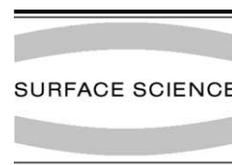




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Probing the reactivity of C₆-hydrocarbons on Au surfaces: cyclohexane, cyclohexyl and cyclohexene on Au(1 1 1)

Denis Syomin, Bruce. E. Koel *

Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482, USA

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Abstract

Au is often added to reduce the activity of Group-VIII transition metals like Ni, Pd and Pt in dehydrogenation catalysts. In order to improve understanding of the fundamental chemistry of hydrocarbons at Au sites, further studies of stable hydrocarbon molecules and reactive intermediates on Au surfaces are needed. The adsorption and thermal chemistry of cyclohexane (C₆H₁₂), cyclohexyl groups (C₆H₁₁) produced by electron-induced dissociation (EID) of cyclohexane, and cyclohexene (C₆H₁₀) on Au(1 1 1) was studied by using primarily temperature programmed desorption (TPD) and Fourier-Transform Infrared Reflection-Absorption spectroscopy (IRAS). Both cyclohexane and cyclohexene are reversibly adsorbed on Au(1 1 1) surfaces, with desorption peak temperatures of 198 and 213 K from the adsorbed monolayer, respectively, and 143 K from both multilayer films. EID with an incident electron energy of 30 eV on a monolayer film of cyclohexane selectively breaks one C–H bond in weakly bound cyclohexane molecules to form adsorbed C₆H₁₁ groups on the Au(1 1 1) surface, as established by TPD and IRAS. The Au(1 1 1) surface can readily and selectively dehydrogenate adsorbed cyclohexyl groups to produce cyclohexene at or below 216 K. Cyclohexyl groups also undergo disproportionation reactions at 273 K to produce cyclohexane and cyclohexene. We suggest that surface Au atoms may play a more important, direct role in the hydrogenation/dehydrogenation selectivity found for transition metal–Au alloys than is commonly discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Gold; Thermal desorption; Infrared absorption spectroscopy; Electron bombardment; Alkanes; Alkenes

1. Introduction

Understanding the fundamental chemistry of stable hydrocarbons and adsorbed intermediates in hydrocarbon reactions on metal surfaces is an important aspect of the surface science of catalysis. Au is often used as a component of bimetallic catalysts containing Group-VIII transition metals

such as Ni, Pd and Pt, for increasing catalytic selectivity [1–9].

The interaction of cyclohexane with metal surfaces has been extensively studied in the past by means of TPD and vibrational spectroscopy, as discussed by Raval and Chesters [10]. Adsorbed cyclohexane is dehydrogenated to benzene on many metal surfaces, e.g., Ru(00 1), Pt(1 1 1), Pd(1 1 0), Pd(1 1 1) [10] and Pt(1 0 0) [11]. On the other hand, on Cu(1 0 0) and (1 1 1) [10], Cu(1 1 0) [12], and Ni(1 1 0) and (1 1 1) [10] surfaces, cyclohexane is reversibly adsorbed and desorbs molecularly.

* Corresponding author. Tel.: +1-213-740-7036; fax: +1-213-740-2701.

E-mail address: koel@chem1.usc.edu (B.E. Koel).

One distinctive feature of the interaction of cyclohexane with metal surfaces is the appearance of “soft” C–H modes in vibrational spectra [10]. The origin of the “soft” mode is not clear, but it has been proposed that electron transfer between the C–H bond and metal surface weakens the C–H bond and shifts the C–H stretching frequency to the red [13]. Overall, the position and intensity of the “soft” mode often depends on the identity of the metal and not much on the crystallographic plane for the same metal. Also, the degree of perturbation in the C–H bond apparently depends on the metal–cyclohexane bond strength. However, Chen et al. [12] recently showed that such a dependence does not exist for Cu and Mo surfaces.

Cyclohexene dehydrogenation and decomposition reactions on metal surfaces have also been extensively investigated in the past. For example, cyclohexene decomposes via C–C bond cleavage on Ru(001) [14] and dehydrogenates primarily to form chemisorbed benzene on Ni(111), (110), and (100) [15,16], Pt(111) [17], and Pd(111) [18].

In this paper, we report on TPD and IRAS investigations of the interaction of cyclohexane, cyclohexene and cyclohexyl groups with Au(111) surfaces. We show that both cyclohexane and cyclohexene reversibly adsorb on Au(111). Cyclohexyl groups, produced via EID of cyclohexane monolayers and multilayers on the Au(111) surface, readily and selectively dehydrogenate to produce cyclohexene at or below 216 K and undergo disproportionation reactions at 273 K to form cyclohexane and cyclohexene.

2. Experimental methods

These experiments were performed in an UHV chamber with a base pressure 6×10^{-10} Torr and equipped for AES, LEED, TPD and FT-IRAS studies. The Au(111) crystal could be resistively heated to 1000 K and cooled to 87 K by direct contact of a copper block on the sample holder with liquid nitrogen. The crystal temperature was measured by a chromel–alumel thermocouple pressed directly into a small hole drilled in the edge of the crystal. The Au(111) surface was cleaned by Ar⁺ ion sputtering (0.5 keV and 1.5 μ A

at $P_{\text{Ar}} = 6 \times 10^{-5}$ Torr) for 12 min with the sample held at 650 K. Sputtering was followed by annealing the sample at 1000 K for 20 min in UHV. After this cleaning procedure, we observed very sharp spots in the LEED pattern which showed the $(\sqrt{3} \times 22)$ reconstruction of the Au(111) surface [19]. No surface carbon was detected by AES.

TPD measurements were made with the sample placed in line-of-sight of the mass spectrometer ionizer at a location of 2 mm in front of a 10-mm diameter entrance aperture to a shield covering the ionizer. A heating rate of 4 K/s was used. Signals at 2, 15, 26, 41, 82, 83, 84, 158, 162, and 166 amu were collected in the TPD experiments, and these signals were used to monitor desorption of H₂, CH₃, C₂H₂, C₃-containing species, C₃H₅, C₆H₁₀, C₆H₁₁, C₆H₁₂, C₁₂H₁₄, C₁₂H₁₈, C₁₂H₂₂ respectively.

Cyclohexane (C₆H₁₂, Aldrich, 99+%) and cyclohexene (C₆H₁₀, Aldrich, 99+%) were degassed by several freeze–pump–thaw cycles before dosing. Exposures were carried out on the Au(111) crystal at 87–90 K through a leak valve connected to a microcapillary-array doser. Exposures reported herein are given in Langmuirs (L) (1 L = 10^{-6} Torr \times s) and are uncorrected for ion gauge sensitivity and doser enhancement factor.

IRAS studies were carried out at a grazing incidence angle of 86° with a Mattson Galaxy[®] 6020 FTIR spectrometer. A narrow-band, liquid-nitrogen cooled, mercury cadmium telluride (MCT) detector was used. IRAS spectra were taken typically with the sample temperature at 87–90 K, spectrometer resolution set to 4 cm⁻¹, and averaging 2000 scans over 8 min. All IRAS spectra reported were ratioed against the clean Au(111) surface.

EID experiments were performed by using a variable-energy electron gun (5–1000 eV, Kimball Physics, Model FRA 2 \times 12). The incident beam current was measured with the sample biased by +50 V to capture secondary and scattered electrons.

Adsorbate coverages are reported herein with respect to saturation of the chemisorbed monolayer ($\theta = 1$ ML) of the corresponding molecule as determined in TPD experiments.

3. Results

3.1. Cyclohexane (C_6H_{12}) and cyclohexene (C_6H_{10}) adsorption

TPD spectra following cyclohexane and cyclohexene exposures on Au(111) at 90 K are shown in Figs. 1 and 2, respectively. Both cyclohexane and cyclohexene were reversibly adsorbed; only molecular desorption of the adsorbed species occurred. Cyclohexane desorption peaks at 198 and 143 K are assigned to the monolayer and multilayer, respectively. Cyclohexene desorption peaks at 213 and 143 K are similarly assigned to desorption from the monolayer and multilayer, respectively.

Using Redhead analysis, and assuming first-order desorption kinetics with a preexponential factor of 10^{13} s^{-1} , the desorption activation energy E_d for cyclohexane and cyclohexene from the monolayer was estimated to be 12 and 13 kcal/mol, respectively. Arrhenius plots of the desorption traces gave $E_d = 10 \text{ kcal/mol}$ for both cyclohexane and cyclohexene multilayers. Because there is no appreciable barrier expected for adsorption of

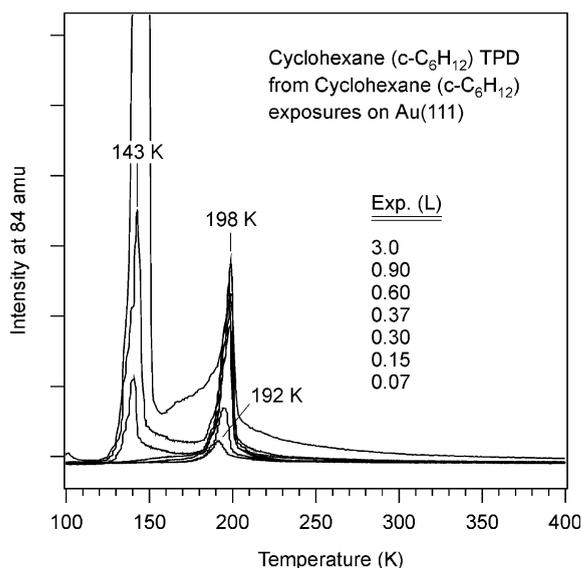


Fig. 1. Cyclohexane TPD spectra after $c\text{-C}_6\text{H}_{12}$ exposures on Au(111) at 90 K.

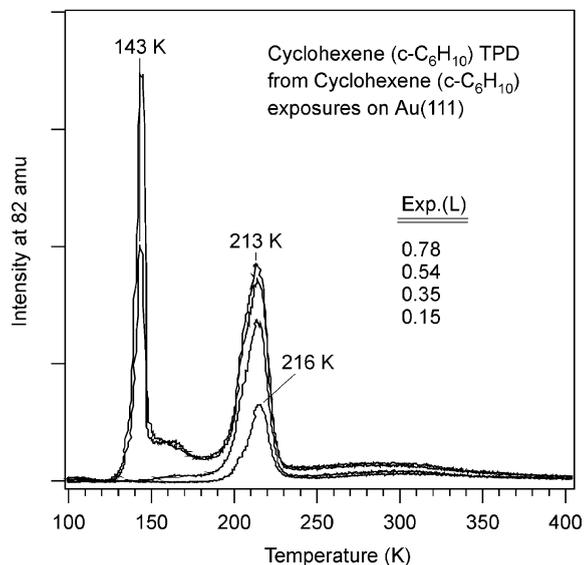


Fig. 2. Cyclohexene TPD spectra after $c\text{-C}_6\text{H}_{10}$ exposures on Au(111) at 90 K.

either of these molecules, these values for E_d are good estimates of the respective adsorption energies on Au(111).

3.2. Preparation of adsorbed cyclohexyl species

Electron bombardment at 30 eV incident energy of the cyclohexane monolayer and three-layer film can greatly reduce C_6H_{12} desorption from the chemisorbed monolayer, as shown in Figs. 3 and 4. For an initial cyclohexane coverage of 1 ML, electron exposure caused a new desorption state of cyclohexane at 273 K. Also, new desorption peaks at 216 and 273 K were detected at 82 amu, as shown in Fig. 5. For an initial, 3-ML C_6H_{12} film, electron bombardment created new 82-amu desorption peaks at 215, 277 and 324 K, as shown in Fig. 6. We assigned these 82-amu signals to cyclohexene desorption. No bicyclohexyl ($C_6H_{11}\text{-}C_6H_{11}$) desorption was detected at 166 amu. These TPD results show that the elimination of the unmodified cyclohexane desorption from the chemisorbed layer and the formation of new product states is quite efficient for EID of monolayer and multilayer initial coverages of cyclohexane.

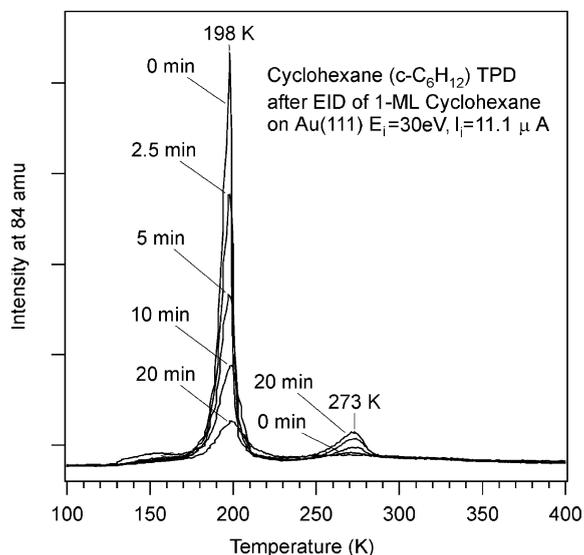


Fig. 3. Cyclohexane TPD spectra after a $c\text{-C}_6\text{H}_{12}$ coverage of 1 ML on Au(111) 90 K was bombarded by electrons.

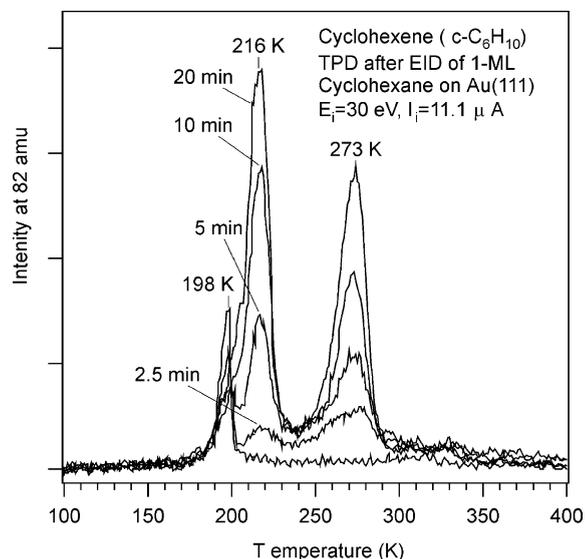


Fig. 5. Cyclohexane TPD spectra after a $c\text{-C}_6\text{H}_{12}$ coverage of 1 ML on Au(111) 90 K was bombarded by electrons.

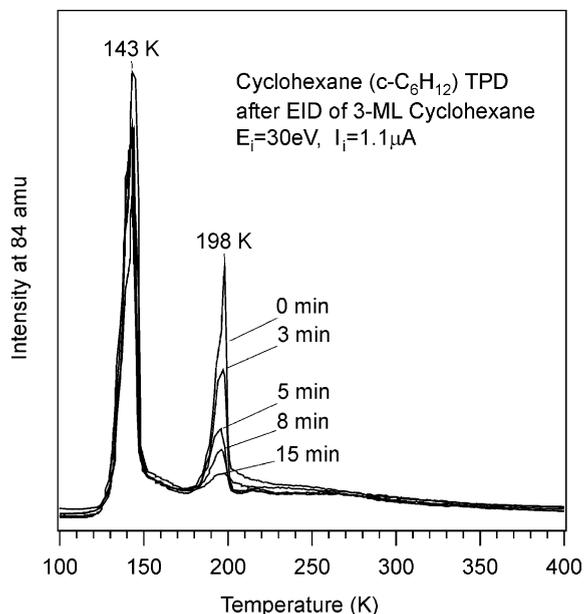


Fig. 4. Cyclohexane TPD spectra after a $c\text{-C}_6\text{H}_{12}$ coverage of 3 ML on Au(111) 90 K was bombarded by electrons.

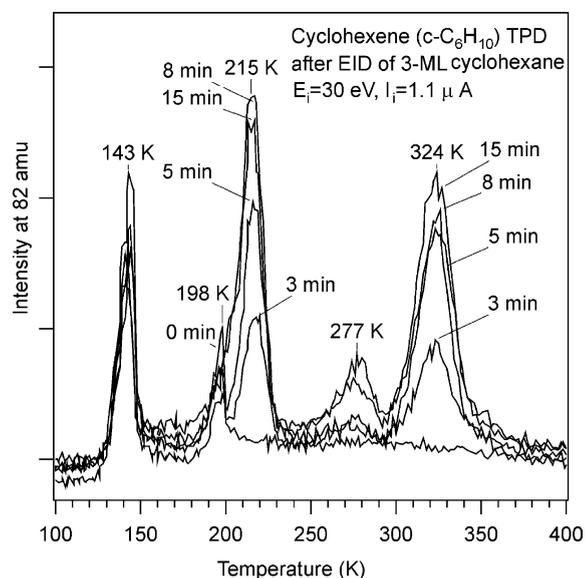


Fig. 6. Cyclohexane TPD spectra after a $c\text{-C}_6\text{H}_{12}$ coverage of 3 ML on Au(111) 90 K was bombarded by electrons.

Fig. 7 compares the effect of electron induced chemistry on the monolayer and the multilayer cyclohexane films as the duration of electron beam

exposure is increased for both initial coverages. After 20 min of electron exposure to the monolayer covered surface, the amount of C_6H_{12} desorbing at 198 K decreased by 0.8-ML, and

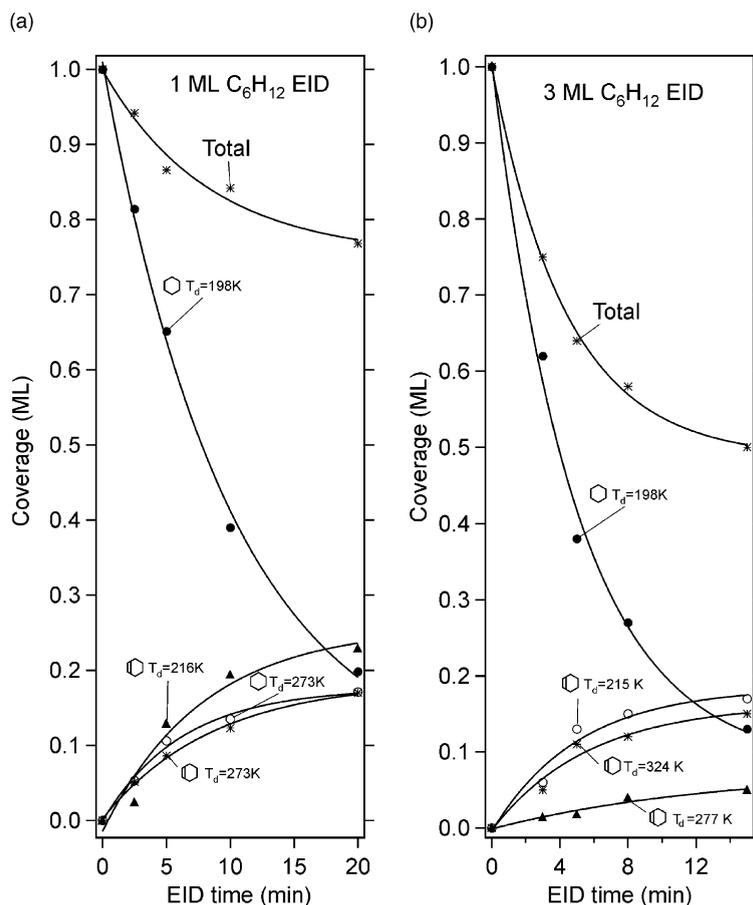


Fig. 7. (a) Amount of cyclohexane and cyclohexene evolution from the surface (in ML) after a $c\text{-C}_6\text{H}_{12}$ coverage of 1 ML on Au(111) at 90 K was bombarded by electrons and (b) amount of cyclohexane and cyclohexene evolution from the surface (in ML) after a $c\text{-C}_6\text{H}_{12}$ coverage of 3 ML on Au(111) at 90 K was bombarded by electrons.

0.17-ML of C_6H_{12} and C_6H_{10} desorbed from the surface at 273 K, and 0.23-ML C_6H_{10} desorbed at 216 K, as shown in Fig. 7(a). We assign C_6H_{12} desorption at 273 K and all C_6H_{10} desorption to be the result of conversion (dehydrogenation or disproportionation) reactions of adsorbed cyclohexyl groups. The simultaneous appearance of both cyclohexane and cyclohexene at 273 K is presumed to result from the disproportionation of two cyclohexyl groups as will be discussed in Section 4. This leads to an estimate of the minimum coverage of cyclohexyl groups adsorbed on the surface as 0.57 ML after 20-min EID on the 1-ML film using $11.1 \mu\text{A}$. This is a lower limit because some low temperature cyclohexyl hydrogenation to reform

cyclohexane can occur during TPD. It is also apparent from this figure that about 20% of cyclohexane monolayer is unaccounted for and we presume that it desorbed during electron bombardment in EID via electron stimulated desorption (ESD).

Similar electron induced chemistry occurs on the multilayer covered surface, Fig. 7(b). After 15 min of electron bombardment $1.1 \mu\text{A}$ of the 3-ML film, the total amount of C_6H_{12} desorbed from the chemisorbed monolayer state decreased by 0.87 ML. About 0.17-ML C_6H_{10} desorbed at 215 K, 0.05-ML C_6H_{10} desorbed at 277 K and 0.15-ML C_6H_{10} desorbed at 324 K. Assuming that all C_6H_{10} desorption to be the result of conversion reactions

of adsorbed cyclohexyl groups and that cyclohexene desorption at 277 K is due to disproportionation reactions and the same amount of cyclohexane desorbed from the surface at 277 K undetected due to its very low intensity in TPD spectra we estimate the coverage of cyclohexyl groups adsorbed on the surface after 15-min EID of the 3 ML film as 0.42 ML. This is clearly a lower limit for the coverage of adsorbed cyclohexyl groups because the observed mass 82 species at 324 K may be a cracking fraction of a larger species such as bi-2-cyclohexen-1-yl ($C_6H_9-C_6H_9$) formed by the surface reaction of adsorbed cyclohexyl groups. In this case we would underestimate the coverage of adsorbed cyclohexyl groups.

EID of cyclohexane may be described by a first order kinetic model according to the expression:

$$\ln \left(\frac{I(t)}{I(0)} \right) = - \left(\frac{i \times t}{e \times A} \right) \times \sigma = -F \times \sigma \quad (1)$$

where $I(0)$ and $I(t)$ are the C_6H_{12} TPD area in C_6H_{12} monolayer peak before and after EID, i is the sample current (A), t is the electron bombardment time (sec), e is the electron charge (C), A is the sample area (cm^2) and σ is the total EID cross-section (cm^2). The value of σ was calculated from the slope of a semi-logarithmic plot of the decrease in the relative amount of C_6H_{12} desorption in the peak at 198 K versus the electron bombardment time, as shown in Fig. 8. Values of σ were $3.0 \times 10^{-16} cm^2$ for an initial cyclohexane coverage $\theta^{init} = 3 ML$ and $1.5 \times 10^{-17} cm^2$ for $\theta^{init} = 1 ML$. These values could be too high if ESD plays an important role, but more likely, these values are lower limits because of possible hydrogenation of cyclohexyl to reform cyclohexane during TPD. Bond breaking process other than simple C–H cleavage that occurs from EID are included in these values because recombination processes to give cyclohexane would be expected to have activation energies that are significantly higher than E_d for cyclohexane desorption.

Fig. 9 gives the energy dependence of the EID cross-section $\sigma(E)$ for $\theta^{init} = 1 ML$. In these experiments the electron flux changed unavoidably from 3.2×10^{13} electrons/ $cm^2 s$ for $E_i = 5 eV$ to 7.2×10^{13} electrons/ $cm^2 s$ for $E_i = 50 eV$. Cyclo-

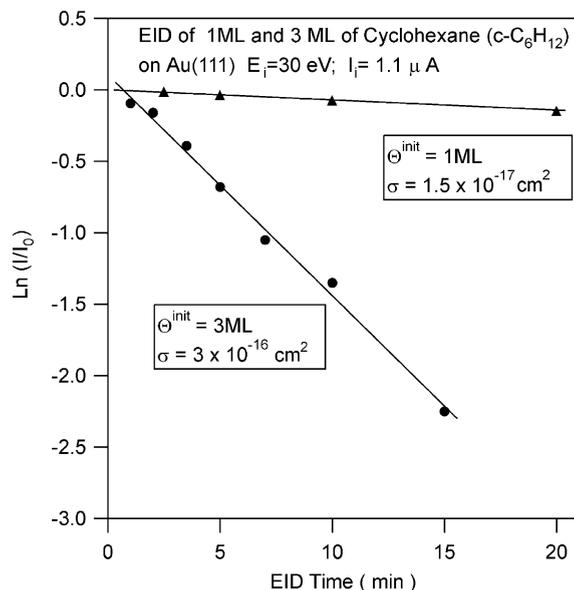


Fig. 8. Semi-logarithmic plot used for determining the EID reaction cross-section for cyclohexane films on Au(111). The molecular cyclohexane desorption in TPD was used to monitor the reaction progress. (1 ML plot was normalized to sample current $I_i = 1.1 \mu A$).

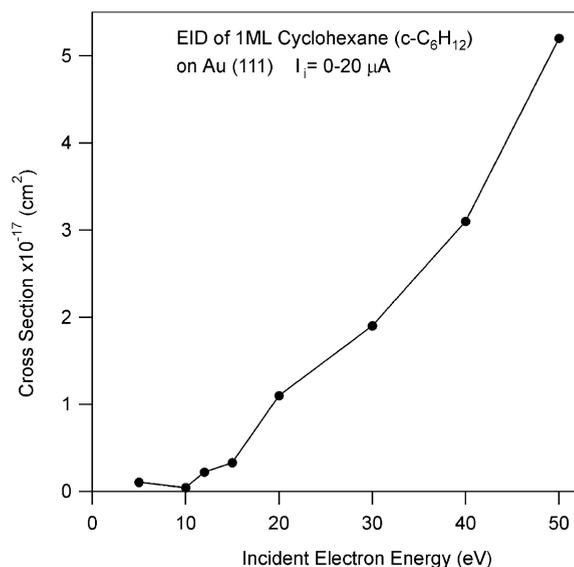


Fig. 9. Influence of the incident electron energy on the EID cross-section in 1-ML cyclohexane films on Au(111).

hexane EID reactions have an onset energy of about 11 eV.

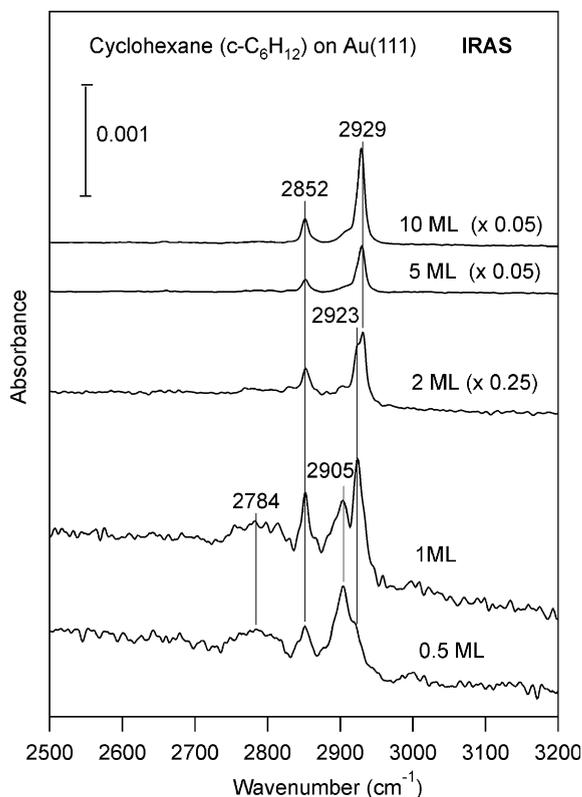


Fig. 10. IRAS spectra of cyclohexane adlayers on Au(1 1 1) at 90 K.

3.3. IRAS

IRAS was utilized to spectroscopically characterize the adsorbed layers. Fig. 10 provides vibrational spectra taken at several different cyclohexane coverages on Au(1 1 1) at 90 K. Vibrational assignments for these spectra are given in Table 1, and these were made based on vibrational

assignments of the IR spectrum of liquid-phase $c\text{-C}_6\text{H}_{12}$ [20] and $c\text{-C}_6\text{H}_{12}$ adsorbed on Cu(1 1 1) [13]. Spectra obtained for films about 5 and 10-layers thick exhibited two bands in the C–H stretching region at 2852 and 2929 cm^{-1} . These correspond to the C–H symmetric $\nu_s(\text{C-H})$ and C–H asymmetric stretching mode $\nu_{as}(\text{C-H})$, respectively. At lower coverages, in the monolayer and submonolayer regime, four bands are observed in the C–H stretching region. The new, broad band centered near 2784 cm^{-1} corresponds to the “soft” C–H mode observed in the IR spectra of cyclohexane adsorbed on many metal surfaces [10–12]. The band at 2852 cm^{-1} can be assigned to a $\nu_s(\text{C-H})$ mode and bands at 2905 and 2923 cm^{-1} can be assigned to $\nu_{as}(\text{C-H})$ modes.

Fig. 11 shows IRAS spectra of cyclohexene adsorbed on Au(1 1 1) at 90 K. In its own right, it is useful to spectroscopically characterize cyclohexene adsorption on Au(1 1 1), but these spectra primarily provide a necessary reference required for evaluating deeper dehydrogenation that may occur during EID of cyclohexane. The vibrational assignments for these spectra are given in Table 2 and were made based on previous assignments for liquid-phase cyclohexene [21] and cyclohexene adsorbed on Pt(1 1 1) [11]. For a 4-ML film, the spectra exhibited four identifiable peaks in the $\nu(\text{C-H})$ region. The band at 3022 cm^{-1} arises from C–H stretching $\nu(\text{CH})$ of the olefinic hydrogens and three bands at 2925, 2860 and 2839 cm^{-1} were assigned to $\nu(\text{C-H})$ modes of aliphatic CH_2 groups. Obviously there is significant additional intensity near 2875 and 2935 in several additional unresolved bands. At coverages of one monolayer and below, the band at 3022 cm^{-1} is not observed because of the surface selection rule and the most

Table 1
Vibrational frequencies (cm^{-1}) in the C–H stretching region of cyclohexane

Mode	Liquid [20]	Au(1 1 1) (this work)			Cu(1 1 1) [13]		
		1/2 ML	1 ML	10 ML	1/3 ML	1 ML	4/3 ML
$\nu_{(a)}(\text{C-H})$	2937					2935	2932
						2925	2926
		2923	2923			2920	–
		2905	2905			2900	2907
$\nu_{(s)}(\text{C-H})$	2852	2852	2852	2852	2848	2851	2853
						2851	
		2784	2784		2770	2776	2770

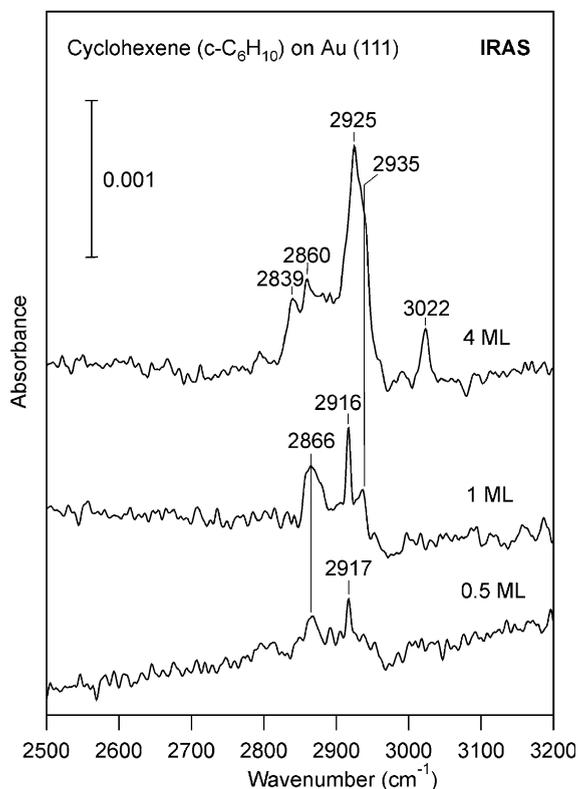


Fig. 11. IRAS spectra of cyclohexene adlayers on Au(111) at 90 K.

intense absorption is the narrow line at 2916 cm^{-1} due to $\nu(\text{C-H})$ modes of aliphatic CH_2 groups. Other bands corresponding to the aliphatic CH_2 -groups appear at 2866 and 2935 cm^{-1} .

IRAS spectra of the cyclohexane-EID products taken for initial cyclohexane coverage θ^{init} of 1 ML are shown in Fig. 12. Electron bombardment strongly reduces the cyclohexane “soft” mode

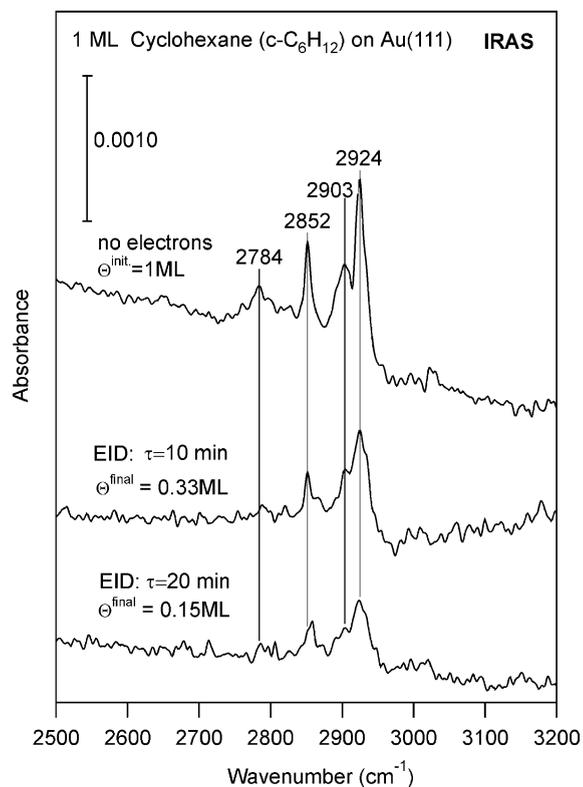


Fig. 12. IRAS spectra after 1 ML of cyclohexane was exposed to 30 eV electrons.

centered at 2784 cm^{-1} and decreases the overall adsorption intensity in both spectra in Fig. 12. Following EID, both spectra closely resemble that of a low coverage of cyclohexane in the absence of electrons. These spectra exhibit three bands due to $\nu_s(\text{C-H})$ at 2852 cm^{-1} and $\nu_{\text{as}}(\text{C-H})$ at 2903 and 2924 cm^{-1} and one band at 2933 cm^{-1} present as a shoulder. Fig. 13 shows results from similar ex-

Table 2
Vibrational frequencies (cm^{-1}) in the C–H stretching region of cyclohexene

Mode	Liquid [21]	Au(111) (this work)			Pt{100}-(1 × 1) [11]
		0.5 ML	1 ML	4 ML	4 ML
Olefinic $\nu(\text{C-H})$	3026	–	–	3022	
Aliphatic $\nu(\text{C-H})$	2940		2935	2935	2928
	2929	2917	2916	2925	2903
	2860	2866	2866	2860	2863
	2840			2839	2768

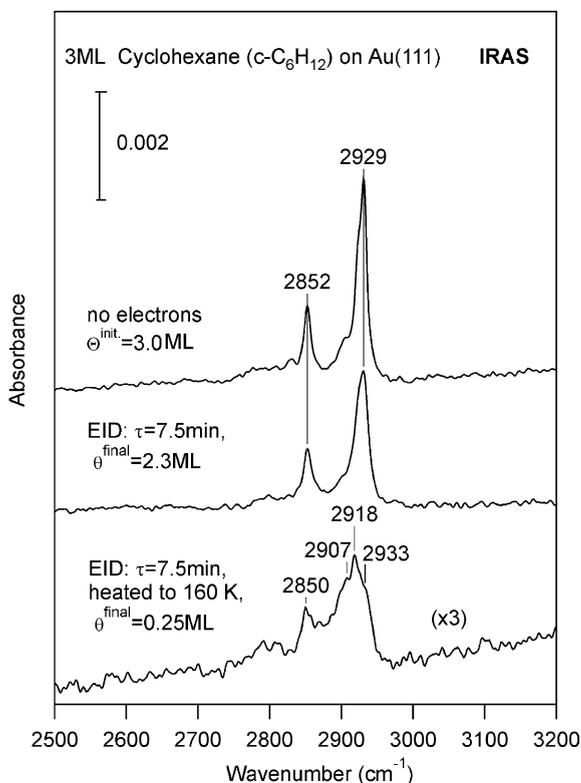


Fig. 13. IRAS spectra after 3 ML of cyclohexane was exposed to 30 eV electrons.

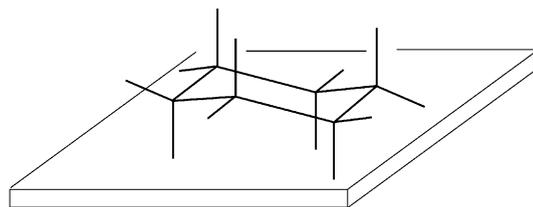
periments in which IR spectra were taken before and after cyclohexane EID at $\theta^{\text{init}} = 3$ ML. Electron bombardment leads to a decrease in the absorption intensity because of cyclohexane desorption via ESD, but physisorbed cyclohexane is still present and obscures the absorption bands of chemisorbed species in the monolayer. An IR spectrum of the 3-ML EID products was taken after annealing the sample to 160 K, which desorbs any remaining cyclohexane from the multilayer film, but we point out that this could also drive some thermal chemistry of the EID products including dehydrogenation of cyclohexyl groups and cyclohexene formation. IR spectra obtained after electron bombardment and annealing of the 3-ML C_6H_{12} film also differ from the cyclohexane spectra. A new band at 2918 cm^{-1} appears in the spectra, and the band at 2933 cm^{-1} present as a shoulder.

4. Discussion

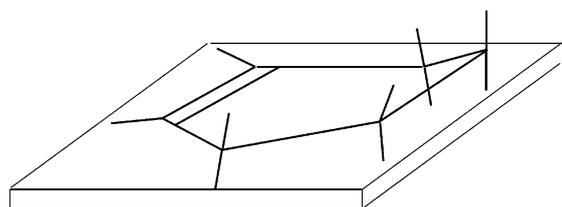
Cyclohexane interacts weakly with Au surfaces, forming a reversibly adsorbed, physisorbed monolayer on Au(1 1 1). It was somewhat surprising that the peak temperature for cyclohexane desorption from the monolayer on Au(1 1 1) occurred at a higher temperature (198 K) than on Cu(1 1 1) (178 K) [12]. One explanation could be that there is a difference in the molecular orientation on the two surfaces at monolayer coverage, as discussed below. Also, despite the higher desorption temperature (larger adsorption energy) on Au(1 1 1), the C–H “soft” modes are shifted less and have lower relative intensity than on Cu(1 1 1). Consequently, cyclohexane adsorption on Au(1 1 1) is another example of the lack of a simple correlation between the position of the “soft modes” and desorption temperature or adsorption energy.

The orientation of adsorbed cyclohexane changes with coverage for adsorption on Cu(1 1 1). At submonolayer coverages, the molecular “plane” is relatively parallel to the surface with 3 axial hydrogens pointed directly into the surface, as shown in Scheme 1.

The molecular plane is more “tilted” with respect to the surface normal at 1-ML coverage [13]. At a coverage of $\sim 1/2$ ML, these two orientations coexist on the surface. This orientational phase transition is characterized by the disappearance of the band at 2905 cm^{-1} and appearance of new strong bands at 2920 and 2925 cm^{-1} . On Au(1 1 1), it is likely that these two phases coexist at 1 ML coverage, because bands at 2905 and 2923 cm^{-1} are both present in the 1-ML spectrum. The position of the $\nu_s(\text{CH})$ mode at 2852 cm^{-1} does not shift with coverage and this behavior is consistent



Scheme 1.



Scheme 2.

with that seen in IR spectra of cyclohexane on Cu(111) [13].

IR spectra for cyclohexene multilayers show bands of the olefinic C–H group stretching mode, but these are absent in the C_6H_{10} spectra at coverages of 1 ML or below. This is similar to that observed on Pt(111) [11]. This arises because of a preferential chemisorption geometry in the monolayer that forces the C=C double bond to be parallel with the metal surface, as shown in Scheme 2.

We now discuss the TPD results obtained by using of EID to “activate” cyclohexane molecules in order to probe the thermal chemistry and reactivity of hydrocarbons on the Au(111) surface, and also discuss the spectroscopic evidence from IRAS that EID cleanly forms cyclohexyl groups on this surface at 90 K.

First, we consider the IRAS spectra, specifically the $\nu(C-H)$ region as shown in Fig. 12 and 13. Fig. 14 replots some of this data to make a direct comparison of the IR spectra of cyclohexane, cyclohexene and cyclohexane EID products. This comparison provides strong evidence supporting the production of cyclohexyl groups by EID. A $\nu(C-H)$ region of the IR spectra of 1-ML cyclohexane EID products closely resembles the IR spectra of adsorbed cyclohexane, and cannot be due to adsorbed cyclohexene. Other than a decrease in the absorption intensity in the 1-ML cyclohexane spectra after electron bombardment in EID, due to ESD of C_6H_{12} , two additional differences in comparing with IR spectra of 1-ML cyclohexane are the disappearance of the “soft” mode of the $\nu(CH)$ band at 2784 cm^{-1} and appearance of the mode at 2933 cm^{-1} present as a shoulder. This is to be expected if EID cleanly forms adsorbed cyclohexyl groups, because one

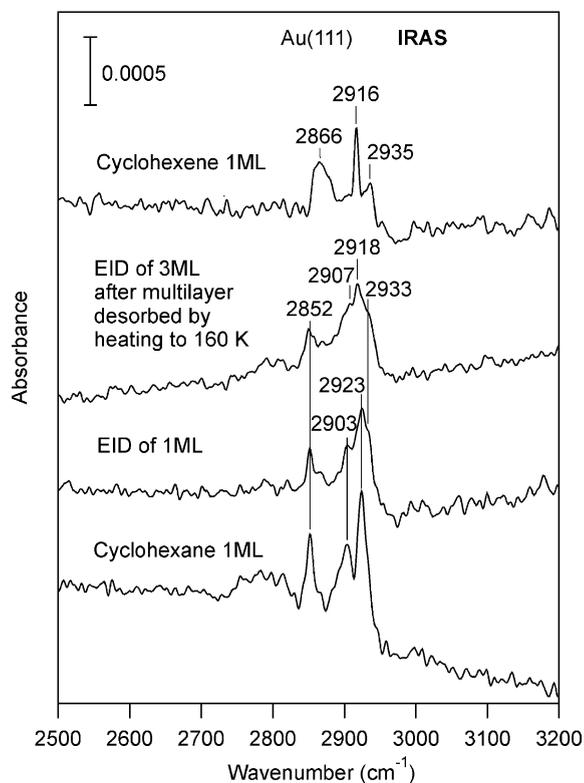
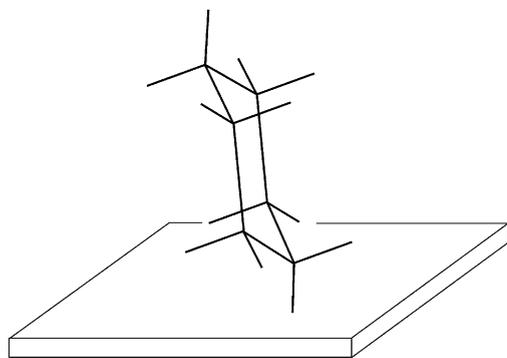


Fig. 14. Comparison of the IRAS spectra obtained for cyclohexane and cyclohexene monolayers along with that for adlayers formed from exposing 1 and 3 ML of cyclohexane to 30 eV electrons.

expects similarity in the IR spectra of weakly adsorbed cyclohexane and adsorbed cyclohexyl groups. The only chemical difference is the replacement of one C–H bond by one C–Au bond which is a weak bond with $D(Au-C)$ estimated to be only about 25 kcal/mol [22]. However, formation of cyclohexyl groups on the surface will cause a change in the orientation of the molecular ring, because these species are bound to the surface through a single Au–carbon covalent σ -bond. This change in orientation of the adsorbate occurs such that no hydrogen atoms project directly into the surface as shown in Scheme 3.

The IR spectrum of the 3-ML cyclohexane EID products annealed to 160 K exhibit a band at 2916 cm^{-1} that we assigned as $\nu(C-H)$ modes of cyclohexene aliphatic CH_2 groups. That indicates that heating to 160 K causes some conversion of the



Scheme 3.

cyclohexyl groups to adsorbed cyclohexene. The $\nu_{(s)}(\text{C-H})$ band at 2852 cm^{-1} in cyclohexane does not change position after EID of either 1 or 3 ML of cyclohexane.

Next, we discuss the thermal chemistry observed following EID. Electron bombardment at 30 eV of a 1-ML cyclohexane film caused changes in the subsequent TPD spectra. Desorption of cyclohexane and cyclohexene occurred coincidentally at 273 K. This cyclohexene peak cannot be explained by cyclohexane cracking in the QMS ionizer because the ratio of the peak intensities at 82 and 84 amu in the TPD spectra is much higher than that for cyclohexane gas and desorption spectra from the cyclohexane multilayer. Both cyclohexane and cyclohexene are formed on the surface at 273 K, and desorb in reaction-rate limited peaks, because cyclohexane and cyclohexene monolayers produced by adsorption of these gases desorb from the surface at 198 and 213 K, respectively.

We assert that no carbon–carbon bonds were broken during these EID experiments because no carbon was detected by AES after TPD subsequent to a prolonged exposure of the surface to electrons. Surface carbon was detected by AES after TPD subsequent to long exposures of the sample to electrons with incident energies higher than 50 eV.

Chemisorbed alkyl groups formed on the Au(111) surface by thermal dissociation of $\text{C}_2\text{--C}_4$ alkyl iodides undergo coupling and disproportionation reactions at comparable rates at $\sim 270\text{ K}$ [23–25]. Disproportionation reactions to form

corresponding alkanes and alkenes could obviously occur by two different mechanisms. In one case reaction would begin with β -hydride elimination to produce the corresponding alkene and hydrogen adatoms that immediately hydrogenate unreacted alkyl groups to produce the corresponding alkane. In the second case, bimolecular reaction directly transferring a H atom. There is apparently a high facility for this reductive elimination of chemisorbed alkyls to form alkanes because although hydrogen atoms recombine and desorb as H_2 at $\sim 100\text{--}140\text{ K}$ [25] on clean Au(111), no H_2 desorption was detected in our experiments during TPD.

β -hydride elimination in adsorbed alkyls occurs over a narrow temperature range of 230–270 K on several different metal surfaces. Coupling reactions are more variable, with reports of these reactions occurring at temperatures from 185 to 250 K on Ag(111), 270 K on Au(111), and 400 K on Cu(111) [25]. Paul and Bent have suggested that the branching ratio between coupling and disproportionation reactions depends on the surface-alkyl and surface-hydrogen bond strength [25]. Specifically, cyclohexyl groups adsorbed on Cu(100) were reported to undergo β -hydride elimination at 239 K to form cyclohexene and adsorbed hydrogen [26].

Based on these results, we attribute the coincident C_6H_{12} and C_6H_{10} desorption at 273 K to disproportionation reactions of adsorbed cyclohexyl groups formed by C_6H_{12} EID. The desorption-rate limited cyclohexene peak at 216 K is evidence that some of the cyclohexyl groups that were formed during EID undergo β -hydride elimination at temperatures below 216 K.

Electron bombardment at 30 eV of a 3 ML cyclohexane film caused almost complete elimination of cyclohexane desorption from the chemisorbed monolayer state. We attribute this to the dissociation of a C–H bond and formation of a cyclohexyl radical in physisorbed layers above the monolayer followed by diffusion of cyclohexyl groups to the surface, similar to that observed in cyclohexane EID experiments on Pt(111) [27]. Cyclohexene desorption at 277 K is due to the disproportionation of cyclohexyl groups. It is possible that the same small amount of cyclohexane

desorbed from the surface at 277 K, but this did not produce a clear peak in the TPD experiments. We do not have a good explanation for the formation of cyclohexene at 324 K. It is possible that EID or subsequent thermal reactions during TPD induces surface oligomerization. Evolution of mass 82 species at 324 K may be explained by the reaction-limited desorption of cyclohexene produced by high temperature decomposition of larger C_{12} molecules such as cyclohexene, 3-cyclohexyl (C_6H_9 – C_6H_{11}) or bi-2-cyclohexen-1-yl (C_6H_9 – C_6H_9) formed by surface reactions. On the other hand, 324 K is in the temperature range where such large molecules are expected to desorb from the Au(111) surface and mass 82 could be a cracking fraction of such desorbing molecules in the mass spectrometer.

The electron-induced decomposition reaction cross-section for a 3-ML cyclohexane film is much larger than that for a 1-ML film. This is because of the stronger interaction of the molecules in the monolayer with the metal surface which decreases the lifetime of the excited states of the species formed by electron bombardment and lowers the decomposition probability. An even more pronounced effect of this was found in EID studies of cyclohexane on Pt(111) [28]. Gold adsorbs cyclohexane more weakly than platinum, and so the EID cross-section for the adsorbed cyclohexane monolayer is fairly high on Au(111) compared to that on Pt(111).

5. Conclusion

Cyclohexane and cyclohexene adsorb molecularly and reversibly on the Au(111) surface, with monolayer desorption energies estimated to be 12 and 13 kcal/mol, respectively. EID reactions induced by 30 eV electrons in monolayer and multilayer ($\theta^{\text{init}} = 3$ ML) films gave only two desorption products in TPD: cyclohexane and cyclohexene. No surface carbon was detected by AES following TPD, and our experimental results suggest that no deep dehydrogenation or extensive C–C bond breaking occurred during EID. We conclude that EID in cyclohexane films causes clean dissociation of cyclohexane to cyclohexyl

species that then chemisorb on the surface. IR data fully support this conclusion. Adsorbed cyclohexyl groups on Au(111) undergo facile, low temperature dehydrogenation to produce cyclohexene below 216 K and disproportionation reactions at 273 K to produce cyclohexane and cyclohexene. EID of 3-ML cyclohexane films on Au(111) are very similar to those using 1-ML films. However, the EID cross-section is much larger in the multilayer film and there is an additional reaction channel that leads to either cyclohexene formation and desorption at 324 K following decomposition reactions of surface bound C_{12} double ring molecules, or larger oligomers, or to the desorption of such larger compounds at 324 K.

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