[2.2]paracyclophane. Thus the equatorial H^c proton is shielded by the aryl faces of the guest, whereas the tropical H^d region of the host is slightly deshielded by the aryl edges of the guest.

The half-lives for guest liberation by 13 of the complexes were measured in $C_2D_2Cl_4$ and (or) $CDCl_3$ by following ^1H NMR signal changes with time, at temperatures of 25–134 °C. Values ranged from a low of 3.2 h at 25 °C for **1**–hexachlorobutadiene in $CDCl_3$ to a high of 19.6 h for **1**–ferrocene at 112 °C. The kinetic stability order was as follows: **1**–ferrocene > **1**–[2.2]paracyclophane > **1**–adamantane > **1**–ruthenocene > **1**–amantadine > **1**–hexamethylenetetramine > **1**–camphor > **1**–anthraquinone ~ **1**–tripropyl phosphate > **1**–anthracene > **1**–menthol > **1**–triethyl phosphate ~ **1**–hexachlorobutadiene. Variable-temperature ^1H NMR kinetic measurements provided activation energies (E_a) for decomplexation of 19 ± 5 and 28 ± 2 kcal mol^{-1} for **1**–adamantane and **1**–ruthenocene, respectively. Notice that adamantane ($C_{10}H_{18}$), which is rigid and nearly spherical, is much more difficult to liberate than flexible tripropyl phosphate ($C_9H_{21}O_4P$).

We have exemplified hemicarceplexes stabilized by constrictive binding, and formable and dissociable by heating. The guests are as large as [2.2]paracyclophane. Similar complexes of drugs might find use as delivery systems.

Identification of Multiple Steps in the Dehydrogenation of Cyclic C_6 Hydrocarbons to Benzene on Pt(111)

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The dehydrogenation of cyclic hydrocarbons to benzene over transition-metal catalysts has been widely studied by ultrahigh vacuum surface science techniques as well as techniques applicable to supported metal catalysts.[1-10] However, only recently has cyclohexene been directly observed as a surface intermediate in the dehydrogenation of cyclohexane to benzene on Pt.[1] When the technique of laser-induced thermal desorption (LITD) combined with Fourier transform mass spectrometry (FTMS) was used, cyclohexene was observed in the reaction mixture. However, measurable quantities of the cyclohexene intermediate were observed only over a narrow range of surface coverages and temperatures, suggesting the existence of other stable surface intermediates. In an effort to further understand this prototypical hydrocarbon dehydrogenation reaction, we have extended our studies to several other C_6 hydrocarbons. The results, presented herein, indicate that although dehydrogenation of cyclohexane begins at ~180 K, benzene is not formed at a substantial rate until the surface reaches ~280 K. Therefore, another stable surface intermediate species must exist, and our results suggest that it has the stoichiometry C_6H_9.

In our experiments, a Pt(111) surface is initially held at low temperature (115 K) so that the reactant (e.g., cyclohexane) is molecularly adsorbed. LITD/FTMS experiments are performed by focusing a pulsed laser beam (Lambda Physik excimer EMG103; 248 nm) down to a small spot (~0.002 cm^2) on the sample surface. This generates an extremely rapid temperature jump within the area of the small spot ($\Delta T \sim 1000$ K in 20 ns),[11-14] and molecular species on the surface are desorbed as intact neutrals. Even molecular adsorbates that decompose on the surface under slower sample heating conditions can be desorbed intact in this manner because of the extremely rapid heating rate of ~10^{10} K/s.[12] The desorbed intact neutral molecules are subsequently ionized by an electron beam and detected by FTMS.[15-18] For each laser pulse a complete mass spectrum is obtained of all the stable molecular species that were on the surface within the irradiated area. Effectively, analysis of the mass spectrum provides a snapshot of the surface species as the reaction progresses. The temperature dependence of a reaction can be followed by increasing the temperature of the Pt crystal in a stepwise manner and obtaining a mass spectrum of the reaction mixture from a new spot on the surface for each temperature step. In a typical experiment we hold the sample at a given temperature for ~30 s before obtaining the mass spectrum. The LITD/FTMS spectrum can be obtained and displayed in a period of ~1.5 s. If the spectrum has not changed from a previous one, we increase the sample temperature to the next step. If a change is observed in the spectrum (indicative of a surface reaction), we typically wait another time period and obtain another spectrum. The reaction is then followed in this manner until no further changes are observed in the spectrum. The sample is then heated to a higher temperature and the procedure repeated. Up to 50 spots can be interrogated without interference in a given experiment. The short time required to obtain and display the LITD/FTMS spectrum is very convenient for these reaction survey types of experiments. While stable molecular adsorbates are easily removed from the surface and identified in the manner just described, more strongly bonded adsorbate species, such as radical-like intermediates, may rearrange or decompose before desorbing.[19]

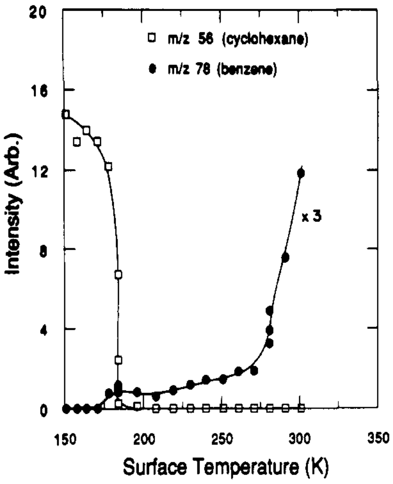

Figure 1. LITD/FTMS signals for cyclohexane (*m/z* 56 peak) and benzene (*m/z* 78 peak) as a function of the Pt(111) surface temperature following low-temperature adsorption of cyclohexane at low coverage (0.03 monolayer).

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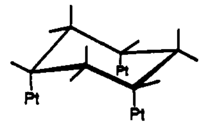
Figure 1 shows the results of a LITD/FTMS experiment in which cyclohexane was adsorbed at low coverage (~0.03 monolayer) on the Pt(111) surface at 150 K. This figure shows the intensity of the *m/z* 56 peak (M – 28, the base peak in the electron ionization of cyclohexane) and the *m/z* 78 peak (base peak for benzene) in the mass spectra which were obtained as the temperature of the Pt(111) sample was increased in a stepwise manner, as described above. At 150 K cyclohexane is stable on the surface and is the only species observed in the mass spectrum. As the Pt(111) crystal is heated to ~180 K, the cyclohexane signal rapidly falls to 0, as shown in the figure. At this temperature, thermal desorption[9] and separate Auger electron spectra show that no thermal desorption is occurring, only surface dehydrogenation. At 180 K a small amount of benzene is observed, but it is not produced in substantial quantities until ~270 K. Indeed, further experiments have led us to conclude that the benzene signal observed in the temperature range of ~180–250 K is due to a surface reaction of a tightly bonded intermediate caused by the laser-induced temperature jump.[20] While it may be coincidental, it should be noted that the onset temperature for benzene production on the surface (~270 K) corresponds closely to onset of recombination and desorption of the hydrogen atoms liberated in the reaction.

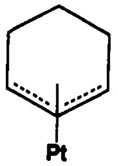
In the temperature range 180–270 K, the only signals observed in our low coverage LITD/FTMS spectra are due to a small amount of benzene which is formed by a laser-driven surface reaction. This suggests that the surface intermediate must be tightly bonded to the Pt(111) surface and is not desorbed in an intact manner by the laser-induced temperature jump. In an attempt to shed light on the nature of this surface intermediate, we have carried out experiments similar to the one described above but with initial adsorption of cyclohexene. In these experiments the starting temperature was reduced to 115 K. At this low surface temperature, cyclohexene is molecularly adsorbed and is easily observed in the LITD/FTMS spectra. At the low coverages used here, as the Pt surface temperature is increased, cyclohexene is stable up to ~150 K, where the surface concentration decreases in a manner similar to that observed for cyclohexane. That is, the cyclohexene signal decreases but no new species appears until the surface temperature reaches ~270 K, where the onset of benzene production is once again observed. While our previous work shows that cyclohexene is an intermediate in the dehydrogenation of cyclohexane, the present results show that cyclohexene is not the surface species that exists in the intermediate range of ~180–270 K, under the low-coverage conditions discussed here. We conclude, therefore, that cyclohexene reacts to form another surface species that is further dehydrogenated.

Additional LITD/FTMS experiments with low coverages of 1,3-cyclohexadiene and 1,4-cyclohexadiene showed that substantial amounts of benzene were observed in the mass spectra even after only 2 min at 115 K. This indicates that the activation energy for conversion of the cyclohexadienes to benzene is very low, and it clearly eliminates them as candidates for the surface species in the 180–270 K temperature range of the cyclohexane experiments.

We have now come to the conclusion that this surface intermediate is beyond cyclohexene (C_6H_{10}) in the conversion to benzene but not yet dehydrogenated to the extent of the cyclohexadienes (C_6H_8). These results suggest a stable surface intermediate of C_6H_9 stoichiometry for the species that exists on the surface in the temperature range 180–270 K in the cyclohexane experiments and 150–270 K in the cyclohexene experiments. Two attractive possibilities for this intermediate are shown herein. Species I would result from the removal of the three axial hydrogens on the surface side of the chair form of cyclohexane. This has been suggested as an intermediate by vibrational spectroscopy studies of cyclohexane dehydrogenation on Pt[5] and investigated by empirical electronic structure calculations.[21] Species II is an allylic C_6H_9 species that could be easily formed from adsorbed cyclohexene by the loss of one α-hydrogen.



I



II

While it seems likely from our experiments that the surface species that is stable in this intermediate range is of C_6H_9 stoichiometry and may be I or II, we should stress that we have no direct evidence of the structure of this surface intermediate at this time and further studies by other surface spectroscopies are needed. Such studies will be greatly facilitated by the present results, which provide a well-defined temperature range and conditions for formation of the stable C_6H_9 surface species. We have also shown here, for the first time, that benzene is not formed in substantial amounts until the surface is heated to ~270 K, coincidental with the onset of recombinative desorption of the surface hydrogen produced in the reaction. These experiments also clearly demonstrate the potential of the LITD/FTMS technique for rapidly surveying the chemistry of complex adsorbate species.

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Mutually Interpenetrating Inorganic–Organic Networks. New Routes into Nonshrinking Sol–Gel Composite Materials

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Control over bulk molecular architecture is a critical challenge in the design of new materials.[1] In the field of new inorganic–organic composites, aspects such as phase continuity, domain size, and molecular mixing at the phase boundaries greatly influence the optical, physical, and mechanical properties of the composite material.[2] Our interest in chemistry at the inorganic–organic interface has led to the design and preparation of new, homogeneous, optically transparent composite materials displaying a remarkably high degree of mixing between the two chemically dissimilar phases. These transparent composites are synthesized through a synchronous application of the aqueous ring-opening metathesis polymerization (aqueous ROMP)[3] of cyclic alkenyl

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