provides a quantitative means to compare, contrast, and consolidate results obtained on high surface area catalysts as well as on single crystal surfaces.

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Kinetic Study of the Initial Stages of Dehydrogenation of Cyclohexane on the Pt(111) Surface

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The initial dehydrogenation in the conversion of cyclohexane to benzene has been studied by laser-induced thermal desorption (LITD) combined with Fourier transform mass spectrometry (FTMS). Our previous work has shown that the initial dehydrogenation of cyclohexane occurs at \sim 180 K while benzene is not formed at a substantial rate until \sim 280 K. A stable surface intermediate exists in the temperature range 180-280 K. We have studied the kinetics of the dehydrogenation of cyclohexane to form this intermediate in the temperature range 175-215 K. LITD combined with FTMS was used to measure the surface concentration of cyclohexane as a function of time. From the kinetic data we find that the initial dehydrogenation is first order in cyclohexane coverage for all cyclohexane starting coverages studied. The activation energy at low coverage (0.05 ML) is 9.5 \pm 0.5 kcal/mol and increases to 13.5 \pm 0.9 kcal/mol at ~0.30 ML. Over this same coverage range the rate constant preexponential factors increase from 2.2×10^9 s⁻¹ at 0.05 ML coverage to 7.4×10^{12} s⁻¹ at 0.30 ML coverage. We discuss the coverage-dependent rate in terms of a simple site-blocking model and pseudo-first-order kinetics, recognizing that the total hydrocarbon coverage on the surface does not change as the reaction proceeds. At higher coverages (0.50 ML), the desorption of cyclohexane contributes significantly to the observed rate. At these high coverages, the rate constant measured by LITD is the sum of the desorption rate constant and the reaction rate constant. The kinetic analysis at this coverage is complicated by the changing surface coverage due to desorption of cyclohexane. Our data also show that the reaction rate is not substantially inhibited by the surface hydrogen which is a product of the reaction.

I. Introduction

The reactivity of hydrocarbons on metal surfaces is an important area of catalysis. The reactivity of cyclohexane and other C_6 hydrocarbons on Pt surfaces in particular has been the topic of a number of works¹⁻²⁰ due to the technological importance of cyclohexane dehydrogenation on platinum catalysts in relation to petroleum processing.²¹ The work presented here reports the kinetics of the initial dehydrogenation of cyclohexane on Pt(111). This work is part of an ongoing study in our laboratory to understand the chemisorption and reactivity of C_6 hydrocarbons on platinum surfaces.

Early studies of the reactivity of C_6 hydrocarbons on a variety of platinum and other transition-metal catalysts have proposed several different cyclic intermediates involved in the hydrogen exchange and reactivity of these molecules.²²⁻²⁵ In one of the first studies of hydrocarbon adsorption on a single-crystal Pt surface,¹ Gland et al. studied the adsorption and reactivity of cyclohexane, cyclohexene, and 1,3-cyclohexadiene on Pt(111). Their results suggested that cyclohexene is an intermediate in the dehydrogenation reaction and the dehydrogenation of cyclohexene is the rate-limiting step in the reaction. Near-edge X-ray absorption fine-structure (NEXAFS) experiments^{11,12} show the C-C bond of cyclohexane lies parallel to the Pt surface and has a bond length of 1.51 ± 0.03 Å (compared to the gas-phase bond length of 1.535 Å). Electron-stimulated desorption ion angular distribution (ESDIAD) experiments by Madey and Yates²⁶ also report cyclohexane bonded parallel to the Pt(111) surface and conclude that three of the 12 C-H bonds were directed into the surface.

Demuth et al.⁴ report a new C-H stretching frequency observed with HREELS (high-resolution electron energy loss spectroscopy) for adsorbed cyclohexane which is unusually low in frequency and broadened and attribute it to H-bonding-like interactions of the adsorbate with the metal. Hoffman and Upton¹⁰ propose a dif-

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ferent origin for the frequency shift. They present evidence that shows C-H mode softening in cyclic hydrocarbons only occurs if there is a geometric match between the lattice and the ring size. A theoretical study of Kang and Anderson¹⁴ presents a molecular orbital explanation for cyclohexane bonding to the surface. The authors find that cyclohexane is bonded most strongly to the surface when the three axial C-H bonds are directly over three surface metal atoms. They propose that the nearness of these three hydrogens to the surface should promote C-H bond cleavage. The infrared spectrum of cyclohexane has been studied by Chesters and Gardner.²⁰ They find a phase transition occurs in the overlayer as the coverage is increased as the molecules are displaced from their preferred geometry and conclude that the perturbation or softening of the C-H bonds by the surface is site specific. A very thorough study of cyclohexane adsorption on clean and Bi-covered Pt(111) by Rodriguez and Campbell¹⁷ reports the first TPD spectrum for this system. They show that cyclohexane is adsorbed in three molecular states: monolayer, second monolayer, and multilayer. The coverage at monolayer saturation was found to be 0.21 cyclohexane molecules per Pt surface atom. The authors report dehydrogenation of the cyclohexane to form benzene at 236 K.

Work in our laboratory has detected the laser desorption of cyclohexene in a narrow window of reaction time and temperature,²⁷ suggesting that other surface intermediates are present. The cyclohexene intermediate is only seen under conditions of very high initial cyclohexane coverages, suggesting the cyclohexene dehydrogenation is rate limiting only at high coverage. We have identified multiple steps in the dehydrogenation of cyclohexane.²⁸ We found that dehydrogenation of cyclohexane begins around 180 K, but benzene is not formed until 280 K. We have previously suggested that at low coverage the surface species, which is stable between 180 and 280 K, has C₆H₉ stoichiometry.²⁸ The results presented here show the coverage dependence of the kinetics for the initial step in the dehydrogenation reaction to form this stable intermediate in the temperature range 175-215 K. Our data provide quantitative results for the activation energy and preexponential factors as a function of hydrocarbon coverage.

II. Experimental Section

These experiments were performed in a stainless steel UHV chamber having a typical base pressure of 8×10^{-11} Torr. The chamber, which has been described in detail previously,^{29,30} is equipped with an ion gun for sample cleaning by argon ion bombardment, a single-pass cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES), optics for low-energy electron diffraction (LEED), and a directed doser for cyclohexane dosing. A side arm extension from the chamber holds an analyzer cell for Fourier transform mass spectrometry (FTMS) and a window allowing passage of the laser light to the sample for performing laser-induced thermal desorption (LITD). The Pt(111)single-crystal sample was mounted on a long -motion manipulator. The manipulator design allows for movement of the sample between the main chamber and the side arm containing the FTMS cell. The side arm is positioned between the poles of a 0.6-T electromagnet. The sample temperature may be varied between 120 and 1300 K by a combination of resistive heating and contact with a liquid nitrogen reservoir for cooling. The crystal temperature is measured by a chromel-alumel thermocouple spotwelded directly to the edge of the sample and referenced to 0 °C in an ice-water bath.

The Pt(111) crystal was cleaned and annealed by a standard procedure.³¹ Routine cleaning following cyclohexane exposure was performed by O₂ treatment (2 min at 900 K in 1×10^{-6} Torr of O_2) followed by annealing at 1200 K for 30 s. The cleanliness of the sample was carefully monitored by AES. The typical C(272 eV)/Pt(237 eV) ratio after a routine cleaning cycle was found to be ≤ 0.03 .

High-purity cyclohexane (C_6H_{12} , Aldrich) was further purified by several freeze-pump-thaw cycles. The purity of the cyclohexane was verified by FTMS which showed the expected cracking pattern for gas-phase cyclohexane with no additional unidentified mass fragments observed. The cyclohexane was dosed through a stainless steel directional doser. The chamber pressure during dosing was 5×10^{-10} Torr (uncorrected for ion gauge sensitivity). The effective dosing pressure at the sample was a factor of 50-100 higher due to the doser arrangement. Detailed coverage calibrations are described in the Results section of this paper. All dosing was carried out at 120 K.

The laser used for these experiments is a Lambda Physik EMG 103 MSC excimer laser. Radiation of wavelength 248 nm (KrF) and 20-ns pulse width was used for these experiments. Low laser powers were used (2 mJ focused to roughly 25 MW/cm^2) so that only neutrals are desorbed from the surface. Under these conditions, virtually all of the cyclohexane is removed from the surface, but no ablation of the platinum crystal occurs. The technique combining LITD with FTMS has been described in greater detail in a previous publication.32

The FTMS experiments are performed with an IonSpec Omega data acquisition system.²⁹ Impulse excitation^{33,34} is used to accelerate the ions. The data were taken with an analog-to-digital conversion rate of 2 MHz, and 4K-16K data points were acquired for each transient. One transient was collected per laser shot.

A typical kinetics experiment is carried out as follows. The clean Pt(111) crystal is cooled to 120 K and dosed with cyclohexane for a specified time (5-50 s for these experiments). The crystal is then moved down the side arm to the FTMS cell. The crystal is positioned in front of a 1-cm-diameter hole in the cell which has been cut in the center of one of the analyzer cell plates. The laser beam passes through a similar hole in the opposite side of the cell and strikes the crystal at normal incidence. The laser spot size is typically 1.8×0.2 mm. When the laser pulse strikes the metal sample, the temperature of the illuminated spot increases rapidly (~1000 K in the 20-ns pulse^{32,35}), causing the molecules to desorb. These desorbed molecules are ionized by a 70-eV, 1-uA electron beam. The ionized molecules are trapped in the 0.6-T magnetic field and are mass analyzed by FTMS.³⁶ Each laser shot provides a complete mass spectrum over the range m/z =10-250. The laser optics are adjusted by a programmable controller to move the laser to a fresh spot on the surface for each laser pulse. Several reference mass spectra are taken at 120 K. The temperature of the crystal is then ramped to the desired reaction temperature at a rate of 3 K/s. Once the temperature of the crystal is stabilized, a series of mass spectra are taken as a function of time with each spectrum taken from a fresh spot on the surface. Up to 50 spots may be taken during a typical kinetics experiment. In this manner we are able to monitor the molecular surface composition as a function of time.

III. Results

A. TPD and Coverage Quantification. Figure 1 shows a series of TPD curves for four different exposures of cyclohexane on the Pt(111) surface. This is the first report of TPD acquired using FTMS as the method of detecting the desorbing molecules. No laser pulse was used in obtaining the TPD spectra. The TPD

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Figure 1. Temperature-programmed desorption spectra showing the molecular desorption of cyclohexane following various exposures to cyclohexane at 120 K using a directional doser. A temperature ramp rate of 3 K/s was used to generate these data.

spectra are acquired in the usual manner by ramping the temperature of the crystal (3 K/s in this case) and monitoring the intensity of the desorbing molecules which have been ionized by electron impact ionization in the gas phase. The only difference between this technique and the usual quadrupole mass spectrometer (QMS) technique lies in the method of detection of the m/z ratio of the ions. The advantage of FTMS is that all masses can be observed simultaneously. We have plotted only mass 56 in Figure 1 since it is the most intense fragment observed in the mass spectrum. It is possible to create a montage plot showing all of the mass spectra as a function of temperature. The disadvantage of detecting the mass signals with FTMS is that the longer time required for signal processing limits the data point density. This disadvantage can be offset somewhat by using low-temperature ramp rates. Unlike conventional QMS detection for TPD, we still observe very good signal levels at low ramp rates even with high chamber pumping speeds since only a few thousand ions are needed for measurable image current detection by FTMS.32

The TPD spectrum shown in Figure 1 is in good agreement with that reported by Rodriguez and Campbell¹⁷ after accounting for differences in ramp rates. We observe three peaks in the desorption spectra for very high coverages, corresponding to monolayer, second monolayer, and multilayer desorption. We can quantify the initial cyclohexane coverages used in the kinetics experiments by using the fact that a 100-s dose at 5×10^{-10} Torr has just begun to populate the second adsorption state (100 s curve in Figure 1). Thus, a 100-s dose just saturates the monolayer state. According to Rodriguez and Campbell,¹⁷ this corresponds to a coverage of 0.21 cyclohexane molecules per Pt atom for molecularly adsorbed cyclohexane.

B. Uptake Measurements. Before any discussion can be made concerning concentrations of surface species as a function of time, it is vital to show that the measured LITD/FTMS signal is indeed proportional to coverage. To do this, we compared the uptake of cyclohexane measured by AES with the uptake measured by LITD/FTMS. Figure 2 shows the carbon 237-eV peak height measured as a function of cyclohexane exposure time. Each data point on the curve is an average of several measurements from different locations on the crystal. Although saturated hydrocarbons are known to be particularly sensitive to electron beam decomposition,³ we find no evidence of electron stimulated desorption under these conditions. Even though the molecule may decompose during the analysis, the carbon AES signal will still provide a good measure of cyclohexane coverage. The data in Figure 2 were taken at a temperature low enough (120 K) to cause condensation of a multilayer. Hence, the curve continues to increase with increasing exposure as multilayers of cyclohexane build up on the surface.



Figure 2. Uptake curve for cyclohexane/Pt(111) showing the peak height of the C (237 eV) Auger transition as a function of exposure time to cyclohexane. Each point plotted is the average of 5-10 data points. The errors bars are for the 95% confidence limit.



Figure 3. FTMS/LITD uptake curve showing the mass 56 signal from laser-induced thermal desorption of cyclohexane as a function of exposure time to cyclohexane. Each point plotted is the average of 5-10 data points. The errors bars are for the 95% confidence limit.

Figure 3 shows the LITD/FTMS uptake curve taken for the same exposure range as in Figure 1. These data were acquired by exposing the crystal to cyclohexane for a set amount of time at 120 K. The crystal was then positioned in the front of the FTMS cell and analyzed with LITD/FTMS. Each data point in this figure is the average of several laser shots, each at a different spot on the crystal. Comparison of Figures 1 and 2 shows that LITD/FTMS provides a good measure of surface coverage and that the signal is linearly proportional to cyclohexane coverage.

C. Survey Experiments. As a first step in studying the reactivity of this system, we performed a series of survey experiments²⁸ to identify the species present on the surface as a function of temperature. We perform a survey experiment by increasing the temperature of the crystal in a stepwise manner and obtaining a mass spectrum of the reaction mixture on the surface from a new spot for each temperature step. Because of the rapid temperature jump from the laser pulse (heating rate = 10^{11} K/s),^{32,35} even molecular species which decompose on the surface under slower heating conditions can be desorbed intact. For each laser pulse, we obtain a complete mass spectrum of all of the stable species present in the area irradiated by the laser.

Figure 4 shows the results of a survey experiment performed on a low-coverage (0.03 ML) cyclohexane adsorbed at 120 K on Pt(111). This figure shows a plot of mass 56 (base peak for cyclohexane) and mass 78 (base peak for benzene) intensity as a function of crystal temperature. At 150 K, cyclohexane is the only species observed in the mass spectrum, indicating the stability of cyclohexane at this temperature. As the temperature is increased, the cyclohexane signal falls to zero by 180 K. Thermal desorption, as in Figure 1, and AES show that no desorption is occurring at this temperature and coverage, indicating that the cyclohexane has begun to dehydrogenate at this temperature. Benzene is not produced in quantity until 270 K. The small amount of benzene in the region between 180 and 270 K is likely



Figure 4. Survey experiment showing LITD/FTMS signals for cyclohexane (mass 56) and benzene (mass 78) as a function of surface temperature. The surface was prepared by exposure to cyclohexane at 120 K for a surface coverage of 0.03 ML.



Figure 5. Typical kinetic experiment following a 30-s exposure to cyclohexane at 120 K ($\theta_0 = 0.3$ ML). Reaction temperature used for this particular run is 205 K. The dark circles are individual data points which correspond to a single laser shot each on a different location on the crystal. The line is a best fit to a single-exponential decay.

due to a laser-driven reaction of the surface intermediate to form benzene. Since no species other than the small amount of benzene laser desorbs between 180 and 270 K, we conclude that the intermediate or intermediates on the surface in this temperature range must be tightly bound to the surface and do not desorb intact. We have previously proposed that a C₆H₉ species may be the stable surface species in the 180–270 K temperature range.²⁸ The kinetic data discussed below follow the initial dehydrogenation step to form this intermediate in the temperature range 175–215 K. We follow the kinetics by following the decrease in cyclohexane concentration on the surface as a function of time at fixed temperature.

D. Kinetics of Dehydrogenation. Figure 5 shows typical kinetic data obtained for the initial dehydrogenation of cyclohexane. This particular experiment was performed using a 30-s exposure of cyclohexane at 120 K and thus corresponds to an initial coverage of 0.30 ML, using the calibration discussed in section III.A. About 3 min is required to move the sample from the dosing chamber to the FTMS analyzer cell, during which the sample temperature is held at 120K. The temperature of the crystal was then ramped to the desired reaction temperature (205 K), and the decrease in cyclohexane coverage was monitored as a function of time by following the mass 56 signal with LITD/FTMS. AES experiments have shown that for low initial coverages nothing desorbs from the surface at this reaction temperature. The solid line in



Figure 6. Logarithm plot of the data shown in Figure 5. Both mass 56 and 84 (the two most intense fragments in the mass spectrum of cyclohexane) are shown. The solid line is the least squares fit through the data points. The slope of this line gives the rate constant for the initial dehydrogenation of cyclohexane.



Figure 7. LITD/FTMS spectrum corresponding to a cyclohexane coverage of 0.05 ML on Pt(111). This is the first spectrum (time = 0) of a kinetics experiment at this coverage. The signal-to-noise ratio for the mass 56 fragment ion is \sim 45.

Figure 5 is a single-exponential fit through the data points. Figure 6 shows the logarithm of the data in Figure 5 plotted versus time as well as the data for mass 84, the second most intense fragment in the cyclohexane mass spectrum. The slope of the least squares line through the data gives the rate constant for the reaction. An important point to note is the dynamic range over which we are able to follow the reaction. The data shown in Figure 5 and 6 follow the reaction over a factor of 50 in surface concentration. We are also able to monitor the reactions over a wide range of times. We have followed reactions as long as 30 min with the only limitation being coadsorption from the background. We have followed reactions for times as short as 10 s. The study of short reaction time is limited by our data collection rate (maximum of one point per second).

We performed experiments like those shown in Figures 5 and 6 for four different initial coverages at several different reaction temperatures to obtain the kinetic parameters of activation energy and preexponential factor as a function of initial cyclohexane coverage. Figure 7 shows a LITD/FTMS spectrum obtained at the beginning of one such experiment following adsorption of 0.05 ML of cyclohexane. The signal to noise for the mass 56 peak (the major electron ionization fragment of cyclohexane) is \sim 45:1 in this spectrum. Thus, even at this low coverage we can easily follow the reaction over a sufficient range of cyclohexane concentrations to accurately determine the kinetics. Figures 8, 9, and 10 show Arrhenius plots for 5-, 15-, and 30-s cyclohexane exposures, respectively. These correspond to estimated initial cyclohexane coverages of 0.05, 0.15, and 0.30 ML. These Arrhenius plots were constructed using rate constants obtained from plots of ln [signal] vs time as illustrated in Figure 6. The error bars on the data points are the errors from the determination of the slope in the ln [signal] vs time plots. From the slope and intercept of the Arrhenius plots, we obtain the activation energy and preexponential factor for the



Figure 8. Arrhenius plot of the rate constants obtained for 5-s exposure to cyclohexane. This corresponds to a coverage of 0.05 ML of cyclohexane. The error bars on the individual data points are obtained from the error in the slope determined from the rate constant plots. The slope of the Arrhenius plot gives an activation energy of 9.5 ± 0.5 kcal/mol. The preexponential factor determined from the intercept is 2.2×10^9 s⁻¹.



Figure 9. Arrhenius plot of the rate constants obtained for 15-s exposure to cyclohexane. This corresponds to a coverage of 0.15 ML of cyclohexane. The error bars on the individual data points are obtained from the error in the slope determined from the rate constant plots. The slope of the Arrhenius plot gives an activation energy of 11.8 ± 1.0 kcal/mol. The preexponential factor determined from the intercept is 3.4×10^{11} s⁻¹.



Figure 10. Arrhenius plot of the rate constants obtained for 30-s exposure to cyclohexane. This corresponds to a coverage of 0.30 ML of cyclohexane. The error bars on the individual data points are obtained from the error in the slope determined from the rate constant plots. The slope of the Arrhenius plot gives an activation energy of 13.4 ± 0.9 kcal/mol. The preexponential factor determined from the intercept is 7.4×10^{12} s⁻¹.

initial dehydrogenation. The Arrhenius parameters (activation energy and preexponent factor) are shown as a function of coverage in Figures 11 and 12. At the lowest coverage, 0.05 ML, the activation energy is 9.5 ± 0.5 kcal/mol. At slightly higher coverage, 0.15 ML, the activation energy increases to 11.8 ± 1.0 kcal/mol. Increasing the coverage further to 0.30 ML increases



Figure 11. Activation energy for the initial dehydrogenation of cyclohexane as a function of initial cyclohexane coverage. The error bars are obtained from the error in the slope of the Arrhenius plots. The line through the points is meant solely to aid the eye.



Figure 12. Preexponential factor for the initial dehydrogenation of cyclohexane as a function of initial cyclohexane coverage. The error bars are obtained from the error in the intercept of the Arrhenius plots. The line through the points is meant solely to aid the eye.

the activation energy to 13.4 ± 0.9 kcal/mol. This higher coverage result is in excellent agreement with the value obtained by Rodriguez and Campbell¹⁷ obtained from a model fit to the sticking probability as a function of temperature. The preexponential factors also increase with initial cyclohexane coverage from 2×10^9 to 7×10^{12} s⁻¹ for 0.05 to 0.30 ML, respectively.

At higher coverages (0.50 ML), the desorption of cyclohexane becomes significant. We have performed Auger measurements monitoring the amount of carbon on the surface before and after reaction and find that no significant desorption is occurring for the low coverages (0.05–0.30 ML). At 0.50 ML, a significant amount of cyclohexane desorbs. Since we are monitoring the disappearance of cyclohexane as a function of time, we are measuring the total rate due to both desorption and reaction. The kinetics parameters for the total process (both desorption and reaction) are $E_a = 15.6 \pm 0.7$ and $v = 3.1 \times 10^{15}$.

IV. Discussion

A. Coverage-Dependent Kinetics. Our results show that each starting coverage the initial dehydrogenation is first order in cyclohexane coverage. The quality of the first-order fit is quite good, covering a factor of 50 in cyclohexane signal. At coverages ≤ 0.30 ML, no carbon-containing species desorb from the surface, and the reaction temperatures are well below the temperature for hydrogen desorption. This means that we are following the reaction in a region where all of the reactants and products remain on the surface. The reaction exhibits a coverage dependence, with the activation energy increasing with increasing initial coverage.

There are several possible origins of the coverage dependence of this reaction. First, the coverage dependence could arise from an ensemble requirement for the reaction. In this case, the reaction could be described as pseudo-first-order, with the actual first-order dependence in the number of open sites. At each initial coverage,



Figure 13. Plot of ln k versus ln $(1 - 5[C_6H_{12}]_0)$ for different reaction temperatures. The inset shows the temperature dependence of the ensemble size n obtained from these plots.

the number of open sites is nearly constant and the total hydrocarbon coverage remains constant during the reaction since we are studying the reaction in a region where no surface species are desorbing. Also, the coverage dependence could arise from a change in the detailed reaction coordinate with coverage and a change in the transition state with total hydrocarbon coverage due to crowding or lateral interactions.

1. Ensemble Site Requirement Model. We have tested the ensemble requirement model by assuming that the coverage dependence of the rate could be described by the equation

rate =
$$-d[C_6H_{12}]/dt = k'[\text{open Pt sites}]^n[C_6H_{12}]$$
 (1)

We can take advantage of the fact that since nothing desorbs from the surface during the reaction it is reasonable to assume that the concentration of open Pt sites does not change as the initial dehydrogenation proceeds and indeed is determined by the initial cyclohexane coverage

$$[\text{open Pt sites}] \approx (1 - 5[C_6H_{12}]_0)$$
 (2)

where the factor of 5 comes from the fact that each cyclohexane covers five Pt atoms.¹⁵⁻¹⁸ Thus, the rate law suggested by an ensemble model is

$$-d[C_6H_{12}]/dt = k'(1 - 5[C_6H_{12}]_0)^n[C_6H_{12}]$$
(3)

The relationship between k' and the previously determined pseudo-first-order rate constants k is then given by

$$k = k'(1 - 5[C_6H_{12}]_0)^n \tag{4}$$

Taking the logarithm of eq 4 yields

$$n k = ln k' + n\{ln (1 - 5[C_6H_{12}]_0)\}$$
(5)

A plot of ln k versus ln $(1 - 5[C_6H_{12}]_0)$ will yield a slope of n and the intercept of ln k', the coverage-independent rate constant. We have performed this analysis and show the results in Figure 13. We obtain values of n between 5 and 7. This indicates that 5–7 open Pt sites are required for dehydrogenation in addition to the Pt sites required for the cyclohexane adsorption, giving a total requirement of 10–12 Pt atoms. From Bi site-blocking studies, Rodriguez and Campbell estimate an ensemble size of eight open Pt atoms required for the dehydrogenation.

While our results are in reasonable agreement with those of Rodriguez and Campbell,¹⁷ the ensemble model does not adequately describe the kinetic data. Our initial analysis, presented in section D, indicates that there is a substantial temperature dependence to the coverage dependence. This is clearly indicated by the coverage-dependent activation energy of the pseudofirst-order rate constants. (E_a ranges from 9.5 to 13.5 kcal/mol over the coverage range studied.) The ensemble model provides no simple explanation for such a temperature dependence. The result is that, in applying the ensemble model to our data, a temperature-dependent ensemble size is obtained (*n* varies with temperature) as shown in the inset of Figure 13. 2. Compensation Effects. There exist many examples of surface processes (both desorption and reactions) for which the coverage dependence of the rates shows the interesting behavior that both the activation energy and the preexponential factors of the rate constants increase with coverage. Increases in the activation energy and the preexponential factor have opposite effects on the magnitude of the rate constant (the activation energy decreasing the rate constant while the preexponential factor increases the rate constant). The widespread nature of such observations has resulted in the use of the general term "compensation effects". Our data clearly illustrate that the dehydrogenation of cyclohexane to benzene exhibits compensation behavior.

Recently, Kevan has discussed compensation behavior of desorption kinetics in terms of statistical thermodynamics³⁷ using a virial coefficient expansion of the adsorbate partition functions. In particular, while the direct applicability of Kevan's analysis to a surface reaction in which no desorption takes place is certainly questionable, he does draw some conclusions which may be useful to us. Kevan points out an obvious result of the compensation effect: there must exist a temperature for which the coverage dependence of the activation energy and the coverage dependence of the preexponential factor will exactly cancel, resulting in no coverage dependence for the rate constant. Keven also conjectures that this temperature is similar conceptually to the Boyle temperature of an imperfect gas. We can use the analysis of Figure 13 to estimate the temperature at which the rate of dehydrogenation of cyclohexane will show no coverage dependence. This is equivalent to an extrapolation of the data in the insert of Figure 13 to n = 0, which would occur at ~ 230 K. Even at a starting coverage of 30% of a monolayer, the rate of the reaction at 230 K would be too fast for our present experimental capabilities. The predicted pseudo-first-order rate constant at this temperature is $k = 1.7 \text{ s}^{-1}$ whereas the fastest rates we have measured to date are $k \approx 0.2 \text{ s}^{-1}$ ($\theta_0 = 0.05 \text{ ML}$ and T = 250 K). Thus, we cannot at this time clearly confirm the predicted coverage independence of the rate at 230 K.

Finally, we must consider possible causes for the change in the transition state and reaction coordinate as a function of coverage. This change would most likely be caused by changes in the ability of the platinum surface to activate the C-H bond due to lateral interactions in the adlayer which increase with increasing surface coverage. There is C-H bond weakening upon adsorption as evidenced by the shift in the C-H stretching frequency as observed by Demuth et al.⁴ It is proposed that C-H σ donation to the platinum delocalizes the bonding electrons and weakens the C-H bond (Kang and Anderson).¹⁴ As the coverage increases, less σ donation occurs and thus the bond is weakened less and is less activated for C-H bond cleavage. As a result, the activation energy for dehydrogenation increases. The most reasonable model for a reaction such as the one studied here is that a number of open Pt sites are required for the reaction to proceed. However, it is likely that this is not an all-or-nothing proposition. If a smaller ensemble of open sites is available, the reaction will not be completely blocked but will proceed with a higher activation energy. It should be recognized that the phenomena discussed here are not exclusive of each other. Thus, while we present here an analysis of our data in terms of these possible origins of the coverage dependence in an independent manner, a more complex situation where multiple mechanisms lead to the coverage dependence cannot be ruled out.

B. Hydrogen-Induced Self-Poisoning. We have also investigated the possibility of self-poisoning of the reaction due to the surface hydrogen generated as the reaction proceeds. For this model we have assumed the following rate expression

$$-d[C_6H_{12}]/dt = k[C_6H_{12}]/[H]^n$$
(6)

It should be noted here that we are using this form for the rate

^{(37) (}a) Peterson, L. D.; Kevan, S. D. J. Chem. Phys. 1991, 94 (3), 2281.

 ⁽b) Wu, K. J.; Kevan, S. D. J. Chem. Phys. 1991, 94 (11), 7494.
 (38) Lewis, R.; Gomer, R. Surf. Sci. 1969, 17, 333.



Figure 14. Plot of the 0.30-ML kinetics data to test the hydrogen poisoning model with an inverse first power for the hydrogen dependence of the rate law. Left axis shows $[C_6H_{12}]_0 \ln [C_6H_{12}] - [C_6H_{12}]$ versus time. Right axis shows standard first-order plot of $\ln [C_6H_{12}]$ versus time.

law to quantify our discussion of hydrogen poisoning without any implication of a microscopic mechanism. To investigate the sensitivity of our experiments to this effect, we look at the case of n = 1. Integration of eq 6 with n = 1 gives

$$[C_6H_{12}]_0 \ln ([C_6H_{12}]) - [C_6H_{12}] = -k''t + [C_6H_{12}]_0 \ln ([C_6H_{12}])_0 - [C_6H_{12}]_0$$
(7)

where we have used $[H] = 3([C_6H_{12}]_0 - [C_6H_{12}])$ assuming the C_6H_9 stoichiometry of the intermediate.

A plot of $[C_6H_{12}]_0$ ln $([C_6H_{12}]) - [C_6H_{12}]$ versus time should be linear if the data can be described by this rate expression. Figure 14 shows the results of this analysis for 30-s exposure data $([C_6H_{12}]_0 = 0.3 \text{ ML})$. The effect of hydrogen poisoning should be largest at this higher coverage. The first-order kinetics fit to the data is also presented in Figure 14. Figure 14 clearly shows that the kinetics of this reaction are best described by a simple first-order process and are not well-described by the hydrogen poisoning model (at least at the level of an inverse first power term in the rate law). Higher powers of the hydrogen exponent in the rate law would be expected to show even greater deviation from the observed results. Hydrogen might not be expected to be an efficient poisoning agent or site blocker if hydrogen is mobile at the reaction temperature. There is evidence that hydrogen is mobile above 100 K;³⁷ thus, we are not surprised by the lack of any evidence of hydrogen poisoning.

V. Conclusion

We have investigated the initial dehydrogenation of cyclohexane to form the surface intermediate which has been previously proposed to have stoichiometry C_6H_9 .^{4,14,28} TPD was used to quantify the surface coverage of cyclohexane. We also have compared the uptake of cyclohexane by LITD/FTMS and AES and find that the LITD/FTMS signal is linearly proportional to cyclohexane coverage and therefore provides a good measure of surface concentration. LITD/FTMS was used to monitor the cyclohexane coverage as a function of time in a reaction region where no species are leaving the surface.

Our kinetic results show that the reaction is first order in surface cyclohexane coverage, with a coverage-dependent activation energy and preexponential factors which increase with increasing coverage. The activation energy was found to be 9.5 ± 0.5 kcal/mol at low coverage (0.05 ML) and 13.5 ± 0.9 kcal/mol at high coverage (0.30 ML). The preexponential factor increases from 2.2×10^9 to 7.4×10^{12} s⁻¹. A simple site-blocking model can provide a reasonable fit to the coverage dependence, with an ensemble requirement of 5–7 open surface atoms around the molecule. However, this simple model is clearly inadequate as indicated by the temperature dependence of the ensemble size. Our higher coverage data ($\theta = 0.3$ ML) can be used to clearly rule out significant self-poisoning of the reaction by surface hydrogen produced as the reaction proceeds.

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