Surface-Aligned Photoreaction of DBr with C_2H_4 on Pt(111)

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Abstract: For ethylene and deuterium bromide coadsorbed on Pt(111) at 52 K, evidence is presented for photon-driven production of ethane and bromoethane. The formation of bromoethane is ascribed to a surface-aligned concerted reaction between photoexcited DBr^-, or its vibrationally excited, electronically quenched form, and C_2H_4. This reaction is more likely when the C_2H_4 is adsorbed over a chemisorbed layer of DBr. Ethane is best accounted for on the basis of photogenerated energetic D atoms reacting with C_2H_4 to form C_2H_4D, and the latter being hydrogenated during temperature-programmed desorption by active D atoms derived from dissociating DBr. When C_2H_4 and DBr are both in the first layer, the π-bonded form of ethylene reacts more readily than the di-σ-bonded form.

1. Introduction

There is growing interest in the photolysis of adsorbates on metals and semiconductors. Despite strong quenching of electronically excited states by metals, it is well established that photon-driven adsorbate bond breaking and desorption occurs for many adsorbed molecules.[1-4] Recently, UV photon-induced reactions between coadsorbed species have been reported and described in terms of either energetic surface atoms or activated molecules. For example, on Pt(111), photons drive a reaction, attributed to energetic oxygen atoms, of peroxo-type dioxygen with coadsorbed CO[5] or H.[6] Recently, however, Ukraintsev and Harrison[7] found on Pt(111) that CO_2 is produced with a *higher* cross section than the photoinduced dissociation of O_2, suggesting that active molecular oxygen, e.g., O_2^- might also be involved. We have reported a photon-driven reaction between chemisorbed N_2O and CO to form CO_2 on Pt(111),[8] a reaction described in terms of chemisorbed N_2O^-, formed transiently by attachment of electrons excited in the Pt, interacting with chemisorbed CO. UV irradiation of H_2S and CO coadsorbed on Cu(111) at 68 K leads to HCO, H_2CO, and OCS,[9] products ascribed to reactions of CO with translationally excited H atoms and vibrationally excited HS fragments produced by the photodissociation of H_2S.

Polanyi and co-workers[4,10,11] coined the term "surface-aligned photoreaction" to describe some of these processes. The term "surface-aligned" implies, as is commonly observed for adsorbates, that there are anisotropic forces between the adsorbate and the substrate which orient the molecular axes with respect to the plane of the surface. There are also forces which position adsorbates in certain surface "sites". For example, on insulator surfaces, e.g., LiF, they found two kinds of photoreactions when HX (X = Cl, Br) was photolyzed with 193-nm photons. In the first, dihydrogen was formed and attributed to an abstraction reaction, $H + HBr(a) \rightarrow H_2(g) + Br(g)$. In the second, $H_2(g) + X_2(g)$ were formed, but photodissociation of HX(a) was not required.

In the present paper, we report on the photochemistry of DBr + C_2H_4 at monolayer and multilayer coverages coadsorbed at 52 K on catalytically active Pt(111). In the gas phase, McNesby et al.[12] have used C_2D_4 to scavenge H atoms produced in the vacuum UV photolysis of H_2O and NH_3. We use this idea here in a surface photochemical process.

Using UV irradiation ($\lambda \geq 230$ nm from a Hg arc lamp), we observe ethane and bromoethane from UV photoexcited DBr reacting with coadsorbed C_2H_4. We attribute both to processes in which DBr and C_2H_4 are positioned with respect to each other and are held by the Pt substrate. Based on temperature-programmed desorption and X-ray photoelectron spectroscopy, we propose that ethane is formed through the photodissociation of DBr, generating translationally energetic D atoms which react with locally coadsorbed and oriented ethylene to produce surface-bound ethyl fragments. During subsequent TPD, these ethyl fragments abstract D from an activated neighboring DBr. The formation of bromoethane is ascribed to a concerted photoreaction involving oriented $DBr-C_2H_4$ pairs. In the proposed model, photons are absorbed in the Pt, and excited electrons attach to DBr, forming DBr^-. The DBr^- either reacts directly with C_2H_4 to form C_2H_4DBr or is quenched to the electronic ground state. The latter can also react with C_2H_4 because it is vibrationally excited. The product yields were significantly higher when ethylene was bound to Pt in a weak π-bonded form, as opposed to a stronger di-σ-bonded form in which each carbon forms a σ bond with Pt. The bromoethane yields increased when ethylene was adsorbed on a monolayer of DBr. As its *thermal* chemistry is significant even at 52 K, the interaction of DBr with Pt(111) was also studied.

2. Experimental Section

A standard turbo-pumped ultrahigh vacuum (2.5×10^{-10} Torr) chamber, equipped with X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and temperature-programmed desorption (TPD) capabilities, was used.[13-15] The Pt(111) sample could be cooled to 50 K by a closed-cycle He cryostat and heated resistively to 1400 K at a controlled rate. A heating rate of 6 K/s was used for TPD. XP spectra were taken with a hemispherical electron analyzer (80-eV pass energy, 0.05-eV step size, and 300-W Mg Kα source).

The Pt(111) sample was cleaned by Ne^+ ion sputtering, oxidation, and high-temperature annealing. The cleanliness of the sample was checked by XPS. Before use, gaseous HBr (Matheson) and DBr (MSD Isotopes, 99% isotopic purity) were purified. They were frozen in a liquid-nitrogen-cooled trap and remaining gases were pumped away to remove D_2 (H_2). An acetone slush bath (208 K), which has a temperature above the boiling point of HBr (206.8 K), but below the melting point of Br_2 (265.2 K) was then used to provide the gas for dosing by backfilling through a variable-leak valve. Both C_2D_4 and $^{13}C_2H_4$ (MS Isotopes) were dosed through a 2-μm pinhole doser.[14]

The light source was a 100-W high-pressure Hg-arc lamp. The power flux to the sample was 100 mW/cm² and the light was incident at 45° off the surface normal. Under these irradiation conditions, the bulk

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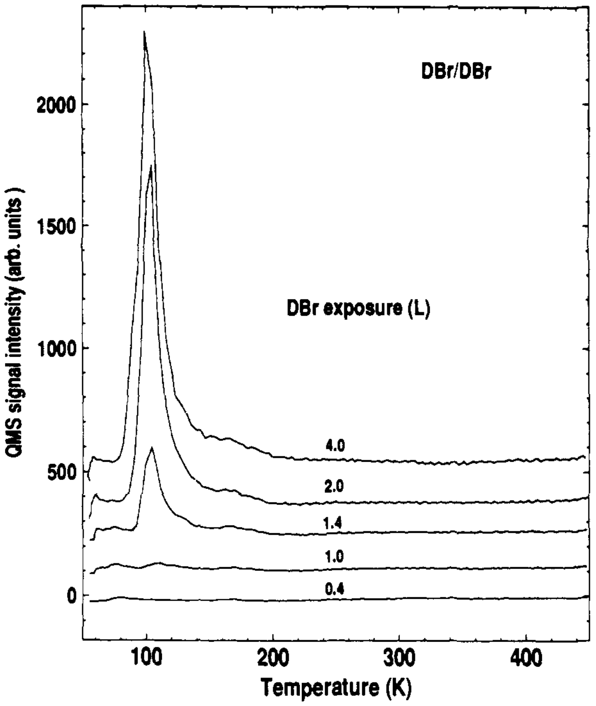

Figure 1. TPD spectra following various exposures of DBr adsorbed on Pt(111). The dosing temperature was 52 K and the temperature ramp was 6 K/s (same as in other figures). Exposures are given in langmuirs (1 L = 1 × 10^{-6} Torr/s).

temperature of the sample rose 5 K and there was no evidence for any thermal desorption.

3. Results and Discussion

3.1. Thermal Chemistry of DBr on Pt(111). In this section, thermal desorption and photoelectron spectroscopic measurements on DBr, made in the absence of irradiation, are described. DBr (HBr) partially decomposes during adsorption at 52 K and the decomposition process is complete between 100 and 120 K.

After low doses of DBr on Pt(111) at 52 K, TPD (Figure 1) shows no molecular DBr desorption; i.e., submonolayer DBr is completely decomposed. Above 1.0 L exposure, a sharp, unsaturable, desorption peak appears at 110 K, moves to slightly higher temperatures with increasing coverage, and is accompanied by a trailing edge signal out to ≈200 K. This molecular desorption is ascribed to DBr adsorbed in the presence of Br on Pt(111) and to physisorbed multilayer DBr, i.e., DBr adsorbed on DBr. These two are indistinguishable under our conditions.

Dihydrogen and atomic bromine desorption are found regardless of the DBr dose (Figure 2). There was no evidence for Br_2 desorption. As in other work, i.e., adsorption of HBr at 300 K[16] and photon-induced reaction of chemisorbed CH_3Br,[17] atomic Br desorbs above 700 K and has a peak temperature at 800 K. At low coverages, there is a D_2 peak at 270 K; it shifts to lower temperatures with increasing coverage. Above 1 L, a second peak develops near 185 K. Except for a 50–60 K shift to lower peak temperatures, these D_2 TPD spectra resemble those found after D_2 adsorption on a clean surface. Since XPS data (below) shows that DBr dissociation is complete at 120 K, well before D_2 desorption starts, D_2 TPD is not limited by DBr dissociation. In control experiments where atomic D was prepared in the presence of preadsorbed bromine, the D_2 TPD peak was weaker but peaked at the same temperature. We suppose that Br blocks sites and, because it is electronegative, lowers the local electron density available to D.

The variations of the TPD intensities with DBr dose (Figure 3) show that molecular DBr desorption sets in at about 1 L, well before Br and D_2 are saturated (≈2 L). Once DBr desorption begins, its intensity grows linearly with exposure, indicating, as expected, a constant sticking coefficient, probably unity. In the early stages, the D_2 and Br signals grow linearly and, as anticipated, extrapolate to zero. After TPD, there are no residual surface species.

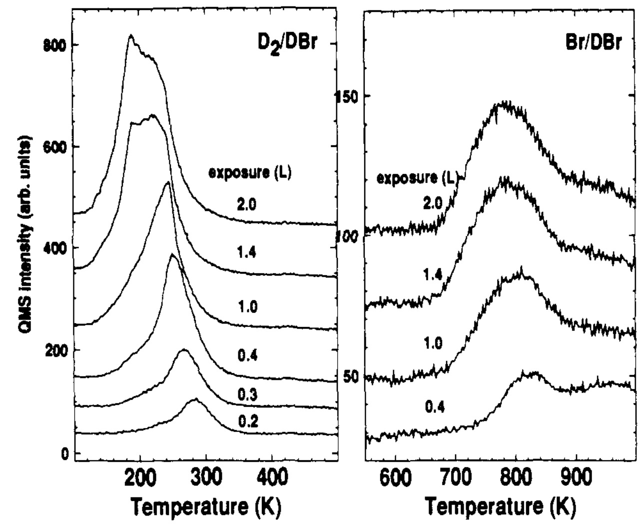

Figure 2. TPD spectra of D_2 and Br following various exposures of DBr adsorbed on Pt(111) at 52 K.

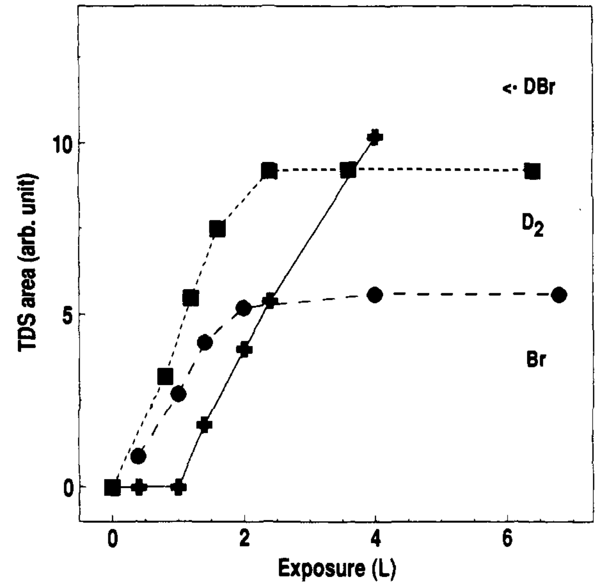

Figure 3. TPD peak areas for DBr, D_2, and Br as a function of DBr exposures.

The Br(3p) XPS after 0.8 L and 2.2 L of DBr exposures at 52 K (Figure 4) can be fit by the sum of two Gaussian peaks centered at 181.5 and 182.8 eV, respectively. The lower binding energy (BE) corresponds to atomic bromine and the higher BE to molecular DBr. The intensity of the latter increases more than the former in passing from 0.8 L to 2.2 L. At 2.2 L, there is roughly equal intensity in both. Upon heating to 140 K and recooling (top curve in Figure 4), the amount of dissociated bromine increased by 30%, the total Br(3p) XPS area decreased by 20%, and the molecular state was no longer observable. For this 2.2 L dose, which saturates the dissociation channel according to TPD, the increased atomic Br signal is attributed to thermally activated dissociation of DBr, while the overall loss of Br intensity is attributed to DBr TPD. From an analysis of the XPS and TPD, we conclude that about 60% of the first layer dissociates upon adsorption and that DBr dissociation is complete by 120 K.

UP spectra (not shown) provide further evidence for both dissociated and undissociated DBr at 52 K. Heating to 120 K removes all evidence of DBr; i.e., all the peaks ascribed to ioni-

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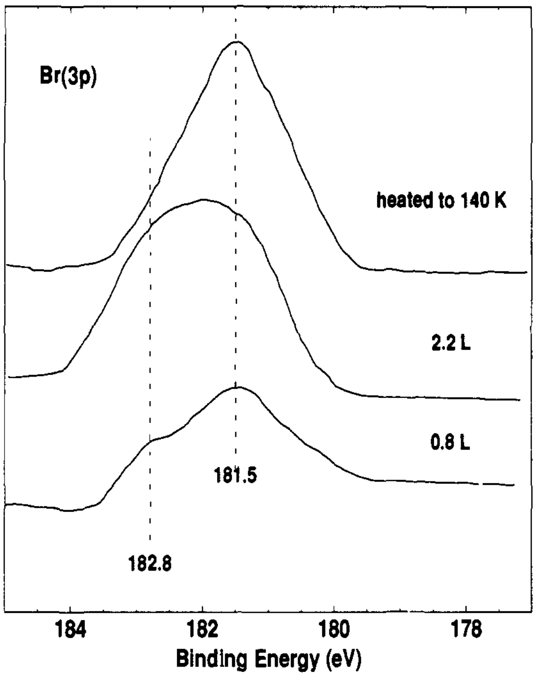

Figure 4. Br(3p) XPS of DBr on Pt(111) at 52 K for 0.8 and 2.2 L doses and after a 2.2 L dose was heated to 140 K (upper spectrum).

zation of DBr molecular orbitals disappear. Consistent with this, Bradshaw and co-workers[17] found no HREELS evidence for the H–Br stretching vibration after dosing HBr on Pt(111) between 150 and 300 K.

3.2. Photochemistry of DBr on Br/Pt(111). In view of the foregoing, the photochemistry of DBr can be studied only on Pt(111) partially covered by bromine and deuterium. The TPD peak intensities, positions, and shapes were the same before and after UV irradiation with an unfiltered Hg arc lamp; i.e., effects of UV are not distinguishable by TPD because of thermal decomposition that occurs during TPD.

To detect the effects of UV, photoelectron spectra were taken at 52 K, before and after irradiation. The XP and UP spectra were slightly different, indicating some photon-driven dissociation. When 2.2 L of DBr was irradiated for 10 min, the XPS results (Figure 5) indicated increased atomic bromine, from 50 to 58%, with no loss of Br. In a control experiment involving no irradiation, a 1 ML dose was warmed to 60 K for 10 min (this temperature is higher by 3 K than the irradiated surface temperature). Subsequent XPS shows no increase of the atomic bromine signal. Our expectations are, thus, confirmed; some photon-driven dissociation of DBr occurs.

The UV photon absorption of gas-phase HBr is continuous above 160 nm, maximizes near 180 nm, and decays exponentially out to 280 nm, where it becomes negligible.[18] In fact, at 250 nm the absorption cross section is only 10^{-22} cm^2. Dissociation is prompt and occurs with unit efficiency. Ground-state Br atoms are a major product and the excess energy is, by momentum conservation, largely in the H atoms, e.g., 1.25 eV at 250 nm.[18] For our light source ($\lambda \geq 250$ nm) and for monolayer coverages, most of the absorption is in the Pt, not the DBr. Thus, we expect, as known for CH_3Br,[19] that direct excitation, i.e., photon absorption by DBr, makes a minor contribution, and substrate-mediated hot electron charge transfer excitation dominates, forming DBr^-. The latter process involves photon absorption in the metal to form excited electrons which are transported to the adsorbate–substrate interface. These hot carriers can, with some probability, attach to and, thereby, activate the adsorbate. The substrate-mediated process was confirmed in control experiments showing that, for multilayers of DBr, only the first layer was photolyzed. In our case, the work function lies between 5.8 and 6.0 eV and, thus, photon energies (<5.3 eV) are insufficient to eject electrons, i.e., no photoelectrons.

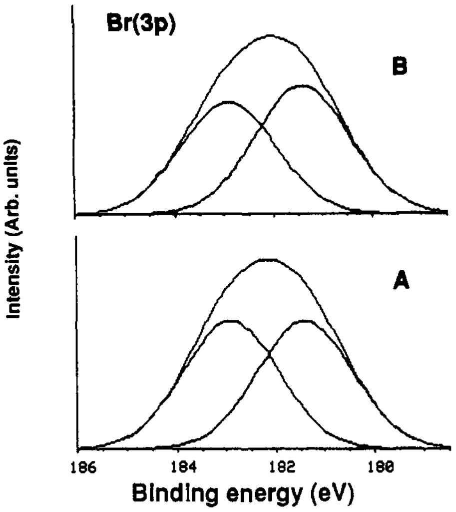

Figure 5. Br(3p) XPS of 2.2 L dose of DBr at 52 K before (A) and after (B) irradiation. Irradiation time was 10 min with full arc. The decomposition used two peaks with fixed fwhm of 2.3 eV.

Substrate-mediated photochemistry induced by energetic electrons is well known, particularly for hydrogen and alkyl halides.[3] As important examples, (1) there is direct evidence for Cl^- desorption in the photolysis of CCl_4 on Ag(111);[20] (2) there is a correlation between photoelectron yield and photon-driven dissociation of CH_3Cl on Pt(111);[13] (3) lowering the work function by potassium coadsorption increases the photochemical dissociation cross section of CH_3Cl on Pd(111)[21] and HCl on Ag(111);[22] and (4) raising the work function by adding atomic Cl decreases HCl photodissociation on Ag(111).[23] We suppose the same excitation dominates the DBr photochemistry observed here.

3.3. Photoinduced Reaction between Adsorbed DBr and C_2H_4. We now turn to the main topic, photochemistry of coadsorbed DBr and C_2H_4 on Pt(111) at 52 K. Ethylene was chosen because it has known H atom scavenging properties for hot hydrogen atoms.[12] To avoid background artifacts, ^{13}C-labeled ethylene was used.

For benchmark purposes, we examined the characteristics of adsorbed ethylene, with and without coadsorbed DBr. Ethylene on Pt(111) has been studied extensively, but most studies involve adsorption above 85 K. Based on HREELS[24–26] at 100 K, ethylene rehybridizes to a di-σ-bonded form upon adsorption at 100 K; each carbon atom forms a covalent σ bond to a surface Pt atom, eliminating the C–C π bond and leaving a single C–C σ bond. Adsorption at 52 K leaves monolayer ethylene in a π-bonded configuration, and further dosing leads to multilayers (not possible at $\geq$85 K).[27,28] The UP spectra become characteristic of di-σ ethylene between 80 and 90 K; i.e., conversion from the π- to the σ-bonded form is complete. For TPD under our conditions (Figure 6), some ethylene desorbs at 86 K when the dosing time exceeds 40 s. This peak grows, but does not fully saturate before an unsaturable peak at 70 K first appears (80-s dosing time). Heating above the range shown in Figure 6, as expected, leads to ethylene

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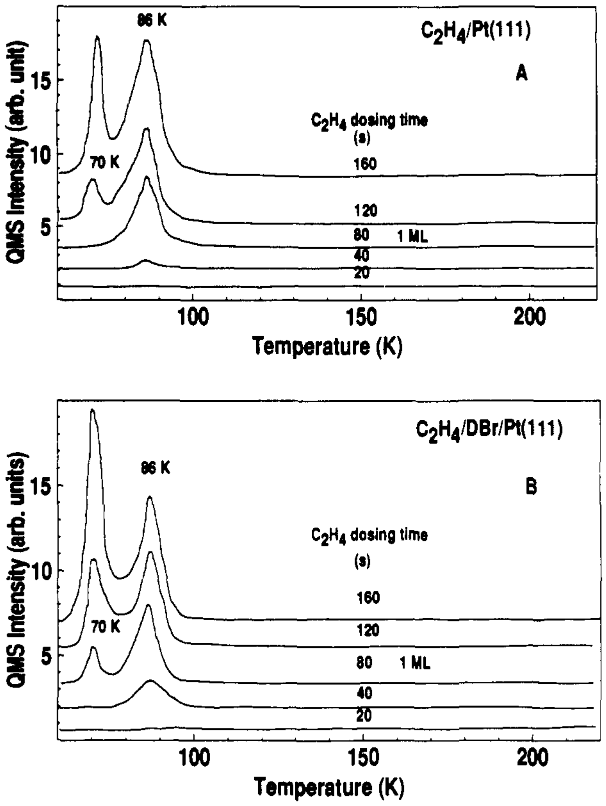


Figure 6. TPD spectra following various exposures of ethylene on clean Pt(111) (A). In (B) the ethylene covered surface was postdosed with 2.2 L of DBr. Adsorption temperature was at 52 K. The desorption of di-σ-bonded ethylene between 250 and 300 K is not shown here. Note that 80-s dosing time corresponds to 1 ML ethylene coverage.

desorption and ethylidyne formation at 280 K.[26] We arbitrarily define one monolayer (1 ML) in terms of the maximum exposure that gave no multilayer TPD peak.

In order to assess the photochemistry observed in this coadsorbed system, we studied, by TPD (Figure 6B), the influence of DBr on C_2H_4 (no light). Ethylene, π-bonded, was adsorbed first and, in each case, was followed by a constant amount of DBr (2.2 L). The DBr dose causes an increased and redistributed low-temperature desorption of ethylene. The increase occurs at the expense of desorption between 250 and 300 K. The redistribution involves more intensity at 70 K and less intensity at 86 K for a given coverage of C_2H_4; i.e., DBr displaces C_2H_4 from the monolayer to the multilayer TPD peak.

Di-σ-bonded ethylene, prepared by heating multilayer ethylene to 100 K and recooling to 52 K, behaves differently. TPD spectra with and without coadsorbed DBr (2.2 L) were almost the same except for a 10 K shift of C_2H_4 TPD to higher temperatures.

Significantly, the extent of thermal dissociation of DBr is not influenced by the type or amount of ethylene, and there is *no thermal chemistry* between adsorbed C_2H_4 and DBr (bottom two curves of Figures 7 and 8). Moreover, ethylene, alone or coadsorbed with H(a) and/or Br(a), is not altered by photolysis; i.e., photoinduced desorption, decomposition and transformations from σ-to-π or π-to-σ states were below detection limits. However, when molecular DBr was coadsorbed with either π- or di-σ-bonded ethylene, illumination caused significant changes (Figures 7 and 8). Both $C_2H_4D_2$ and C_2H_4DBr desorb during postirradiation TPD. Product desorption during irradiation was below detection limits.

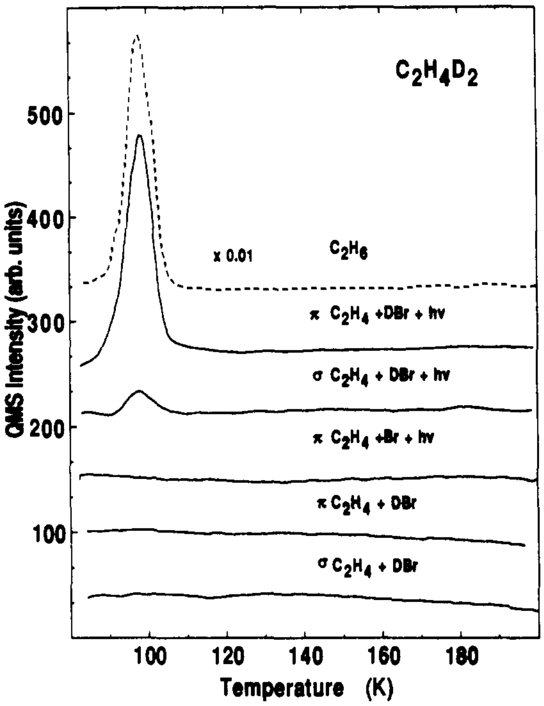


Figure 7. TPD signals for desorption of $C_2H_4D_2$ with and without irradiation of C_2H_4 + DBr coadsorbed on Pt(111) at 52 K. Irradiation time was 10 min. In each case, 2.2 L of DBr was postdosed at 52 K. Di-σ-bonded ethylene was prepared by heating the adsorbed layer to 100 K. The surface concentrations of π- and di-σ-bonded ethylene were the same (40 s dosing time; 0.5 ML). When using no illumination, the coadsorbed system was held in dark at 52 K for 10 min before starting TPD.

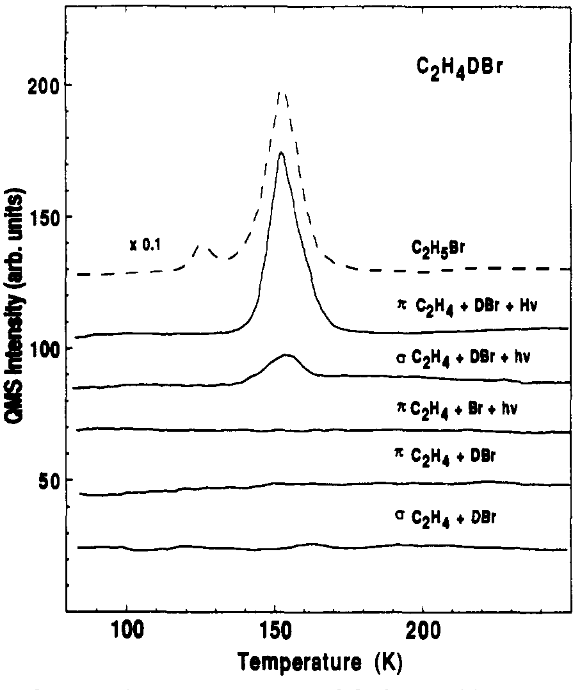


Figure 8. TPD signals for desorption of C_2H_4DBr with and without irradiation of C_2H_4 + DBr coadsorbed on Pt(111) at 52 K. Irradiation time was 10 min. The adsorbed layer was prepared as indicated in Figure 7.

The TPD spectra of ethane and bromoethane, dosed at 52 K on Pt(111), are also shown in Figures 7 and 8 (dashed curves). Ethane desorbs at 99 K and bromoethane at 152 K. Since the photoproducts desorb at the same temperatures, we conclude that they are desorption-limited, not reaction-limited. In other words, ethane and bromoethane already exist at 99 and 152 K, respectively, and we conclude that they form either during irradiation or the early stages of TPD. As a control experiment, we used $^{12}C_2D_4$ and HBr. As expected, labeled ethane, $^{12}C_2D_4H_2$, and bromoethane, $^{12}C_2D_4HBr$, dominated the products.

XPS data (Figure 9) confirm UV photolysis on the basis of Br(3p) signals before (A) and after (B) irradiation. After irradiation for 6 min, there is no change in the total peak area, but a shift to the lower BE. The peak at 181.5 eV, due to atomic bromine, increased by 14%, a greater increase than observed for

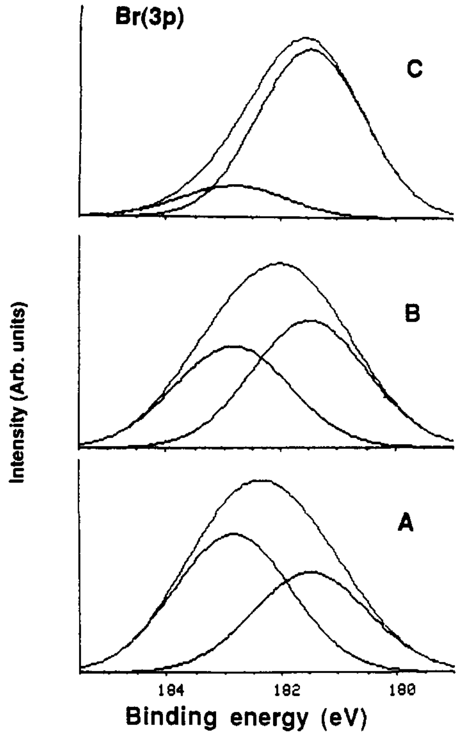


Figure 9. Br(3p) XPS of C_2H_4 + DBr system on Pt(111) at 52 K before (A) and after (B) irradiation, and subsequent heating to 130 K (C). Irradiation time was 6 min with full arc. The preadsorbed C_2H_4 concentration was 1.5 ML, and 2.2 L of DBr was postdosed.

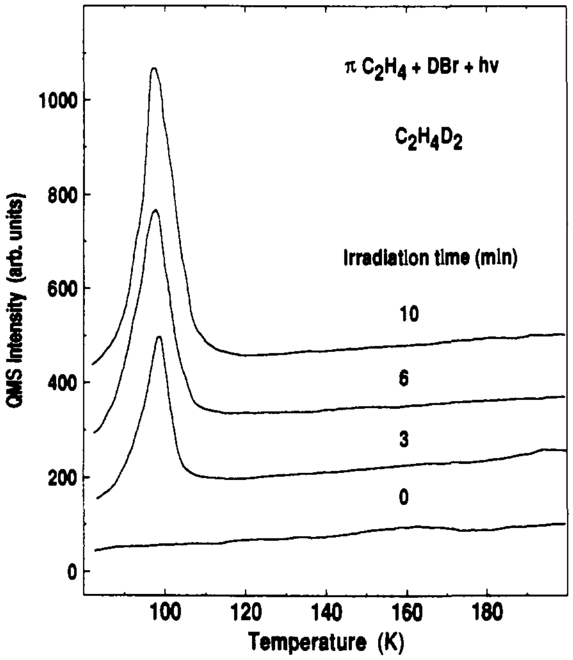


Figure 10. Formation of $C_2H_4D_2$ from C_2H_4 + DBr coadsorbed on Pt(111) as a function of irradiation time; 1 ML (80 s) of ethylene was dosed at 52 K and 2.2 L of DBr was postdosed.

a 10-min exposure in the absence of C_2H_4 (8% in Figure 5). Upon heating to 130 K, the Br(3p) peak area decreases 20% because DBr desorbs. The decomposition shows a weak peak at 182.8 eV, which is attributed to C_2H_4DBr (Figure 9C). Upon heating to 200 K, the high binding energy shoulder disappeared, leaving a symmetric peak (181.5 eV) due to the adsorbed atomic bromine. Separate experiments showed that Br(3p) XPS binding energies are almost the same for undissociated DBr and C_2H_5Br.

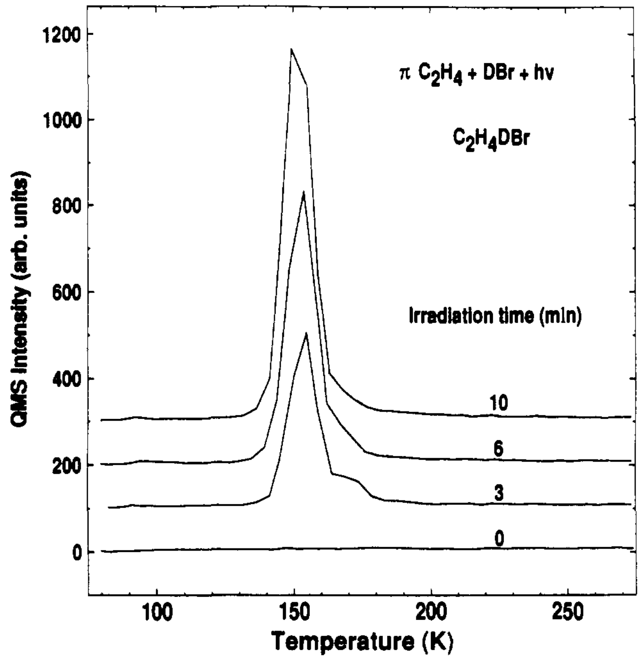


Figure 11. Formation of C_2H_4DBr from the C_2H_4 + DBr coadsorbed on Pt(111) as a function of irradiation time; 1 ML (80 s) of ethylene was dosed at 52 K and 2.2 L of DBr was postdosed.

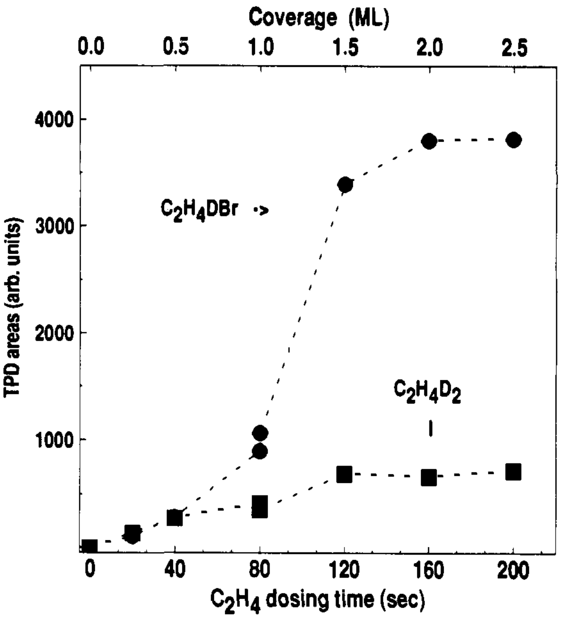


Figure 12. TPD areas of ethane and bromoethane formed during irradiation as a function of ethylene concentration. Irradiation time was 6 min and the DBr exposure was 2.2 L. The TPD areas are corrected with the mass spectrometer sensitivity.

The photon-driven reactions are sensitive to the form of ethylene; the π-bonded form is much more reactive than the di-σ-bonded form (Figures 7 and 8). Figures 10 and 11 show postirradiation TPD of ethane and bromoethane formed by photolysis of π-bonded ethylene and DBr for several irradiation times. Figure 12 summarizes the peak areas (adjusted with mass spectrometer sensitivities) as a function of surface coverage of preadsorbed ethylene at a constant DBr concentration (2.2 L) and at a constant irradiation time (6 min). The yields follow different coverage dependences; the amount of ethane increases monotonically up to 1 ML and then saturates, whereas the amount of bromoethane rises with ethane up to 1 ML and then sharply increases before saturating near 2 ML. Below 0.5 ML the two products form in equal amounts, but at higher ethylene coverages they diverge and, at saturation (≥2 ML), 6-fold more bromoethane is formed. Mechanistic proposals must account for these differences in coverage dependence, assuming both are initiated by the formation of DBr^-.

The formation of ethane increases with irradiation time and with the amount of preadsorbed ethylene, but only through the first monolayer, indicating the strategic importance of the surface. Comparison with the gas phase, where free radical chain reactions dominate, and, for ethylene mixed with hydrogen chloride, where C_2H_5Cl is the only significant photochemical product,[29] underscores the important role played by the Pt(111). Photoinduced dissociation of DBr, clearly indicated by XPS, is taken to be the primary step. This process produces a translationally hot D atom, D*:

$$\mathrm{DBr(a)} + h\nu = [\mathrm{DBr}^-] = \mathrm{Br(a)} + \mathrm{D}^* \tag{1}$$

The D* can be quenched or can react with coadsorbed ethylene to form adsorbed ethyl fragments:

$$\mathrm{C_2H_4(a)} + \mathrm{D}^* = \mathrm{C_2H_4D(a)} \tag{2}$$

To form dideuteroethane, we consider two possibilities: adsorbed ethyl either reacts thermally during TPD or reacts with a neighboring DBr within a few picoseconds after its formation (while it retains vibrational excitation). We rule out the reaction of ethyl with a second photoexcited deuterium atom; the probability of this kind of process will be very low, particularly in the early stages of the photon-driven reaction, and the yield of $C_2H_4D_2(a)$ should be very nonlinear, contrary to our observations. Based on other work involving ethyl fragments derived from the thermal dissociation of C_2H_5I[30] and photodissociation of C_2H_5Cl[31] the hydrogenation of ethyl intermediates, by chemisorbed atomic hydrogen, occurs in a reaction rate-limiting step at around 250 K on Pt(111), which is much too high to be relevant in our experiments. A thermally activated reaction with DBr that is dissociating or with nascent D atoms thus formed is more likely since they are certainly being produced in the temperature interval where ethane is formed, ≈100 K (Figure 6), i.e.,

$$\mathrm{C_2H_4D} + [\mathrm{DBr}^*] = \mathrm{C_2H_4D_2} + \mathrm{Br} \tag{3}$$

where [DBr*] denotes thermally activated DBr.

Another plausible explanation involves a vibrationally excited ethyl radical which either scavenges a neighboring D atom or abstracts D from DBr. In order to clarify the role of scavenging, we produced extra hydrogen atoms (0.2 ML) by dosing H_2 at 100 K before preparing the C_2H_4–DBr coadsorbed layer at 52 K. C_2H_5D was not detected in post-irradiation TPD, suggesting that thermalized chemisorbed atomic hydrogen is not involved.

It is plausible that the vibrationally excited ethyl group formed in reaction 2 reacts with chemisorbed DBr, i.e.,

$$\mathrm{C_2H_2D}^* + \mathrm{D{-}Br(a)} = \mathrm{C_2H_4D_2(a)} \tag{4}$$

Of these possibilities, we intuitively favor (3).

We now propose and discuss pathways that can account for the photon-driven bromoethane formation. In homogeneous processes, alkenes, including ethylene, have a tendency to act as Lewis bases and react with electrophilic reagents. This kind of chemistry is probably not important here since DBr^-, the presumed initial excited species, is not electrophilic. Because of strong coupling of Br and D to the Pt(111) surface, neither is the free radical chain chemistry that is prevalent in the gas-phase photochemistry of hydrogen halides.[29]

In another possible path, a fraction of the nascent bromine, formed by photodissociation of DBr, reacts with the adsorbed ethylene:

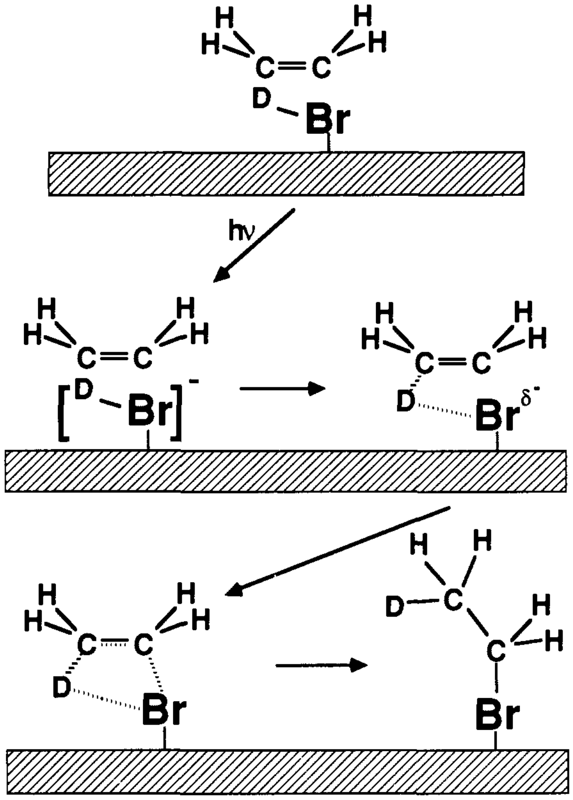
$$\mathrm{C_2H_4(a)} + \mathrm{Br}^* = \mathrm{C_2H_4Br(a)} \tag{5}$$

and then with chemisorbed deuterium during TPD

$$\mathrm{C_2H_4Br(a)} + \mathrm{D(a)} = \mathrm{C_2H_4DBr(a)} \tag{6}$$

to form bromoethane. To test this, hydrogen atoms were preadsorbed. In postirradiation TPD, there was no C_2H_5Br, but, significantly, the same amount of C_2H_4DBr was observed as when no H was preadsorbed. In other words, preadsorbed H is not incorporated into the bromoethane; only the D and Br from DBr are involved. It appears that we can rule out any reaction that involves equilibrium of atomic Br and D with the Pt(111) surface.

Scheme I. Schematic of Proposed Surface-Aligned Reactants and Photon-Driven Reaction Path



These considerations, and the fact that the photon-driven loss of DBr increases in the presence of coadsorbed ethylene, lead us to a concerted reaction between surface-aligned DBr and C_2H_4. We propose two possibilities: (1) DBr^-, formed transiently by electron attachment, reacts with adjacent and aligned ethylene:

$$\mathrm{C_2H_4(a)} + \mathrm{DBr}^- = \mathrm{C_2H_4DBr(a)} \tag{7}$$

or (2) DBr^- forms and is quenched to a vibrationally excited, and activated, ground-state molecule, DBr*, which reacts with ethylene:

$$\mathrm{C_2H_4(a)} + \mathrm{DBr}^* = \mathrm{C_2H_4DBr(a)} \tag{8}$$

Our experiments do not allow these to be distinguished, but it is worth pointing out that reaction 8 extends the available time scale since vibrationally excited DBr* will have a longer lifetime (10^{-10} to 10^{-12} s) than DBr^- (10^{-13} to 10^{-14} s).

From the coverage dependence of the yield of C_2H_4DBr, C_2H_4 aligned over chemisorbed DBr (Scheme I) appears to be key. Assuming reaction 7, in which the negative charge tends to localize on the Br during the lifetime of DBr^-, we would describe the formation of C_2H_4DBr as follows: the accelerating D reacts with prealigned C_2H_4 to form $\{C_2H_4D\}$ in proximity to Br^-, which attaches to the other carbon on a sub-picosecond time scale, i.e., before the Br^- becomes equilibrated with the Pt. In the process, the electron charge is returned to the Pt substrate.

Assuming DBr* is the key intermediate (reaction 8), the formation of C_2H_4DBr can be described in much the same way as above. There are two qualitative differences: first, the electron is returned to the Pt before the bonds to C_2H_4 begin to form, and, second, compared to DBr^-, the DBr* can make a relatively large number of attempts during its longer lifetime.

As can be seen when working on the time scales associated with molecular vibrations, with charge transfer and with acceleration of atoms, the term *concerted* requires refined definition. *Any set*

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of processes that occur during a single encounter should be considered parts of a concerted event even though the members of the set do not necessarily begin and end simultaneously.

Above 1 ML, bromoethane is clearly preferred. We now estimate a lower limit for the percentage of consumed DBr which enters this channel. Assuming that the extent of DBr dissociation is the same with and without ethylene, we compute the following percentages: 75%, 12.5%, and 12.5% for bromoethane formation, ethane formation, and DBr dissociation, respectively. The product, bromoethane, is itself photoactive,[3] but its concentration is not high enough here to compete with the reaction between deuterium bromide and ethylene.

It is interesting that the photoreactivity depends on the structure of ethylene. At the same surface concentration, π-bonded ethylene produces $\approx$10 times more ethane and bromoethane than di-σ-bonded ethylene. These differences emphasize the role played by the substrate; different adsorption sites involve different adsorbate substrate bonding. In turn, intraadsorbate electronic structures differ. Both can play important roles indicating surface photoreactivity.

4. Summary

1. DBr adsorbed on Pt(111) partially decomposes at 52 K. Irradiation with UV light from a Hg arc lamp causes further dissociation, a substrate-mediated process attributed to excitation by attachment to DBr of subvacuum hot electrons. Only the first layer of multilayer DBr is photoactive.

2. There is no thermal reaction between coadsorbed C_2H_4 and DBr. Ethylene alone is not photolyzed; i.e., no photoinduced desorption, decomposition or transformation among its adsorption states occur. There is no photoassisted hydrogenation reaction between ethylene and chemisorbed hydrogen.

3. Coadsorbed DBr and C_2H_4 are photoactive, producing adsorbed ethane and bromoethane which desorb subsequent TPD.

4. The photoinduced ethane formation is attributed to the photodissociation of DBr, generating energetic D atoms. These react with coadsorbed ethylene to produce surface-bound ethyl species, which react thermally with DBr, probably during TPD, to form ethane.

5. The proposed pathway to bromoethane involves a concerted reaction involving surface-aligned and oriented reactant pairs, i.e., DBr–C_2H_4. The excitation is provided by electrons, excited in the substrate, which attach to DBr.

6. The photoproducts form with higher probability when ethylene is π-bonded rather than di-σ-bonded.

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The Electronic Nature of the Metal–Metal Quadruple Bond: Variable Photon Energy Photoelectron Spectroscopy of $Mo_2(O_2CCH_3)_4$

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Abstract: Variable-energy photoelectron spectroscopy of thin film $Mo_2(O_2CCH_3)_4$ on a GaAs substrate in ultrahigh vacuum is used to examine the valence ionizations of the quadruple metal–metal bond. The changes in photoionization cross sections with photon energy over a range of 40 to 90 eV are examined. The metal-based σ, π, and δ ionizations of the quadruple bond are strongly enhanced relative to the acetate-based ionizations in the region of photon energies from 40 to 50 eV. This is consistent with a molybdenum 4p to 4d resonance and super-Coster–Kronig Auger enhancement of the metal-based ionizations. The extent of resonance enhancement is related to the amount of Mo 4d character associated with the ionization. The π ionization of the Mo–Mo quadruple bond has the largest contribution from the Mo 4d orbitals. The δ and σ ionizations of the metal–metal bond contain smaller amounts of Mo 4d character, and some Mo 4d character is observed in the acetate-based ionizations. This is explained in terms of significant overlap and mixing of the δ and σ components with the ligand orbitals. Also, in the case of the σ component, there is a possible filled/filled interaction between the Mo $4d_{z^2}$ orbital on one metal and the Mo $4p_z$ orbital on the adjoining metal. These interactions have significant impact on the properties of these complexes.

Introduction

Following the recognition that certain molybdenum dimer complexes possess metal–metal quadruple bonds,[1] there has been a continuing effort directed toward obtaining a better understanding of these compounds.[2-4] Recent investigations range from studies of general reactivity[5] to studies of these compounds as precursors for cluster formation[6] and as monomeric units in inorganic polymerization reactions.[7] There have even been several industrially useful catalysts identified which contain Mo–Mo quadruple bonds.[8] In each of the studies, the focus of the effort

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