

20030220238

KEEP THIS COPY FOR REPRODUCTION PURPOSES

AD-A249 266



ATION PAGE

Form Approved
OMB No. 0704-0188

2

average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Avenue, Washington, DC 20503, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE January 27, 1992		3. REPORT TYPE AND DATES COVERED	
4. TITLE AND SUBTITLE The Activation of Chemical Bonds at Surfaces				5. FUNDING NUMBERS DAAL03-89-K-0001	
6. AUTHOR(S) John T. Yates, Jr.					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Pittsburgh Department of Chemistry Surface Science Center Pittsburgh, PA 15260				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P. O. Box 12211 Research Triangle Park, NC 27709-2211				10. SPONSORING/MONITORING AGENCY REPORT NUMBER ARO 26238.19-CH	
11. SUPPLEMENTARY NOTES The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.					
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Studies of the chemisorption, thermal decomposition, and photo decomposition of small molecules on metal and semiconductor oxide surfaces have been carried out. In addition, new methods for research in surface science have been developed.					
14. SUBJECT TERMS chemisorption, photodesorption, surface chemistry				15. NUMBER OF PAGES	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL		

DTIC
SELECTE
MAY 01 1992
S D D

THE ACTIVATION OF CHEMICAL BONDS AT SURFACES

FINAL TECHNICAL REPORT

JOHN T. YATES, JR.

JANUARY 27, 1992

U.S. ARMY RESEARCH OFFICE


RESEARCH AGREEMENT NO. DAA103-89-K-0001

UNIVERSITY OF PITTSBURGH

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

APPROVED FOR PUBLIC RELEASE
DISTRIBUTION UNLIMITED

92 4 28 240

92-11567




FINAL TECHNICAL REPORT
THE ACTIVATION OF CHEMICAL BONDS AT SURFACES
Research Agreement No. DAAL03-89-K-0001

John T. Yates, Jr.
R.K. Mellon Professor of Chemistry
Director, Pittsburgh Surface Science Center
University of Pittsburgh
Pittsburgh, PA 15260
412-624-8320

January 27, 1992

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 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 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-CH₃, on Pd(111) does not thermally dissociate into reaction channels which produce either CO or methanol by recombination.
- The chemisorption of O₂ 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, C₂N₂ 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 (CH₃)₂N₂, 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.

- 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 O₂(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 CH₃ group occurs as the O-H bond in ethanol dissociates, resulting in the C_{3v} axis of the group becoming more parallel with the surface.
- The oxidation of chemisorbed P on a high area supported MoO₃ 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 O₂ 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 O₂ 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

1. A. Winkler and J. T. Yates, Jr., "Capillary Array Dosing and Angular Desorption Distribution Measurements. A General Formalism.," J. Vac. Sci. Technol. A6(5), 2929 (1988).

2. I. Chorkendorff, P. L. Hagans, J. N. Russell, Jr., and J. T. Yates, Jr., "Scanning Kinetic Spectroscopy for Determination of Major Reaction Pathways on Single Crystals," Proceedings of 2nd Nordic Conference on Surface Science, Linköping University, Linköping, Sweden, 1987.
3. X. Guo, J.T. Yates, Jr., V.K. Agrawal and M. Trenary "A Fourier Transform Infrared Reflection Absorption Spectroscopy Study of Chemisorbed PF_3 on Ni(111): Coverage and Temperature Dependence", J. Chem. Phys. 94 (1991) 6256.
4. X. Guo, L. Hanley, and J. T. Yates, Jr., "Thermal Stability of the C-O Bond of Methanol on the Pd(111) Surface: An Isotopic Mixing Study," J. Am. Chem. Soc. 111, 3155 (1989).
5. X. Guo, A. Hoffman, and J. T. Yates, Jr., "Adsorption Kinetics and Isotopic Equilibration of Oxygen Adsorbed on the Pd(111) Surface," J. Chem. Phys. 90(10), 5787 (1989).
6. X. Guo, A. Hoffman, and J. T. Yates, Jr., "HCN Adsorption on the Pd(111) Surface: Surface Temperature and Coverage Dependence," J. Phys. Chem. 93, 4253 (1989).
7. X. Guo and J. T. Yates, Jr., "Dependence of Effective Desorption Kinetic Parameters on Surface Coverage and Adsorption Temperature: CO on Pd(111)," J. Chem. Phys. 90(11), 6761 (1989).
8. L. Hanley, X. Guo, and J. T. Yates, Jr., "Thermal Decomposition of Chemisorbed Azomethane on Pd(111)," J. Phys. Chem. 93, 6754 (1989).
9. X. Guo, J. Yoshinobu, and J. T. Yates, Jr., "Decomposition of an Organophosphonate Compound (Dimethyl Methyl Phosphonate) on the Ni(111) and Pd(111) Surfaces," J. Phys. Chem. 94, 6839 (1990).
10. J. G. Chen, M. L. Colaianni, W. H. Weinberg and J. T. Yates, Jr. "Direct Vibrational Detection of Surface Reaction Channels Leading to CO Dissociation and to its Inhibition on Mo(110)," Chem. Phys. Lett., 177, 113 (1991).
11. J. Xu, X. Zhang, R. Zenobi, J. Yoshinobu, Z. Xu and J.T. Yates, Jr. "Ethanol Decomposition on Ni(111)-Observation of Ethoxy Formation by IRAS and Other Methods", Surface Science 256, 288 (1991).

12. M. L. Colaianni, J. G. Chen, W. H. Weinberg and J. T. Yates, Jr. "The Adsorption and Dissociation of Carbon Monoxide on Clean and Oxygen-Modified Mo(110) Surfaces", submitted to J. Am. Chem. Soc.
13. D. K. Paul, L.-F. Rao and J. T. Yates, Jr. "Catalytic Oxidation of Phosphorus on MoO₃ 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 O₂ Dissociation and Desorption on Pd(111)," J. Chem. Phys. 90(9), 5200 (1989).
15. A. Hoffman, X. Guo, J. T. Yates, Jr., J. W. Gadzuk, and C. W. Clark, "Electron-Stimulated Desorption and Surface Species Conversion: The Observation of a Desorption Resonance for Atomic Oxygen on the Pd(111) Surface," J. Chem. Phys. 90(10), 5793 (1989).
16. L. Hanley, X. Guo, and J. T. Yates, Jr., "Photolysis of Chemisorbed Dioxygen on Pd(111): Dependence on Photon Energy," J. Chem. Phys. 91, 7220 (1989).
17. X. Guo, J. Yoshinobu, and J. T. Yates, Jr., "Photon-Induced Desorption of CO Chemisorbed on the Oxidized Ni(111) Surface," J. Chem. Phys. 92, 4320 (1990).
18. J. Yoshinobu, X. Guo, and J. T. Yates, Jr., "Photodesorption of NO from Chemically Modified Ni(111) Surfaces," J. Chem. Phys. 92, 7700 (1990).
19. L. Hanley, X. Guo, and J. T. Yates, Jr., "Photolysis of Azomethane Adsorbed on Pd(111)," Surface Science 232, 129 (1990).
20. J. Yoshinobu, X. Guo and J. T. Yates, Jr. "Photo-Induced Processes for Chemisorbed O₂ on Pd (111): Effect of Light Polarization," Chem. Phys. Lett. 169, 209 (1990).
21. J. Yoshinobu, X. Guo and J. T. Yates, Jr. "Photodesorption of CO, NO and O₂ from Modified Ni(111) Surfaces," J. Vac. Sci. Technol. A 9(3) (1991) 1726.
22. J. Yoshinobu, T. H. Ballinger, Z. Xu, H. J. Jänsch, M. I. Zaki, J. Xu, and J. T. Yates, Jr. "Ultraviolet Photodesorption of CO from NiC As Measured by Infrared Spectroscopy", Surface Science, 255 (1991) 295.
23. J. T. Yates, Jr., X. Guo, L. Hanley and J. Yoshinobu "Photochemical Studies of Adsorbed Species on Metal Surfaces," 1990 U.S. Army Chemical Research Development and Engineering Center Conference.

24. J. T. Yates, Jr., X. Guo, and L. Hanley, "Photolysis of Molecules Adsorbed on Metal Surfaces," published, proceedings of 4th Japan-China-USA Symposium on Catalysis, July 3-7, 1989, Sapporo, Japan.
25. H. R. Siddiqui, A. Winkler, X. Guo, P. Hagans, and J. T. Yates, Jr., "Chemisorption Site Retention During Thermal Desorption - A Study of O₂ Chemisorption on Pt(112)", Surface Science 193, L17 (1988).
26. A. Winkler, X. Guo, P. L. Hagans, H. R. Siddiqui, and J. T. Yates, Jr., "Coadsorption of Oxygen and HCN on Pt(111) and Pt(112)," Proceedings of Symposium on Surface Science (Kaprun, Austria 1988) Varga & Betz, Eds., p. 105.
27. A. Winkler, X. Guo, H. R. Siddiqui, P. L. Hagans, and J. T. Yates, Jr., "Kinetics and Energetics of Oxygen Adsorption on Pt(111) and Pt(112) - A Comparison of Flat and Stepped Surfaces," Surface Science 201, 419 (1988).

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)

- | | |
|-----------------------------|--|
| 8. Dr. Ling Fea Rao | Postdoctoral -
University of Pittsburgh |
| 9. Mr. Luigi Colaianni | 5th year graduate
student - University of
Pittsburgh |
| 10. Professor W.H. Weinberg | University of
California -
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.