

Surface Science Letters

Electron-induced dissociation of hydrocarbon multilayers

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We have recently observed large cross sections ($\sigma = 1.8 \times 10^{-15} \text{ cm}^2$) for electron induced dissociation (EID) of physisorbed cyclohexane in multilayers on Pt(111) surfaces. This is a general phenomenon for hydrocarbon multilayers and for other physisorbed hydrocarbon species at monolayer or submonolayer coverages. While it is certainly not new to identify electron induced effects in adsorbed layers, the large EID cross sections reported here and their implications for physisorbed hydrocarbons is not generally appreciated. Two consequences of this chemistry are discussed. First, these EID cross sections are so large that serious artifacts in temperature programmed desorption (TPD) can be caused even in the short time it takes to perform a TPD experiment using a conventional quadrupole mass spectrometer (QMS) which can bombard the sample with electron fluxes in the μA regime. This problem in TPD can be overcome by utilizing a biased grid between the sample and the QMS ionizer region to stop low energy electrons. However, the secondary electron emission inherent in many electron spectroscopies (XPS, UPS, AES, etc.) may cause similar effects that are difficult to eliminate. Secondly, the large difference in EID cross sections between physisorbed and chemisorbed species has the exciting consequence that well-defined, complex hydrocarbon surface intermediates, e.g., cyclohexyl, can be prepared cleanly on reactive metal surfaces for chemistry studies.

1. Introduction

The electron induced dissociation and desorption of adsorbed molecules are well-known phenomena [1–11]. These effects often prevent the application of conventional AES, LEED, and other electron spectroscopies to investigate adsorbate covered surfaces. This is especially true in the case of weakly adsorbed molecules because the damage caused by low energy electrons is much larger for weakly adsorbed molecules than for strongly adsorbed molecules [12,13]. In contrast, temperature programmed desorption (TPD) is generally thought to be one of the “damage-free” methods in surface science even though there have been many reports to the contrary due to electrons coming out of the quadrupole mass spectrometer (QMS) ionizer region and impinging on the sample. For example, Swanson et al. [1] have pointed out that low energy electrons from the QMS can readily decompose adsorbed transition metal carbonyls. In this paper, we show

that large cross sections for electron induced dissociation (EID) are a general phenomena for multilayer and physisorbed hydrocarbon adsorbates, and estimate the cross section for dissociation of cyclohexane multilayers caused by the stray electrons emerging from the QMS during TPD.

An exciting consequence of this result is that we have a new method to prepare well-defined hydrocarbon intermediates on reactive surfaces. Recently, Zhou and White [12] have shown that electrons can be used to selectively break one C–H bond of ethylene adsorbed on Ag(111), since ethylene is weakly adsorbed on Ag(111). Because the probability of breaking a second C–H or C–C bond is much lower once the C_2H_3 radicals are bound to the surface, they were able to produce a pure layer of C_2H_3 species adsorbed on the surface. As described above, this method is limited to weakly bound adsorbates such as ethylene and benzene on Ag(111) [12,13]. Our finding that a single hydrocarbon intermediate can be formed

very selectively on Pt(111) via EID of multilayers of hydrocarbon molecules greatly widens the application of this method to more catalytically interesting systems and reactive substrates.

2. Experimental methods

The experiments were performed in two ultra-high vacuum chambers, with one equipped for AES, LEED, TPD, XPS and ISS, and the second one equipped with AES, TPD, LEED, XPS, UPS and HREELS [14]. The base pressures of both chambers were $(5-6) \times 10^{-11}$ Torr. TPD measurements were made using a UTI Model 100C quadrupole mass spectrometer in line-of-sight with the sample surface and using a linear heating rate of ~ 4 K/s. The mass spectrometer was surrounded with a shield having a small (6 mm diameter) entry hole. As shown in ref. [15], the contribution of the crystal edges and back is insignificant in our system. The electron bombardment was carried out simply by using electrons coming out from the QMS ionizer. The electron flux was estimated by measuring the current from the sample to ground. As pointed out in ref. [13], the scattered electrons (both primary and secondary) are not counted. Therefore, this measurement only gives a lower limit of the electron flux. In one series of experiments, we used the QMS without modification, which allowed a large electron flux ($6.6 \mu\text{A}$ at near 55 eV) to reach the sample surface. In a second series of experiments, we put a fine Ni screen biased -50 V in front of QMS ionizer. The electron current on the sample was suppressed in this way by a factor of 40.

The Pt(111) crystal was cleaned using a standard procedure [16]. After TPD measurements, the surface was contaminated with carbon, which was easily removed by heating the sample in 2×10^{-8} Torr O_2 at 800 K and then annealing to 1200 K.

Cyclohexane and the other hydrocarbons used in these experiments were purified by freeze-thaw cycles while pumping. The purity was checked with gas chromatography (GC) and in-situ mass spectroscopy.

3. Results and discussion

Fig. 1 shows two series of cyclohexane TPD spectra from different cyclohexane coverages on the Pt(111) surface. The spectra in the left panel were taken using a commercial UTI QMS without modification, while the spectra in the right panel were obtained with a biased screen in front of the QMS ionizer to suppress electron emission. At low cyclohexane coverages, both sets of TPD spectra are very similar and are in good agreement with published data [17,18], with one exception. We only see two cyclohexane peaks, which can be assigned to the first, or chemisorbed, layer and multilayer desorption. A third peak (β state) between the first layer and the multilayer desorption peaks has often been observed [17,18]. This β state has been assigned either to desorption from the sample holder and crystal edges or

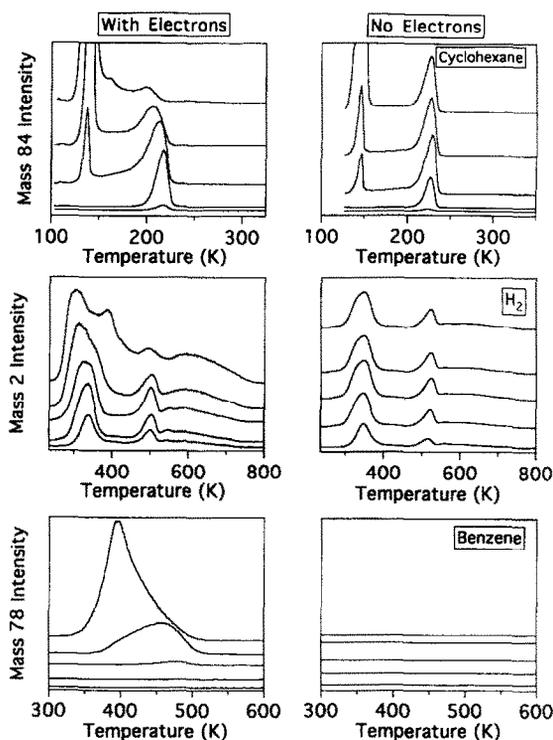


Fig. 1. C_6H_{12} (top panels), H_2 (middle panels), and C_6H_6 (bottom panels) TPD spectra after different cyclohexane exposures on Pt(111) surfaces. The TPD spectra on the left and right were taken with and without electron influence, respectively.

to desorption from the second layer [17]. In a separate paper [15], we have shown that precovering the surface with carbon, oxygen, or other contamination shifts the first chemisorbed peak to this β state.

With increasing cyclohexane exposures, the TPD spectra in the right and left panels of fig. 1 show very different development. In the right panel, where the electron emission from the QMS is strongly suppressed by the additional screen, no changes occur in the H_2 and C_6H_6 TPD spectra with increasing initial cyclohexane coverage. Also, the C_6H_{12} TPD spectra show only a continued growth of the multilayer peak. However, in the left panel, where a large electron flux from the QMS reaches the surface, dramatic changes in all of the H_2 , C_6H_6 and C_6H_{12} TPD spectra accompany the formation of a cyclohexane multilayer. In the C_6H_{12} TPD spectra, the multilayer peak grows with increasing initial coverage and the monolayer peak loses intensity, which indicates a decreasing amount of chemisorbed cyclohexane desorption. Consistent with the C_6H_{12} TPD changes, we see a large benzene desorption peak and a new hydrogen desorption peak in the presence of the multilayer. From a comparison of the right and left panels in fig. 1, it is obvious that electrons enhance cyclohexane decomposition in the multilayer phase.

We have observed very similar effects for cyclohexene, methylcyclohexane, heptane, butane, and isobutane on Pt(111) and other bimetallic Pt(111) surfaces. *In contrast, the chemistry of a monolayer of cyclohexane on Pt(111) is not affected substantially by similar electron bombardment.* This is because the strong interaction between Pt and the adsorbed cyclohexane in the monolayer effectively quenches excitations in the adsorbate molecules induced by electrons; dissociation pathways cannot compete with quenching in the chemisorbed monolayer. At higher coverages, the second and third physisorbed layers are isolated from the surface by the first layer. The electron induced excitations in the second or third layer have a prolonged lifetime which strongly promotes the dissociation pathway. In the case of cyclohexane, the most favorable process is C-H bond cleavage (see below). The dis-

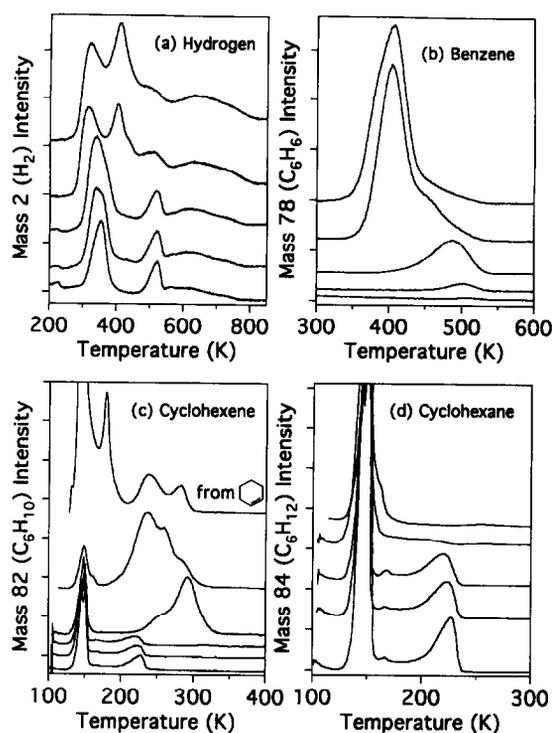


Fig. 2. H_2 , C_6H_6 , C_6H_{10} , and C_6H_{12} TPD spectra after a 3-layer cyclohexane film was subjected to electron bombardment for different lengths of time. To compare, a C_6H_{10} TPD spectrum after cyclohexane exposure is also provided in (c).

sociation product can either diffuse to the surface and replace (displace) the cyclohexane in the first adsorbed layer or abstract a hydrogen atom from neighboring cyclohexane in the first layer. The cyclohexyl intermediates thus formed bind more strongly to the surface than cyclohexane and dehydrogenate further upon heating in TPD.

To estimate the relevant cross sections and get some insight into electron induced cyclohexane decomposition in the multilayer, TPD spectra were taken after different lengths of time of low energy (< 50 eV) electron bombardment of a 3-layer film of cyclohexane. The current measured to the sample was $0.21 \mu A$. The results are summarized in fig. 2. With increasing time, cyclohexane desorption in the peak at 225 K decreases gradually, corresponding to a decrease in desorption from the first chemisorbed layer. After electron bombardment for 20 min, almost no cyclohexane desorption from the first chemisorbed

layer was observed. A slight decrease in the amount of desorption of the multilayer phase was also observed which was probably due to some electron induced desorption or perhaps the surface accommodating a higher coverage of the dissociation products than adsorbed cyclohexane. With the decrease of molecular cyclohexane desorption, a new hydrogen desorption peak was formed. Benzene desorption was also observed.

First, we consider the cross section for electron-induced dissociation. This can be estimated by a semi-logarithmic plot of the relative decrease of molecular cyclohexane desorption from the first chemisorbed layer versus the electron bombardment time. The cross section is calculated from the slope using the following equation:

$$\ln(I_t/I_0) = -(i_e t/eA)\sigma, \quad (1)$$

where I_0 is the cyclohexane TPD area from the first layer before electron bombardment, I_t is the cyclohexane TPD area from the first layer after electron bombardment for a period of time t at a electron current i_e , e is the electron charge, A is the surface area, and σ is the EID cross section. Such a plot is shown in fig. 3. The slope yields a cross section of $1.8 \times 10^{-15} \text{ cm}^2$ for a 3-layer cyclohexane film. As we can see in fig. 3, the cross section for the monolayer is much smaller than for the multilayer. Our measurements place a crude upper limit on this value as $5 \times 10^{-17} \text{ cm}^2$, although it may be much smaller. In the work described here, we are only trying to grossly differentiate two categories: monolayer and multilayer. We expect that coverage is an important variable, but without better energy discrimination we did not attempt to make detailed, thickness-dependent measurements of the EID cross section.

Secondly, we consider the dissociation pathway involved in electron-induced dissociation. We propose that dissociation by low energy electrons is limited to only one C-H bond in one cyclohexane molecule. There is strong evidence to support this assertion. Both the H_2 and benzene TPD spectra after extensive electron bombardment in fig. 2 are very similar to the H_2 and benzene TPD spectra after cyclohexene exposures [19]. Consistently, we also observed cyclohexene de-

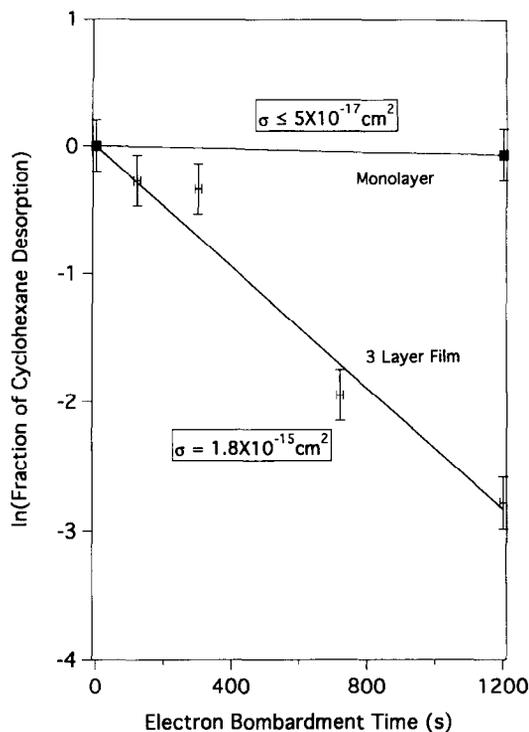


Fig. 3. Semi-logarithmic plot of the relative decrease of molecular cyclohexane desorption in the state corresponding to the first chemisorbed layer versus the electron bombardment time for a 3-layer cyclohexane film and a cyclohexane monolayer on Pt(111).

sorption at large electron bombardment times. Another important result from the TPD series in fig. 2 is that *benzene and cyclohexene are the only products observed in addition to hydrogen desorption*. (Also, similar EID experiments on cyclohexane multilayers on Sn/Pt(111) surface alloys yielded only cyclohexene in subsequent TPD spectra [15].) This indicates that the electron induced dissociation mechanism prefers a reaction channel that preferentially breaks a C-H bond much more readily than a C-C bond, and that extensive C-H bond breaking does not take place.

A comparison of the desorption temperature of cyclohexene formed from the dissociation products with that after cyclohexene exposures [15] offers additional insight into electron induced cyclohexane decomposition in the multilayer. In order to compare this directly, a cyclohexene TPD spectrum after cyclohexene expo-

sure is also provided as the top curve of fig. 2c. One can see significant differences. Cyclohexene desorption after cyclohexene exposures is characterized by 3 different states at 179, 238 and 282 K from the monolayer, and a multilayer desorption peak at 140 K. Electron bombardment following cyclohexene dosing on the surface only produces peaks at 238 and 282 K. The peak at 179 K was never seen after cyclohexene exposures. Instead, a peak at 258 K was observed. This suggests that cyclohexene is first formed from some other intermediate by the subsequent heating in TPD. The cyclohexene desorption temperature is determined by three processes: forming cyclohexene from the cyclohexene dissociation product, cyclohexene dehydrogenation, and cyclohexene desorption. A rationale choice for the dissociation product is cyclohexyl radical. Once cyclohexyl is formed, it is transferred to the surface either indirectly through abstraction of one hydrogen atom from the first chemisorbed layer or directly by diffusion to the surface before a second electron-induced reaction occurs. The covalent bond of adsorbed cyclohexyl to a surface Pt atom strongly inhibits further electron induced dissociation. Very similar results have been observed for other weakly adsorbed hydrocarbon monolayers on Ag [12,13]. Strong support for this interpretation comes from our HREELS studies of this system (see below). Very importantly, we can estimate from the TPD area that at least 95% of the adsorbed cyclohexane in the first layer after electron bombardment is converted to cyclohexene and to benzene during subsequent heating in TPD. This result indicates again the high selectivity of C-H bond cleavage over C-C bond cleavage induced by low energy electrons.

The dissociation products after electron bombardment have been studied with HREELS and the results are seen in fig. 4. The bottom spectrum was taken after ~ 3 layers of cyclohexane were formed at 110 K and then annealed to 155 K to remove the multilayer. The top spectrum was taken after a similar cyclohexane exposure at 110 K, but subjected to electron bombardment at 100 K, and then annealed to 155 K. Recently, the adsorption of cyclohexane on Pt(111) has been reinvestigated by Land et al. [20]. They found

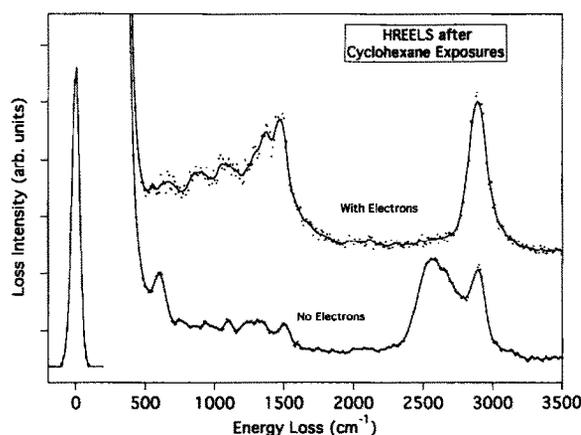


Fig. 4. HREELS spectra of cyclohexane with and without prior electron bombardment as explained in the text.

that cyclohexane adsorbed parallel on the surface with C_{3v} symmetry. Our HREELS spectrum of monolayer cyclohexane is in good agreement with their results. A detailed assignment of the observed bands can be found in the paper by Land et al. [20]. Most importantly, the broad band at 2600 cm^{-1} was attributed to the C-H stretch of three axial hydrogens of the cyclohexane which are directed toward the surface. The red shift (softening) and broadening of C-H stretch vibration are a result of strong interactions between C-H and Pt, similar to the agostic C-H-Pt interaction found in transition metal compounds [21]. In the top HREELS spectra of fig. 4, where the multilayer was bombarded with low energy electrons before excess physisorbed cyclohexane was removed by annealing to 155 K, dramatic changes occur. First, the broad band at 2600 cm^{-1} disappeared completely. Instead, only one sharp C-H band is observed at 2900 cm^{-1} , the same frequency as the C-H stretch of the cyclohexane C-H bond which does not interact with the surface. These results indicate that the dissociation intermediates produced by the electrons are not bonded to the surface through agostic C-H-Pt bonding interaction anymore, rather a C-Pt bond must be formed, consistent with the higher binding energy and reactivity of the dissociation intermediates. In addition, no deep dehydrogenation has taken place. The carbon atom must still be

sp^3 -hybridized. Otherwise, we should see a blue shift of the C–H stretch frequency. Second, the relative intensities of the bands between 500 and 1600 cm^{-1} change significantly, although the frequencies of the individual peaks do not change. It is interesting to note that the top HREELS spectrum in fig. 4 is almost identical to the off-specular HREELS spectrum of monolayer cyclohexane [20], but significantly different from the HREELS spectrum of monolayer cyclohexene [22]. The former observation implies that the dissociation intermediate has a structure not far from molecular cyclohexane and that an adsorption geometry change occurs which reduces the symmetry from C_{3v} of cyclohexane to C_1 for the dissociation intermediate. Therefore, all vibrations of the dissociation intermediate are dipole-allowed, breaking the dipole selection rule analogously accomplished in off-specular measurements. Both observations are consistent with the conclusion from TPD that only one C–H bond is broken by low energy electron bombardment and the resultant cyclohexyl radical is covalently bonded through one carbon atom to the Pt(111) surface.

As a final point, we note again that the high cross section of electron induced decomposition ($\sigma = 1.8 \times 10^{-15}\text{ cm}^2$) reported here is not limited to hydrocarbons in multilayers. It is quite a general effect for weakly adsorbed species on the surface. For example, a high cross section for electron induced dissociation has been found previously for adsorbed transition metal complexes [1,8,9] and weakly adsorbed hydrocarbons and alkyl halides on Ag [3,5,11]. Also, we have found that coadsorption of monolayer or submonolayer coverages of hydrocarbons with Sn, C, or K adatoms, which reduce the binding energy of chemisorbed hydrocarbon on Pt(111), enhanced the electron induced dissociation strongly. A high cross section is also to be expected for all adsorbates in the multilayer phase which have a high cross section for electron induced dissociation in the gas phase. One example is NO_2 , which can be easily dissociated in the gas phase by electrons. With increasing NO_2 exposures on Pd(111), a multilayer state desorbs at 140 K [23]. At high NO_2 coverages (2–3 layers), an additional NO_2 desorption peak at 170 K was observed on Pd(111)

and on several other surfaces studied previously [23–25]. The origin of this state has never been explained and the spectroscopic separation and identification of this state was also unsuccessful [23]. With our current findings, we can easily explain this state. Electrons from the QMS can cause NO_2 dissociation to form $\text{O}_{(a)}$ during TPD measurements. NO_2 desorbs at 170 K if NO_2 is dosed to an O-precovered Pd(111) surface or if N_2O_3 is formed [26].

Summarizing, we can say that the electron induced dissociation in physisorbed cyclohexane is strongly localized in the C–H bond. C–C bond breaking has a much smaller cross section than C–H bond cleavage. Once one C–H bond is broken, the cyclohexyl radical is somehow transferred to the surface. The strong C–Pt bond prevents further electron driven dissociation, at least until much larger incident electron fluxes are reached. This high selectivity of electron induced dissociation offers experimentalists a great opportunity to selectively and cleanly prepare reaction intermediates at the surface that have been proposed as reaction intermediates at high pressures, but which are not normally accessible under UHV conditions. In this example, adsorbed cyclohexyl species on Pt(111) were prepared and were observed to undergo dehydrogenation reactions to form cyclohexene and benzene during subsequent heating in TPD. This ability on reactive metals such as Pt has not been widely appreciated previously and it certainly will be very helpful in the future for understanding the mechanisms of hydrocarbon conversion reactions on working catalysts.

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