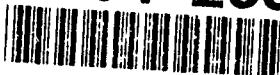


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13. ABSTRACT (Maximum 200 words)

The research is in the area of chemical reactions on surfaces and deals with molecules and solids that model systems of technological and environmental significance to ARO. In particular, we study heteroatom organic adsorbates containing halogens, sulfur, oxygen, phosphorus and nitrogen. The fundamental surface chemical decomposition kinetics of selected molecules, especially simulants, are studied on metal and metal oxide substrates that model technological materials used to destroy and render them harmless. Our goal is to acquire fundamental and quantitative molecular level descriptions of heterogeneous chemical reactions at gas-solid interfaces.

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Phosphorus-, Nitrogen-, Sulfur-, and Chlorine-Containing Molecules on Surfaces

ARO PROPOSAL # 26822-CH

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Statement of the Problem Studied

The research is in the area of chemical reactions on surfaces and deals with molecules and solids that model systems of technological and environmental significance to ARO. In particular, we study heteroatom organic adsorbates containing halogens, sulfur, oxygen, phosphorus and nitrogen. The fundamental surface chemical decomposition kinetics of selected molecules, especially simulants, are studied on metal and metal oxide substrates that model technological materials used to destroy and render them harmless. Our goal is to acquire fundamental and quantitative molecular level descriptions of heterogeneous chemical reactions at gas-solid interfaces.

Summary of Results

Overview. Potentially hazardous materials, both natural and man made, are commonplace. While they often serve useful purposes, above certain concentrations, they are, as their name implies, hazardous. Issues associated with their storage, their utilization, their destruction and their control are being dealt with politically and culturally; in this context chemical sciences, particularly chemical reaction science, can and must provide relevant fundamental factual data if we are to realize reasoned decisions and practices.

Our ARO-supported work has centered on three molecules of direct relevance, phosgene, 2-chloroethyl ethyl sulfide and dimethyl methyl phosphonate, and a number of others whose chemistry is related to hazardous molecule destruction and which are tractable at the molecular level, e.g., phosphines, fluorinated phosphines, chlorobenzene, ammonia, and thiols. The heterogeneous reactions of these have been studied on catalytically active metals, e.g., Pt, Ag, Ni and Ru, often promoted or poisoned with other atoms, e.g., Cl, K, I, S and O. The goal is to characterize the chemical reaction paths through which the hazardous molecules adsorb, rearrange to new species and desorb, and to determine kinetic parameters for these processes in as much detail as our best instrumentation, skills and time will allow. In addition to traditional thermal activation methods, we have turned heavily to photon-activated and electron-activated surface chemistry. We measure and report kinetic parameters that should be useful to engineers who must design and evaluate procedures for safely handling hazardous chemicals in environmentally acceptable and responsible ways.

DMMP, DFP and 2-chloroethyl ethyl sulfide on Pt(111). We are studying the chemistry of dimethyl methyl phosphonate (DMMP), di-isopropyl fluorophosphate (DFP) and 2-chloroethyl ethyl sulfide on Pt(111). In the case of DMMP and DFP on Pt(111), we find that both molecules adsorb molecularly at 85 K and that TPD is dominated by parent desorption. At most, 0.03 monolayer (ML) of adsorbed DMMP decomposes; this leads to gaseous carbon monoxide, hydrogen and water and surface P. No more than 0.01 ML of adsorbed DFP decomposes, producing gaseous carbon monoxide and hydrogen and surface carbon and phosphorus.

For 2-chloroethyl ethyl sulfide, we have examined its adsorption and thermal decomposition on clean and oxygen-covered Pt(111) using FTMS/LITD, temperature programmed desorption and Auger electron spectroscopy. 2-chloroethyl ethyl sulfide is strongly, yet molecularly, adsorbed on Pt(111) at 85 K. For a monolayer coverage, molecular desorption, which occurs between 250 and 380 K, is a minor channel. Extensive decomposition and reaction occur between 300 and 400 K, producing gaseous

hydrogen, hydrogen chloride, ethylene and diethyl sulfide, and surface sulfur and ethylidyne. Ethylidyne dehydrogenates at higher temperatures, leaving carbon along with the sulfur, thereby poisoning the substrate. On atomic oxygen-covered Pt(111), additional reaction products, water and carbon dioxide, are found. Compared to oxygen-free Pt(111), the extent of decomposition does not change significantly and, after temperature programmed desorption, there is less carbon but nearly the same amount of sulfur.

Pre-dosed oxygen temperature programmed desorption (POTPD).

Aiding our insight, we have developed a novel method, pre-dosed oxygen temperature programmed desorption (POTPD), for examining C-H bond cleavage kinetics on Pt surfaces. POTPD is a thermal desorption and reaction technique based on scavenging surface H(a) by small amounts of preadsorbed O(a) to form water. On Pt, this water desorbs at very low temperatures and is easily detected mass spectrometrically. More importantly, when hydrocarbon fragments supply H(a) at temperatures *exceeding* that for H₂O desorption, this water monitors C-H bond cleavage and, thus, characterizes the kinetics of hydrocarbon fragment dehydrogenation. While one must always exercise care in the application of this kinetic approach, it is proving useful in a variety of problems, including the one-armed mustard (2-chloroethyl ethyl sulfide) studies outlined above.

As an example of the detail this technique provides, consider the conversion of CHCH₂(a) to CCH₃(a) on Pt(111). If the pathway involves an intramolecular 1,2-hydrogen shift, then no H₂O will be formed during this process, since no H atoms are bonded to Pt, even transiently. However, if a transient H-Pt bond is involved, then H₂O will be formed. Our results indicate that transient Pt-H bonds are formed beginning about 130 K, consistent with earlier TPSSIMS results, and the conversion from vinyl to ethylidyne has an overall *effective* activation energy of 2.4 ± 0.2 kcal/mol and a pre-exponential factor of $10^{1.4 \pm 0.2}$ s⁻¹.

Contact with Army Laboratories. On October 29, 1991, the PI visited CRDEC (Aberdeen Proving Ground) at the invitation of Dr. Chen Hsu and gave an invited seminar reviewing the Texas work on agent simulants. The day also included substantive discussions with Drs. F. R. Longo, J. Rossin, and Yu-Chu Yang. It is our intention to maintain communication with CRDEC.

Publications and Technical Reports Arising from Contract

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13. M. E. Castro, L. A. Pressley and J. M. White, "Kinetics of the Interaction of Azomethane with Low Energy Electrons on Ag(111)", Surface Sci. 256 (1991) 227.
14. M. E. Castro and J. M. White, "Decomposition of Methanethiol on Ni(111): a TPD and SSIMS Study", Surface Sci. 257 (1991) 22.
15. X.-Y. Zhu, C. R. Flores and J. M. White, "Wavelength Dependent Mechanism of Metal-Adsorbate Photochemistry: Phosgene on Pd(111)", Surf. Sci. 256 (1991) L585.
16. C. R. Flores, X.-Y. Zhu and J. M. White, "The Photodissociation of Phosgene on Pd(111) at 193 nm", J. Phys. Chem. 95 (1991) 9431.

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1. Z.-M. Liu, X.-L. Zhou, J. Kiss and J. M. White, "Interaction of CF₃I with Pt(111)," Surf. Sci. (submitted).
2. X.-L. Zhou and J. M. White, "Predosed Oxygen Temperature Programmed Desorption (POTPD) as a Kinetic Probe of Dehydrogenation on Pt(111)," J. Vac. Sci. Tech. (submitted).
3. X.-L. Zhou, Z.-J. Sun and J. M. White, "Adsorption and Decomposition of 2-Chloroethyl Ethyl Sulfide on Pt(111): A TPD and LTID/FTMS Study," J. Vac. Sci. Tech. (submitted).

Participating Scientific Personnel and Degrees Awarded

Miguel Castro -	Ph.D. May 1991
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Inventions or Patents

None