Fundamental Studies of Hydrocarbon Organization and Reactivity on Platinum Surfaces

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The strength of the interaction occurring between a hydrocarbon and a metal substrate is a major determinant of the molecular organization and its reactivity. In many cases, the strength of the adsorbate-substrate interaction can be divided into two general classes: physisorption and chemisorption.

Physisorption is commonplace for saturated hydrocarbons (both linear and cyclic) on many metal surfaces.¹ Despite the weak nature of the adsorbate-substrate interaction seen for these systems, we observe that there are large perturbations to certain C-H bonds due to significant C-H…M interactions. These perturbations are manifested in a typical reflectionabsorption infrared (RAIR) spectrum by large red shifts of certain C-H stretching modes (usually referred to as "softened modes").^{2,3} Spectroscopic indicators of the perturbed C-H bonds for adsorbed monolayers of *n*-alkanes on Pt(111) (see Figure 1)⁴ exhibit linewidths that are very narrow when compared to those seen for cyclic hydrocarbons on this same substrate (FWHMs of 50 vs. 150 cm⁻¹, respectively). We have convincingly illustrated that the line width of the softened mode(s) observed for monolayers of the *n*-alkanes (and other hydrocarbon systems) on Pt(111) is largely related to site bonding heterogeneity. Narrow softened modes (structured envelope with an intense feature at ~2760 cm⁻¹) for monolayers of *n*alkanes on Pt(111) are observed for three reasons: first, there is a registry of the adsorbate on the surface, second, the octane overlayers order on the surface, and, third, the adsorbates have a small degree of conformational, rotational, or translational disorder (Figure 2).⁵

Since the nature of the softened mode is acutely sensitive to the disorder present in an n-alkane monolayer, we use it as a spectroscopic indicator to monitor phase transitions occurring in monolayers of n-hexane, n-octane, and n-decane on Pt(111). RAIRS data convincingly illustrates that these systems undergo two phase transitions involving reversible two-dimensional to one-dimensional (order-order) and one-dimensional to disordered transformations. Our results are consistent with theory that predicts that the melting of physisorbed monolayers does not have to be a single discontinuous transition; rather, there can exist an intermediate phase whose properties are between those of the ordered solid and the disordered liquid and that the melting of a monolayer can be *continuous*. ⁶⁻⁹

With chemisorption, the adsorbate-substrate strength of the interactions are much greater than those manifested in physisorbed systems. As a consequence, most hydrocarbon overlayers will react rather than desorb upon thermal treatment; unsaturated cyclic hydrocarbons adsorbed on Pt(111) were shown to dehydrogenate/hydrogenate and/or undergo C-C bond scission.¹⁰⁻¹⁷ The nature of the reactions occurring at higher temperatures and the thermolysis products they generate provide important insights into the processes relevant to heterogeneous catalysis.



Figure 1. Reflection-absorption infrared spectrum for a monolayer of *n*-octane on Pt(111).



Figure 2. Proposed disposition of *n*-octane molecules adsorbed on a Pt(111) surface.

Using a combination of temperature-programmed reaction (TPR) and RAIR spectroscopies, we have identified various reaction intermediates of the unsaturated cyclic hydrocarbons (C_5 - C_8) formed as a function of the temperature. The thermal chemistry of 1,3-cycloheptadiene on Pt(111) provides an illustrative example of the reaction intermediates identified spectroscopically in this work. Shown in Figure 3 are the RAIR spectra for a monolayer of 1,3-cycloheptadiene on Pt(111) along with the reaction intermediates formed as a function of temperature. The appearance of new bands (and the disappearance of others) marks the formation of these intermediates. The identification of these intermediates was further assisted by analyzing the C/H stoichiometries of the surface-bound species by TPRS.

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Figure 3. Reflection-absorption infrared spectra for a monolayer of 1,3-cycloheptadiene adsorbed on Pt(111) taken after annealing at the listed temperatures.

Our studies revealed that various types of electronic perturbations occur to the C-H bonds of the hydrocarbons upon adsorption on Pt(111). Not only do we observe the aforementioned "mode softening" due to C-H···M but also we observe that some unsaturated cyclic hydrocarbons exhibit unusually low-frequency C-H stretches due to hyperconjugation. These latter bands appear between 2700 and 2800 cm⁻¹ and are much narrower than those arising from C-H···M interactions. An example of this hyperconjugation effect is seen for η^5 -cycloheptadienyl formed from the thermolysis of 1,3-cycloheptadiene (the mode appearing at ~2770 cm⁻¹, see Figure 3 at 275 K).

Interestingly, all the unsaturated cyclic hydrocarbons dehydrogenate to some extent to form planar intermediates in varying yields:

- cyclopentene and 1,3-cyclopentadiene form a pentahaptopentadienyl (η^{5-} Cp) intermediate;
- cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene form benzene;
- cycloheptene, 1,3-cycloheptadiene, and 1,3,5-cycloheptatriene form a heptahaptoheptrienyl intermediate;
- *cis*-cyclooctene, *cis*, *cis*-1,3-cyclooctadiene, 1,5-cyclooctadiene, and 1,3,5,7-cyclootatetraene form a pentalenyl intermediate.

References

- 1. Somorjai, G. A. Introduction to Surface Chemistry and Catalysis; Wiley: New York, 1994.
- 2. Chesters, M. A.; Gardner, P. Spectrochim. Acta. 1990, 46A, 1011-1015.
- 3. Raval, R.; Chesters, M. A. Surf. Sci. Lett. 1989, 219, L505-L514.
- 4. Hostetler, M. J.; Manner, W. L.; Nuzzo, R. G.; Girolami, G. S. J. Phys. Chem. 1995, 99, 15269-15278.
- 5. Firment, L. E.; Somorjai, G. A. J. Chem. Phys. 1977, 66, 2901-2913.
- 6. Kosterlitz, J. M.; Thouless, D. J. J. Phys. C 1973, 6, 1181-1203.
- 7. Nelson, D. R.; Halperin, B. I. Phys. Rev. B 1979, 19, 2457-2484.
- 8. Zippelius, A.; Halperin, B. I.; Nelson, D. R. Phys. Rev. B 1980, 22, 2514-2541.
- 9. Young, A. P. Phys. Rev. B 1979, 19, 1855-1866.
- 10. Campbell, C. T.; Campbell, J. M.; Dalton, P. J.; Henn, F. C.; Rodriguez, J. A.; Seimanides, S. G. J. Phys. Chem. **1989**, 93, 806-814.
- 11. Henn, F. C.; Diaz, A. L.; Bussell, M. E.; Hugenschmidt, M. B.; Domagala, M. E.; Campbell, C. T. J. Phys. Chem. **1992**, 96, 5965-5974.
- 12. Hugenschmidt, M. B.; Diaz, A. L.; Campbell, C. T. J. Phys. Chem. 1992, 96, 5974-5978.
- 13. Muetterties, E. L. Pure & Appl. Chem. 1982, 54, 83-96.
- 14. Pettiette-Hall, C. L.; Land, D. P.; McIver, R. T., Jr.; Hemminger, J. C. J. Am. Chem. Soc. 1991, 113, 2755-2756.
- 15. Tsai, M.-C.; Stein, J.; Friend, C. M.; Muetterties, E. L. J. Am. Chem. Soc. 1982, 104, 3533-3534.
- 16. Avery, N. R. Surf. Sci. 1984, 146, 363-381.
- 17. Pearlstine, K. A.; Friend, C. M. J. Am. Chem. Soc. 1985, 107, 5898-5901.