Photochemistry of adsorbed molecules. XII. Photoinduced ion–molecule reactions at a metal surface for CH3X/RCl/Ag(111) (X=Br, I)

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A photoinduced ion–molecule reaction is reported between superimposed molecular layers of alkyl halides on a metal substrate $CH_3X/RCl/Ag(111)$ (where X=Br or I and R=CCl_3, $CHCl_2$, or CH_2Cl) to form CH_3Cl(ad) (wavelengths 193, 248, and 350 nm). The reaction is mediated by charge-transfer (CT) photodissociation, in which photoelectrons from the metal surface transfer to the lower layer of adsorbate RCl to form RCl^-. These negative ions then react with the upper layer CH_3X in an ion–molecule reaction to form CH_3Cl+X^-. The yield of product CH_3Cl is found to be enhanced at ~1 ML of adsorbed CH_3X (upper layer) due to a decrease in the local potential in the region of the adsorbate–adsorbate interface that enhances the probability of CT to the lower layer. In addition to lowering the local potential at the interface, the adsorbed CH_3X also lowers the surface work function; as a result changes in the microscopic local potential correlate (via the CT reaction rate) with changes in the observed macroscopic work function. The yield of CH_3Cl decreases at still higher CH_3X coverage in the upper layer as the work function increases. The ion–molecule reaction gives evidence of being a concerted process in which the Cl^- reacts as it separates from RCl^- rather than following separation. The reagent RCl^-, as in the surface reaction discussed in the previous paper, is formed by CT from "hot" electrons rather than free photoelectrons.

I. INTRODUCTION

Photoelectron induced dissociation of molecules at surfaces has been implicated in a number of studies of the photodissociation of molecules at metal surfaces.[1] The study of these "half-reactions" is therefore important to a full understanding of photoinduced chemical processes. In recent work,[2] we have studied photoelectron induced charge-transfer (CT) dissociation of chloromethanes on the Ag(111) surface. The most significant observations were (i) Cl^- anions desorbing from the surface following UV laser irradiation and (ii) CT photoreaction of adsorbed chloromethanes with the metal surface to form Cl–Ag(111). We now report the observation of a photoreaction between the anions formed by photoinduced CT and a coadsorbed overlayer.

The principal observation of the present study is the formation of CH_3Cl by a photoinduced reaction between CCl_4 (or $CHCl_3$ or CH_2Cl_2) on the Ag(111) surface and an overlayer of CH_3X (X=Br, I). The experimental situation is depicted in Fig. 1; the bottom layer A (usually CCl_4) and the top layer B (CH_3X; X=Br, I) are shown adsorbed on the Ag(111) surface. Our findings point to the fact that the mechanism for this photoinduced reaction is the formation of RCl^- ions due to a charge-transfer process from the surface to the adjacent RCl (R=CCl_3, $CHCl_2$, CH_2Cl) followed by an ion–molecule reaction of the negative ion RCl^- with CH_3X to yield CH_3Cl+X^-,

$$CH_3X/RCl/Ag(111) \xrightarrow{h\nu} CH_3X/(RCl^-)^{\ddagger}/Ag(111)$$

$$\rightarrow X^- + CH_3Cl/R/Ag(111). \qquad (1)$$

In this equation, we have indicated the transitory nature of the unbound negative ion RCl^- by designating it as a transition state ($\ddagger$). This study extends the previous work on the CT photochemistry of chloromethanes on Ag(111) by demonstrating the important role that CT processes can play in photochemical reactions between coadsorbates at surfaces.

II. EXPERIMENTAL METHOD

The experiments were performed in an ultrahigh vacuum chamber[3] with a base pressure of 1×10^{-10} Torr. The Ag(111) single crystal was prepared according to a published recipe[4] and its surface cleanliness was monitored using Auger electron spectroscopy. The sample was mounted on a tantalum plate that was electrically isolated by sapphire sheets from a liquid-N_2 cooled mount that could maintain a sample temperature of 105 K. The sample could be heated to 800 K by electron bombardment heating using a tungsten filament located behind the sample holder.

Ultraviolet radiation was obtained from an excimer laser (Lumonics TE-860) using ArF, KrF, and XeF laser lines giving 193, 248, and 350 nm radiation, respectively. Light from the laser was directed upon the sample at a glancing angle of 77° from the surface normal. For the photoinduced reaction experiments, laser fluences of ~1 mJ/cm² were used. The amount of surface heating due to the incident laser pulse was estimated[5] to be less than ~2 K, so thermal effects could be excluded. The photoelectron emission from the sample was monitored using a charge-sensitive preamplifier (Canberra 1405) connected to the sample at laser fluences ~1 μJ/cm².
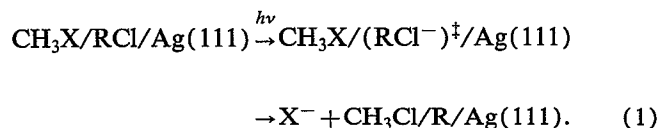
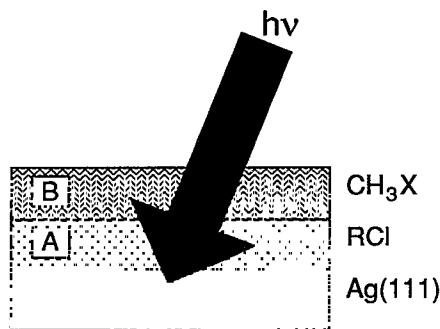FIG. 1. A schematic diagram of the surface used in these experiments; layers A (CCl_4,$CHCl_3$) and B (CH_3X; X=Br, I) are adsorbed sequentially on top of the Ag(111) surface.

Temperature programmed desorption (TPD) of molecules from the Ag(111) surface was measured by means of a quadrupole mass spectrometer (Extrel 4-270-9). The TPD spectra were obtained by monitoring the mass spectrometer signal as the sample temperature was raised by radiative heating using the sample heating filament. Temperatures were measured by a chromel–alumel thermocouple mechanically connected to the sample. The thermocouple voltage was measured by a digital voltmeter (Fluke 8860A). Both the sample temperature and mass spectrometer signal outputs were read as the sample temperature was increased at a heating rate of ~4.5°/s.

The CCl_4, $CHCl_3$, CH_2Cl_2 (Caledon Laboratories), and CH_3I (Fischer Scientific) liquids were placed in Pyrex bulbs on the gas handling rack, and were degased by freeze/pump/thaw cycles. The room temperature vapor was used to fill the Pyrex and Teflon gas-handling line. The CH_3Br and CH_3Cl gases (Matheson) were used without further purification. The gases were background dosed onto the crystal. Gas doses were measured in Langmuirs (1 L=1×10^{-6} Torr s) and were corrected for the relative ion-gauge sensitivity[6] as follows: CCl_4, 6.0; $CHCl_3$, 4.8; CH_2Cl_2, 3.7; CH_3I, 4.2; CH_3Br, 3.7; CH_3Cl, 3.0.

III. RESULTS AND DISCUSSION

A. Observation of photoreaction between CCl_4 and CH_3X

Irradiation of the bilayer system $CH_3X/CCl_4/$ Ag(111) with UV excimer laser light resulted in the formation of CH_3Cl product. Figure 2(a) shows a sequence of thermal desorption spectra obtained from 1 ML CH_3Br on top of 2 ML CCl_4 after irradiation by 248 nm light. Figure 2(b) shows the total integrated yield of CH_3Cl plotted as a function of the number of 248 nm photons used. For this range of laser fluence, the yield of CH_3Cl photoproduct was linear with the number of incident photons. We have also measured the yield of CH_3Cl as a function of the incident laser power in the 0.2–2.5 mJ/cm^2 range for a fixed number of laser shots; the yield was once again linear with laser power, indicating a single-photon photoreaction mechanism consequent on single-photon charge-transfer dissociation.[2]
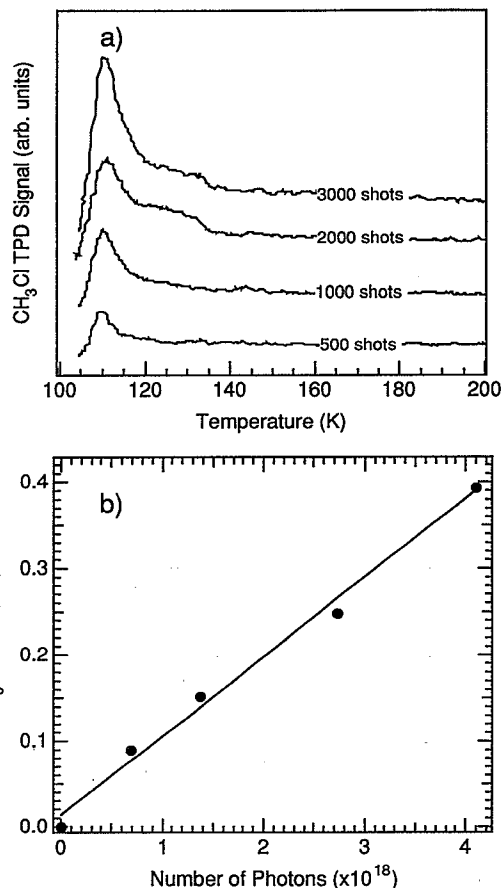

FIG. 2. (a) A series of thermal desorption spectra of CH_3Cl is shown after photoreaction between CH_3Br and CCl_4 on Ag(111) as a function of the number of laser shots. (b) The yield of CH_3Cl in monolayers as a function of the number of incident photons.

B. The effect of layer "B" thickness—varying the CH_3X coverage

In Fig. 3, we show the measured yield of CH_3Cl photoproduct formed at the surface as a function of the amount of CH_3Br reagent adsorbed as layer B on top of a 2 L dose of layer A CCl_4/Ag(111). The two layers were adsorbed by dosing CCl_4 first and then CH_3Br. The sample was irradiated with 3000 laser pulses of ~1 mJ/cm^2. The CH_3Cl yield was measured by integrating the thermal desorption signal at 50 amu. Figure 3(a) shows the yield of CH_3Cl obtained using 248 nm radiation and Fig. 3(b) shows the yield curve at 350 nm. Qualitatively, the yield of CH_3Cl increases for low coverages of CH_3Br and then decreases for coverages above ~1 L. The decrease in yield is steeper for 350 than for 248 nm. In Fig. 4, we observe that the photoyield of CH_3Cl from $CH_3I/CCl_4/$Ag(111) has the same qualitative features as in the case of layer B being CH_3Br (Fig. 3). The yield increases at low coverage and eventually decreases beyond ~2 L coverage. Once again the decrease is steeper for 350 nm.

Comparison between the data for CH_3Br (Fig. 3) and CH_3I (Fig. 4) shows that the rates of increase and decrease in product yield (CH_3Cl) were more pronounced when
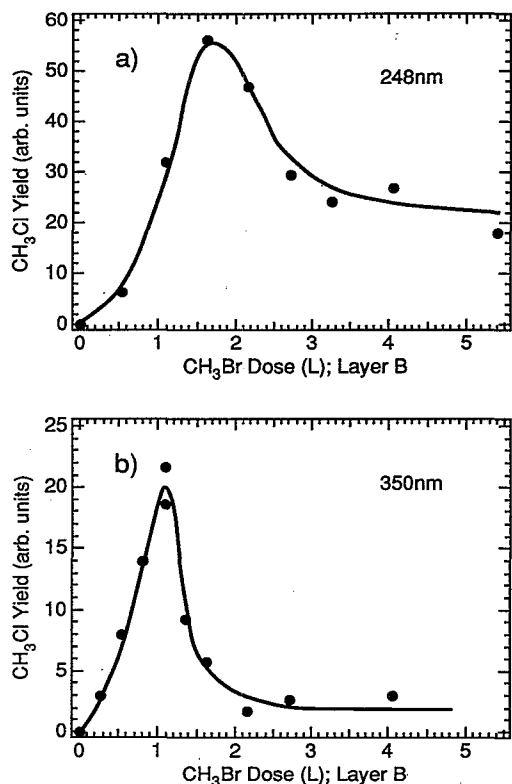
FIG. 3. Photoyield of CH_3Cl after irradiation of $CH_3Br/CCl_4/Ag(111)$ with (a) 248 and (b) 350 nm light, as a function of the CH_3Br (layer B) dose. The CCl_4 coverage (layer A) was fixed at 2 L.

FIG. 4. Photoyield of CH_3Cl after irradiation of $CH_3I/CCl_4/Ag(111)$ with (a) 248 and (b) 350 nm light as a function of the CH_3I (layer B) dose. The CCl_4 coverage (layer A) was fixed at 2 L.

layer B was CH_3Br. Similar results (not shown) were obtained at 193 nm for both CH_3Br and CH_3I on CCl_4, but with a less pronounced peak in the CH_3Cl yield than at 248 or 350 nm. For either layer B, the peak in product yield grew progressively more pronounced in going from 193 to 248 and then to 350 nm. These observations are consistent with photoinduced charge transfer to form RCl^- followed by ion–molecule reaction to yield CH_3Cl (see Sec. III D below).

Temperature programmed desorption experiments showed that the two-layer system $CH_3X/CCl_4/Ag(111)$ was composed of a distinct bottom layer (A) of CCl_4 in contact with $Ag(111)$ and a top layer (B) of physisorbed CH_3X. On bare $Ag(111)$, it was found that CH_3Br desorbed at 135 K and CH_3I desorbed at 195 K, in agreement with Zhou et al.[7] The desorption of CCl_4 from $Ag(111)$ is complex,[2] but the ~2 L CCl_4 layer that we used in the present experiment desorbed between 170 and 210 K. When CH_3X (X=Cl, Br, I) was adsorbed as layer B on top of $CCl_4/Ag(111)$, CH_3X desorbed at ~110 K [i.e., lower than on bare $Ag(111)$], indicating that the physisorption bond of CH_3X with the CCl_4 layer beneath was weaker than that between CH_3X and $Ag(111)$. The CCl_4 desorption temperature (170–210 K) was not affected by the CH_3X adsorption. When the order of dosing was reversed (CH_3X first as layer A, then CCl_4 as B), the TPD features were unchanged, i.e., CH_3X desorbed alone at 110
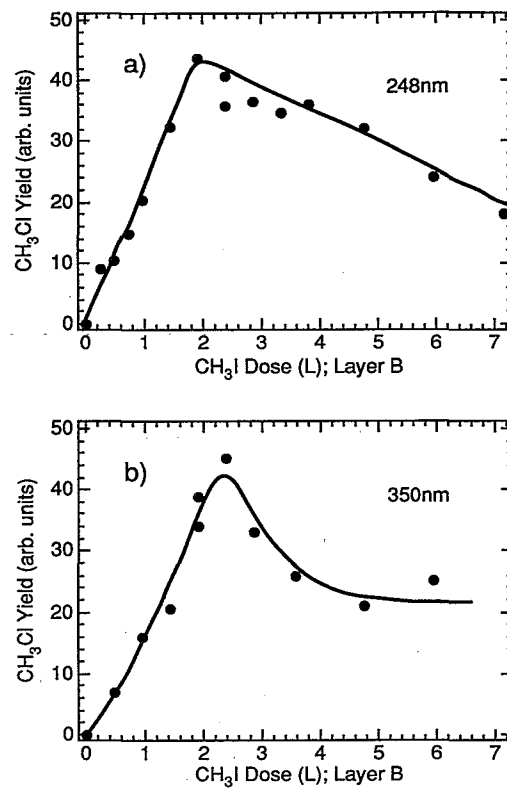
K, indicating that CCl_4 had displaced CH_3X from the surface due to its higher heat of adsorption. [At submonolayer CCl_4 coverage plus ~1 ML of CH_3Br, it was possible to see both the $CH_3Br/Ag(111)$ and the $CH_3Br/CCl_4/Ag(111)$ thermal desorption peaks.]

The higher binding energy for the adsorbed CCl_4, evidenced by the above experiments, coupled with the observations in regard to successive dosing of CCl_4 and CH_3X, indicated that there was little mixing between the CCl_4 and CH_3X adlayers. The observed reaction between these adlayers can be viewed as occurring at the interface between them.

C. Reaction mechanism

A mechanism mediated by direct photolysis in which neutral radicals (CH_3 from CH_3X, or Cl from CCl_4) react with the adjacent layer to form CH_3Cl can be discounted. This is because the wavelength dependence of the photoreaction cross section differs markedly from the gas-phase photolysis cross sections for CH_3Br, CH_3I, or CCl_4. Specifically, the gas-phase cross section for CCl_4 photolysis to produce Cl decreases by three orders of magnitude in going from 193 to 248 nm (Ref. 8) and decreases still further at 350 nm. By contrast, the surface reaction between CH_3X and CCl_4 were observed with comparable yield at 248 and 350 nm (Figs. 3 and 4). Thus direct photolysis of CCl_4 can be excluded as the source of Cl that forms CH_3Cl from

CH_3X. Similarly, the cross section for CH_3Br photolysis decreases by two orders of magnitude between 193 and 248 nm.[9] The photolysis cross section for CH_3I decreases by two orders of magnitude in going from 248 to 350 nm,[10] so the observed yields in Figs. 3 and 4 are also not consistent with CH_3X photolysis as the primary step in forming CH_3Cl. It would appear that direct photolysis of the reagents was not the dominant mechanism in forming the CH_3Cl product.

The wavelength dependence of the product (CH_3Cl) yield was consistent with a mechanism involving photoelectron and/or hot electron formation as a required step. Photons incident upon the metal substrate can excite valence-band electrons into states above the Fermi level E_F, creating excited electrons with energies between E_F and $E_F + h\nu$. Electrons having sufficient energy to escape the surface are referred to as "free" photoelectrons and those having energies between the Fermi level and the vacuum level as "hot." In our experiments, both free and hot photoelectrons could be generated at 248 and 193 nm, while at 350 nm ($h\nu = 3.5$ eV), only hot electrons could be formed. The CT photodissociation mechanism requires electrons of appropriate energy[2] to be captured by the target molecule RCl in order to cause dissociation.

We can also exclude the possibility that it is the layer B (CH_3X) molecules that are dissociated by photoelectrons $e^- + CH_3X \rightarrow CH_3 + X^-$, with subsequent reaction $CH_3 + CCl_4 \rightarrow CH_3Cl + CCl_3$. The cross sections for photoreactions to give CH_3Cl in $CH_3Br/CCl_4/Ag(111)$ and $CH_3I/CCl_4/Ag(111)$ (see Figs. 3 and 4) are similar. However, the gas-phase dissociative attachment of CH_3I has a cross section $\sim 10\times$ greater than that for CH_3Br.[11] If the observed photoreaction was mediated by the dissociation of layer B (CH_3X), then one would expect a substantially larger reaction cross section for $B = CH_3I$ than for $B = CH_3Br$. Furthermore, the neutral reaction $CH_3 + CCl_4 \rightarrow CH_3Cl + CCl_3$ has a barrier of ~ 0.45 eV,[12] hence CH_3 that collides inelastically in the adsorbed state prior to encountering RCl will no longer be able to surmount the barrier to form CH_3Cl.

The most probable reaction mechanism is CT photodissociation of the adsorbed RCl (CCl_4, $CHCl_3$, or CH_2Cl_2) in layer A, followed by a reaction between the resulting negative ion and CH_3X in layer B. We have recently found that photoinduced CT is an efficient mechanism for the formation of $(RCl^-)^\ddagger$ adsorbed on Ag(111).[2] In the gas phase, electron attachment to CCl_4, $CHCl_3$, and CH_2Cl_2 has an extremely large cross section for very low electron energies [$\sigma_{tot}^g \rightarrow \sim 1 \times 10^{-14}$ cm^2 for $E \sim 0$ eV (Ref. 13)]. This cross section is larger than the physical extent of the molecule ($\pi r^2 \sim 2 \times 10^{-15}$ cm^2). The ion–molecule reaction $Cl^- + CH_3X \rightarrow CH_3Cl + X^-$ has been studied extensively in the gas phase; it has no energy barrier[14] and exhibits the large cross-section characteristic of ion–molecule reactions. We shall argue that in the present case, it is more reasonable to write the reaction as $(RCl^-)^\ddagger + CH_3X \rightarrow CH_3Cl + R + X^-$ to stress that Cl^- need not escape from RCl^- before entering into an ion–molecule reaction.
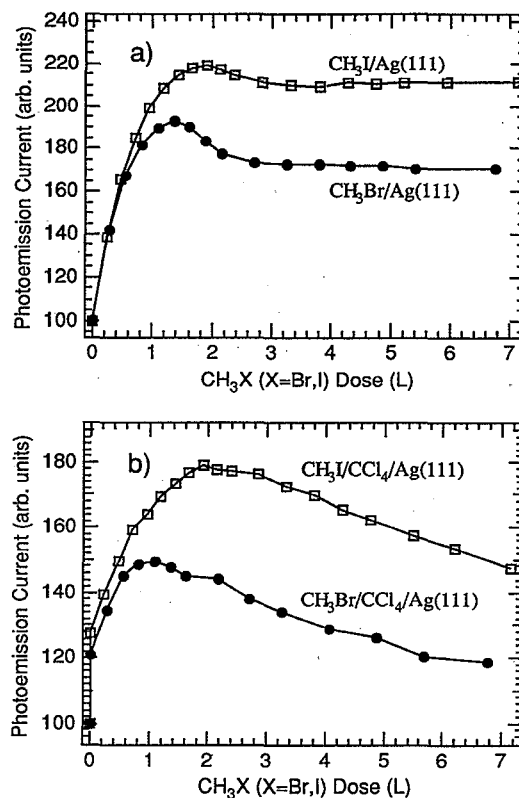

FIG. 5. Photoelectron emission from the sample, measured during 248 nm laser irradiation. (a) Photoemission from $CH_3X/Ag(111)$ from CH_3Br (circles) and from CH_3I (squares). (b) Photoemission from $CH_3X/CCl_4/Ag(111)$; CH_3Br (circles); CH_3I (squares).

D. Correlation of reaction yield with photoelectron emission

Evidence for the role of photoexcited electrons in the CH_3Cl reaction yields of Figs. 3 and 4 was obtained by measuring the amount of photoelectron emission from the surface as CCl_4 and CH_3X were adsorbed (Fig. 5). As CH_3X (X=Br, I) was adsorbed alone on the Ag(111) surface, the photoelectron yield at 248 nm [Fig. 5(a)] was found to increase up to a maximum value, decrease slightly, and then remain essentially constant for further CH_3X coverage. These features mirror the changes in work function measured by Zhou et al. for $CH_3X/Ag(111)$ (Ref. 7) and validate the method. This probe of the work function was then used to examine the photoelectron emission in the two layer system $CH_3X/CCl_4/Ag(111)$ appropriate to the present experiments. Figure 5(b) shows two curves, corresponding to X=Br and X=I. The initial 2 L dose of CCl_4 decreased the work function from the clean Ag(111) value, as shown by the enhanced photoelectron emission at zero coverage of CH_3X. As layer B (CH_3X; X=Br, I) was dosed on top, the emission increased still further until it reached a maximum at 1 L for CH_3Br and at 2 L for CH_3I. At higher CH_3X coverage, the emission was found to decrease monotonically, indicating that the surface work function was increasing.

The work function decreases upon initial adsorption of CH_3X on Ag(111) because the dipolar molecules are pref-

erentially oriented on the surface with the halogen end of the molecule pointing down.[7] As 1 ML coverage is approached, the neighboring CH_3X molecules can be expected to begin to interact and eventually depolarize the fields at the surface,[7] resulting in the increase in work function observed at higher coverage.

It is significant that the features in the photoemission yield curves of Fig. 5(b) correlate with the yield of reaction product CH_3Cl shown in Figs. 3 and 4. This confirms the important role of photoexcited electrons in the reaction between layer A (CCl_4) and layer B (CH_3X). In Fig. 3(a), the yield of CH_3Cl is observed to reach a maximum at a dose of 1.5 L of layer B (CH_3Br) and decrease for higher coverage. Similarly, in Fig. 3(b), the reaction yield reaches a maximum at a 1 L dose of layer B. Two effects produce the observed peak in CH_3Cl yield. At low coverage of layer B, the number density of B molecules at the interface with CCl_4 is increasing and the surface work function is decreasing, facilitating the photoelectron emission. At greater than 1 L dose, the number of B molecules at the interface has reached a maximum (one monolayer of B). However, the surface work function now begins to increase, reducing the probability that photoexcited electrons can reach the interface, and hence reducing the amount of reaction.

It is also significant that the peak in the CH_3Cl yield curve is more pronounced at 350 nm [Fig. 3(b)] than at 248 nm [Fig. 3(a)]. At 350 nm, only hot electrons are generated, and yet in this case, the changes in the work function induced by the CH_3X adlayer are crucial in allowing the charge-transfer reaction to proceed. Thus, at 350 nm [Fig. 3(b)] a sharp peak in the reaction product (CH_3Cl) yield is observed at 1 L CH_3Br dose [where a minimum work function is measured Fig. 5(b)] and very little product is observed above 2 L dose. The increase in work function that occurred above 1 L CH_3Br dose was evidently sufficient to inhibit photogenerated *hot electrons* from reaching the interface between CCl_4 and CH_3Br, so the reaction "turned off."

Similar results were obtained for the $CH_3I/CCl_4/$ Ag(111). Figure 5(b) shows that the decrease in work function was more pronounced for $CH_3I/CCl_4/Ag(111)$ than for CH_3Br. The maximum yield of photoproduct CH_3Cl occurred at 2 L dose irrespective of wavelength (Fig. 4) and the yield decreased slowly for higher CH_3I doses. The surface work function increased at these higher coverages, but was lower than for equivalent coverages of CH_3Br [Fig. 5(b)]. Hence, the reaction did not "turn off" for higher coverages of CH_3I, since the work function was low enough to allow photoelectrons to reach the interface between CCl_4 and CH_3I.

Here again we note the direct correlation between the work function and the rate of ion–molecule reaction, even at 350 nm, where only hot electrons were involved in the charge transfer. In order for the ion–molecule reaction to occur, photoelectrons must reach RCl at the interface—the observation of an enhanced rate of CT [and hence reaction (Figs. 3 and 4)] suggests that the local potential for the photoelectrons at the interface was lowered by the CH_3X adlayer at the same time that the macroscopic work func-
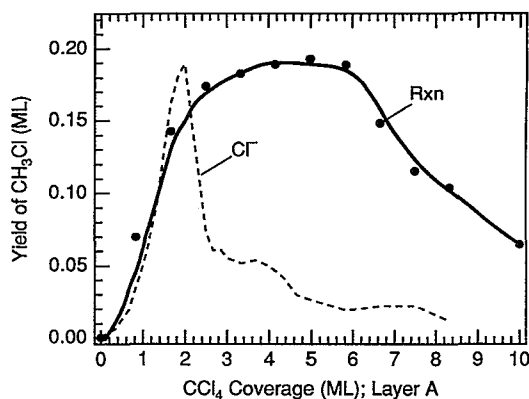

FIG. 6. Filled circles give the photoyield of CH_3Cl from 1 ML, CH_3Br (layer B) on a variable amount of CCl_4 (layer A). The measured amount of $Cl^-(g)$ emission from $CCl_4/Ag(111)$ is shown for comparison as a dotted line (from Ref. 2).

tion was observed to have been lowered [Fig. 5(b)]. Just as the work function governs the probability that a free electron escapes, the local potential in the adsorbed layers governs the probability that a hot electron can tunnel out of the surface into the adsorbate layer. By analogy with the case of the $(RCl^-)^{\ddagger}$ reaction with the substrate,[2] it seems most probable that reaction with the overlayer depends on the availability of hot electrons at all wavelengths, despite the fact that free electrons are also available at the shorter wavelengths. The reason for this is that RCl^- is stabilized (i.e., lowered in energy) in the neighborhood of the metal substrate[15] and surrounding molecules to the extent that the electron capture resonance, which in the gas phase is at $E \sim 0$ eV,[13] will lie at a negative energy $E \sim -1$ eV (with respect to the vacuum level). Hot electrons have the requisite "negative energy" relative to the free state. Free electrons would exhibit a decreased capture-cross section.

E. The effect of layer "*A*" thickness—Varying the CCl_4 coverage

Further evidence of the role of photoexcited electrons in the reaction between CCl_4 and CH_3X is given in Fig. 6, in which the yield of the CH_3Cl product is plotted as a function of the amount of CCl_4 in the lower layer (A). The CH_3Br coverage in the upper layer (B) was 1 L. The yield of $Cl^-(g)$ ions as a function of CCl_4 coverage (obtained in other work[2]) is shown for comparison. The results indicate that the amount of ion–molecule reaction yielding CH_3Cl increased with the increase in $Cl^-(g)$ emission from the CCl_4 layer in the range of 0–2 ML of CCl_4. The CH_3Cl yield then remained constant until about 6 ML CCl_4 dose, while the $Cl^-(g)$ emission decreased dramatically (the latter is discussed in Ref. 2). At about 6 ML CCl_4 dose, the CH_3Cl yield began to decrease with increasing coverage, indicating that for a thick layer A, the amount of ion–molecule reaction was decreasing.

These findings are in accord with the picture of CT photodissociation that we presented in an earlier study.

There we observed a dramatic decline in $Cl^-(g)$ emission from the second molecular layer of CCl_4 on $Ag(111)$ when compared with the first. We ascribed the enhanced yield of $Cl^-(g)$ from the layer adjacent to $Ag(111)$ to energy release in the reaction between the residue (CCl_3) and the substrate. At higher CCl_4 coverage, Cl^- lacks the extra translational energy necessary to escape. Nonetheless, RCl^- would continue to be formed at the surface.

The relatively constant yield of CH_3Cl reaction product between 2 and 6 ML CCl_4 dose observed in the present study (Fig. 6) leaves no doubt that photoinduced CT was continuing to occur in this coverage range. However, the Cl^- ions, lacking the translational energy from surface reaction, were unable to escape. Instead, RCl^- reacted with the CH_3X overlayer to give CH_3Cl.

The decline in CH_3Cl yield at greater than ~ 6 ML CCl_4 dose (Fig. 6) is thought to be due to attenuation of the total electron flux at the top of layer A. This would decrease the amount of RCl^- produced at the interface with layer B (CH_3Br) and so reduce the amount of ion–molecule reaction. This is in accord with the notion that the bulk of the reaction occurs at the B/A interface.

F. The cross section for ion–molecule photoreaction

The cross section for the ion–molecule photoreaction forming CH_3Cl was estimated using the data of Fig. 2. The cross section was calculated from

$$N_{CH_3Cl} = N_{h\nu} N_0 \sigma_{I/PRXN}^{CT}, \qquad (2)$$

where N_{CH_3Cl} is the area density of CH_3Cl product molecules, $N_{h\nu}$ is the total photon flux, N_0 is the area density of CH_3Br reagent molecules, and $\sigma_{I/PRXN}^{CT}$ is the photoreaction cross section. The quantity N_0 was estimated from the number density of CH_3X monolayers on $Ag(111)$,[7,16] $N_{h\nu}$ was the measured photon flux on the sample and N_{CH_3Cl} was estimated from the integrated thermal desorption yield of CH_3Cl product, which was compared to the TPD yield from a known dose of $CH_3Cl/Ag(111)$. In Fig. 2(b), the CH_3Cl yield N_{CH_3Cl} is plotted as a function of $N_{h\nu}$. The slope of this line gives an estimate of $\sigma_{I/PRXN}^{CT} \approx 2 \times 10^{-19}$ cm^2 for CH_3Br/CCl_4 at 248 nm. This is an order of magnitude larger than the direct gas-phase photolysis cross sections for CH_3Br and CCl_4, further evidence that the photoreaction mechanism involves CT and not direct photolysis followed by reaction of an uncharged photofragment.

G. Comparison between the gas-phase and surface ion–molecule reaction

Ion–molecule reactions at a metal surface, electron induced rather than photon induced, have been reported by Sanche and Parenteau.[17] They studied electron-beam-induced reactions between low energy electrons and coadsorbed $O_2 + C_nH_{2n+2}$. The impacting electrons gave rise to dissociative attachment in O_2, and the O^- ions then reacted with C_nH_{2n+2}, yielding $OH^-(g)$.

The gas-phase ion–molecule reaction between Cl^- and CH_3Br has been studied in great detail as a prototypical
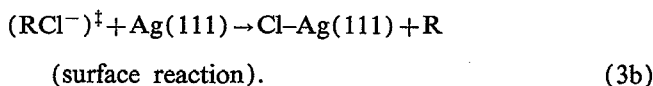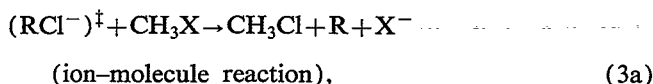
S_N2 substitution reaction.[14] This class of S_N2 reactions are of much interest due to their central role in organic chemistry. In the gas phase, the potential energy surfaces governing these S_N2 reactions have a double minimum. In the case of $Cl^- + CH_3Br$, the reactive transition state is lower in energy than the reagents,[14] hence the reaction has no overall energy barrier. Recent studies have found evidence that the products of this reaction are left vibrationally excited, little of the energy appearing as translation.[14] In the present instance, we believe that the ion–molecule reaction is more properly written as $(RCl^-)^\ddagger + CH_3X \rightarrow CH_3Cl + R + X^-$. We looked for the negative ion product X^- (Br^- or I^-) from the reaction using a time-of-flight mass spectrometer,[2] but found none. This would suggest that the RCl^- reaction in the adsorbed state resembles the Cl^- reaction in the gas, in giving low product translational energy, since it would require ~ 1 eV of kinetic energy for the X^- fragment to escape its image charge. We also looked for desorbing CH_3Cl using a time-of-flight quadrupole mass spectrometer, but saw none; it appears that the bulk of the product of photoreaction stays trapped at the B/A layer interface.

In a previous study, we reported the observation of Cl^- ions desorbing from the surface under UV laser radiation of $CCl_4/Ag(111)$. The Cl^- formed by DA of gas phase CCl_4 is known to have an energy distribution that peaks at very low energies [< 0.1 eV (Ref. 18)]. Since the Cl^- ions that desorb from the surface must escape the ~ 1 eV polarization attraction, they are likely to be in the high-energy tail of the initial energy distribution. By contrast, for the ion–molecule reaction at the surface, there is no energy barrier to reaction, thus all of the negative ions formed at the CCl_4/CH_3X interface can react to form the CH_3Cl product. Ion–molecule reaction constitutes an in situ detector for the RCl^- formed at the metal surface. In this it resembles the surface reaction studied in the previous paper in this series.[2]

H. The relationship between ion–molecule and surface photoreaction

The parallel between ion–molecule photoreaction, with cross section $\sigma_{I/PRXN}^{CT}$, and surface photoreaction[2] with cross section $\sigma_{S/PRXN}^{CT}$, is evident from the fact that at all wavelengths for which data are available (193, 248, and 350 nm for layer $A = CCl_4$) and for all types of layer A studied (CCl_4, $CHCl_3$, and CH_2Cl_2), the absolute values of the cross sections for the two reaction pathways are comparable, namely, $\sigma_{I/PRXN}^{CT} \sim \sigma_{S/PRXN}^{CT} \sim 10^{-19}$ cm^2. The actual values have been included in Table I of the previous paper,[2] in which a wide range of salient variables were brought together. Not only are these photoreaction cross sections many orders of magnitude larger ($> 10^6 \times$) than those for $RCl/Ag(111) + h\nu \rightarrow Cl^-(g) + R/Ag(111)$ [termed σ_{PDIS}^{CT} (see Table I of Ref. 2)], but in addition, they differ from σ_{PDIS}^{CT} in remaining virtually unchanged as RCl goes from CCl_4 to $CHCl_3$ to CH_2Cl_2. By contrast, σ_{PDIS}^{CT} drops by four orders of magnitude along this series (Table I of Ref. 2).

The parallelism between $\sigma_{I/\text{PRXN}}^{\text{CT}}$ (this work) and $\sigma_{S/\text{PRXN}}^{\text{CT}}$ [previous paper (Ref. 2)] taken together with the lack of correlation with $\sigma_{\text{PDIS}}^{\text{CT}}$ indicate that Cl^- does not need to separate fully from RCl^- prior to ion–molecule reaction with a superimposed layer B, or surface reaction with the metal substrate [to form Cl–$Ag(111)$]. We therefore write the two photoreactions as

$$(RCl^-)^{\ddagger} + CH_3X \rightarrow CH_3Cl + R + X^-$$

$$\text{(ion–molecule reaction)}, \tag{3a}$$

$$(RCl^-)^{\ddagger} + Ag(111) \rightarrow Cl\text{–}Ag(111) + R$$

$$\text{(surface reaction)}. \tag{3b}$$

All these symbols should carry the suffix (ad), since the entire process takes place in the adsorbed state. The choice of reaction pathway is likely to be determined by the orientation of the dissociating bond in $(RCl^-)^{\ddagger}$ which may be directed upwards ($\rightarrow$ ion–molecule reaction) or downwards ($\rightarrow$ surface reaction). Rotation of $(RCl^-)^{\ddagger}$ on the time scale of dissociation can be neglected. Since $\sigma_{I/\text{PRXN}}^{\text{CT}} \sim \sigma_{S/\text{PRXN}}^{\text{CT}}$, it would seem that, with layer B present, $(RCl^-)^{\ddagger}$ is as likely to be oriented up as down.

Experiments were performed to ascertain the effect of layer B (CH_3X) on the photoreaction of layer A (RCl) with the $Ag(111)$ substrate (the latter, in isolation, being the subject of the previous paper[2]). For layer A consisting of $CHCl_3$ (2 ML), the rate of formation of Cl–$Ag(111)$ at 248 nm was determined by Auger spectroscopy, and thereafter was redetermined in the presence of 1 ML of superimposed CH_3Br (layer B). The rate of formation of Cl–$Ag(111)$ was reduced by one-third in the presence of layer B, despite the fact that the work function was observed to decrease in the presence of this overlayer, so that one would expect increased CT. This marked decrease in the yield of Cl–$Ag(111)$ in the presence of layer B confirms that the two processes—ion–molecule and surface reaction—have comparable cross sections.

For the case of the surface photoreaction, we found persuasive evidence that hot electrons rather than "free" electrons played the dominant role in forming the $(RCl^-)^{\ddagger}$ reagent. The evidence, which applies again in the present case, came from a comparison of the change in electron photoemission efficiency with wavelength with the corresponding change in photoreaction probability. The photoemission of free electrons decreases with increasing wavelength (193:248:350 nm) in the ratio 1:0.1:0. The relative cross sections for ion–molecule photoreaction $\sigma_{I/\text{PRXN}}^{\text{CT}}$ by contrast are 1:1:0.5 [layer $A = CCl_4$, layer $B = CH_3Br$ (Table I of Ref. 2)]. Since there are no free electrons being formed at the third wavelength (350 nm), it is evident that the presence of free electrons is not required for the ion–molecule photoreaction, any more than for the surface photoreaction. This finding is not unexpected, since the reagent is the same $(RCl^-)^{\ddagger}$ in both cases, and $RCl(\text{ad}) \rightarrow (RCl^-)^{\ddagger}$ has its peak electron-capture cross section for electrons of energy ~ 1 eV below the vacuum level.[2]

IV. SUMMARY

A photoinduced ion–molecule reaction is described for the two-layer system $CH_3X/RCl/Ag(111)$ ($X = Br$, I) forming CH_3Cl as product. The mechanism for the reaction was found to be photoinduced charge transfer of substrate electrons to RCl to form $(RCl^-)^{\ddagger}$, which then reacts with CH_3X to form CH_3Cl. The variation in CH_3Cl yield as the top layer CH_3X coverage was increased correlated with changes in the surface work function, even though the electrons involved in CT tunneled to the RCl adsorbate (i.e. were hot rather than free electrons). The CH_3Cl yield was also studied as a function of the bottom layer thickness CCl_4 for a fixed amount of CH_3Br. The yield of CH_3Cl photoproduct was constant for 2–6 ML of CCl_4, but decreased for higher CCl_4 coverage due to the attenuation of the photoelectrons reaching the CH_3Br/CCl_4 interface.

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