Steric Effect in Electron–Molecule Interaction

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A steric effect has been identified and measured in the interaction of electrons with oriented molecules, for the first time. Photoelectron mediated reactivity has been determined, with a cross section of $\sigma = (3.0 \pm 0.4) \times 10^{-19}$ cm$^2$ (methyl down) for an adsorbed CD$_3$Br on O/Ru(001). A three times smaller cross section was obtained for the bromine down configuration, controlled by oxygen precoverage. A qualitatively similar molecular orientation dependent effect was measured by direct bombardment with 10 eV electrons, however, at much larger cross sections. The significance of the steric effect reported here for electron-transfer processes in general is discussed.

Introduction

Steric effects are among the oldest and most intuitive concepts in chemical reactivity. Chemists have recognized very early that proper mutual orientation of reactants is almost as important as energetic requirements for a successful reactive encounter. One experimental approach to study molecular orientation dependent reactivity has been via molecular beam studies in the gas phase, a focus of interest two decades ago. In these studies, electrostatic hexapole technology has been employed to orient molecules in a beam and then collide them with alkali metals$^{1-4}$ and other electron-donating atoms.$^5$

For many years the multiple and diverse aspects of electron–molecule interactions have been at the focus of basic science research in both chemistry and biology. Studies in this field have included inter- and intramolecular electron transfer,$^6$ transmission$^7-9$ conduction within and through molecules,$^{10,11}$ and dissipative electron attachment (DEA) processes.$^{12-14}$ Recent interest in molecular electronics has brought the basic science in this field closer to modern technology than ever before.$^{8-11}$

Here we present, for the first time, the phenomenon of molecular orientation dependent electron–molecule interaction. Specifically, by tuning of the oxygen coverage on ruthenium, the orientation of methyl bromide could be controlled bromine down or methyl down on O/Ru(001). Similar behavior was reported in the coadsorption system of potassium with water on Pt(111).$^{15,16}$

UV irradiation at a photon energy of 6.4 eV revealed enhanced reactivity of substrate-mediated DEA and electron-stimulated desorption (ESD) of the methyl down orientation by a factor of 3. Similar sensitivity to the molecular orientation, although with a smaller effect, was measured by low-energy electrons directly bombarding the oriented adsorbates, approaching the molecules from the opposite direction, namely the vacuum side.

Experimental Section

The photochemistry experiments described below were performed in an ultrahigh vacuum (UHV) apparatus, described elsewhere in detail.$^{17}$ It is equipped with LEED/Auger, a quadrupole mass spectrometer (QMS) for temperature-programmed desorption (TPD) and for real time detection of desorbing molecules during laser irradiation and electron bombardment. Adsorbates orientation could be determined by means of a Kelvin probe, operated in a differential $\Delta\Phi$-TPD mode as explained elsewhere in detail.$^{17,18}$ A mini excimer laser was operated at 193 nm, 1 mJ/pulse, at variable repetition rate up to 100 Hz. Low-energy electrons at 10 eV kinetic energy bombarded the adsorbate system via a retarding grid that decreased the electrons energy from 100 eV at a typical sample current of 0.1 $\mu$A. The Ru(001) sample, oriented to within 0.1 deg of the (001) plane, could be cooled to 82 K by pumping over a liquid-nitrogen reservoir attached to the sample and heated to 1650 K for annealing, with temperature stabilized to 0.5 deg or ramping of its temperature via resistive heating ac coupled routine. The temperature was monitored by means of a W5Re/W26Re thermocouple.

Results and Discussion

Methyl bromide thermally dissociates on a clean Ru(001) at coverages below 0.2 ML.$^{19}$ Adsorbing 0.25 ML of oxygen on Ru(001) and annealing to 400 K results in an ordered (2 $\times$ 2)O–Ru(001) structure.$^{20,21}$ This oxygen coverage suffices to completely passivate the ruthenium surface against dissociation of CD$_3$Br, as indicated by the absence of any D$_2$ signal in $\Delta P$-TPD (not shown) following CD$_3$Br adsorption on that surface at 82 K. Gradually increasing the annealed oxygen precoverage above 0.25 ML and then covering it by 1.5 ML of CD$_3$Br results in the $\Delta P$-TPD and differential ($d(\Delta\phi)/dT$) $\Delta\Phi$-TPD spectra shown in Figure 1. There are three distinct peaks in $\Delta P$-TPD, denoted $\beta_1$, $\beta_2$, and $\alpha$. The relatively high temperature of the $\beta_1$ peak and its width are associated with binding energy ($E_b$) of 17.8 kcal/mol (resulting from full TPD line shape analysis) of CD$_3$Br molecules to O/Ru and a significant repulsive interaction among the adsorbates. The $d(\Delta\phi)/dT$ spectrum indicates (positive change) that all the $\beta$ molecules adsorb with their bromine end down toward the surface. The $\alpha$ peak at 120 K is due to molecules desorbing from the second layer ($E_a = 7.7$ kcal/mol). As previously discussed in detail,$^{19}$ the second layer of CD$_3$Br on the clean Ru(001) is adsorbed with its methyl
end down (negative change in the $d(\Delta \phi)/dT$ spectrum). Increasing the oxygen coverage above 0.25 ML introduces a new adsorption site ($\beta_2$). These molecules desorb at 160 K ($E_b = 9.6$ kcal/mol).

The total desorption peak area ($\alpha + \beta_1 + \beta_2$ sites) of the methyl bromide $\Delta \Phi$-TPD spectra is invariant with oxygen precoverage to within 5\% of our experimental uncertainty, indicating that the sticking probability of CD$_3$Br is insensitive to the oxygen coverage. The appearance of the $\beta_2$ molecules suggests that as the oxygen precoverage increases, CD$_3$Br molecules are displaced from the $\beta_1$ adsorption sites into the $\beta_2$ sites.

The interesting observation in Figure 1 is that the orientation of the $\beta_2$ molecules is sensitive to the local surface density of adsorbed oxygen. This is inferred from the opposite sign of the relevant $d(\Delta \phi)/dT$ peak at 160 K (Figure 1). This is a justified interpretation of the work function change spectrum as long as no molecular dissociation takes place. In fact, work function interpretation of the work function change spectrum as long as no molecular dissociation takes place. In fact, work function change spectrum as long as no molecular dissociation takes place. In fact, work function change spectrum as long as no molecular dissociation takes place. In fact, work function change spectrum as long as no molecular dissociation takes place.

Once the ability to control molecular orientation has been confirmed it becomes an ideal model system to examine the sensitivity of electron–molecule interaction to molecular orientation by employing substrate-mediated photoelectrons and direct electron-induced desorption and dissociation.

Differential $\Delta \Phi$-TPD spectra following 6.4 eV photons irradiation of 0.8 ML CD$_3$Br adsorbed on 0.6 ML O/Ru(001) (A) and 0.35 ML O/Ru(001) (B), following the indicated irradiation times by 193 nm UV laser irradiation. The photons flux was $2.4 \times 10^{16}$ photons/s at the sample surface. (C) Cross section determination for depletion of the $\beta_1$ and $\beta_2$ differential work function change peaks shown in (A) and (B).

The cross sections obtained this way can clearly be separated into two groups: the removal of the $\beta_1$ molecules (bromine down = BD) in both oxygen coverages and that of the $\beta_2$ molecules on top of 0.6 ML O/Ru is at a cross section $\sigma_{BD} = (1.0 \pm 0.2) \times 10^{-19}$ cm$^2$. In contrast, the $\beta_2$ molecules that reside on top of 0.35 ML O/Ru, and are oriented methyl down (MD), are removed at $\sigma_{MD} = (3.0 \pm 0.4) \times 10^{-19}$ cm$^2$.

We find that molecules adsorbed at the same orientation (BD) but at different binding sites at different adsorption energies ($\beta_1$ and $\beta_2$ over 0.6 ML O/Ru) possess the same overall removal (desorption + dissociation) cross section. At the same time, the more weakly bound molecules that are flipped to the MD configuration are removed at a cross section that is three times larger. It is interesting to note that despite the different electronic configurations of the surface dictated by different oxygen coverage, the molecular orientations MD and BD within the $\beta_2$ sites are bound at exactly the same energy to the surface, as indicated by the TPD data in Figure 1. This, we believe, emphasizes the dominance of the molecular orientation in determining the cross section for the electron–molecule interaction.

Orientation-dependent electron–molecule interaction could be detected also by following the real-time desorption of CD$_3$Br molecules during the UV irradiation. The QMS signal at mass 97 during continuous exposure to photons is shown in Figure 3 (left frames), for the oxygen and CD$_3$Br coverages discussed above. The cross section is extracted from the expression $I(t) = I(0)e^{-\sigma F}$, where $I(t)$ is the QMS signal, $F$ is the photons flux in photons/cm$^2$, and $\sigma$ is the photoelectron-mediated desorption cross section in cm$^2$. As before, only the...
initial $6 \times 10^{18}$ photons are considered. This is important to minimize the influence of photofragments on the tail of the decay curve. The measured cross sections are $\sigma_{BD} = (2.0 \pm 0.1) \times 10^{-19}$ cm$^2$ and $\sigma_{MD} = (2.9 \pm 0.1) \times 10^{-19}$ cm$^2$ for the 0.6 ML O/Ru (BD) and 0.35 ML O/Ru (MD), respectively.

The QMS signal includes photodesorption from both $\beta_1$ and $\beta_2$ sites, but it is insensitive to photofragmentation (DEA). The identical cross section obtained by the real-time QMS detection and the work function change measurements is explained assuming that photoelectron-mediated desorption is the dominant process in the MD configuration (0.35 ML O/Ru). Dominance of the electron-mediated dissociative channel in the MD configuration of the $\beta_2$ molecules would have resulted in smaller integrated differential work function change near 160 K. This is due to the negative work function change contribution of the two dissociation fragments, methyl and bromine,$^{19,22}$ if they separately adsorb on the surface. If fragments (e.g. methyl) are ejected to the gas phase, the overall work function change and thus the measured cross section are again expected to be similar to the electron-mediated parent molecular desorption. A total of $15 \pm 5\%$ of the parent molecules dissociate, and their methyl fragments stay on the surface and further dissociate. This is established by the postirradiation TPD of D$_2$, obtained due to several consecutive photogenerated dissociation events of methyl and smaller fragments on the surface.$^{23,24}$

Real-time desorption was measured also for irradiation with 10 eV electrons, as seen in Figure 3 (right frames). The cross sections for direct electron-stimulated desorption are 4 orders of magnitude larger than those for the photoelectron-mediated desorption. Observations of similar nature were previously reported for a related system.$^{25}$ A steric effect has been measured also in the case of the direct ESD, although a smaller magnitude was detected. As expected, however, the difference between the two orientations has the opposite trend, namely the removal cross section of MD molecules is smaller than that of the BD molecules. As in the photoelectron-mediated case discussed above, also here the difference in the cross section is attributed to steric effect in electron–molecule collision, where the reaction CD$_3$Br $+ e^-$ has a larger cross section when the electron approaches the molecule from the methyl end.

One should consider alternative mechanisms to explain the enhanced probability for both photoinduced and electron-induced desorption of methyl bromide from the O/Ru(001) surface when the methyl faces the direction of approach of the electrons. One such explanation is the enhanced quenching rate at the bromine down (BD) configuration. Such a mechanism may be justified if we consider that most of the negative charge resides on the bromine side of the molecule following electron attachment. In this case, the larger charge density on the bromine side should overlap higher electron density of the metal when the bromine faces the surface since it is closer to the surface than when it is in the methyl down (MD) configuration. Larger charge density overlap often results in shorter excited-state lifetime or faster quenching back to the ground state. Shorter lifetime results, therefore, in a smaller probability for electron-induced desorption, as preliminary wave packet dynamical simulations indicate.$^{26}$ While this argument qualitatively explains the steric effect found in the photoinduced substrate-mediated desorption of methyl bromide at photon energy of 6.4 eV, it cannot simultaneously rationalize the opposite steric effect found in the enhanced electron-stimulated desorption data.

Figure 3. QMS signal at mass 97 (open circles) during irradiation of 0.8 ML CD$_3$Br on 0.35 ML O/Ru(001) (top) and 0.6 ML O/Ru(001) (bottom). Irradiation consisted of photoelectrons generated from 193 nm photons (left panels) and direct 10 eV electrons from the gas phase (right panels). The initial decay was fitted to an exponent (solid line) to extract the cross section for desorption.
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Conclusions

We conclude that the steric effect has indeed been identified and measured, for the first time, within the initial attachment step of the interaction of collimated electrons with preoriented molecules. Control over the molecular orientation of adsorbed CD$_3$Br was achieved by varying oxygen precoverage on Ru(001). When a flux of photoelectrons generated at the bulk metal strikes adsorbed methyl bromide from the methyl end, the overall electron mediated reactivity has a cross section of $\sigma = 3.0 \times 10^{-19}$ cm$^2$, which is three times larger than the cross section determined for the bromine down configuration. Qualitatively similar results were obtained by direct bombardment with 10 eV electrons from the gas phase but at cross sections that are 4 orders of magnitude larger.

The steric effect reported here is central for our basic understanding of electron-transfer processes, among the most fundamental concepts in chemical reactivity. Photosynthesis is an example of a biological system that functions via a cascade of electron-transfer processes. Only in recent years the detailed analysis of the relevant proteins has been scrutinized by means of X-ray diffraction and other structural techniques.

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References and Notes

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