

THE ACTIVATION OF CHEMICAL BONDS AT SURFACES

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FINAL TECHNICAL REPORT

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### THE ACTIVATION OF CHEMICAL BONDS AT SURFACES

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This is a summary of the results of a three year effort in surface chemistry research. The ultimate objective is to understand the chemical reactivity of metal and semiconductor oxide surfaces with simple molecules, and to supply fundamental information of importance to the Army as it deals with surface phenomena in diverse technologies such as environmental protection, and chemical cleanup. The work of the three years may be roughly divided into four categories: (1) Development of new surface measurement methods for observing molecular behavior at surfaces; (2) Study of the thermal decomposition of molecules on well defined metal and semiconducting oxide surfaces; (3) Study of the photochemical behavior of adsorbed molecules, and (4) Review articles/presentations.

Twenty seven papers and reviews have been produced in the three years, and these are listed separately later in this report.

A list of research highlights is given below:

#### I. DEVELOPMENT OF NEW SURFACE MEASUREMENT TECHNIQUES

- The behavior of the gas emitted from a collimated beam doser has been mathematically modelled as an aid to the now widespread use of these dosers for accurate exposure control in chemisorption experiments on single crystals.
- High quality infrared reflection absorption spectroscopy has been applied to the study of the thermal activation of a chemisorbed  $\text{PF}_3$  molecule. From an analysis of the variation of the symmetric P-F lineshape with temperature, it was discovered that the thermally induced rotation of the  $\text{PF}_3$  molecule could be detected.

- The use of infrared reflection absorption spectroscopy to follow kinetically the photodesorption of a CO molecule from a NiO surface was demonstrated. This is the first use of this method to study photodesorption, opening up a more incisive way to understand the details of photodesorption.

## II. THERMAL DECOMPOSITION OF ADSORBED MOLECULES

- Isotopic exchange methods were employed to show that the C-O bond in chemisorbed methoxy, O-CH<sub>3</sub>, on Pd(111) does not thermally dissociate into reaction channels which produce either CO or methanol by recombination.
- The chemisorption of O<sub>2</sub> as a molecule has been observed on Pd(111) and its thermal desorption kinetics and interconversion kinetics into adsorbed atomic oxygen species has been characterized.
- The decomposition channels for HCN on Pd(111) have been investigated. Surprisingly, cyanogen, C<sub>2</sub>N<sub>2</sub> desorption as well as HCN polymerization have been detected.
- A thorough investigation of the kinetics of desorption of CO from Pd(111) has revealed that the kinetic parameters measured depend upon the thermal history of the adsorbed layer prior to desorption. This suggests that local structural effects are of great importance in determining the kinetics of desorption. This work employed the threshold temperature programmed desorption method (TTPD) to make very accurate kinetic measurements. TTPD was developed under ARO support here.
- The thermal decomposition of (CH<sub>3</sub>)<sub>2</sub>N<sub>2</sub>, azomethane, was investigated as a starting point for using this molecule in surface photochemistry experiments. It was found that the thermal decomposition in the first chemisorbed layer led to HCN production. Undecomposed molecules, suitable for photochemical studies, exist in the second layer.

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- The CW simulant molecule, dimethyl methyl phosphonate, was studied on Ni(111) and Pd(111), as a function of temperature. Destruction of the molecule by exposure to O<sub>2</sub>(g) occurs on Pd(111) at 1075 K. However, for Ni(111), no such reaction is observed at 1075 K. This experiment, coupled with earlier studies on Mo(110), suggests that the earlier transition metals may be more catalytically active for phosphorus oxidation which is the rate limiting step in maintenance of catalytic activity.
- The decomposition of CO on the Mo(110) surface has been studied carefully by vibrational spectroscopy. An intermediate CO species, bound by both the C and O atoms to the Mo(110) surface has been detected by its unusually low vibrational frequency. This species can decompose thermally, or, if the CO coverage is raised, it can be converted to less strongly bound CO species which will not dissociate.
- The dissociation of ethanol on the Ni(111) surface has been monitored by infrared reflection absorption spectroscopy and other methods. Conformational changes in the orientation of the CH<sub>3</sub> group occurs as the O-H bond in ethanol dissociates, resulting in the C<sub>3v</sub> axis of the group becoming more parallel with the surface.
- The oxidation of chemisorbed P on a high area supported MoO<sub>3</sub> catalyst has been studied by transmission IR spectroscopy. A H-P=O species has been detected in the first stage of oxidation, followed by the production of a phosphoric acid-like species upon extensive oxidation. This surface chemistry, at Torr pressure of oxygen, occurs at 800 K, and may form the basis for the catalytic oxidation of organophosphorus compounds.

### III. PHOTOCHEMICAL BEHAVIOR OF ADSORBED MOLECULES

- The photodissociation of chemisorbed O<sub>2</sub> has been studied thoroughly on Pd(111) surfaces. It was found that excitation of the solid was involved in the activation process leading both to O<sub>2</sub> desorption and decomposition.

- An unusual resonance was observed for the electron impact excitation of chemisorbed O on Pd(111) at about 5eV. The cross section for O desorption is strongly enhanced at this resonance energy, and then falls back at higher electron energies. A model to explain this effect was developed, in which a temporary negative ion is produced and is attracted by coulomb forces to the metal. Deexcitation of this ion places the O atom formed into a repulsive electronic state, causing efficient desorption. This effect is novel and has not been observed previously.
- The photochemical decomposition of  $(\text{CH}_3)_2\text{N}_2$  in the multilayer has been studied carefully. Methyl groups formed photolytically either recombine to produce ethane or extract H from the Pd surface to form methane.
- Chemisorbed CO and NO have been studied as photochemical molecules on Ni and NiO surfaces. For NiO, an interband electronic transition is postulated to be involved in the photodesorption process. High cross sections for photodesorption are observed in the ultraviolet region.

#### IV. REVIEWS

- The photolysis of molecules on well defined surfaces was reviewed at the 4th Japan-China-USA Symposium on Catalysis, July 3-7, 1989, Sapporo, Japan. During this visit, I met many workers from Japan and China, and one outstanding postdoctoral scholar, Dr. Ling Fen Rao, has been brought to my laboratories for work in surface chemistry, some of which is supported by ARO.
- The photochemical behavior of molecules on metal surfaces was reviewed at the 1990 U.S. Army Chemical Research and Development Conference, Aberdeen Proving Grounds.

#### V. RESEARCH AND REVIEW CONTRIBUTIONS

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13. D. K. Paul, L.-F. Rao and J. T. Yates, Jr. "Catalytic Oxidation of Phosphorus on MoO<sub>3</sub> as Studied by Infrared Spectroscopy, submitted to J. Phys. Chem.
14. X. Guo, L. Hanley, and J. T. Yates, Jr., "Photolysis of a Simple Molecule on a Metal Surface - Adsorbed O<sub>2</sub> Dissociation and Desorption on Pd(111)," J. Chem. Phys. 90(9), 5200 (1989).
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## VI. PERSONNEL

The following people have been associated with this project and their current status is shown below:

<u>Name</u>	<u>Status</u>
1. Dr. Xingcai Guo	Oppenheimer Fellow, Cambridge University; Humboldt Fellow, Fritz Haber Institute, Berlin
2. Dr. Adolph Winkler	Faculty, Graz University Austria
3. Dr. Alon Hoffman	Faculty, Australia
4. Dr. Luke Hanley	Faculty, University of Illinois at Chicago
5. Dr. Jun Yoshinobu	Staff Member, Riken Saitama, Japan
6. Ms. Amy Linsebigler	3rd year graduate student - University of Pittsburgh
7. Ms. Xiping Zhang	MS expected (1992)



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|-----|-------------------------|--|
| 8.  | Dr. Ling Fen Rao        | Postdoctoral -<br>University of Pittsburgh                 |
| 9.  | Mr. Luigi Colaianni     | 5th year graduate<br>student - University of<br>Pittsburgh |
| 10. | Professor W.H. Weinberg | University of<br>California -<br>Santa Barbara, CA         |

#### VII. INVENTIONS

One patent was obtained during this period:

V.S. Smentkowski, P.L. Hagans, and J.T. Yates, Jr.  
"Heterogeneous Catalytic Oxidation of Organophosphonate  
Esters", U.S. Patent # 4,871,526, dated October 3, 1989.

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