Electron-Transfer–Mediated and Direct Surface Photochemistry: CH_3Cl on Ni(111)

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Direct photolysis and electron-induced fragmentation of CH_3Cl on a Ni(111) surface was observed in time-of-flight studies using 193-nm radiation. With 248-nm radiation, only electron-induced fragmentation was observed. With 351-nm radiation no fragments were observed. The electron-induced process was surface specific, occurring within a limited adsorbate thickness determined by the penetration depth of the excited substrate electrons into the adsorbate. Cross sections are reported as a function of coverage.

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In the photochemistry of molecules on a metal or semiconductor, the surface can play a very important role by perturbing, promoting, or inhibiting the process.[1] Excitation to repulsive states is an important class of surface photochemical processes, since they may be fast enough to escape electronic quenching (5 to 100 fs). However, charge-transfer processes are still fast enough to be important on this time scale.[2] This paper reports a study of CH_3Cl on Ni(111), which clearly shows both a charge-transfer-mediated fragmentation and a direct photolysis. Studies of CH_3Cl and CH_3Br on Pt(111) by Costello *et al.*[3] show fragmentation which is also consistent with such charge-transfer processes.

The ultrahigh-vacuum chamber and experimental conditions were similar to those previously reported.[4] The adsorbed molecules were illuminated with 193-, 248-, and 351-nm laser radiation, at 45° from the surface normal. The laser was pulsed at 10 Hz for 1 to 400 shots; the power was measured every shot and was spatially uniform to within 10%. To avoid significant surface heating, low laser fluences were used, typically 2, 5, and 10 (mJ/cm^2)/pulse for cross section, time of flight (TOF) at 193 nm, and TOF at 248 nm, respectively (fluences defined perpendicular to the direction of light propagation). Molecular desorption due to surface heating was observable at a "threshold" laser fluence of 35 (mJ/cm^2)/pulse for 248-nm radiation, giving a 0.03-eV TOF peak (distinct in arrival time from the fragmentation products). The desorption signal was negligible for all data-collection fluences. The photofragments were detected by a quadrupole mass spectrometer, and time resolved with a Transiac transient digitizer. The ionizer to crystal distance was 7.0 cm; the ion flight times through the detector were 8.0 ± 0.1 μs for CH_3. The surface was monitored by Auger-electron spectroscopy (AES) and thermal desorption spectrometry (TDS), and was cleaned (C, Cl, and S coverages less than 1%) when needed by radiative heating, and/or neon sputtering.

The adsorption of CH_3Cl on Ni(111) was studied by use of TDS and AES, and was similar to CH_3Cl on Ni(100).[5] Adsorbed CH_3Cl desorbs intact with a submonolayer desorption peak at 150 K, shifting to 135 K by 1 monolayer. 1 monolayer is defined as the highest coverage yielding a single TDS peak. The absolute coverage accuracy was about ±50%, but relative coverages are known to better than 1%. The time-integrated TDS spectra were linear with exposure from 0 to at least 10 monolayers. After TDS experiments, AES showed no increase in surface C or Cl. However, after irradiation of the surface with either 193- or 248-nm laser light, surface Cl was observed, increasing with photon exposure to a saturation. The Cl was removed (as $NiCl_2$),[6] and the surface annealed, by heating to 1000 K after each experiment.

The TOF studies of CH_3Cl at 193 nm showed the ejection of CH_3, Cl, and CH_3Cl. The TOF spectra of CH_3 fragments, Fig. 1(a), show two distinct peaks corresponding to fragment energies of 0.6 and 1.3 eV. For coverages less than 1.5 monolayers, no CH_3 TOF fragments were observed. However, fragmentation did take place at coverages of 0.1 to 1.5 monolayers as shown by the production of surface Cl (AES). At coverages above 10 monolayers the slow CH_3 peak height rapidly decreased, being barely visible by 20 monolayers. The *very* broad, slow CH_3 peak is due to cracking of ejected CH_3Cl in the ionizer.[4] The TOF spectra of Cl fragments at 193 nm showed two peaks for coverages of 0.7 monolayer and up; however, one peak was due to CH_3Cl cracking. The Cl fragment signal increased with coverage from 0.7 to 5 monolayers, then remained roughly constant.

TOF spectra of CH_3 at 248 nm showed only one peak, Fig. 1(b), which was nearly identical to the 0.6-eV peak in the 193-nm TOF spectra. No CH_3 TOF signal was observed for coverages below 1.5 monolayers, even though surface Cl production was observed. At coverages above 3 monolayers, molecular ejection was observed due to collisions with fast fragments from neighboring molecules.[4] There was *no* Cl TOF peak observed at this wavelength (except from the cracking of CH_3Cl). Irradiation with 351-nm light gave no TOF fragments or surface Cl.

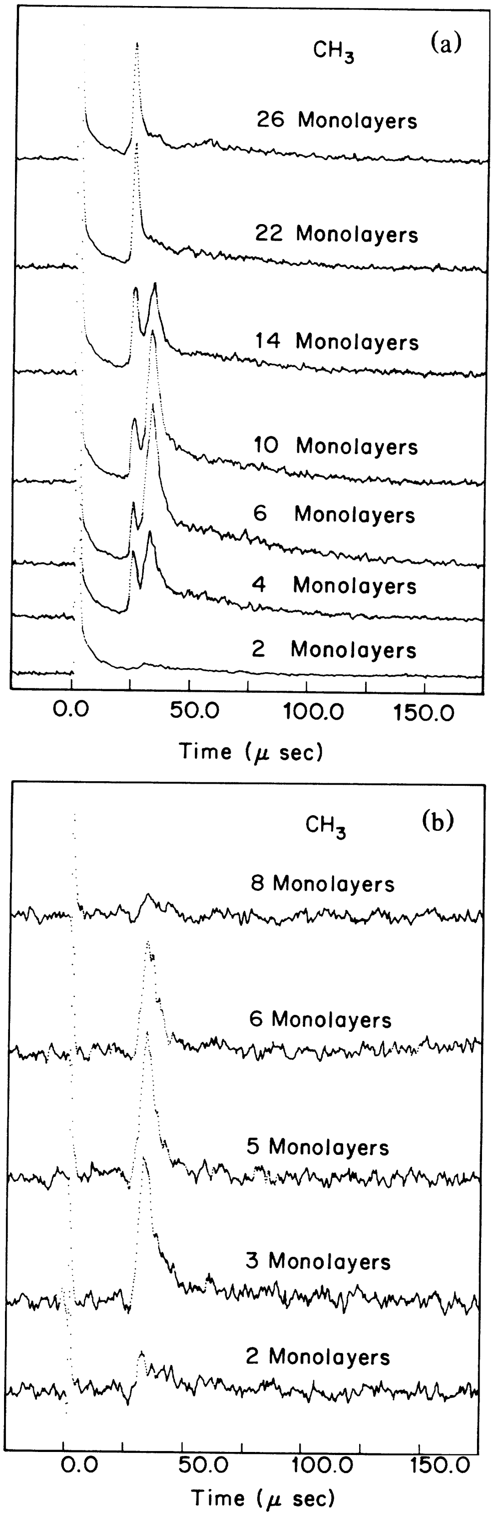

FIG. 1. Time-of-flight signal of CH_3 for CH_3Cl on Ni(111), signal averaged for running at 10 Hz. The peak at time zero is due to scattered light. (a) Use of 100 pulses of 193-nm laser light at a fluence of 4 (mJ/cm^2)/pulse at the crystal; (b) use of 200 pulses of 248-nm laser light at a fluence of 10 (mJ/cm^2)/pulse at the crystal.

Photolysis of CH_3Cl in the gas phase has been studied.[7] From the bond strength, photon energy, and vibrational energy for CH_3 (about 0.5 eV),[8] one would expect CH_3 radicals of about 1.7 eV.[4] This is in very close agreement with the energy of the fast peak's *onset* in the CH_3 TOF $(1.7 \pm 0.06$ eV). Such a well resolved peak could only be due to fragments from the topmost layer of the deposit. Above 5 monolayers this peak remains fairly constant in shape and approaches a limit in intensity, as expected for direct photolysis. No photolysis is seen in the gas phase at 248 nm,[7] and appropriately the fast peak is *not* observed at 248 nm.

The presence of fragmentation at 248 nm has a simple explanation: dissociative attachment by either free or subvacuum excited electrons from the metal. Dissociative electron attachment of CH_3Cl, via a repulsive state, is known to take place in the gas phase.[9] The dissociation energy of CH_3Cl is 3.57 eV,[10] and Cl has an electron affinity of 3.61 eV.[11] In the gas phase the maximum in the attachment cross section is near 0 eV,[12] favorable for interaction with photoexcited substrate electrons.

At 248 nm the CH_3 TOF peak shows complete extinction by 10 monolayers. At or above 10 monolayers the electrons coming from the substrate can no longer reach the top layer, having either attached, or backscattered in the intervening layers. This suggests an effective mean free path for the electrons through the adsorbate of about 7 monolayers, implying a cross section on the order of 10^{-16} cm^2, reasonable for an electron attachment cross section.[13]

The coverage dependences at 248 nm could be attributed to geometric effects. However, this is not the case, since direct photolysis at 193 nm shows that CH_3Cl's are oriented for direct ejection up to the maximum coverage investigated, and the studies at 248 nm are carried out with the same structure.

Electron attachment should lead to Cl^- production for all coverages, *not* neutral Cl. This is consistent with the observation that at 248 nm, there is an increase in surface Cl, but *no* Cl fragments are seen in the TOF spectra (except from cracking). The Cl^- produced would be attracted to the surface by its image charge, which would tend to prevent it from escaping the surface. Escaping Cl^- would not have been detected by our present system.

Electron attachment was also seen at 193 nm as expected. This process was evident in the CH_3 TOF, by the 0.6-eV peak, showing a coverage dependence qualitatively similar to that seen at 248 nm.

Even when electrons cannot reach the topmost layers, dissociative electron attachment should occur in the lower layers. This was shown by measurement of the total cross section for the removal of CH_3Cl per incident photon. The measurement was carried out by use of TDS to determine the amount of CH_3Cl removed as a

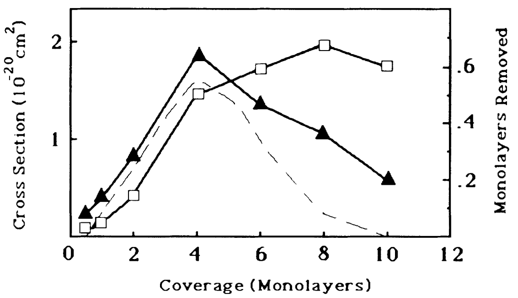

FIG. 2. Coverage dependence of fragmentation at 248 nm: monolayers removed due to fragmentation at constant laser fluence (3×10^{17} photons/cm^2) (□), the cross section for removal of CH_3Cl molecules (▲), integrated TOF signal (arbitrary units) for ejected CH_3 fragments (---).

function of photon fluence.[14]

As shown in Fig. 2, the amount of CH_3Cl removed with a fixed laser fluence at 248 nm increases with coverage to a roughly constant value by 5 monolayers. This coverage is about the same as that required to shield the topmost molecules from surface electrons. The cross sections, shown in Fig. 2, show a decrease at high coverage because they represent the loss of molecules (occurring only in the bottom 5 layers) divided by the *total* coverage.

Figure 2 also shows the CH_3 TOF yield (248 nm). Note that even though the TOF yield is zero at high coverage, fragmentation is still clearly occurring. At 0 to 1.5 monolayers, where the CH_3 TOF yield is also near zero, the cross section is still substantial, showing that C—Cl bond breaking is occurring *without* ejection of fragments.

Measurements at 193 nm yielded cross sections of $(0.43\pm0.04)\times10^{-19}$, $(0.49\pm0.05)\times10^{-19}$, $(0.56\pm0.06)\times10^{-19}$, $(1.8\pm0.07)\times10^{-19}$, $(1.5\pm0.07)\times10^{-19}$, and $(0.84\pm0.06)\times10^{-19}$ cm^2 for coverages of 0.5, 1, 2, 4, 6, and 10 monolayers. This is an order of magnitude greater than seen at 248 nm, which was expected, since at 193 nm direct photofragmentation is possible, and the excited electron flux should be greater.[15]

Studies by Costello *et al.* of CH_3Cl and CH_3Br on Pt(111) showed that fragmentation took place with wavelengths "red shifted" from the gas-phase absorption peaks.[3] It seems likely that their red-shifted fragmentation is due to the *same* mechanism responsible for fragmentation of CH_3Cl on Ni(111) at 248 nm, i.e., charge transfer. However, they specifically concluded that charge transfer was *not* responsible in their case. This was based on the observation that turning on the system filaments, biasing the crystal to +10.4 V, and collecting 100 nA for 4000 s did *not* effect fragmentation.[16] This procedure would have dosed the surface with roughly 3×10^{15} electrons/cm^2 at 10.4 eV or higher. Electron attachment cross sections are known to be *very* energy dependent. So an impact energy of 10.4 eV is likely to be irrelevant for a photoexcited electron attachment process, where the electron energies should be near the vacuum energy level. Additionally, the electron dose would have allowed detection of cross sections of about 10^{-17} cm^2. Trends for energy-resolved electron attachments for alkyl halides (in the gas phase) show peak values on the order of 10^{-16} cm^2, but only very near zero energy.[13,17] Though interesting, the results of Costello *et al.* do not preclude the importance of photoexcited electron-transfer fragmentation in their system.

The fragmentation cross sections at coverages of 1 monolayer or less are about half that seen at 2 monolayers at either wavelength. Below 1 monolayer, very few ejected fragments could be detected, yet the probabilities for the basic processes leading to both the electron attachment and direct photolysis would *not* be expected to decrease at low coverages. At low coverages the coupling to the surface could be *too* strong to allow fragmentation. Before the fragmentation is complete (15 fs) the attached electron (for CH_3Cl^-) or the excited electron (for CH_3Cl^*) can tunnel over to the metal, returning the molecules to a nonrepulsive potential.[18]

Since the gas-phase electron attachment cross section is strongly peaked in energy, only those electrons with the appropriate energy may contribute to the dissociative attachment. Hence, even though the energy distribution of the photoexcited electrons would be different at 193 and 248 nm, the attaching electron could have the same kinetic energy in both cases. The different electron energy distributions could explain the variation in penetration depth with wavelength. At 351 nm, the 3.5-eV photons might have been expected to induce electron attachment, particularly as the CH_3Cl dipolar layer in Ni(111) has been shown to reduce the work function by over 2.5 eV.[19] However, to reach the dipole layer, the electrons should have to surmount a potential close to the clean-surface potential. We believe that the lack of photolysis at 351 nm reflects a negligible electron tunneling rate through this potential barrier.

In summary, we have found that two fragmentation processes took place when CH_3Cl adsorbed on Ni(111) was irradiated with 193-nm light: direct photofragmentation and dissociative electron attachment. The latter process was somewhat dominant at low coverage. The direct photolysis channel was absent when the exciting wavelength (248 nm) was red shifted from the gas-phase absorption region but the electron attachment process was still present. The electron attachment process was surface specific, with its range depending on the excitation wavelength. This process may be important in much of uv surface photochemistry involving adsorbates showing dissociative electron attachment in the gas phase. In addition, this process may take place even when the energy of the exciting photon is less than the substrate work function. Thus, such a system could have applications for the detection of "hot" electrons in the substrate. Alternatively, the process could be used to produce reactive radicals or ions within a variable distance from the surface.

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