant expression of this energy difference in the relative transition-state energies for dissociation in UHV. Our belief is that the differing strengths of the Al-X bonds being formed must help compensate for this difference. This implicitly suggests that the mechanisms of C-X bond cleavage which operate in UHV and solution may not be the same.

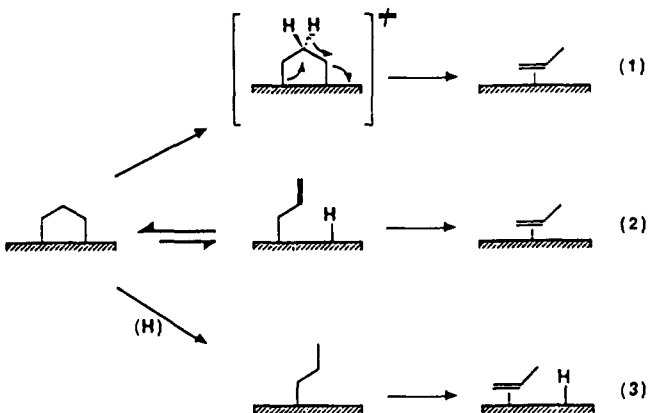
We have also shown that the dissociation of dihalides yields stable surface species on aluminum as long as the methylene chain bearing the halogens is at least three carbon atoms long. EELS data show that the hydrocarbon fragment derived from either 1,3-diiodopropane (Figure 1) or 1,3-dibromopropane is bonded to the substrate at *both* ends of the methylene chain. This offers a striking contrast to the well-known solution-phase reactions of 1,3-dihaloalkanes with active metals where cyclopropanes are efficiently produced at low temperature.^{17,18} Again, the data suggest that a clear mechanistic distinction exists between UHV and solution-phase reactivity patterns for at least this adsorbate.

4.2. Thermal Decomposition of Surface Metallacycles. The thermal decomposition of the C₃ and C₄ metallacycles can be described by a simple mechanistic picture that unites the differing

Scheme II



Scheme III



reactions seen in the two systems. This mechanism is outlined in Scheme I for the specific case of the C₄ metallacycle. We exclude from this picture the halogen atoms coadsorbed with the hydrocarbon based on the kinetic and spectroscopic arguments presented earlier.¹

The intermediacy of a butenyl species as shown is supported by the results of studies conducted with 4-bromo-1-butene, in which it was noted that similar products are evolved at comparable rates to the C₄ metallacycle (the small differences observed are consistent with the lower surface hydrogen coverage in the former case). The preequilibrium denoted by k_1/k_{-1} is implicated by the partially deuterated products formed in studies conducted on a deuterium atom dosed surface (Figure 3B). The partitioning between k_2 and k_3 must favor k_3 given that the product formed is principally diene. We show k_2 as being small compared to k_3 , given that the methylated C₃ metallacycle formed by the decomposition of 1,3-dibromobutane produces predominantly butene. Control experiments involving coadsorbed olefins and hydrogen atoms suggest that k_3 and k_4 are irreversible under UHV conditions, as shown.

On the basis of this simple model, the formation of butadiene from the C₄ metallacycle can be viewed as arising from sequential β -hydride eliminations. Consistent with this interpretation, the energetics for butadiene formation are similar to those found for β -hydride elimination by *n*-alkyls.¹ In the case of the C₄ metallacycle, however, the deuterium coadsorption studies show that the first β -hydride elimination step is reversible, while the latter (the rate-limiting step) is irreversible under our experimental conditions. The butene(s) detected reflect the partitioning of this butenyl intermediate into a secondary reaction channel (k_2).

The rate constant in the scheme denoted as k_4 brings us to a consideration of the mechanisms which operate in the decomposition of a three-carbon metallacycle. The data presented above suggest that k_4 must represent a series of elementary steps. Foremost among these is the isotopic cross-exchange observed in the decomposition of mixed monolayers prepared from 1:1 ratio of 1,3-dibromopropane-*d*₀ and -*d*₆ (Figure 5B and ref 3). As implicated by these results and supported by studies with allyl iodide and allyl bromide, the reversible formation of a surface allyl moiety, as shown in Scheme II, appears likely. There are at least two possible bonding geometries, as shown above, for this type of intermediate. EELS studies of the product formed by the reaction of allyl iodide with Al(100) (Figure 6) suggest that the favored structure for this intermediate is that shown in a. Since

(14) This is in contrast to the reactivities of low molecular weight monohalides which show a strong dependence of the reactive sticking coefficient on the identity of the halogen atom.¹⁸

(15) Rogers, H. R.; Hill, C. L.; Fujiwara, Y.; Rogers, R. J.; Mitchell, H. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 217. Rogers, H. R.; Deutch, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 226. Rogers, H. R.; Rogers, R. J.; Mitchell, H. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 231 and reference cited therein.

(16) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; 3rd ed.; J. Wiley: New York, 1972; p 113.

(17) Coates, G. E.; Wade, K. *Organometallic Compounds. Volume 1: The Main Group Elements*; Methuen: London, 1967; p 324 and references cited therein.

(18) See, selected examples: Lindsell, W. E. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon: New York, 1982; Vol. 1, p 155.

(19) Although concerted rearrangements formally involving six electrons are fairly common in organic reactions (numerous examples can be found: March, J. *Advanced Organic Chemistry*, 3rd ed.; J. Wiley and Sons: New York, 1985, pp 1000-1045), similar precedents in surface-mediated processes under UHV conditions have yet to be demonstrated.

allyl iodide efficiently scavenges H atoms on H-precovered Al surfaces to form propylene at 500 K, a temperature over 100 K above where hydrogen atoms recombine to form H₂ on Al surfaces (Figure 5D), we infer that the equilibrium described above greatly favors the saturated form.

It should be emphasized that this allyl/metallacycle equilibrium does not necessarily lie along the olefin-forming reaction coordinate. Several other pathways can be envisioned as outlined in Scheme III.

Pathway 1 shows a concerted 1,2-hydrogen shift,¹⁹ pathway 2 a β -hydride elimination coupled to a reductive elimination, and pathway 3 reductive elimination followed by β -hydride elimination. This latter mechanism requires hydrogen atoms (from the metallacycle/allyl equilibrium, for example) for initiation, with the overall reaction regenerating hydrogen necessary to perpetuate the chain process. While we cannot determine from our data which pathway is operative, the important observation to note is that each pathway contains either a hydrogen shift or a reductive elimination step, chemistries *not* observed for either the *n*-alkyls or the C₄ metallacycle on aluminum. The fact that the kinetics for C₃ metallacycle decomposition are similar to those for β -hy-

dride elimination suggests that either ring strain in the C₃ metallacycle or π -allyl character in the propenyl intermediate enhance the rate of one of these new processes.

5. Conclusions

Surface metallacycles can be prepared on aluminum in ultrahigh vacuum by the low-temperature dissociative adsorption of suitable dihaloalkanes. Bromo- and iodoalkanes yield similar results, suggesting that the nature of the halogen does not significantly affect the surface reaction chemistry. The C₃ metallacycles derived from 1,3-dihalopropanes or 1,3-dibromobutane yield alkanes at ~500 K, while C₄ species formed by dissociative adsorption of 1,4-dihalobutanes produce predominantly butadiene. The observed rates are very similar for these two mechanistically distinct processes. The predominant formation of butadiene by C₄ metallacycles can be accounted for by sequential β -hydride elimination reactions. With regard to the C₃ metallacycle, the products as well as the results of isotope exchange studies suggest that the thermal decomposition of this species must involve additional surface chemistries, most notably reductive elimination and/or 1,2-hydrogen atom shifts.

Stabilities of Complexes of Br⁻ with Substituted Benzenes (SB) Based on Determinations of the Gas-Phase Equilibria Br⁻ + SB = (BrSB)⁻

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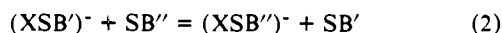
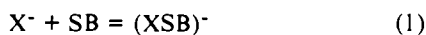
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Abstract: Equilibria involving some forty substituted benzenes (SB) and the bromide ion (SB + Br⁻ = SBBr⁻) in the gas phase were determined with a pulsed electron, high-pressure mass spectrometer (PHPMS). The resulting $-\Delta G_f^\ddagger$ provide information on the stabilities of the SBBr⁻ complexes. Previous work, involving gas-phase thermochemical data for X⁻ (CH₃O⁻, F⁻, Cl⁻, Br⁻, I⁻) and quantum chemical calculations, indicate that the most stable SB·X⁻ complexes might have a variety of structures, depending on X⁻ and the nature of the substituents. Thus X⁻ may engage in hydrogen bonding to an aromatic hydrogen atom, or lead to a σ -bonded (Meisenheimer) complex, or form a complex where X⁻ is on an axis perpendicular to the benzene plane. A Taft substituent analysis of the $\delta\Delta G_f^\ddagger$ indicates that Br⁻ and Cl⁻ form aromatic C-H hydrogen-bonded complexes with all singly substituted benzenes. The field effects of the substituents provide the dominant contribution to the bonding in these complexes. Similar conclusions are reached also for the singly substituted nitrobenzenes and Br⁻. A clearcut analysis of the bonding to Br⁻ when triply substituted benzenes with strongly electron withdrawing substituents like CF₃, CN, and NO₂ are present could not be obtained. In these cases all three bonding structures mentioned above may have similar stabilities.

Introduction

The formation of complexes between X⁻ (CH₃O⁻, F⁻, Cl⁻, Br⁻, and I⁻) and substituted benzenes (SB) is of interest in gas-phase ion chemistry and condensed-phase organic chemistry.

The formation energies of complexes (XSB)⁻ from X⁻ and SB can be obtained by measurement of equilibria 1 and 2 in the gas phase with suitable mass spectrometric apparatus.¹ Many



measurements involving X⁻ and particularly F⁻ and Cl⁻ and a variety of compounds other than substituted benzenes have been reported by this² and other laboratories.^{3,4} In the present work,

we restrict the discussion to substituted benzenes. Furthermore we will exclude substituents which have protic hydrogens such as CO₂H, OH, and NH₂, which engage in strong hydrogen bonding to X⁻. These benzoic acids, phenols, and amines represent a different class of compounds which are considered elsewhere.⁵

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