to stand at room temperature, no changes in the relative amounts of the isomers can be detected, even after 12 h, and hence it can be inferred that the distribution of exo and endo products is under kinetic control.

The lack of reactivity of the furan complex **2** toward maleic anhydride (>10^4 decrease in the pseudo-first-order rate constant compared to the free ligand) is expected upon metal 2,3-η^2-coordination, which causes loss of diene character in the ring. However, the pyrrole complex **1**, albeit also forming a 2,3-η^2-species with pentaammineosmium(II), displays unprecedented facile reactivity with maleic anhydride. The contrasting reaction patterns for the isostructural species **1** and **2** may be ascribed to their differing intramolecular dynamics. In contrast to what is observed for **2**, complex **1** undergoes a rapid 2,3- $\leftrightarrow$ 4,5-η^2-tautomerization, passing through an isomer in which the 2- and 5-positions are available for cycloaddition.

If the metal were to isomerize to the ring nitrogen, Diels–Alder addition of maleic anhydride to the diene fragment could ensue, and this might be followed by an N $\rightarrow$ π rearrangement. However, this hypothesis loses validity in view of the reactivity observed for the η^2-bound *N*-methylpyrrole analogue:[9] in this complex, both the tautomerization and the cycloaddition rates are at least twice as fast as those observed for **1**, thereby making an attack at the hindered nitrogen an unlikely possibility. Alternatively, an intermediate is shown in Chart I which would be stabilized by the π-basic metal center. Addition of maleic anhydride to the 2- and 5-positions of **6** could fully account for the observed products, the reaction taking the form of a 1,3-dipolar cycloaddition to the azomethine ylide portion of the complex. The failure of the furan complex (**2**) to undergo cycloaddition can be understood by considering the decreased stability of the corresponding oxonium intermediate.

Our attempts to liberate the cycloadduct from either osmium(II) or osmium(III) have thus far been unsuccessful.

Acknowledgment. Support of this work by National Science Foundation Grants CHE85-11658 and CHE84-14329 (400 MHz NMR) and National Institutes of Health Grant GM13638-23 is gratefully acknowledged.

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[9] The complex $[(NH_3)_5Os(\eta^2\text{-}N\text{-methylpyrrole})]^{2+}$ was prepared as for **1**.

Detection of Reaction Intermediates in the Conversion of Cyclohexane to Benzene on Pt(111)

Donald P. Land, Claire L. Pettiette-Hall,
Robert T. McIver, Jr.,* and John C. Hemminger*

Institute for Surface and Interface Science and
Department of Chemistry, University of California
Irvine, California 92717

Received March 30, 1989

Dehydrogenation reactions catalyzed by transition-metal surfaces have long been of great interest because of their importance in petroleum processing.[1] In the conversion of cyclohexane to benzene on Pt, cyclohexene has been suggested as an intermediate, but it has never been directly detected.[1-10] Presented here is the first direct observation of cyclohexene as an intermediate in this reaction. In addition, a second intermediate which is believed to be a bis(alkylidene) species is also detected.

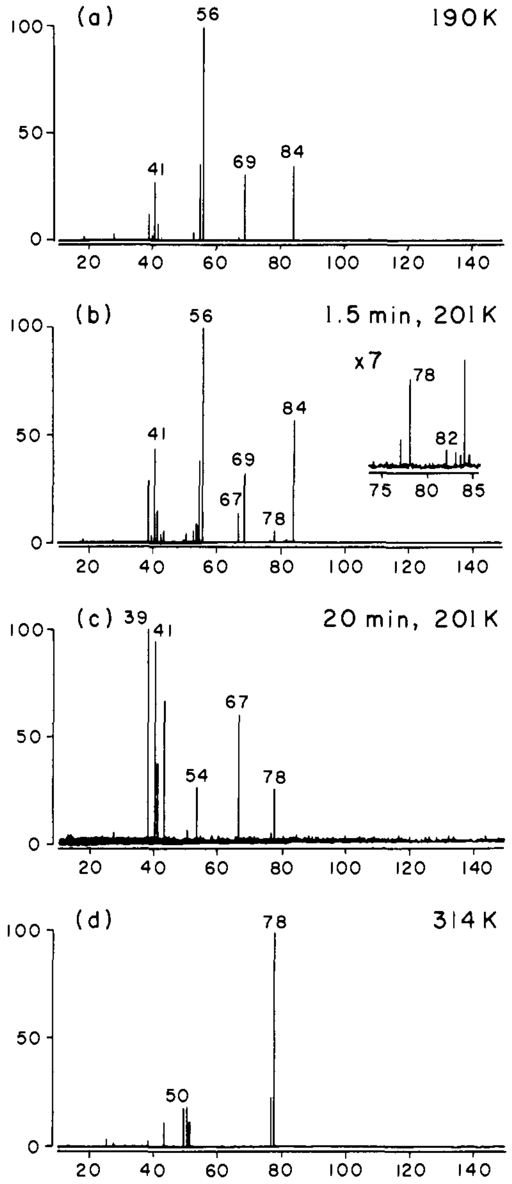

Figure 1. Laser-induced thermal desorption Fourier transform mass spectra, each resulting from a single laser shot at a fresh spot, obtained from a Pt(111) crystal surface after dosing with less than one molecular layer of cyclohexane. (a) After about 3 min at 190 K showing only molecular cyclohexane. (b) Shortly after warming to 201 K, showing the presence of cyclohexane at *m*/*z* 84 and benzene at *m*/*z* 78 (using the same scaling as 1a) and, cyclohexene, in the inset (with scaling expanded by a factor of 7) at *m*/*z* 82. (c) After 20 min at 201 K, cyclohexane and cyclohexene are gone, but benzene and another intermediate, 1,6-hexadialkylidene, remain. (d) Warming to 314 K gives only benzene.

The reaction is studied as a function of temperature and time by laser-induced thermal desorption and Fourier transform mass spectrometry (LITD/FTMS).[11-16] In the experiments described

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below, an excimer laser operated at low power (20 MW/cm^2, 248 nm, approximately 20 ns pulsewidth) is used to desorb molecules adsorbed on a Pt(111) single crystal. The Pt surface is not ablated, and the adsorbates are removed as neutrals. The desorbed neutrals are ionized by a 70-eV electron beam and detected by FTMS.[14,15] The use of FTMS allows one to obtain a complete mass spectrum (*m/z* 10–600) for each single laser shot. Analysis of the mass spectra can provide molecular information about the composition of adsorbates on the surface.[17]

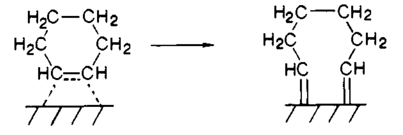
A clean Pt(111) surface, supported in an ultrahigh vacuum system, was cooled to 190 K and exposed to gas-phase cyclohexane. Figure 1 contains four mass spectra obtained by laser-induced thermal desorption from the Pt(111) surface following a cyclohexane exposure of 2.5 Langmuir (1 Langmuir = 10^{-6} Torr-s), which results in submonolayer coverage (Auger electron spectroscopy gives C(272)/Pt(237) = 0.22). Figure 1a is the LITD/FTMS spectrum obtained with a single laser shot after the cyclohexane has been on the surface for 3 min at 190 K. This spectrum shows all the peaks expected for cyclohexane (mass 84 is the parent mass) and confirms that cyclohexane is stable on the surface at this temperature. In addition, there is no indication in Figure 1a of any unexpected peaks due to laser-induced cracking or pyrolysis of the cyclohexane adsorbate.

A survey was then carried out by warming the sample in steps of about 3 K. Several LITD/FTMS spectra were taken at each temperature (each at a *different* spot on the crystal) until there appeared to be no change between successive spectra taken several minutes apart. Three representative mass spectra are shown in Figure 1b–d. Warming to 194 and 197 K for several minutes at each temperature produced mass spectra which did not differ significantly from Figure 1a. Figure 1b was obtained a few minutes after warming to 201 K. There is no noticeable change in the cyclohexane intensity in Figure 1b relative to Figure 1a, as expected from TDS experiments by Rodriguez and Campbell which indicate no significant desorption between 190 and 201 K.[4] In addition to the peaks due to cyclohexane, however, there are new peaks at *m/z* 50, 77, and 78 which indicate that benzene has formed on the surface. Also apparent in Figure 1b are new peaks at *m/z* 54, 67, and the expanded view shows a peak at *m/z* 82. These peaks are indicative that there is cyclohexene on the surface. To our knowledge, this constitutes the first direct observation of cyclohexene as a surface intermediate in this reaction. Additional experiments have shown larger cyclohexene concentrations and that the relative concentrations of benzene and cyclohexene in the reaction mixture at this point are sensitive to the details of the reaction conditions. Previous direct desorption of benzene in this reaction was only recently achieved by Campbell et al., using Bi-postdosing techniques.[3] Conventional thermal desorption conditions (heating rates 5–100 K/s) result in dehydrogenation of benzene and cyclohexene at low coverages, as shown by Rodriguez and Campbell,[18] so that neither product would be observed as desorption products in traditional thermal desorption spectroscopy of this reaction.

The spectrum in Figure 1c was taken after 20 min at 201 K. The absence of a peak at *m/z* 84 indicates that cyclohexane is no longer present on the surface, and the absence of a peak at *m/z* 82 indicates that cyclohexene has also disappeared. There are several peaks that may be assigned to benzene (*m/z* 77 and 78), but the most prominent peaks in the spectrum at *m/z* 39, 41, 42, 54, and 67 are not due to benzene. This is clearly shown by comparing spectra c and d of Figure 1. Figure 1d was obtained after warming the crystal to 314 K. It has been reported that at this temperature only benzene and H_2 are on the surface.[4] The LITD mass spectrum in Figure 1d agrees with this and shows only the peaks normally expected for benzene.[19] The additional peaks in Figure 1c indicate that a distinctly different surface intermediate has formed. While the cyclohexene exists for less than 10 min at 201 K, the other intermediate persists beyond 20 min at this temperature.

Although many C_6 hydrocarbons produce electron ionization fragment ions with masses similar to those in Figure 1c, the relative abundances are quite distinctive for each parent compound. Thus, if one compares Figure 1c with reference mass spectra for the C_6 hydrocarbons,[20] only 1,5-hexadiene shows a close correspondence for both mass numbers and relative abundances. The distinctive features of the 1,5-hexadiene mass spectrum are a lack of parent ion and abundant fragment ions for cyclopropenyl ($C_3H_3^+$, *m/z* 39) and allyl ($C_3H_5^+$, *m/z* 41) as well as significant intensities at *m/z* 54 and 67.[21]

At the low temperatures used in this experiment, it is reasonable to assume that cyclohexene is bonded to the Pt substrate in a di-σ fashion, similar to what is known for ethylene.[22] The di-σ bonded cyclohexene may undergo conversion analogous to olefin metathesis to form the bis(alkylidene), 1,6-hexadialkylidene, shown below. This species is similar to several μ-bis(alkylidene) compounds identified in the organometallic literature.[23-26] Laser desorption of this species would be expected to give a mass spectrum similar to that of 1,5-hexadiene and Figure 1c. Further support for the suggested mechanism is afforded by Macomber et al., who have observed the reverse of this type of reaction.[23] They report the conversion of a (μ-bis(carbene))ditungsten compound to a cyclopentene derivative via an intramolecular carbene–carbene coupling reaction.



cyclohexene 1,6-hexadialkylidene

The high sensitivity of the LITD/FTMS technique has enabled us to identify the reaction product benzene and two intermediates which, when laser desorbed, give cyclohexene and 1,5-hexadiene. Although laser desorption occasionally induces decomposition of surface species during the desorption process, the evolution of a series of spectra taken under identical conditions with only reaction time as a variable must reflect changes occurring on the surface. Our results show that cyclohexene is present in this reaction only over a narrow window of reaction time and temperature. This is consistent with the idea that the initial dehydrogenation of cyclohexane is the slow step, followed by more facile removal of subsequent hydrogens to give benzene. The short lifetimes of the intermediates, combined with the fact that a mixture of several species is present during the conversion, may explain why numerous attempts to detect cyclohexene in this reaction by surface spectroscopic probes have been unsuccessful. However, now that the lifetime and necessary temperature conditions for forming cyclohexene are known (201 K and reaction time less than 20 min), we intend to search again for this species and the bis(alkylidene) intermediate using surface vibrational spectroscopic techniques. In addition, further LITD/FTMS experiments, including kinetics measurements, are being carried out to give a more complete understanding of the dehydrogenation processes involved.

Acknowledgment. We thank Frank J. Feher for many enlightening discussions and acknowledge financial support from

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the donors of the Petroleum Research Fund, administered by the American Chemical Society, from the National Science Foundation (CHE8511999), and from IBM Corporation Research Division.

Registry No. Pt, 7440-06-4; cyclohexane, 110-82-7; benzene, 71-43-2; cyclohexene, 110-83-8; 1,5-hexadiene, 592-42-7.

Geometric Evidence on the Ribonuclease Model Mechanism

Eric Anslyn and Ronald Breslow*

Department of Chemistry, Columbia University
New York, New York 10027

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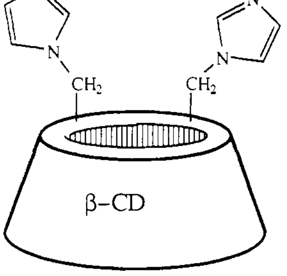
We have described the use of cyclodextrin–bis(imidazole) compounds (**1**) as catalysts for the hydrolysis of 4-*tert*-butylcatechol cyclic phosphate (**2**).[1,2] The reaction exhibited a bell-shaped profile for the plot of V_{max} (the rate at kinetic saturation) vs pH. There was also excellent selectivity for cleavage of one bond of **2**, related to the expected direction of approach of a water molecule assisted by the catalytic imidazole group.[1] This selectivity was reversed to some extent when we changed the geometry of the catalyst by use of a mercaptomethylimidazole, moving the catalytic group further from the binding site.[2]



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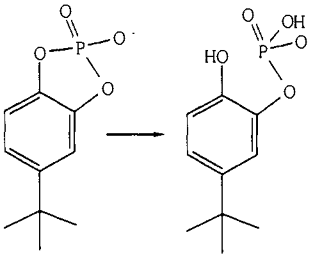

2

The bis(imidazoles) were prepared by imidazole displacements on β-cyclodextrin disulfonates difunctionalized by the Tabushi procedure,[4] by using a rigid disulfonyl capping reagent. We showed that this procedure actually gave a mixture of 6A,6C and 6A,6D isomers (the glucose rings are lettered A to G), different mixtures with different reagents.[2] Tabushi later[5] developed reagents that are rather selective for the three possible isomers—A,B and A,C and A,D—and we have used these procedures to prepare the corresponding bis(imidazoles) by displacement of the sulfonate groups with iodide ion and then imidazole. For the preparation of the A,B disubstituted isomer we cap with 1,3-dimethoxybenzene-4,6-disulfonyl chloride, which we find[6] to be better than the original Tabushi reagent. All three β-cyclodextrin-6,6′-bis(1-imidazole) compounds were carefully purified[7] and evaluated as catalysts for the hydrolysis of **2**.

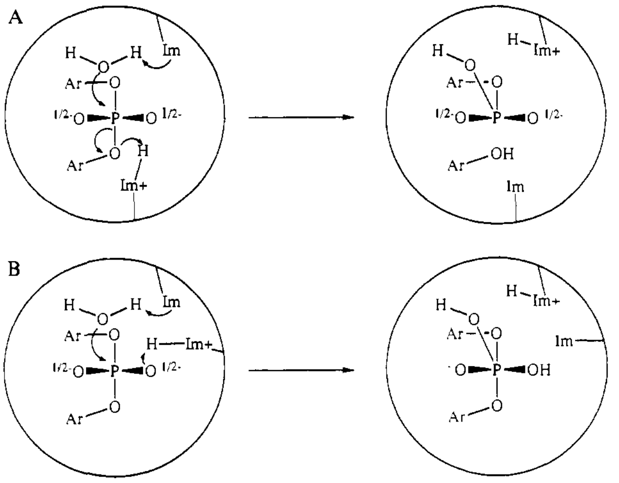

Figure 1. A top view of the bifunctional-catalyzed addition of water to substrate **2**, by the direct displacement mechanism (A) or the proton-assisted addition mechanism (B), forming a phosphorane that cleaves in a later step.

In our original work[1] we invoked a mechanism (Figure 1A) in which one imidazole ring of the catalyst delivers H_2O to the phosphate as the ImH^+ group protonates the leaving phenoxide ion. Models showed that this mechanism was possible with both the 6A,6C and 6A,6D isomers of the catalyst, and it would explain the pH maximum for k_{cat} at catalyst half protonation. The mechanism of Figure 1A is also related to that commonly written[8] for ribonuclease A; an imidazole acts as base, while the ImH^+ is suggested to protonate the leaving group. However, we have recently questioned this picture.[9,10]

The cleavages of RNA (polyU)[11] or of the dimer UpU by imidazole buffers[9] also show bell-shaped pH vs rate plots, but we

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(7) Compound characterizations. Primed atoms represent imidazole atoms. A,B bis(imidazole)–β-cyclodextrin: ^{1}H NMR (D_2O, 297 K) δ 7.51 (1 H, s, H2′), 7.36 (1 H, s, H2′), 6.97 (1 H, s, H4′), 6.82 (1 H, s, H4′), 6.80 (1 H, s, H5′), 6.40 (1 H, s, H4′), 4.97 (1 H, d, H1), 4.87 (3 H, d, H1), 4.84 (1 H, d, H1), 4.80 (1 H, d, H1), 4.72 (1 H, d, H1), 2.90–3.90 (35 H, m with fine structure, H2 & H3 & H4 & H5 & H6); $^{13}C\{^{1}H\}$ NMR δ 47.03, 47.03 (C6 with N attached), 50.36, 60.42, 60.83, (C6), 70.41, 71.53, 71.98, 72.74, 73.33 (C2–C5), 80.62, 81.47, 81.87, 83.43 (C4), 101.15, 102.09 (C1), 120.72 (C5′), 127.80 (C4′), 138.42 (C2′); MS *m/z* 1236 $(M + 1)^+$; Anal. Found (Calcd for $C_{48}H_{74}N_4O_{33} + 6H_2O$) C, 43.12 (42.92), H, 6.42 (6.45), N, 4.05 (4.17). A,C bis(imidazole)–β-cyclodextrin: ^{1}H NMR (D_2O, 297 K) δ 7.53 (2 H, s, H2′), 7.02 (1 H, s, H4′), 6.99 (1 H, s, H4′), 6.88 (1 H, s, H5′), 6.67 (1 H, s, H5′), 4.87–4.82 (7 H, m, H1), 2.90–3.90 (35 H, m with fine structure, H_2 & H3 & H4 & H5 & H6); $^{13}C\{^{1}H\}$ NMR δ 47.64 (C6 with N attached), 59.58, 60.34, 60.66 (C6), 70.99, 71.92, 73.00, 73.19 (C2–C5), 80.88, 81.30, 81.69, 82.94, 83.16 (C4), 101.40, 101.59, 102.06 (C1), 120.54 (C5′), 127.88 (C4′), 138.54 (C2′); MS *m/z* 1236 $(M + 1)^+$; Anal. Found (Calcd for $C_{48}H_{74}N_4O_{33} + 4H_2O$) C, 43.93 (44.07), H, 6.27 (6.35), N, 4.11 (4.28). A,D bis(imidazole)–β-cyclodextrin: ^{1}H NMR (D_2O, 297 K) δ 7.53 (2 H, s, H2′), 7.07 (2 H, s, H4′), 6.89 (1 H, s, H5′), 6.86 (1 H, s, H5′), 4.87–4.82 (7 H, s, H1), 2.90–3.90 (35 H, m with fine structure, H2 & H3 & H4 & H5 & H6); $^{13}C\{^{1}H\}$ NMR δ 47.71 (C6 with N attached), 59.72, 60.39, 60.72 (C6), 70.98, 71.94, 72.46, 73.39 (C2–C5), 81.08, 81.41, 81.85, 83.10, 83.21 (C4), 101.55, 102.17, C1), 120.89 (C5′), 127.85 (C4′), 138.50 (C2′); MS *m/z* 1236 $(M + 1)^+$; Anal. Found (Calcd for $C_{48}H_{74}N_4O_{33} + 4H_2O$) C, 44.19 (44.07), H, 6.32 (6.35), N, 4.05 (4.28). The differing imidazole separations in the three isomers lead to characteristic ^{1}H NMR signals and p*K*'s reflected in Figure 2.

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