AD-A282 726

TATION PAGE

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OMB No 0704-0188

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len to Washington Headquarters Services, Directorate for information Operations and Reports, 1215 Jefferson
ice of Management and Budget Paperwork Reduction Project (0704 0188), Washington DC 20503

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE

3. REPORT TYPE AND DATES COVERED
Annual- 1 Mar 93 - 30 Jun 94

4. TITLE AND SUBTITLE
Gas-Surface Interactions Near Dissociation Threshold

5. FUNDING NUMBERS
61102F 2303 ES

(1)

6. AUTHOR(S)
Hanna Reisler and Curt Wittig

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JUL 27 1994
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Univ of Southern California
University Park MC 1147
Los Angeles, CA 90089-1147

8. PERFORMING ORGANIZATION REPORT NUMBER
AEOSR-TR- 94 0458

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR/~~NC~~ NL
Building 410, Bolling AFB DC
20332-6448
Dr Berman

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
F49620-92-J-0168

94-23428

opy

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*
Photodissociation, Molecule-Surface Interaction,
Adsorption, Photodesorption

The 365 nm photodissociation of nitrosyl chloride adsorbed on smooth MgO(100) surfaces at 90 K has been studied with mass spectrometric product detection, as well as state-selective ionization detection of NO. Results of photofragment time-of-flight (TOF) spectra of Cl and NO, state-selective detection of the NO photofragment and temperature programmed desorptions can be rationalized by a mechnism in which ClNO grows on the surface in islands with MgO defects serving as nucleation centers. No significant differences are observed between the rough and smooth surfaces, although the number of defect sites, especially oxygen vacancies, on the latter is substantially reduced. An attempt was made to determine the geometry of the adsorbates on the surface using FTIR. The results did not show any particular order, reinforcing the conclusions of clustering and lack or orientation. Preliminary attempts to dissociate ClNO by impact of hyperthermal Xe atoms led to deposition of Xe on the surface without evidence of dissociation. Collision induced dissociation (CID) of highly excited NO_2 has been observed for well characterized MgO(100) surfaces with parent and product angular resolution at various internal and incident translational energies.

94 7 25 070

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)

AFOSR-TR- 94 0458

AFOSR Grant No. F49620-92-J-0168

Annual Technical Report
March 1993 - June 1994

GAS-SURFACE INTERACTIONS NEAR DISSOCIATION THRESHOLD

Prepared by: Hanna Reisler and Curt Wittig
Chemistry Department
University of Southern California
Los Angeles, CA 90089-0482

Submitted to: Dr. Michael Berman
Program Manager
Directorate of Chemical and Atmospheric Sciences
Air Force Office of Scientific Research
Bolling Air Force Base
Washington, D.C. 20322

I. SUMMARY

The 365 nm photodissociation of nitrosyl chloride adsorbed on smooth MgO(100) surfaces at 90 K has been studied with mass spectrometric product detection, as well as state-selective ionization detection of NO. Results of photofragment time-of-flight (TOF) spectra of Cl and NO, state-selective detection of the NO photofragment and temperature programmed desorptions can be rationalized by a mechnism in which ClNO grows on the surface in islands with MgO defects serving as nucleation centers. No significant differences are observed between the rough and smooth surfaces, although the number of defect sites, especially oxygen vacancies, on the latter is substantially reduced. An attempt was made to determine the geometry of the adsorbates on the surface using FTIR. The results did not show any particular order, reinforcing the conclusions of clustering and lack or orientation. Preliminary attempts to dissociate ClNO by impact of hyperthermal Xe atoms led to deposition of Xe on the surface without evidence of dissociation. Collision induced dissociation (CID) of highly excited NO_2 in the mixed $^2A_1/^2B_2$ electronic system has been observed for well characterized MgO(100) surfaces with parent and product angular resolution at various internal and incident translational energies.

II. PROGRESS REPORT, MARCH. 1993 - JUNE 1994

During this period we submitted a large manuscript, describing our results on the photodissociation of ClNO. The photochemistry of adsorbed ClNO was examined on different MgO(100) crystals, *i.e.* rough versus relatively defect-free. In these studies, it was possible to demonstrate a large, qualitative difference in the photophysics and photochemistry of surface-bound versus gas phase moieties. Namely, the enormous dynamical bias that characterizes the gas phase system was eliminated in the corresponding surface-bound system. In addition we reported the first demonstration of the collision-induced dissociation of highly internally excited NO_2. Specifically, NO_2 seeded in a supersonic molecular beam was excited to levels below D_0 by photoexcitation via its broad ultraviolet absorption system. This prepares excited levels of mixed $^2B_2/^2A_1$ character, since the zeroth-order $^2B_2$ excited and $^2A_1$ ground states are known to be strongly coupled at all energies. Because of the larger $^2A_1$ statistical weight, on average the levels are of predominantly ground electronic state character, ensuring a unimolecular decomposition mechanism. Note that in these experiments it is the *combination* of internal and translational energies which must exceed D_0 for fragmentation to be possible. All our experiments were carried out with well-defined initial conditions and with product-state-resolved detection — an experimental approach that we found very useful and which provided uniquely detailed mechanistic insights.

1. Photodissociation of ClNO on MgO(100)

During this year we completed our studies of the photodissociation of ClNO on smooth Mgo(100) single crystals and summarized them in a comprehensive publication to appear in the Journal of Chemical Physics. Temperature programmed desorption (TPD) and 365 nm photolysis of ClNO adsorbed on MgO(100) at 90 K were investigated under ultrahigh vacuum conditions. The crystal was treated in a way that largely eliminated oxygen vacancies and yielded a relatively smooth surface. Angularly resolved time-of-flight (TOF) mass spectra and state-selective resonance-enhanced multiphoton ionization (REMPI) spectra of NO photoproducts were obtained. The TPD data indicate that ClNO desorbs at surface temperatures above 160 K for exposures (Θ) below 0.2 Langmuirs (L), while for higher values of Θ the main desorption peak is near 120 K. The higher temperature feature, which saturates at $\Theta \sim 0.3$ L is probably associated with binding to defect sites. Thermal desorption is believed to be molecular at all coverages. Irradiation at 365 nm for $0.1 \leq \Theta \leq 5.0$ L yields products having low average translational energies and broad translational energy distributions. NO fragment REMPI spectra were recorded at $\Theta \geq 0.7$ L. The rotational distributions could be fit with a temperature of 110 ± 10 K, *i.e.* comparable to that of the substrate. These results differ from those obtained in the photodissociation of gas-phase ClNO, where the NO fragment has high translational and rotational energies. However, the present results are similar to those obtained on rougher MgO(100) surfaces.

2. Collision-Induced Dissociation of NO_2^* on MgO(110)

Combinations of translational and internal energies were employed for the first time to investigate the CID of molecules incident on a single crystal surface. NO_2 was chosen because of its absorption features and its long excited state lifetimes (*e.g.* ~ 50 µs), which are needed to achieve high concentrations of excited molecules striking the crystal surface. The surface used in the experiment was MgO(100), an inert crystal that should minimize electron induced processes such as those seen on metal surfaces. Specifically, dissociation will be less likely due to electronic interactions with the crystal. The experiment was performed at various internal and incident translational energies, E_{inc}, with parent and product angular resolution and typical crystal temperatures of ~ 400 K. Besides the importance of this experiment to our understanding of activating chemical reactions, as well as intramolecular and crystal excitation, it is also relevant to the recombination of $O(^3P)$ with adsorbed NO.

When the probe laser is set to monitor a specific quantum state of NO and the excitation laser is scanned, a CID yield specrum is obtained. Comparing this spectrum to a similar one obtained under similar conditions in collisions with Ar reveals similar features for NO_2^* CID on MgO(100) and in the gas phase. Both curves carry the fingerprint of the NO_2 absorption spectrum confirming the CID mechanism. For example, the peaks in both CID spectra are the same as those observed in LIF spectra of expansion cooled NO_2.

The NO rotational distributions obtained for two different NO_2^* internal energies and two different values of the angle of incidence are rather similar. The lower and upper spin-orbit states, $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, respectively, have similar populations, with a slightly higher population in the lower spin-orbit state. Overall, the rotational distributions are similar, and correspond to 450 K Boltzmann distributions. Significant differences are only observed at high J".

The angular dependence of the NO state distribution on the scattering angle, θ_s, was investigated at $\theta_i = 40°$. The yield was most intense near the specular angle, $\theta_s = \theta_i$. When monitoring NO at $\theta_s = 70°$, the signal dropped, as with scattered NO, indicating that NO_2^* CID on MgO(100) occurs via direct inelastic scattering rather than trapping-desorption.

The NO rotational distributions are similar for the cases of NO_2^* CID and NO scattered inelastically from MgO(100), and the degree of spin-orbit excitation is also similar for these two experiments, *i.e.* the $[^2\Pi_{3/2}]/[^2\Pi_{1/2}]$ ratio is ~ unity. This is noteworthy, since gas phase NO_2 unimolecular decomposition is known to result in significantly colder spin-orbit ratios, which are thought to be established at large interfragment distances. However, if scattered NO_2 acquires enough internal energy to cause its unimolecular decomposition rate to be in the subpicosecond regime, it will fragment a few Å from the surface, and interaction of the NO product with the surface is inevitable. In this case, the decomposition step cannot be taken as separate from the molecule-surface interaction. The θ_i dependence of the NO distributions suggests that the normal component of E_{inc} contributes more to dissociation than does the parallel component.

3. Work in Progress

Currently two experiments are being carried out. In collaboration with Bruce Koel, the FTIR spectrum of ClNO on MgO(100) is being investigated as a function of coverage. Good signals are obtained even for submonolayer coverages. The preliminary results suggest that ClNO adsorbs without preferred orientation, which is in accord with the interpretation that it aggregates in islands on the surface. Polarization experiments do not show a significant polarization dependence.

In the second experiment we are attempting to dissociate ClNO adsorbed on MgO(100) by impact of hyperthermal Xe atoms. So far, no dissociation products have been detected, but we find that Xe is deposited on the surface. These experiments are continuing.

III. PUBLICATIONS

1. *The photodissociation of ClNO on rough MgO(100) surface*, G. Ziegler, H. Ferkel, L. Hodgson, H. Reisler, and C. Wittig, Can. J. Chem., in press.
2. *365 nm photo-induced dynamics of ClNO on MgO(100)* H. Ferkel, L. Hodgson, J. Singleton, P. Blass, H. Reisler and C. Wittig, J. Chem. Phys., in press.
3. *Molecule-surface collision-induced dissociation of highly excited NO_2 on MgO(100)*, H. Ferkel, J. Singleton, C. Wittig and H. Reisler, Chem. Phys. Lett., **221**, 447 (1994).

IV. PRESENTATIONS AT MEETINGS

1. L. Hodgson, G. Ziegler, H. Reisler and C. Wittig, *Photodissociation of ClNO adsorbed on MgO(100)*, ACS Meeting, San Francisco, April 1992.
2. H. Reisler, *Photodissociation Dynamics of Fast Evolving States*, ACS Meeting, Washington, D.C., August 1992.
3. H. Reisler, *Unimolecular and bimolecular reactions in crossed molecular beams and on surfaces*, Gordon Research Conference on Molecular Energy Transfer, June 1993.
4. H. Ferkel, J. Singleton, L. Hodgson, H. Reisler and C. Wittig, *The photochemistry of ClNO on MgO(100)*, Gordon Research Conference on the Dynamics of Surface Interactions, Aug. 1993.
5. H. Ferkel, J. Singleton,, H. Reisler and C. Wittig, *The collision-induced dissociation of highly excited NO_2 on surfaces*, ACS Meeting, San Diego, March, 1994.
6. H. Reisler, *Unimolecular and bimolecular reactions in crossd molecular beams and on surfaces*, Inf. Conference on Photochemistry, Toronto, May 1994.

V. RESEARCH PERSONNEL

Lori Hodgson — graduate student
James Singleton — graduate student
Peter Blass — postdoctoral fellow
Hans Ferkel — postdoctoral fellow
Bruce Koel — senior collaborator

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