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Correlation of Cyclohexene Reactions on Platinum Crystal Surfaces over a Ten-Order-of-Magnitude Pressure Range

Variations of Structure Sensitivity, Rates, and Reaction Probabilities[1]

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The hydrogenation and dehydrogenation of cyclohexene have been studied in the pressure range 10^{-7} to 10^2 Torr. The reaction of cyclohexene in excess hydrogen over the Pt(223) stepped platinum crystal surface at 25–150°C predominantly produces benzene at low pressures ($\sim 10^{-7}$ Torr) and cyclohexane at high pressures ($\sim 10^2$ Torr). While the low-pressure reactions are structure sensitive and proceed on the clean metal surface, the high-pressure reaction is apparently structure insensitive due to the continuous presence of a near monolayer of carbonaceous species. Widely differing coverages of reactive, weakly adsorbed hydrogen influence the reversal in selectivity between high and low pressures. The reaction probabilities decrease markedly with increasing pressure.

INTRODUCTION

The reactions of cyclohexene at low total pressures (10^{-8}–10^{-5} Torr) over platinum crystal surfaces have been investigated extensively (*1–3*). The hydrogenation and dehydrogenation reactions are structure sensitive as indicated by the striking variations in catalytic behavior which exist between crystal surfaces of different atomic structure. At much higher pressures (10–10^3 Torr) over silica supported platinum catalysts, Boudart and co-workers (*4*) have convincingly shown that cyclohexene hydrogenation is structure insensitive. The change of the reaction rate dependence on surface structure as the pressure is increased indicates that the reaction mechanism is changed. In order to explore how the reaction mechanism was altered we have investigated the catalyzed hydrogenation and dehydrogenation of cyclohexene over a ten-order-of-magnitude pressure range, from 10^{-8} to 10^2 Torr. Our catalyst was a Pt(223) single crystal of surface area of about 1 cm^2. The atomic surface structure of this sample consists of terraces of (111) orientation that are five atoms wide, separated by steps, one atom in height, and of (100) orientation. The structure and composition of the surface was monitored by low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) before and after the reaction studies, *in situ*, in the reaction chamber.

Our results indicate that at low reactant pressures the reaction occurs on an initially clean platinum surface and the kinetics are characteristic of the uncovered metal. The catalyst deactivates rapidly, however, due to the buildup of a monolayer of carbonaceous deposit on the metal surface. Platinum in the presence of this carbon-containing overlayer is quite active, however, at high reactant pressures. At high pressures the deposit builds up within seconds and steady-state rates are obtained in its presence. It appears that while the hydrogenation and dehydrogenation of cyclohexene are structure sensitive on the clean platinum surface these reactions are structure

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insensitive in the presence of this carbonaceous deposit. This explains in part the pressure dependence of the structure sensitivity of these reactions.

The turnover numbers increase by four to six orders of magnitude for the dehydrogenation and hydrogenation reactions, respectively, as the reactant pressure is increased from 10^{-8} to 10^{2} Torr. The initial reaction probabilities, however, decrease by two to six orders of magnitude with increasing pressure. Thus the platinum surface becomes much less efficient for carrying out the surface reactions at high pressures.

EXPERIMENTAL

High- and low-pressure experiments were performed in a UHV apparatus equipped with electron optics for low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES), an argon ion-sputter gun, a quadrupole mass analyzer, and an internal isolation cell which operates as a microbatch reactor (V = 160 cm^3) in the pressure range 10^{-4}–1 atm (*5*). The high-pressure enclosure was attached to an external gas recirculation loop which was fitted with an isolable Wallace & Tiernan gauge, metering valves for gas admission and mass spectral analysis, a gear pump for gas circulation, and a gas chromatograph sampling valve. Research-grade hydrogen (Matheson) and cyclohexene (Matheson "Spectroquality," 99.5+ mol%) were mixed in the circulation loop before expansion into the isolation cell. While cyclohexane was the major impurity present in the cyclohexane, trace amounts of adsorbed chlorine and sulfur species were also detected by AES following the high-pressure reactions. The sulfur coverage increased slightly with increasing reaction temperature but never exceeded 3–5% of a monolayer (*6*, *7*). These low levels of sulfur surface impurities appear to have no effect on the results described here (*8*).

Turnover frequencies for the batch reactions were calculated from the slopes of initially linear product accumulation versus reaction time curves. Reaction rates did not depend on the recirculation rate, and initial rates were reproducible to within about ±10%. At 150°C and 77 Torr (1 Torr = 133 N m^{-2}) the maximum hydrogenation rate of 33 molec $site^{-1}$ sec^{-1} represented a cyclohexene conversion rate of about 4% min^{-1}. However, total conversion after 100 min of reaction never exceeded ~75% as a result of self-poisoning. The sample was cooled to 25°C before evacuating the reaction mixture and then flashed to the reaction temperature prior to Auger analysis. The pumpdown time required for Auger analysis was about 3 min. Detailed procedures for low-pressure flow reactions, crystal preparation and cleaning, and surface characterization have been described previously (*2*, *3*).

RESULTS AND DISCUSSION

The Buildup of the Carbonaceous Overlayer

The product accumulation as a function of reaction time for the stepped platinum crystal surface is shown in Fig. 1 for a total pressure of 77 Torr. At temperatures *below* ~100°C, self-poisoning does not occur at 77 Torr or is slow and *largely reversible* at 10^{-6}

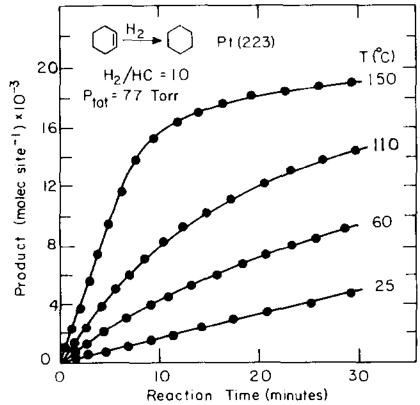

FIG. 1. Product accumulation versus reaction time for cyclohexene hydrogenation over Pt(223) at several temperatures. Rapid sampling was facilitated by the combined use of a mass spectrometer and gas chromatograph.

Torr (*2*). After reactions at these low temperatures most (~70% or more at 25°C) of the adsorbed species that accumulate on the surface can be reversibly desorbed at ~120°C as molecular benzene. At temperatures *higher* than ~120°C, self-poisoning becomes rapid and *largely irreversible* with the formation of extensively dissociated species with multiple metal–organic bond multiplicity (*9*). This strongly chemisorbed overlayer decomposes on further heating under vacuum with the evolution of hydrogen and only traces of benzene (*2*).

Between 0.3 and 1.1 monolayer of disordered carbonaceous materials is deposited during the first 10–200 sec of the reaction essentially independent of the cyclohexene pressure. The overlayer coverage depends significantly on the reaction temperature increasing from $\theta \sim 0.3$ at 25°C and 10^{-6} Torr to $\theta \sim 1.1$ at 150°C and 77 Torr ($C_{273}/Pt_{237} = 2.8$ corresponds to monolayer coverage for this surface (*10*)). Thus at low temperatures (~25°C), cyclohexene chemisorption displays a high degree of reversibility and a low, but still appreciable, saturation coverage ($\theta \sim 0.3$). This coverage increases with increasing reaction temperature, and an effectively irreversible form of adsorption is observed at temperatures in excess of 120°C.

In Fig. 2 the rate of the dehydrogenation reaction as a function of time is shown at low pressures along with the buildup of the carbonaceous deposit with time. The overall rate of self-poisoning at low pressures correlates closely with the buildup of the carbon containing irreversibly chemisorbed overlayer. The rapid self-poisoning at 150°C demonstrates that the irreversibly chemisorbed overlayer is particularly effective in blocking sites that catalyze dehydrogenation. The reaction rates at low pressures were obtained before the buildup of the deposit. *The catalytic activity observed at low pressures is therefore characteristic of the clean metal surface. At high pressures the initially clean surface rapidly becomes covered with a near monolayer of reversibly and irreversibly chemisorbed species. The catalytic behavior is then characteristic of an extensively precovered platinum surface.*

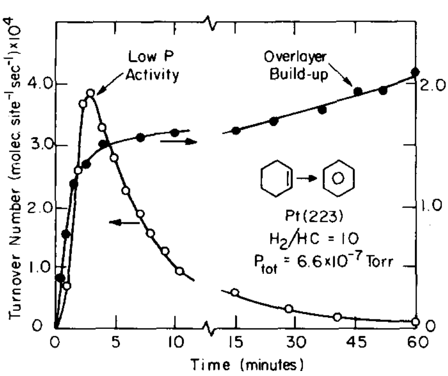

FIG. 2. A comparison at 150°C of the cyclohexene dehydrogenation rate over Pt(223) at low pressures with the simultaneous buildup of the irreversibly chemisorbed carbonaceous overlayer. A C_{273}/Pt_{237} ratio of 2.8 corresponds to monolayer coverage.

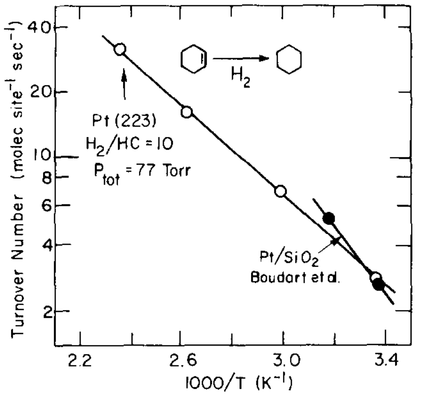

FIG. 3. Arrhenius plot for cyclohexene hydrogenation over Pt(223). For comparison, the results of Segal *et al.* (*4*) are included for $P_{HC} = 13$ Torr and $P_{H_2} = 76$ Torr.

In Fig. 3 the initial turnover frequencies obtained for the hydrogenation reaction as a function of temperature over the stepped crystal surface are compared with those reported by Segal *et al.* (*4*) for dispersed platinum. The two sets of data agree well, supporting the view (*4*) that the reaction at high pressures is structure insensitive. The apparent activation energy for hydrogenation is 5.0 ± 0.5 kcal/mol on the stepped surface at 77 Torr.

The transition of the active platinum surface from being clean to being continuously covered by the carbonaceous deposit is accompanied by a change from structure-sensitive to structure-insensitive catalytic behavior for the hydrogenation of cyclohexene. A change in mechanism is also indicated by the changing apparent activation energy for this reaction. It is less than 1 kcal/mol at low pressures while it is 5 kcal/mol at high pressures. Similarly, the apparent activation energy for the dehydrogenation of cyclohexene is at least 8 kcal/mol at 77 Torr, while it is near zero at low pressures in the same temperature regime. A more pronounced increase in apparent activation energy with increasing pressure has also been observed during cyclohexane hydrogenolysis and dehydrogenation (*11*). The apparent activation energy for metal-catalyzed hydrocarbon reactions always appears to increase with increasing reactant pressures (*12*).

The Hydrogenation and Dehydrogenation Rates of Cyclohexene Over a Ten-Order-of-Magnitude Pressure Range

The turnover frequencies and reaction probabilities at 150°C for the hydrogenation and dehydrogenation of cyclohexene in excess hydrogen are summarized in Fig. 4. All the results were obtained on the stepped Pt(223) crystal face. The error bars at low pressures span the range of structure sensitivity for two to six different platinum crystal surfaces. Overall, the turnover numbers for hydrogenation and dehydrogenation vary by factors of 10^7 and 10^4, respectively, for a 10^9-fold increase in the cyclohexene pressure. The fraction of reacting molecules dehydrogenating to benzene decreases from 94 to 100% at low pressures to just over 1% at a total pressure of 77 Torr. The dehydrogenation reaction probability—that is, the fraction of incident cyclohexene molecules converted to benzene—declines steadily from ~0.05 at 10^{-7} Torr to less than 10^{-6} at 77 Torr. In contrast, the hydrogenation probability varies by only two orders of magnitude (~10^{-3}–10^{-5}) over the entire range of pressure, surprisingly exhibits a minimum at a total pressure of 10^{-2}–10^{-1} Torr, and thereafter increases with increasing total pressure. In the pressure range of increasing reaction probability the hydrogenation rate is 1.3 order with respect to total pressure.

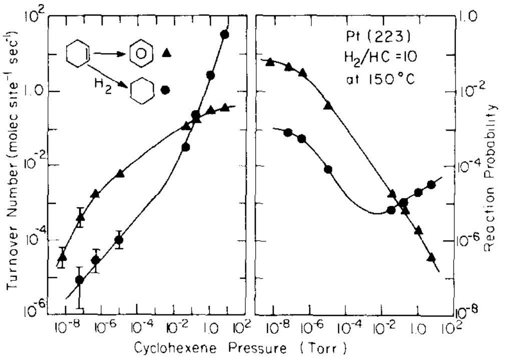

FIG. 4. Correlation of cyclohexene reaction rates and reaction probabilities over a ten-order-of-magnitude pressure range. The reactions were performed at 150°C over the stepped Pt(223) crystal surface with H_2/HC = 10.

The enormous decline in the dehydrogenation probability with increasing pressure is mainly associated with the lengthy mean reaction time which is required for the dehydrogenation and desorption processes to occur. The 2- to 5-min induction period observed before appreciable benzene desorption in our low-pressure experiments (cf. Fig. 2) (*1–3*) indicates that the mean reaction time is on the order of 10 sec at 150°C and certainly no shorter than 10^{-1} sec. When the cyclohexene pressure is 10^{-7} Torr, the dehydrogenation probability is high (~0.05) because the time required for adsorption, surface reaction, and product transport away from the surface is short in comparison to the time between collisions of the reactant molecules with the surface (ca. 10^{-14} sec cm^2 at 10^{-7} Torr). At higher pressures the dehydrogenation efficiency decreases rapidly as the intercollision period becomes much shorter than the mean reaction time. Under these conditions, most of the adsorption sites are continuously blocked from incident cyclohexene molecules by carbonaceous deposits.

In order to assure that thermodynamic equilibrium considerations do not influence the rate data that are shown in Fig. 4, the equilibrium constants and conversion concentrations of cyclohexane and benzene were calculated at low pressures ($\sim 10^{-7}$ Torr) and high pressures (77 Torr) at two temperatures, 25 and 150°C. These data along with turnover frequencies are listed in Table 1. It can be seen that at 150°C there are no thermodynamic boundary conditions that influence the rates reported in Fig. 4 with the exception of the low-pressure hydrogenation rate.

There could be another reason, in addition to the presence of the carbonaceous deposit, for the change in hydrogenation mechanism and reversal in selectivity at higher pressures. Reactive, weakly adsorbed hydrogen (with heats of adsorption in the range 8–10 kcal/mol) is identifiable on platinum only at pressures exceeding $\sim 10^{-1}$ Torr (*13–16*). At about this pressure the cyclohexene hydrogenation probability begins to increase, and hydrogenation becomes the prevailing reaction pathway. While weakly adsorbed hydrogen hydrogenates benzene readily (*14, 17*), studies by Basset *et al.* (*14*) indicate that strongly chemisorbed hydrogen ($-\Delta H_a \gtrsim 15$ kcal/mol) does not add to benzene at all, or at least not at an easily accessible rate. More general considerations (*12*) suggest that at pressures of practical application this new type of weakly adsorbed hydrogen is responsible for most, perhaps all, metal-catalyzed hydrogenation reactions. Reversibly chemisorbed hydrogen must also be present under low-pressure reaction conditions. However, the surface concentration, σ, at 10^{-6} Torr will be exceedingly small because its residence time, $\tau = \tau_0 e^{-\Delta H_a/RT} = 10^{-8}$–$10^{-5}$ sec, is short compared to the period between H_2 collisions with the surface ($1/F \cong 10^{-15}$ sec cm^2 at 10^{-6} Torr), so that $\sigma = F\tau$ is less than $\sim 10^{10}$ cm^{-2}, i.e., less than $10^{-3}\%$ of a monolayer. At high pressures the steady-state concentration of weakly adsorbed hydrogen will become appreciable as a result of the increased H_2 flux, and as a consequence, hydrogenation will become kinetically facile.

It should be noted that Hattori and Burwell (*19*) recently considered the role of carbonaceous deposits during ethylene and cyclopropane hydrogenation at −31–0°C over silica-supported platinum. There is evidence that the platinum surface is extensively covered by carbonaceous species ($\theta \sim 0.2$–0.5) during the reactions at these low temperatures. The reversibly adsorbed species that prevail under these conditions (pulse reactor, ~1 atm) are quantitatively converted to alkane by one pulse of hydrogen. Low coverages ($\theta \leq 0.1$) of more

TABLE 1

Equilibrium Constants and Turnover Frequencies for Cyclohexene Reactions at High and Low Pressures over Pt(223)

Reaction	T (°C)	TN^a		log $K_p{}^b$	$C_{eq}{}^a$ (%)	
		Low P	High P		low P	high P
Hydrogenation	25	3–8 × 10^{-6}	2.8	13.08	99.9	99.9
	150	3–8 × 10^{-6}	33	6.95	0.8	99.9
Dehydrogenation	25	2 × 10^{-4}	—	−3.96	99.9	0.2
	150	4 × 10^{-4}	0.4	0.65	99.9	99.7

[a] Turnover frequencies (uncertainty ± 10%) and equilibrium conversions refer to initial pressures of 6 × 10^{-8} Torr C_6H_{10} and 6 × 10^{-7} Torr H_2 at low P; 7 Torr C_6H_{10} and 70 Torr H_2 at high P (1 Torr = 133 N m^{-2}).

[b] Refers to ideal gas state at 1 atm (*18*).

strongly adsorbed and slowly reacting deposits also accumulate after an 11-pulse sequence. The latter species can be rehydrogenated in flowing hydrogen at 50–100°C. These authors conclude that a hydrogenation mechanism based on intermolecular hydrogen transfer between adsorbed carbonaceous species is very unlikely. These results closely parallel those reported here for the hydrogenation of cyclohexene at low temperatures. At 25°C, for example, reversible cyclohexene adsorption prevails, deactivation does not occur, the apparent steady-state coverage by adsorbed species is a significant fraction of a monolayer, and there is no evidence for intermolecular hydrogen exchange. It is important to note that intermolecular hydrogen transfer can occur and apparently does occur between adsorbed cyclohexene molecules at temperatures in excess of ~ 100°C. The disproportionation of cyclohexene to cyclohexane and benzene occurs at a high rate in the absence of hydrogen on the stepped Pt(223) crystal surface; at 150°C with $P_{C_6H_{10}}$, $TN_{BZ} \simeq 1.7$ sec^{-1}, $TN_{CH} \simeq 1.2$ sec^{-1}, and $E_a \sim 18$ kcal/mole. Benzene and cyclohexane are both *initial* products of this reaction, which clearly must proceed in the presence of a carbonaceous monolayer (*8*).

ACKNOWLEDGMENTS

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