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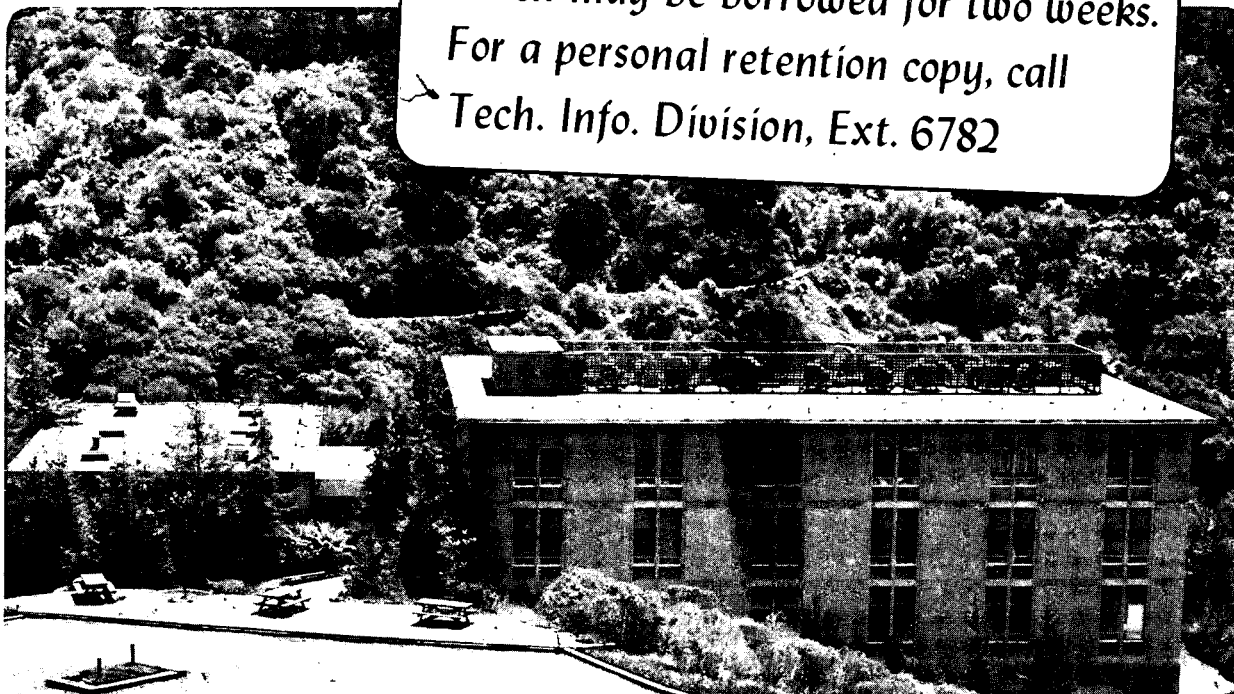
DEHYDROGENATION OF CYCLOHEXANE, CYCLOHEXENE, AND
CYCLOHEXADIENES TO BENZENE ON NICKEL AND PLATINUM SURFACES

M.-C. Tsai, C.M. Friend, and E.L. Muetterties

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Summary Abstract

Dehydrogenation of Cyclohexane, Cyclohexene, and
Cyclohexadienes to Benzene on Nickel and Platinum Surfaces

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The coordination chemistry of cyclic hydrocarbons on single crystal nickel and platinum surfaces has been investigated by thermal desorption spectroscopy, chemical displacement reactions and isotopic labelling experiments. Specifically described here is the dehydrogenation reactions of cyclohexane, cyclohexene and cyclohexadiene to chemisorbed benzene on four low Miller index planes: Ni(111), Ni(110), Ni(100) and Pt(111), and two stepped surfaces: Ni 9(111)x(111) and Pt 6(111)x(111).

Benzene chemisorption is largely molecular in character^{1,2} on single crystal nickel and platinum surfaces; the definitive experiment was the displacement of benzene by trimethylphosphine at room temperatures. No hydrogen-deuterium exchange between chemisorbed C_6H_6 and C_6D_6 was observed on these metal surfaces with the exception of the stepped platinum surface where hydrogen-deuterium exchange was relatively fast at temperatures above 130°C.

Conversion of 1,3- and 1,4-cyclohexadiene to benzene occurred on all the nickel and platinum surfaces at room temperature as established by trimethylphosphine displacement of benzene from the chemisorption state generated by cyclohexadiene adsorption at 20°C. Thermal desorption experiments following adsorption of cyclohexadiene on all the nickel and platinum surfaces also showed desorption of benzene with maximal rates that corresponded closely to those observed for benzene adsorbed on the respective surface. However, there were additional features: (a) For Ni(100)- \underline{c} - C_6H_8 , an additional benzene desorption maximum was observed at 75-100°C, significantly lower than that for Ni(100)- C_6H_6 ; whereas for Ni(110)- \underline{c} - C_6H_8 , the additional benzene desorption maximum was at ~200°C, about 100° higher than that for Ni(110)- C_6H_6 . (b) For Pt(111)- \underline{c} - C_6H_8 , the higher temperature (200-220°C) benzene desorption peak characteristic²

of Pt(111)-C₆H₆ was not observed, and an additional lower temperature benzene desorption maximum was observed at 50°C. Hydrogen-deuterium exchange (C-H bonds) was only evident on the platinum surfaces as established in the experiments wherein D₂ and c-C₆H₈ were co-adsorbed. The surface coordination chemistry of 1,3- and 1,4-cyclohexadiene isomers was qualitatively the same.

Cyclohexene was converted to benzene on all the nickel and platinum surfaces, and this conversion was a more activated process than that for cyclohexadiene conversion to benzene. The rate of the dehydrogenation process was dependent upon the topographic features of the metal surfaces. For example, the rate of dehydrogenation of cyclohexene was high only at temperatures of 100-130°C on Ni(100) and ~70°C on Pt(111). In contrast, the stepped platinum and nickel surfaces converted cyclohexene to benzene at 25°C as established by chemical displacement of benzene by trimethylphosphine after adsorption of cyclohexene on these surfaces at 25°C.

Hydrogen-deuterium exchange reactions for chemisorbed cyclohexene were studied by co-adsorption of a 1:1 mixture of c-C₆H₁₀ and c-C₆D₁₀. None of the nickel surfaces exhibited evidence of hydrogen-deuterium exchange in the process of dehydrogenation of cyclohexene: only C₆H₆ and C₆D₆ were detected in either thermal desorption or displacement reactions. Earlier studies¹ of benzene chemistry on nickel surfaces had also shown no evidence of hydrogen-deuterium exchange between adsorbed C₆H₆ and C₆D₆ (in the case of Ni(100), annealing to 150°C of the surface with a chemisorbed mixture of C₆H₆ and C₆D₆ gave no evidence of hydrogen-deuterium exchange between chemisorbed benzene molecules).

In the dehydrogenation of cyclohexene on the two platinum surfaces, a mixture of all possible C₆H_xD_{6-x} molecules were observed in both the thermal desorption and the displacement reactions, conducted at ~125°C

and $\sim 100^\circ\text{C}$, respectively, for the stepped and (111) surfaces. Since hydrogen-deuterium exchange was not observed² between adsorbed C_6H_6 and C_6D_6 on Pt(111) up to $\sim 130^\circ\text{C}$, the hydrogen-deuterium exchange process in the cyclohexene dehydrogenation on Pt(111) must occur at some intermediate state before chemisorbed benzene is formed. Probably, a similar intermediate exchange occurs for cyclohexene on the stepped platinum surface.

Cyclohexane did not react with any of the nickel surfaces at room temperature or above. Probably, the residence time of cyclohexane was too short for any significant dehydrogenation to occur under these conditions. Only the Pt 6(111)x(111) surface displayed a high activity for the dehydrogenation of cyclohexane to benzene. Dehydrogenation of cyclohexane to benzene had a higher activation energy than the dehydrogenation of cyclohexene to benzene on this surface. Evidence of hydrogen-deuterium exchange between adsorbed $\underline{\text{c}}\text{-C}_6\text{H}_{12}$ and $\underline{\text{c}}\text{-C}_6\text{D}_{12}$ on the Pt 6(111)x(111) was obtained from a thermal desorption study subsequent to an attempted trimethylphosphine displacement whereby all possible $\text{C}_6\text{H}_x\text{D}_{6-x}$ molecules were desorbed at $170\text{-}190^\circ\text{C}$ —a feature similar to that observed for benzene chemisorbed on the stepped platinum surface.

Dehydrogenation reactions were studied over carbon-contaminated surfaces (sub-monolayer coverage). The Ni(110)-C surface was far more reactive in dehydrogenating both cyclohexene and cyclohexadiene than the clean Ni(110) surface. A substantial carbon effect on the chemistry of the other surfaces was not detected.

Rate data for the dehydrogenation to benzene establish the cyclohexadiene transformation as the most facile process, cyclohexene next and cyclohexane least. Thus, the data are not inconsistent with chemisorbed intermediates of cyclohexadiene in the cyclohexene transformation and of cyclohexene and cyclohexadiene in the cyclohexane transformation. In the cyclohexadiene and cyclohexene reactions, it is presumed that the initial chemisorption states primarily involved an interaction of appropriate metal surface orbitals with the π and π^* orbitals of the olefinic or diolefinic systems. This necessarily places one C-H hydrogen atom of the saturated CH_2 centers proximate to the metal surface thus enabling C-H bond scission at these sites and the subsequent generation of chemisorbed benzene. Reversible C-H bond breaking was not detectable for any of the nickel surfaces under the ultra high vacuum conditions, but was for platinum—a result consistent with the relative electronic properties of nickel and platinum.

There is some generality to the metal surface conversion of a cyclic hydrocarbon to a chemisorbed C_nH_n species. Exploratory experiments have demonstrated the conversion of 1,5-cyclooctadiene to cyclooctatetraene on Pt(111).

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References

1. Friend, C.M., and Muetterties, E.L., J. Am. Chem. Soc., 103, 773 (1981).
2. Tsai, M.-C., and Muetterties, E.L., to be published.

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