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FINAL REPORT

1. ARO PROPOSAL NUMBER: 23591-CH
2. PERIOD COVERED BY REPORT: 15 June 1986 through 31 August 1989
3. TITLE OF PROPOSAL: Organo Phosphorus-, Nitrogen-, and Sulfur-Containing Molecules on Surfaces
4. CONTRACT OR GRANT NUMBER: DAAL03-86-K-0054
5. NAME OF INSTITUTION: University of Texas at Austin
6. AUTHOR OF REPORT: J. M. White

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1. Statement of the Problem Studied

This research focused on the surface chemistry of organo phosphorus-, nitrogen-, and sulfur-containing molecules, which have relevance for the Army in the area of hazardous chemical environments. These studies were of a fundamental nature, with efforts to understand the molecular level chemistry occurring on both metal and metal oxide surfaces. In many cases, the surfaces chosen have technical/practical relevance, particularly the metal oxides. Studies were carried out in highly controlled environments where surface composition and structure were controlled and measured. A variety of optical, electron, and mass spectroscopies were employed.

2. Summary of the Most Important Results

We successfully examined the detailed surface chemistry of a simulant, dimethyl methylphosphonate (DMMP), dosed onto iron oxide and silicon dioxide. The former is very reactive, and at temperatures in the range of 300 - 500 K, DMMP is decomposed and the iron oxide is converted into a phosphate-type species. On silica, reactions are extremely slow. We also examined the adsorption and decomposition of DMMP on a catalytically active metal, Pt(111). DMMP binds strongly and molecularly to Pt at very low temperatures, but decomposition occurs upon heating to room temperature or higher. The products are carbon monoxide and hydrogen, which desorb, and phosphorus and some carbon, which are retained by the substrate. It remains to be seen whether this material could be operated truly catalytically without self-poisoning by the phosphorus. In any case, on zero-valent Pt, the decomposition reaction is extremely facile and the products are, by comparison to the parent, not particularly hazardous. We have also examined the adsorption and decomposition of phosgene on ruthenium. Ru was selected on the basis of convenience and our long experience with it. While the short supply limits its feasibility for use in a field environment, Ru can be taken as representative of transition metals from the left-hand side of the periodic table. We find that phosgene adsorbed at low temperatures will not decompose readily. It simply desorbs back into the environment. By working at room temperature and above, however, the decomposition of phosgene is rapid but leaves behind chlorine atoms, which are strongly bound to the Ru surface. It does appear possible to remove these chlorine atoms as HCl at elevated temperatures, around 800 K.

In other work, we have used molecules smaller than DMMP in an effort to build up a surface chemistry of phosphorus-containing molecules. In particular, we have studied PF_3 , PH_3 , and $\text{P}(\text{CH}_3)_3$ on clean, K-covered, and Cl-covered Ag(111). This work shows that silver may be a good candidate for a field-based catalytic converter of phosphorus-containing molecules, particularly when the hazardous environment is short-term. The latter appears to be a constraint because the silver surface eventually becomes covered with silver halides if chlorine atoms are involved. These can be removed as silver chloride by momentarily heating the substrate, but some silver is obviously lost in the process.

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As noted in the list of publications, we have also pursued several other small molecule studies on a variety of metal surfaces. These studies, which have been detailed in earlier reports, provide the basis for developing a systematic chemistry of organophosphorus-, sulfur-, and nitrogen-containing compounds on metals.

3. Publications Resulting from the Contract

Published:

1. "A TPD/AES Study of the Interactions of Dimethyl Methylphosphonate with α -Fe₂O₃ and SiO₂," M. A. Henderson, T. Jin, and J. M. White, J. Phys. Chem. **90** (1986) 4607.
2. "The Reaction of H₂S with Adsorbed Oxygen Atoms on Platinum(111)," G. E. Mitchell, M. A. Schulz, and J. M. White, Surface Sci. **197** (1988) 379.
3. "Adsorption and Decomposition of Trimethylphosphine on Pt(111)," G. E. Mitchell, M. A. Henderson, and J. M. White, J. Phys. Chem. **97** (1987) 3808.
4. "The Adsorption of PH₃ on Pt(111) and Its Influence on Coadsorbed CO," G. E. Mitchell, M. A. Henderson, and J. M. White, Surface Sci. **191** (1987) 425.
5. "The Adsorption of Ammonia on Ru(001) and its Effect on Coadsorbed CO," Y. Zhou, S. Akhter and J. M. White, Surface Sci. **202** (1988) 357.
6. "The Adsorption and Decomposition of Dimethyl Methylphosphonate on Pt(111)," M. A. Henderson and J. M. White, J. Amer. Chem. Soc. **110** (1989) 6939.
7. "Comparative Study of PF₃ Chemisorbed on Ru(001), Cu/Ru(001), and Pt(111)," Y. Zhou, G. E. Mitchell, M. A. Henderson, and J. M. White, Surface Sci. **214** (1989) 209.

In press:

1. "The Structure of Phosgene on Ru(001)," M. A. Henderson, Y. Zhou, K. G. Lloyd, and J. M. White, J. Phys. Chem. (in press).
2. "A Comparative Study of PF₃, PH₃, and P(CH₃)₃ on Clean, K-Covered, and Cl-Covered Ag(111)," X.-L. Zhou and J. M. White, Surface Sci. (in press).

Submitted for publication:

1. "Interactions of NH₃, Coadsorbed with PF₃, on Ru(001)," Y. Zhou, Z.-M. Liu and J. M. White, Surface Sci. (submitted).
2. "Initial Cross Section for Phosodissociation of Phosgene on Ag(111)," X.-L. Zhou and J. M. White, J. Chem. Phys. (submitted).
3. "Low Energy Electron-Induced Decomposition of Phosgene on Ag(111)," X.-L. Zhou, S. R. Coon and J. M. White, J. Chem. Phys. (submitted).
4. "Surface Photochemistry of Phosgene on Clean and Iodine-covered Ag(111)," X.-L. Zhou and J. M. White, J. Phys. Chem. (submitted).

4. Scientific Personnel Supported and Degrees Earned

S. Akhter
A. B. Boffa
M. L. Collins
S. D. (Rose) Coon
C. M. Greenlief--(Ph.D. awarded 1987)
B. K. Hance
E. L. Hardegree
M. A. Henderson--(Ph.D. awarded 1988)
G. E. Mitchell--(Ph.D. awarded 1987)
T. Okuhara
Y. Zhou --- (Ph.D. awarded 1989)

The views, opinions, and/or findings contained in this report are those of the author and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.