Surface photochemistry of CH$_3$Cl: dissociative electron attachment through D$_2$O spacer layers

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Received 29 November 1990; accepted for publication 2 April 1991

The rates of photo-induced dissociation of chloromethane, CH$_3$Cl, on D$_2$O-precovered Pt(111) at 55 K were correlated with the measured yields of substrate-excited photoelectrons, for a variety of D$_2$O-precoverages. An excellent quantitative correlation was obtained, consistent with the expected dissociative electron attachment (DEA) mechanism for the C–Cl bond cleavage. Measured electron energy distributions suggest that very low energy (< 0.4 eV) electrons are most effective for CH$_3$Cl dissociation.

1. Introduction

This work is a sequel, adding water spacer layers, to our earlier work on multilayer CH$_3$Cl surface photochemistry. In that study [1] we confirmed and extended earlier work [2,3] showing that C–Cl bond dissociation is due to the dissociative attachment of substrate-excited (above vacuum-level energy) photoelectrons.

Recently, Cowin and co-workers employed multilayer CH$_3$Cl on Ni(111) [2] and monolayer CH$_3$Cl on H$_2$O layer-precovered Ni(111) [3] to elucidate the underlying mechanism for the photo-driven C–Cl bond cleavage. After 248 nm (5 eV) laser pulses, they monitored time-of-flight (TOF) CH$_3$ signals and post-irradiation temperature-programmed desorption (TPD) areas of CH$_3$Cl as a measure of photolysis for various initial CH$_3$Cl coverages. With increasing CH$_3$Cl coverage, the photolysis cross section (σ) obtained from the post-irradiation TPD area measurements, sharply increased initially, and then decreased asymptotically to zero. Similar behavior was found for a covering, single layer of CH$_3$Cl with increasing H$_2$O spacer-layer thickness. Maximum cross sections were obtained at 4 ML CH$_3$Cl [2] and 2 ML H$_2$O [3] for the multilayer and spacer-layer systems, respectively. From the initial increase and subsequent decay of both the cross section and the CH$_3$ TOF signal as a function of layer thickness, they concluded a (metal-to-absorbate) charge-transfer (DEA) mechanism and a strong perturbation (back-charge-transfer resonance quenching) of the CH$_3$Cl photolysis by the substrate metal.

Recently, we studied the same multilayer system [1], but on Pt(111) and with a CW light source. These changes appear not to cause any significant differences in the results. We extended Cowin et al.’s work [2,3] by directly measuring the ejected photoelectrons during irradiation, and correlated the yield with the photolysis rate assuming DEA is the dominant process. It was also found that only those photons with energies greater than 4.3 eV were effective in photolyzing C–Cl bonds, indicating that those (hot) electrons excited into the range between the Fermi level and ~ 0.2 eV below the vacuum level are not participating.

The pseudo-first-order rate coefficient (first order with respect to the surface concentration, or coverage, of CH$_3$Cl), a parameter comparable to the photolysis cross section, was obtained from the post-irradiation TPD areas of CH$_3$Cl for 0.25 to 9 ML CH$_3$Cl coverages. This pseudo-first-order rate coefficient (k') showed a fast monotonic decay with increasing coverage over the entire
coverage range. This trend disagrees with that found by Cowin et al. [2], which shows a maximum at 4 ML. A more meaningful parameter is a rate coefficient, $k$, which takes account of the strong electron attenuation across layers of CH$_2$Cl. This $k$ was coverage-independent for $\geq 2$ ML on Pt(111) and for all coverages on C-covered Pt(111). This indicates that the surface photochemistry of CH$_2$Cl is dominated by the dissociative attachment of substrate-excited photoelectrons and that substrate quenching, if it occurs, is largely offset by substrate promotion effects [1].

The purpose of this work is twofold: (1) to confirm, using a simpler system, the layer-by-layer analysis and consequently concluded mechanism in the earlier work [1]; and (2) to clarify the discrepancy in the coverage-dependent variation of two comparable kinetic parameters, i.e., the pseudo-first-order rate coefficient in our work [1] and the photolysis cross section in earlier work [2] – a study important in assessing the quenching and promotion of the photolysis by the substrate metal.

2. Experimental

A UHV ($2.5 \times 10^{-10}$ Torr) chamber equipped with X-ray photoelectron spectroscopy (XPS), ultra-violet photoemission spectroscopy (UPS), quadrupole mass spectroscopy (QMS), and an ion gun was used. The substrate, a Pt(111) single crystal (8 mm diameter and 1 mm thick), could be resistively heated to 1500 K with a linear ramp (0.1–50 K/s) and subsequently cooled to 55 K within 5 min by a closed-cycle He cryostat. A pin-hole (2 mm) doser mounted on a linear motion device, which provided reproducible (±3%), uniform and localized (to the crystal surface) exposures, was used to dose D$_2$O and CH$_2$Cl. The crystal temperature was kept at 55 K during dosing and irradiation. The full emission (≤ 5.4 eV) of a high-pressure Hg-arc lamp was used to irradiate the adsorbate-covered surface. At these wavelengths, both D$_2$O and CH$_2$Cl are transparent. The UV-light was incident (from outside of the chamber through a UV-grade sapphire window) at 45° off the surface normal, and ejected substrate-photoelectrons were counted by a hemispherical electron energy analyzer at the surface normal. Post-irradiation temperature-programmed desorption (TPD) of molecular CH$_2$Cl was used to quantify the photolysis. Line-of-sight TPD was performed with a 6 K/s ramp rate. Secondary electron thresholds of HeI UPS were used to establish work-function changes.

Deuterium oxide, D$_2$O (Aldrich; 99.8 at.% D), was further purified with freeze–pump–thaw cycles before dosing. Methyl chloride, CH$_2$Cl (Linde; 99.9%), was dosed without further purification. Gas purities were confirmed using QMS in the UHV chamber. A more detailed description of the apparatus has been previously reported [1,4].

3. Results

Fig. 1 shows (non-irradiation) 1 ML TPD spectra of CH$_2$Cl on 0, 1 and 2 ML D$_2$O-precovered Pt(111). One monolayer coverage of CH$_2$Cl was defined as the maximum area measured without multilayer desorption in the absence of D$_2$O. The
D₂O-free spectrum of fig. 1 is in agreement with earlier work [1]. The desorption of 1 ML CH₃Cl on the D₂O-precovered surface coincides with the desorption of multilayers (105–110 K) in the absence of D₂O. This implies that the CH₃CL–CH₃CL and CH₃CL–D₂O interactions are of similar strengths. The residual high-temperature (~135 K) desorption signals for the 1 and 2 ML D₂O-precovered surfaces are attributed to the desorption from Pt atoms which are not covered by D₂O molecules even with two layers of D₂O, a result consistent with a highly ordered bilayer structure of D₂O on Pt(111) [4,5]. Also shown (dashed curve) is the 3 ML D₂O TPD spectrum. Clearly, even multilayers of D₂O desorb at > 20 K higher temperature than CH₃Cl. This, together with the quick suppression of the clean-surface CH₃Cl desorption (>135 K) as the D₂O-precoverage increases, establishes the integrity (stability) of D₂O layers as a spacer.

Fig. 2 shows the UV-irradiation effects on 1 ML CH₃Cl with and without D₂O-precoverage. Monotonic decays of 1 ML CH₃Cl desorption intensity with increasing irradiation time are observed. In an earlier CH₃Cl photolysis study [1], we established the absence of photon-driven desorption of molecular CH₃Cl or Cl on Pt(111) at 50 K, from which it was concluded that the loss of CH₃Cl TPD intensity measures the C–Cl photodissociation yield. We, therefore, can use post-irradiation TPD areas as a measure of photolysis, thereby obtaining the kinetic parameters (see below).

The rate of CH₃Cl photolysis (−d[CH₃Cl]/dt), assuming it occurs via DEA (CH₃Cl + e⁻ → (CH₃Cl)⁻ → CH₃ + Cl⁻), is given as follows [1]:

\[-d[CH₃Cl]/dt = k'[CH₃Cl] = k[e][CH₃Cl],\]

where \(k'\) is the pseudo-first-order rate coefficient, [CH₃Cl] the concentration or coverage of CH₃Cl (=1 ML), [e] the concentration or total yield of photoelectrons, and \(k\) the rate coefficient (=\(k'/[e]\)).

Integrating eq. (1), we obtain

\[\ln\left\{\frac{[CH₃Cl]}{[CH₃Cl]₀}\right\} = -k't = -k[e]t.\]  (2)

Fig. 3 shows a semilogarithmic plot of the CH₃Cl TPD area ratios versus irradiation time for the initial CH₃Cl coverage ([CH₃Cl]₀) of 1 ML on the 0 to 6 ML D₂O-precovered surfaces. The observed linearity of each curve establishes the validity of our first-order approach with respect to [CH₃Cl].

Fig. 4 shows the measured total yield of photoelectrons [e], the pseudo-rate coefficient \(k'\), ex-
Fig. 3. Plot of natural logarithm of CH$_3$Cl TPD area ratios versus irradiation time for 0–6 ML, indicated on each curve, of D$_2$O-precoverages. The slopes are the pseudo-first-order rate coefficients ($k'$). $I_t$ and $I_0$ represent TPD areas after $t$ min and 0 min irradiation, respectively.

Fig. 4. Total photoelectron yield ([e]), pseudo-first-order rate coefficient ($k'$), rate coefficient ($k$), and work-function change ($\Delta \phi$) as a function of D$_2$O spacer-layer thickness. See the text for details.

Fig. 5. Energy distributions of the substrate-excited photoelectrons for 1 ML CH$_3$Cl adsorbed on 0–6 ML (top to bottom) D$_2$O-precovered Pt(111). The scale factors represent the multiplications needed to bring the low-energy leading edges to coincidence.
accounting for the results of fig. 4. As an approximate measure of the photoelectron flux in the effective energy range (referred to as effective photoelectron yield, [e]*, hereafter) for each D₂O-spacer thickness, we used the scale factors in fig. 5. This seems reasonable even without the knowledge of the maximum-DEA energy for the condensed phase CH₃Cl, since the average energies of photoelectrons do not vary significantly with D₂O-coverage, except at very low coverages.

Fig. 6 shows the correlation of k and [e]*. The effective rate coefficient, k*, obtained from the relation k' = k*[e]*, does not change with coverage. This invariant k*, the most important result in this work, will be discussed in the following section. Evidently, the high energy (> 0.4 eV) electrons do not contribute significantly to DEA.

4. Discussion and comparison with other work

In separate papers, we presented detailed studies of D₂O adsorbed alone on Pt(111). Briefly, we obtained TPD evidence for the highly ordered bilayer structure of water at 55 K [4] and a strong exponential attenuation of very low energy (< 0.7 eV) electrons via elastic scattering in thin D₂O films [9]. An electron attenuation length of 2.3 ML was obtained [9], indicating that the electron flux decreases by ~ 64% every 2.3 ML of D₂O [3]. This, together with the stability of the underlying D₂O layers described in the previous section, makes D₂O-precoverage an ideal choice as a spacer, since there is a large variation of the electron flux (by the variation of the D₂O layer-thickness) to the overlayer probe molecules (CH₃Cl).

No photofactors by < 4.3 eV photons were observed here, as for the multilayer CH₃Cl on clean or C-covered Pt(111) [1]. Two points can be made from this: (1) the threshold photon energy is 4.3 eV or higher, and (2) electrons excited above the vacuum level account for the photon-driven chemistry in this work.

The monotonic decrease of k' with increasing thickness of water layers (~ factor-of-five decrease from 0 to 2 ML D₂O-precoverage) in fig. 4 is in sharp contrast with the behavior of σ (~ order-of-magnitude increase from 0 to 2 ML H₂O-precoverage) in Cowin et al.'s work [3]. We obtained a similar decrease for multilayer CH₃Cl photolysis [1], which partly motivated this work. The surface work functions of clean Ni(111) and Pt(111) differ by < 0.2 eV, and work-function changes by CH₃Cl or H₂O are expected to be quite similar for the two surfaces. In our earlier work [1], we showed that a significant fraction of the CH₃ photofragments are retained on the surface, particularly for low coverages. This suggests that the CH₃ TOF signal can not be a true reflection of the top most layer DEA. Our result, showing a quantitative correlation for the two empirical variables (k' and [e]*) and consistent with the multilayer photolysis results, convincingly demonstrates (fig. 6) that the dissociation probability (rate coefficient) is not lower in the first monolayer and, for this case, quenching is not overwhelming for CH₃Cl in direct contact with the metal substrate.

In conclusion, our direct correlation of the measured photoelectron yields and the photolysis rates suggests that the effective photolysis cross section (not accounting for electron flux variation) decreases monotonically with increasing D₂O thickness (decreasing photoelectron yield), consistent with a DEA mechanism.
5. Summary

The results in this work can be summarized as follows.

(1) The pseudo-first-order rate coefficient \( k' \), characterizing the photolysis with respect to the surface concentration of CH\(_2\)Cl, decays monotonically with increasing \( \text{D}_2\text{O} \)-precoverage. This indicates that the substrate quenching, if any, is not strong enough to offset the fast decay of the photoelectron yield.

(2) The total yields of photoelectrons, which also decayed rapidly with increasing thickness of \( \text{D}_2\text{O} \) spacer layers, were correlated with the pseudo-first-order rate coefficients. The characteristic rate coefficient \( k^* \), a coefficient accounting for the decaying photoelectron yield assuming the electrons with energies > 0.4 eV are not active, was constant over the entire range of the spacer thickness.

(3) This strong quantitative correlation firmly establishes the underlying C–Cl dissociation mechanism, i.e., photoelectron attachment to CH\(_2\)Cl, confirming the earlier conclusions, and indicates that only very low energy (< 0.4 eV) electrons are active.

Acknowledgement

This work was supported in part by NSF Grant CHE 8505413.

References