nated k_{2A} and k_{2B}), the data yield the following rate constants ($M^{-1}\ s^{-1}$) at 25.0 °C: $k_{2A} = (1.9 \pm 0.1) \times 10^7$; $k_{2B} = (5.9 \pm 0.7) \times 10^6$; $k_{5A} = (1.28 \pm 0.06) \times 10^7$; $k_{5B} = (5.2 \pm 0.2) \times 10^6$. The minor differences between acidic and basic forms are not unexpected; protonation occurs at a site far removed from the reaction center and produces a small effect in the direction expected from inductive effects.[17]

Reactions typified by eq 2 and 5 appear quite general for aliphatic radicals (except benzyl), and most organocobaloximes (except aryls) react similarly. Although the phrase homolytic displacement has been used, it is recognized that a mechanism consisting of radical addition and reductive elimination also agrees with the results. Further kinetic and stereochemical studies are in progress.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract No. W-7405-ENG-82.

Registry No. $PhCH_2Co(dmgH)_2OH_2$, 38721-38-9; $\cdot C(CH_3)_2OH$, 5131-95-3; $\cdot CH(CH_3)OC_2H_5$, 2229-06-3.

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[17] Effects of a similar magnitude were noted in the reaction of Cr^{2+} with benzylaquocobaloxime, a process that also proceeds by the S_H2 mechanism, for which k_A and k_B are 7.3 and 5.0 $M^{-1}\ s^{-1}$, respectively [Espenson, J. H.; Shveima, J. S. *J. Am. Chem. Soc.* **1973**, *95*, 4468].

Chemistry of Cyclic Olefins and Polyenes on Nickel and Platinum Surfaces

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Acyclic olefins and alkynes chemisorb on clean metal surfaces in a largely irreversible fashion because of the facility with which C–H bond breaking occurs from thermally excited states derived from the initial, π-bound chemisorption states. In contrast, cyclohexene and the cyclohexadiene isomers undergo dehydrogenation on clean Ni and Pt surfaces at 0–130 °C to form chemisorbed benzene.[1] Facile dehydrogenation of chemisorbed cyclic olefins is expected because some of the hydrogen atoms bonded to saturated carbon centers will closely approach the metal surface.[2] Accordingly, we projected a dehydrogenation process general to cyclic olefins on clean, atomically flat metal surfaces (1) whereby a delocalized $c\text{-}C_nH_n$ state might be generated at

$$M\text{-}(c\text{-}C_nH_m) \rightarrow M\text{-}(c\text{-}C_nH_n) + M\text{-}H \qquad (1)$$

moderate temperatures. We describe here an ultra high vacuum study[3,4] of C_4–C_8 cyclic olefin and polyene chemisorption on Ni and Pt surfaces. A mechanistic definition for the novel surface mediated conversions of cycloheptatriene and norbornadiene to benzene is also presented.

If the postulated (eq 1) dehydrogenation process prevails, then even-membered rings would produce species *potentially* displaceable as C_nH_n molecules. In fact, cyclobutene chemisorbed irreversibly on Ni and Pt; no hydrocarbon species could be either desorbed thermally or displaced by $P(CH_3)_3$. As noted above, cyclohexene and cyclohexadiene are converted to benzene on all Ni and Pt surfaces.[1] Cyclooctene and 1,5-cyclooctadiene were partially converted to chemisorbed cyclooctatetraene on Pt(111) as established by $P(CH_3)_3$ displacement reactions. Thus, sequence 1 appears to be a common but not necessarily *dominant* one for cyclic olefins with $n(C_n)$ an even number on these[3] surfaces. Only for $n(C_n) = 6$ is sequence 1 the dominant one *established*[1,5] for the surfaces[3] investigated.

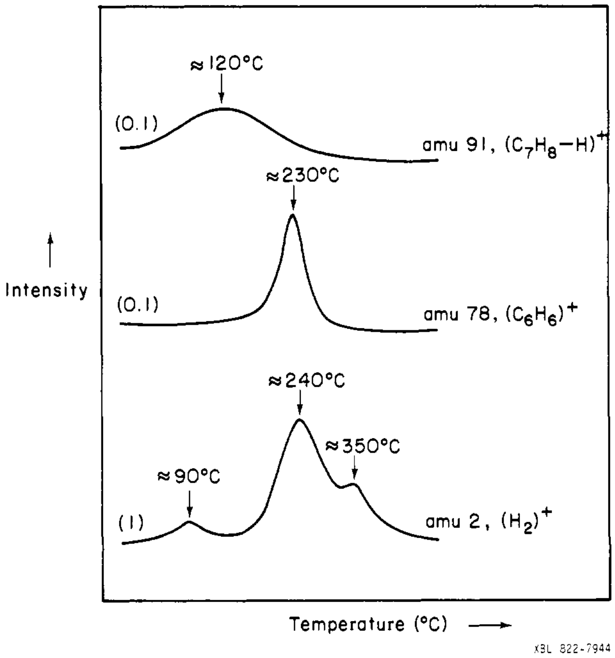

Figure 1. In the rapid heating (20 °C s^{-1}) of Ni(100)–cycloheptatriene, three different species desorbed from this surface: cycloheptatriene, hydrogen, and benzene; these competing thermal processes of reversible cycloheptatriene desorption, decomposition, and benzene formation, respectively, are illustrated with the intensities of the major ions of 91, 2, and 78 plotted as a function of temperature. For normalization of intensities, the parenthetical numbers should be used. The (0.1) value simply indicates that the intensities relative to the (1.0) set should be decreased by a tenth for direct comparisons of intensities of all three molecular species. The low-temperature H_2 desorption maximum observed for Ni(100)–cycloheptatriene coincides with that for Ni(100)–H at comparable H atom coverages—presumably this hydrogen is formed from hydrogen atoms generated in the $C_7H_8 \rightarrow C_7H_7$ process. The two high-temperature H_2 desorption maxima observed for this system and also for Pt(111)–norbornadiene (Figure 2) show that the gross decomposition of the major hydrocarbon fragments is a multistepped process; however, no mechanistic interpretation is warranted based on available data.

For the odd-membered cyclic olefins, sequence 1 would produce a bound C_nH_n "radical" that would not be thermally desorbable or chemically displaceable as a C_nH_n radical. Cyclopentene chemisorption was irreversible on Pt(111) as expected (eq 1),[6]

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[1] Tsai, M.-C.; Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 0000.

[2] (a) Such a stereochemistry in the initial chemisorption state invariably leads to carbon–hydrogen bond breaking on metal surfaces.[1,2b] (b) Muetterties, E. L. *ACS Symp. Ser.* **1981**, *155*, 273.

[3] The metal surfaces studied were Ni(111), Ni(100), Ni(110), Pt(111), Pt 6(111) × (111), and Pt(100) for $n(C_n) = 6$ and Ni(100), Pt(111), and Pt(100) for the others.

[4] (a) The general experimental procedure for these ultra high vacuum studies, the metal surface cleaning protocols, and the Auger spectroscopic and calibration techniques have been described earlier.[1,4b–d] (b) Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 773. (c) Friend, C. M.; Stein, J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 767. (d) Friend, C. M.; Gavin, R. M.; Muetterties, E. L.; Tsai M.-C. *J. Am. Chem. Soc.* **1980**, *102*, 1717.

[5] Reaction sequence 1 may be more general and more dominant than it appears from our thermal desorption and chemical displacement reactions; spectroscopic studies, now in progress, are required to pursue this possibility. A problem in characterization of the reaction 1 hypothesis by desorption or displacement studies is that the binding of a C_nH_n species to a specific metal surface may be too strong for facile displacement and thermal reactivity may be too high to allow characterization by thermal desorption. In the decomposition of cyclobutene on the Pt(111) and Pt(100) surfaces, there were two H_2 desorption maxima of relative intensities of ~2 and 4 with lower temperature maxima at 135 and 100 °C, respectively. These data are consistent with, but do not define, the process

$$Pt\text{-}c\text{-}C_4H_6 \xrightarrow{<100\text{-}135\ °C} Pt\text{-}c\text{-}C_4H_4 + Pt\text{-}H$$

[6] Presumably, cyclopentene generates $\pi\text{-}C_5H_5$ states but our spectroscopic studies of this system are presently incomplete.

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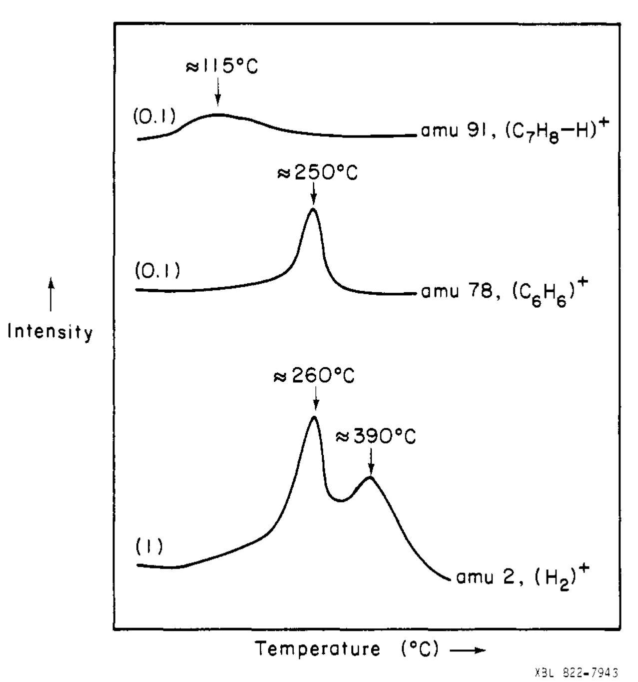
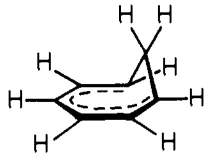


Figure 2. Pt(111)–norbornadiene, formed at 20 °C, when heated at ~20 °C s^{-1} undergoes three competing thermal processes: molecular desorption of norbornadiene[9] (mass 91), decomposition to give hydrogen (mass 2), and conversion to benzene (mass 78). For normalization of intensities, the parenthetical numbers should be used. The (0.1) value simply indicates that the intensities relative to the (1.0) set should be decreased by a tenth for direct comparisons of intensities of all three molecular species. Note that at low coverages, Pt(111)–H yields in the thermal desorption experiment an H_2 maximum at ~130 °C.

and the surface behavior of cycloheptatriene suggested a C_7H_7 intermediate state on Ni(100). Cycloheptatriene chemisorption on Ni(110), Ni(100), Pt(111), and Pt(100) is partially thermally reversible only at high coverages as shown by the respective C_7H_8 desorption maxima at 100, 120, 115, and 115 °C. Cochemisorption of D_2 and cycloheptatriene on these surfaces followed by thermal desorption yielded cycloheptatriene free of deuterium. Hence, the states preceding desorption are molecular. One plausible stereochemistry for molecularly bound cycloheptatriene is **1**, which also can explain a competing C–C bond-breaking process on Ni(100) as discussed below.



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Heating of Ni(100)–cycloheptatriene led to three competing processes: reversible desorption, benzene desorption, and gross decomposition (Figure 1). Benzene formation was a fast reaction only at ~100 °C as shown by $P(CH_3)_3$ displacement of benzene from Ni(100)–C_7H_8 if the crystal was first heated to 100 °C (none was displaced with a 70 °C pretreatment). Consistently, there was a small H_2 desorption maximum at ~90 °C (Figure 1), characteristic of Ni(100)–H. For Ni(100)–cycloheptatriene-7-d_1 desorption, the cycloheptatriene desorbed was C_7H_7D, and the benzene molecules desorbed at 230 °C consisted of C_6H_5D and C_6H_6 in a 6:8 molar ratio. We suggest that a significant fraction of chemisorbed cycloheptatriene can be represented as in **1** and that subsequent processes can represented as in sequence 1. Formation of a Ni(100)–C_7H_7 and Ni(100)–H state below ~100 °C as the precursor state to chemisorbed benzene is consistent with key observations: (i) displacement by $P(CH_3)_3$ of benzene from a Ni(100)–C_7H_8 state heated to 100 °C, (ii) hydrogen desorption at ~90 °C consistent with the formation of Ni(100)–C_7H_7 and Ni(100)–H from **1** below 100 °C, and (iii) the ratio of C_6H_5D to C_6H_6 formed in the conversion of C_7H_7D to benzene.[7] Conversion of chemisorbed C_7H_8-d_1, **1**, to a delocalized C_7H_7 or C_7H_6D surface species would yield a statistical ratio of C_6H_5D to C_6H_6 of 6:8 as observed. No cycloheptatriene was converted to benzene on Ni(110), Pt(111), and Pt(100); why benzene formation from cycloheptratriene is unique to the Ni(100) surface is not understood.

Norbornadiene chemisorption on Pt(111) and Pt(100)[8] was partially reversible with a desorption maximum at ~115 °C. Competitive with desorption of the diene[9] were gross decomposition and benzene formation at high temperatures (Figure 2). Reversible norbornadiene chemisorption on these Pt surfaces only occurs at high coverages. Benzene formation from the chemisorbed norbornadiene on Pt(111) is a high-temperature process occurring at 225–250 °C as established by the thermal desorption spectra in which benzene desorbed at ~250 °C, by the absence of hydrogen desorption below ~180 °C, and by $P(CH_3)_3$ displacement of benzene but only at temperatures above 220 °C.

Adsorption of norbornadiene-7-d_1 on Pt(111) followed by thermal desorption showed that the thermally generated benzene molecules contained no deuterium. Thus, the bridging carbon atom in norborndiene is regioselectively removed in the benzene formation process.[11] The yield of benzene was low (10–20%). For Pt(100), the norbornadiene chemistry was analogous to that for Pt(111) with benzene desorbing at 250 °C (maximum rate); the only substantive difference was the H_2 desorption maxima at ~160, 260, and 400 °C. The benzene produced from Pt(100)–norbornadiene-7-d_1 contained about 15–20% C_6H_5D. Benzene *appears* not to be formed regioselectively from the diene on this surface, but this system is more complicated because of H–D exchange between chemisorbed C_6H_6 and D atoms on Pt(100). We have established that such an exchange process is operative on Pt(100)[12] but not on Pt(111).[10]

Acknowledgment. We thank the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, and the National Science Foundation for support of this research, the Miller Institute for Basic Research in Science for a grant in the form of a Miller Professorship (E.L.M.), and Professor J. R. Wiseman for information concerning the synthesis of cyclobutene.

Registry No. Cyclobutene, 822-35-5; *cis*-cyclooctene, 931-87-3; 1,5-cyclooctadiene, 111-78-4; cyclopentene, 142-29-0; cycloheptatriene, 544-25-2; norbornadiene, 121-46-0; cycloheptatrien-7-d_1, 1541-12-4; norbornadiene-7-d_1, 20504-32-9; 7-chloronorbornadiene, 1609-39-8; cyclooctatetraene, 629-20-9; 1,3-cyclooctadiene, 1700-10-3; Pt, 7440-06-4; Ni, 7440-02-0.

Supplementary Material Available: Synthesis, purification, and spectral characterization data for cycloheptatriene-7-d_1 and norbornadiene-7-d_1 and the desorption and displacement data for cyclooctatetraene and 1,5-cyclooctadiene on Pt(111) (3 pages). Ordering information is given on any current masthead page.

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[7] No conversion of cycloheptatriene to toluene was detected for the Ni(100) surface.

[8] The norbornadiene chemisorption state formed at 20 °C showed that the metal substrate had Pt(100)–(1 × 1) crystallography—an analogous surface crystallography prevails for the benzene chemisorption state formed at 20 °C on this surface plane.

[9] Our mass spectrometric characterization of the hydrocarbon desorbing at this temperature does not distinguish between three plausible C_7H_8 isomers; however, toluene is not the species desorbing from Pt(111) based on established chemistry.[10] We cannot make this distinction for Pt(100).[12] If cycloheptatriene were formed from the norbornadiene on these surfaces, the resultant chemistry would be different and no benzene would be detected.

[10] Tsai, M.-C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 0000.

[11] Regioselective scission of CH_2 from norbornadiene to give benzene cannot proceed directly from an η^4-norbornadiene surface chemisorption state on a flat surface because the CH_2 group would project away from the surface plane in such a state. Possibly, that fraction of the diene molecules converted to benzene molecules is chemisorbed initially through a single olefinic bond with the CH_2 bridging group projected toward the surface plane.

[12] Tsai, M.-C.; Muetterties, E. L., to be published.