Chapter 20

Mass Effects in Photodissociation of Chloromethane

Quenching by Substrate Metal

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The rates of photolysis of CH_3Cl and CD_3Cl on Pt(111) at 100 K were measured using a conventional mercury arc lamp. The rate is significantly faster for the lighter halide and, quantitatively, the rate ratio is $CH_3Cl:CD_3Cl::1.27:1$. This difference is explained by the Menzel-Gomer-Redhead (MGR) model, which predicts a mass-dependent variation of the competition between substrate quenching and dissociation. The rate ratio corresponds to the successful dissociation of 2.4~8% of the excited molecules.

This study extends our earlier work on CH_3Cl surface photochemistry *(1)* and investigates how mass influences the probability of photon-driven dissociation of the C-Cl bond, thereby quantifying the extent of substrate quenching. In the earlier work *(1)*, we confirmed and extended the pioneering investigations of Cowin and co-workers *(2, 3)* who showed that the C-Cl photodissociation can be accounted for by dissociative attachment of substrate-excited photoelectrons. That work employed multilayer CH_3Cl on Ni(111) *(2)* and monolayer CH_3Cl on H_2O-precovered Ni(111) *(3)* to elucidate the underlying mechanism. 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_3Cl as measures of photolysis for various initial CH_3Cl and H_2O spacer-layer coverages. As a function of layer thickness, they observed an initial increase and subsequent decay of both the photolysis cross section (s) and the CH_3 TOF signal, and concluded the importance of both a metal-to-adsorbate charge-transfer (dissociative electron attachment, DEA) mechanism and a strong perturbation (resonance quenching) of the CH_3Cl photolysis by the substrate metal. The decay at high coverages was ascribed to the attenuation of electrons coming from the substrate through several layers.

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Recently, we studied the same multilayer *(1a)* and D₂O-precovered monolayer CH3Cl systems *(1b)*, but on Pt(111) and with a CW Hg-arc light source. We directly measured the yield of ejected photoelectrons during irradiation, and successfully correlated it with the photolysis rate, confirming that DEA alone is sufficient to account for all the dissociation chemistry. Only those photons with energies greater than 4.3 eV were effective, indicating that hot electrons with energies in the range between the Fermi level and ~0.2 eV below the vacuum level are ineffective.

One remaining issue is the extent to which the substrate metal quenches the photolysis *(1b)*. The measured photolysis rate coefficient (**k'** in **d[CH3Cl]/dt = -k'·[CH3Cl]**), although approximately constant over small coverage ranges, generally drops with increasing CH3Cl coverage *(1)*. We have, however, pointed out that the coverage-dependent variation of either the cross section or the (pseudo-) rate coefficient (**k'**) is not an appropriate parameter for an assessment of quenching because, as the coverage increases, the exponentially decaying electron flux contributes to their variation *(1a, 4)*. Taking account of the exponentially decreasing photoelectron yield gave a rate coefficient (**k**), which was *higher* for low coverages than for high coverages *(1a)*. This was attributed to the overwhelming effect, for molecules at the metal surface, of promotion over quenching. The possible origins for the net enhancement of the low-coverage photolysis, as discussed earlier *(1)*, are: (**i**) an additional contribution from direct photon excitation of the "metal-adsorbate complex" consisting of the surface metal layer and first adsorbate layer *(5)*; and, more likely, (**ii**) enhanced tunnelling attachment of "hot" electrons excited to levels between the vacuum level and ~0.2 eV below it.

Our earlier results *(1)*, however, still could not provide a quantitative estimate of the probabilities of quenching and dissociation. This very important branching ratio issue is addressed in this paper. Excitation and quenching both involve coupling between the adsorbed molecule and the metal *(6)*. This coupling takes the form of induced-dipole/induced-dipole coupling, electron-hole pair formation in the metal, and charge transfer mediated processes. Direct dissociation times along repulsive potential energy curves can be as short as 10^{-13} to 10^{-14} s *(7, 8)*; thus, quenching must operate on an equal or faster time scale to inhibit bond cleavage. Depending upon the resonant or non-resonant character of the relaxation process, theory predicts characteristic quenching times relatively close to this, lying between 10^{-15} and 10^{-13} s *(9, 10)*.

From an experimental point of view, one way to gain insight into the branching ratio is to compare photon-driven rates for hydrogenated molecules with those for deuterated ones. Within the MGR model *(11, 12)*, more quenching, and therefore a smaller dissociation cross section, is expected for heavier isotopes. As applied to surface photochemistry, this method was used by Wolf et al. *(13)* with the H₂O/Pd(111) system. Here we report results for CH3Cl and CD3Cl on Pt(111). The measured dissociation rate coefficient is a factor of 1.27 larger for CH3Cl than for CD3Cl. Depending on the effective reduced mass chosen, we estimate that, of the excited CH3Cl molecules, between 2.4 and 8 % dissociate. The implications are discussed in relation to previous results *(1-3)*.

Experimental.

A UHV (2.5×10^{-10} torr) chamber equipped with X-ray photoelectron spectroscopy (XPS), ultra-violet photoemission spectroscopy (UPS), quadrupole mass spectroscopy (QMS), and an ion gun w used. The substrate, a Pt(111) single crystal (8 mm diam. and 1 mm thick), could be resistively heated to 1500 K with a linear ramp (0.1 - 50 K/sec) and subsequently cooled to 50 K within 5 min by a

closed-cycle He cryostat. A collimated doser containing an inner pin-hole conductance (2   m), mounted on a linear motion device, provided reproducible, uniform and localized (to the crystal surface) exposures of the adsorbate molecules. The crystal temperature was kept at 60 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 CH_3Cl and its deuterated counterpart are transparent. The ultraviolet (UV) light was incident (from outside the chamber through a UV-grade sapphire window) at 45° off the surface normal. Post-irradiation temperature-programmed desorption (TPD) of molecular CH_3Cl and CD_3Cl was used to quantify the photolysis. Line-of-sight TPD was performed with a 6 K/sec ramp rate. CH_3Cl (Linde; 99.9%) and CD_3Cl (MSD-Isotope; 99.9 atom % D) were dosed without further purification. Gas purities were confirmed using the QMS.

Results and Discussion.

Assuming the photolysis is first order with respect to the surface concentration of CH_3Cl (CD_3Cl), the rate equation can be written as $dI/dt = -k'\cdot I$ or $Ln\{I/I_0\} = -k'\cdot t$, where I_0 and I are the parent molecular TPD areas after 0 and t min irradiation, respectively, and k' is the rate coefficient. Thus, the rate coefficient (k') can be obtained from a semilogarithmic plot of the TPD area ratio (post- and pre-irradiation) as a function of irradiation time (t).

Figure 1 summarizes the results in first-order kinetic form. The nicely linear fits demonstrate the adequacy of our first order analysis for the C-Cl dissociation reaction. To obtain each data point, the clean (as judged by XPS) surface was covered with a full chemisorbed layer (±3%) and irradiated at 60 K for the time indicated. As described earlier, one monolayer coverage was taken as that of maximum TPD area without multilayer desorption. After irradiation, the residual parent TPD signal was measured and integrated to give, after division by the initial TPD area, the ordinate of Fig. 1. Clearly, with increasing irradiation time, the number of remaining parent molecules goes down, reflecting the photodissociation (other work shows the formation of Cl and CH_3 bound to Pt(111) *(1)*). The slopes of the two curves give the relative cross sections; that for CH_3Cl is 1.27 times larger than that for CD_3Cl. This is the new, key observation reported here.

We now turn to an interpretation and analysis of this isotope effect. We employ a model that is often used to describe electron stimulated desorption (ESD) *(15-17)*. In 1964, Menzel, Gomer *(11)* and Redhead *(12)* proposed a model (MGR) for these kinds of processes that is analogous to direct photodissociation of a gas phase diatomic molecule. An adsorbate is assumed to be electronically excited to a repulsive excited state potential energy curve. After excitation, bond elongation (i.e. nuclear motion) occurs and can lead to dissociation. The presence of the metal surface opens up efficient quenching channels that are not available in the gas phase, and these operate to bring the adsorbate back to its ground state. The probability of successful dissociation is then proportional to a product of two parameters: the initial excitation probability, times the probability of survival on the excited state potential energy surface (PES) long enough to gain the required kinetic energy (bond elongation).

There is a mass dependence in these considerations. First, it is assumed that the dissociative, repulsive potential energy surfaces of negative ion states are the same for both isotopes. Then, the mass dependence occurs because of timing; that is, it takes longer to move the heavier (deuterated) methyl group through the distance required for dissociation. Since the electronic couplings are assumed to be the same and since these are responsible for the quenching, we expect the effective average quenching times to be identical and, thus, the average distance travelled by CD_3 to
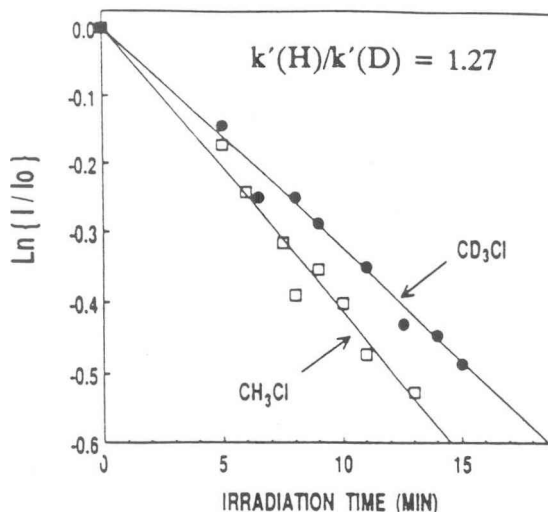
Figure 1: Ln (I/I_0) as a function of irradiation time for 1 ML initial coverage of CH3Cl and CD3Cl on Pt(111). I_0 and I are the CH3Cl (or CD3Cl) TPD areas before and after irradiation, respectively. The ratio of the slopes (rate coefficients, **k'**) is also shown. See the text for details.

be smaller. On the average then, the dissociation probability is higher, as observed, for the H-labelled, compared to the D-labelled, chloride.

This can be described in mathematical form. Following the formulation by Wolf et al. (*13*) and Madey et al. (*15*), the probability, P_d, of C-Cl bond dissociation from the adiabatically excited negative ion (CH3Cl⁻*) is given by

$$P_d = \exp\left(-\int_{x_0}^{x_c} \frac{dx}{\tau v}\right) \qquad (1)$$

where x is the coordinate of the bond being broken, x_0 is the starting value (equilibrium C-Cl distance) and x_c the critical value beyond which dissociation occurs, t is the quenching lifetime, and v is the velocity of the methyl fragment. The mass dependence appears when P_d is rewritten in terms of the potential energy change that occurs between x_0 and x_c.

$$P_d = \exp\left(-\sqrt{\frac{\mu}{2}}\int_{x_0}^{x_c} \frac{dx}{\tau\sqrt{V(x_0)-V(x)}}\right) \qquad (2)$$

where m is the reduced mass of the dissociating *quasi* two-particle system, and $V(x_0)$ and $V(x)$ are the potential energies at x_0 and x_c. The Cl ends of CH3Cl and CD3Cl are known to be oriented toward the Pt(111) substrate (*1, 14*). Thus, it is reasonable to take the Pt into account in the reduced mass calculation ($\mu = m_1 \cdot m_2/[m_1+m_2]$; $m_1 = Pt_n + Cl$ ($n \to \infty$) and $m_2 = CH_3$ or CD_3). Since, then, m_1 is so large compared to m_2, the μ value can be approximated as m_2 (15 amu for CH3Cl and 18 amu for CD3Cl). At the other extreme, ignoring the Pt mass will give a reduced mass of 10.5 amu for CH3Cl and 11.9 for CD3Cl. These can be used to establish limiting dissociation probabilities within the MGR formulation.

As noted above, the observable total cross section for dissociation, σ_d, is a product:

$$\sigma_d = P_d \cdot \sigma_{ex} \qquad (3)$$

where σ_{ex} is the excitation cross section. The repulsive negative ion states of CH_3Cl and CD_3Cl are assumed to be the same; thus, the σ_{ex} are the same for the two isotopes. Taking the σ_d ratio for two isotopes, after inserting the mass dependent formula from Eq. (2) and cancelling mass independent terms, leads to:

$$\sigma_d(H)/\sigma_d(D) = P_d(H)^{1-M}, \qquad (4)$$

where $M = \{\mu_D/\mu_H\}^{1/2}$. Using the $\sigma_d(H)/\sigma_d(D)$ of 1.27 obtained from the rate coefficient ratio in Figure 1 and $M = (18/15)^{1/2}$ or 1.095, we obtain $P_d(H) = 0.08$. Using $M = (10.5/11.9)^{1/2}$ gives $P_d(H) = 0.024$. The values for $P_d(D)$ are 0.06 and 0.02, respectively. These calculations, as noted above, set bounds on the dissociation probability within the framework of the MGR model and indicate that dissociation and quenching are competitive.

This range of P_d, 2.4~8%, is comparable to that (14%) obtained by Wolf et al. (13) for H_2O on Pd(111). The results of this work provide an important quantitative assessment of substrate quenching (>90%) and confirm the operation of strong quenching of the excited negative molecular ion by the substrate metal, in agreement with the suggestion of Cowin et al. (2, 3). Nonetheless, the photolysis rate coefficient in the submonolayer is higher than in the multilayer regime, and we have suggested the importance of enhanced tunneling attachment of hot electrons within 0.2 eV of the vacuum level (1-3).

Summary.
Based on measurements of photon-driven (<5.4 eV photons) dissociation for CH_3Cl and CD_3Cl on Pt(111), we have established that the dissociation cross section for CH_3Cl is 1.27 times that for CD_3Cl. Within the framework of the Menzel-Gomer-Redhead model, and assuming limiting values for the reduced mass of the Pt-methyl chloride system, we conclude that between 2.4 and 8% of those molecules excited actually dissociate. The remaining 92 to 98 % are quenched on a timescale that precludes dissociation.

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