

Photochemical reactions of cis and trans-1,2-dichloroethene adsorbed on Pd(111) and Pt(111)

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Citation: *The Journal of Chemical Physics* **88**, 4484 (1988); doi: 10.1063/1.453807

View online: <http://dx.doi.org/10.1063/1.453807>

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Photochemical reactions of *cis*- and *trans*-1,2-dichloroethene adsorbed on Pd(111) and Pt(111)

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(Received 14 September 1987; accepted 1 December 1987)

The photochemical behaviors of *cis*- and *trans*-1,2-dichloroethene (DCE) adsorbed on Pd(111) and Pt(111) surfaces have been studied using electron energy loss spectroscopy (EELS). For multilayer coverage on either metal surface, irradiation of physisorbed DCE at 110 K with broad band irradiation ($\lambda > 200$ nm) results in photoisomerization, *cis* \rightleftharpoons *trans*. For monolayer coverage on Pt(111) at 110 K, photolysis of chemisorbed DCE causes loss of the two chlorine atoms to form a single hydrocarbon product, chemisorbed acetylene. Apparently, for $\lambda > 237$ nm, the chlorine atoms remain bound to the platinum surface whereas for shorter wavelengths, $\lambda > 200$ nm, the chlorine atoms leave the surface. These results are interpretable in terms of singlet excitation of the chemisorbed alkane followed by chlorine elimination on an excited singlet reaction surface. This study indicates that photochemistry of molecules chemisorbed on a metal surface is possible despite the proximity of the conducting surface. It shows that energy relaxation processes connected with this proximity are not prohibitively fast.

INTRODUCTION

There has been little study of the photochemistry of molecules adsorbed on metal surfaces. A variety of processes have been discussed that tend to discourage such study. The major concern is connected with energy transfer from the adsorbate to the metal, which is thought to be prohibitively rapid and operating through several decay channels, as summarized by Chuang.²

A number of photolysis studies have focused on photo-desorption using both ultraviolet and infrared light sources. For example, McAllister and White³ examined UV-induced photodesorption of carbon monoxide from Ni surfaces, while Chuang⁴ used high power CO₂ laser pulses of infrared light to study the photodesorption of pyridine from Ag(110) and from polycrystalline silver films. The latter work indicated that substrate heating promoted desorption of the more weakly bound molecules.

Other photophysical studies have measured phosphorescent lifetimes of electronically excited states held near a cold metal surface by an inert spacer layer, such as solid argon. An inverse cube distance dependence has been found for the energy transfer rate from the excited molecule to the solid surface for distances down to about 10 Å.⁵⁻⁷ Attempts to measure excited state lifetimes for molecules in contact with a smooth metal surface have been unsuccessful. However, this experimental dependence, as well as classical predictions,⁸ if applicable at close approach, would indicate subpicosecond deactivation times.⁹

In this paper we report the photochemistry of *cis*- and *trans*-1,2-dichloroethenes (1,2-DCE) chemisorbed on the Pt(111) surface. The photochemistry of the 1,2-dichloroethenes have been studied in the gas^{10,11} and liquid phase¹² as well as in cryogenic matrices.¹³ We have used electron energy loss spectroscopy to monitor the chemical reactivity of the adsorbed dichloroethenes, with and without UV irradiation, as a function of temperature and surface coverage. In a separate paper¹ we discuss in detail the structure and

thermochemistry of the dichloroethenes adsorbed on Pt(111). (Hereafter, we will designate Ref. 1 as I).

EXPERIMENTAL

The ultrahigh vacuum chamber used for these experiments has been described previously.¹⁴ The chamber is equipped with Auger electron spectroscopy, low energy electron diffraction, and electron energy loss spectroscopy (EELS). An incident beam energy of 3 eV was used in the EELS experiments. The spectral region from 0–4000 cm⁻¹ was scanned, with a spectral resolution, as defined by the half-width of the elastic peak, of 70–80 cm⁻¹. A quadrupole mass spectrometer was used to measure background gases. The Pt(111) crystal was cleaned by repeated oxygen and heat treatments as well as Ar bombardment, which has been described elsewhere.¹⁴

A General Electric medium pressure mercury arc lamp (AH-4), with its envelope removed, was used as the broad band photolysis source. A quartz lens focused the light into the vacuum chamber and onto the platinum crystal through a 1 in sapphire window (Varian). The crystal temperature was 110 K during each EELS scan as monitored by a Chromel–Alumel thermocouple spot welded to the bottom of the crystal.

The purity of the *cis*- and *trans*-1,2-dichloroethene samples (Aldrich, *cis*-DCE, 97%, *trans*-DCE, 98%) was checked by both gas chromatography and infrared spectroscopy. These liquids were freeze–pump–thawed several times before being introduced into the vacuum chamber. Gas exposures were done using a needle valve doser.

RESULTS

Photolysis of DCE adsorbed on Pd(111) at multilayer coverage at 120 K

Figure 1 shows the EEL spectrum of *trans*-DCE adsorbed on Pd(111) at multilayer coverage before photolysis

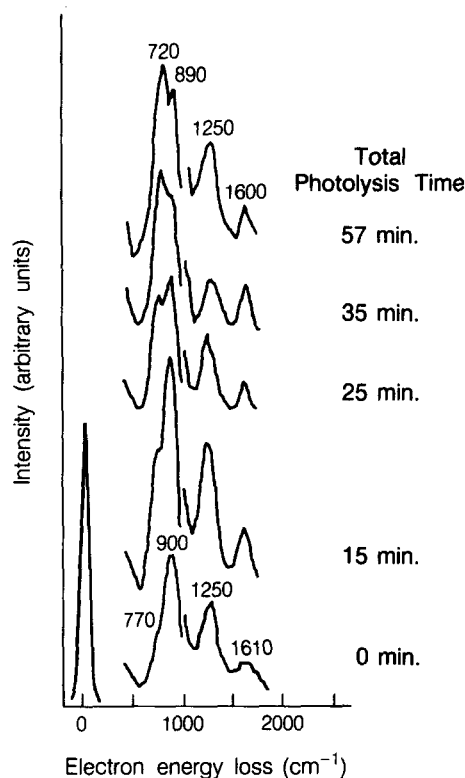


FIG. 1. EEL spectra (specular angle) of a multilayer coverage of *trans*-DCE on Pd(111) at 120 K following photolysis ($\lambda > 200$ nm); total photolysis time as shown.

and then after successive irradiations with the unfiltered mercury lamp. The spectrum before photolysis is quite close to the multilayer EEL spectrum of *trans*-DCE on Pt(111); both spectra resemble closely the IR spectrum of liquid *trans*-DCE (see I). On photolysis, the EEL peak at 900 cm^{-1} decreases and a peak at 720 cm^{-1} grows.

Figure 2 shows the EEL spectrum of *cis*-DCE adsorbed on Pd(111) at multilayer coverage before photolysis [Fig. 2(a)] and then after 52 min of irradiation [Fig. 2(b)]. Again the spectrum is quite close to the multilayer EEL spectrum of *cis*-DCE on Pt(111) and it closely resembles the IR spectrum of liquid *cis*-DCE (see I). Spectrum (b) in Fig. 2 shows that on photolysis, an intense EEL peak at 890 cm^{-1} grows in. Most notable, the spectrum (b) closely resembles the top spectrum in Fig. 1. The spectra indicate that photolytic isomerization is taking place in the multilayer adsorbates. A plot of the intensity of these two features, 720 and 890 cm^{-1} , as a function of photolysis time is shown in Fig. 3. Intensities were measured by normalizing peak intensities to the elastic peak, subtracting the background, and integrating the resulting area. A corrective factor was included to account for any contribution from the *cis* isomer to the intensity of the loss peak around 900 cm^{-1} , as well as any contribution from the *trans* isomer to the intensity of the loss peak around 720 cm^{-1} . Despite the scatter, it is clear that an hour of photolysis of either the *cis*- or *trans*-DCE reaches a steady state with about 0.4 ± 0.1 *cis*-DCE. This implies a steady state mole ratio, $cis/trans = 0.67 \pm 0.20$.

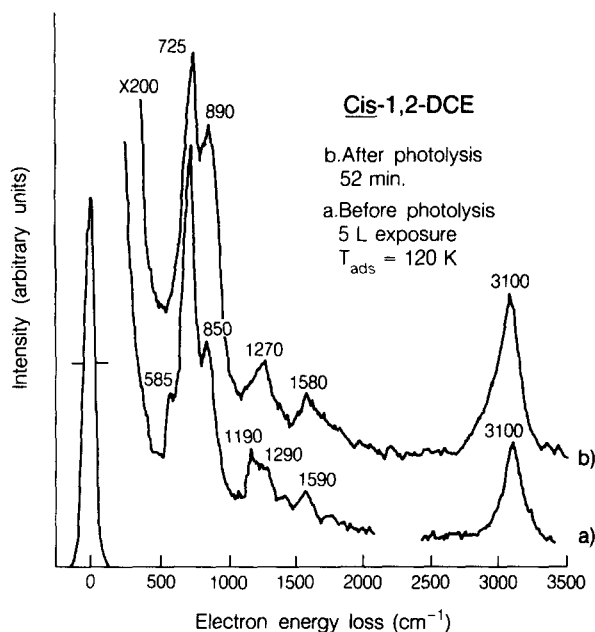


FIG. 2. EEL spectra (specular angle) of a multilayer coverage of *cis*-DCE on Pd(111) at 120 K. (a) Before photolysis; (b) after 52 min photolysis, $\lambda > 200$ nm.

Photolysis of *trans*-DCE adsorbed on Pt(111) at multilayer coverage at 110 K

Figure 4(a) shows the EEL spectrum of *trans*-DCE adsorbed on Pt(111) at multilayer coverage before photolysis and then after successive irradiations with the unfiltered mercury lamp. In I we have already noted that the multilayer EEL spectrum closely resembles the IR spectrum of liquid *trans*-DCE. Figure 4(b) shows that after only 10 min of photolysis, a loss peak at 730 cm^{-1} has appeared. After 20 min, the spectrum includes intense loss peaks at 725 and 890 cm^{-1} in about the same relative intensity as those seen in EEL spectrum (e) in Fig. 1 and (b) in Fig. 2. As on the Pd surface, photolysis of *trans*-DEC causes isomerization, and presumably to the same steady state ratio.

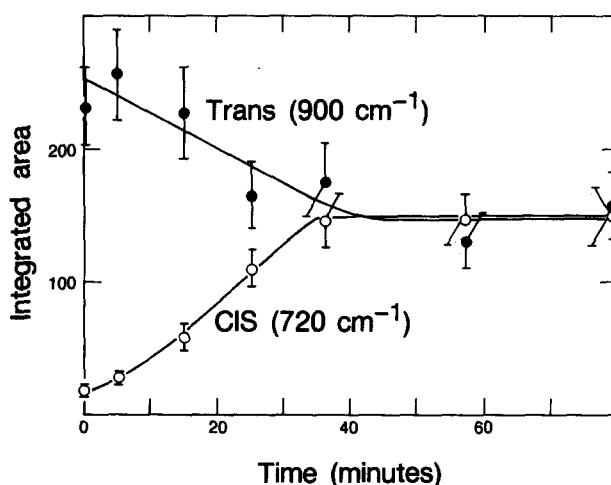


FIG. 3. Growth and decay curves for loss peaks at 720 and 900 cm^{-1} , respectively, during photolysis of a multilayer sample of *trans*-DCE on Pd(111) at 120 K.

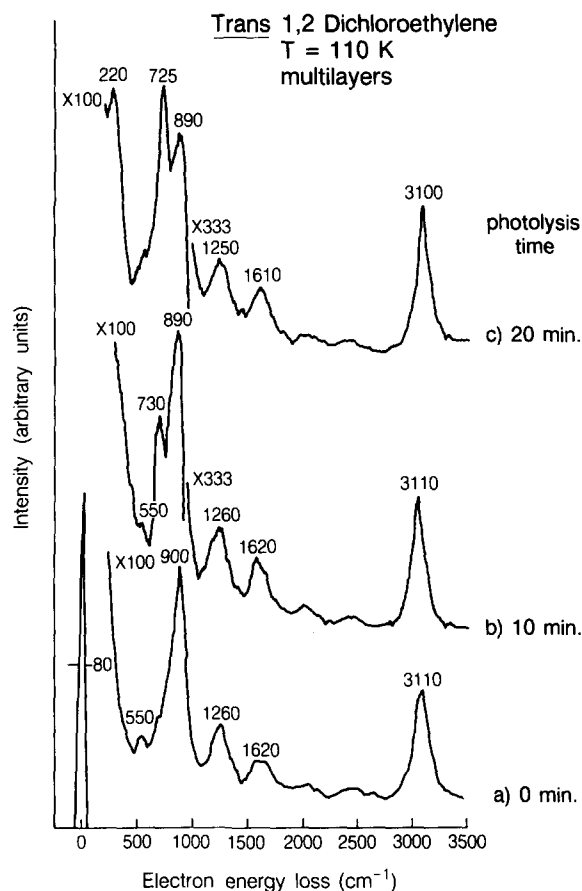


FIG. 4. EEL spectra (specular angle) of a multilayer coverage of *trans*-DCE on Pt(111) at 110 K following photolysis ($\lambda > 200$ nm); total photolysis time as shown.

Photolysis of DCE adsorbed on Pt(111) at monolayer coverage at 110 K

Figure 5(a) shows the EEL spectrum of a multilayer sample of *cis*-DCE after warming to 158 K and then recooling to 110 K. This spectrum is essentially the same as that obtained initially with exposures calculated to provide less than monolayer coverage (see I) and we interpret it to represent a monolayer coverage. Such a sample was photolyzed for 90 min through a CsI filter ($\lambda > 237$ nm) to give the EEL spectrum 5(b). Then another monolayer sample, prepared like the first, was photolyzed for 90 min but without the CsI filter [spectrum 5(c)]. During photolysis, the Pt block temperature rose 1° . Both photolysis spectra 5(b) and 5(c) have rather intense CO EEL peaks at 2080 cm^{-1} due, almost certainly, to carbon monoxide accumulated during the 90 min photolysis period. Both spectra include intense EEL peaks at $785\text{--}790$ and $3020\text{--}3025\text{ cm}^{-1}$. Weaker peaks are observed at 1010 and 515 cm^{-1} in spectrum 5(c), with counterparts at 990 and 520 cm^{-1} in spectrum 5(b), though apparently at rather higher intensity. The major difference is that spectrum 5(b) has a prominent absorption at 290 cm^{-1} whereas spectrum 5(c) has only an indistinct feature at 260 cm^{-1} .

Essentially identical results were obtained with samples prepared by 75 s exposure to 5×10^{-9} Torr *cis*-DCE, conditions that give directly a surface coverage estimated to be 0.70 monolayers. In particular, the absorption at 300 cm^{-1}

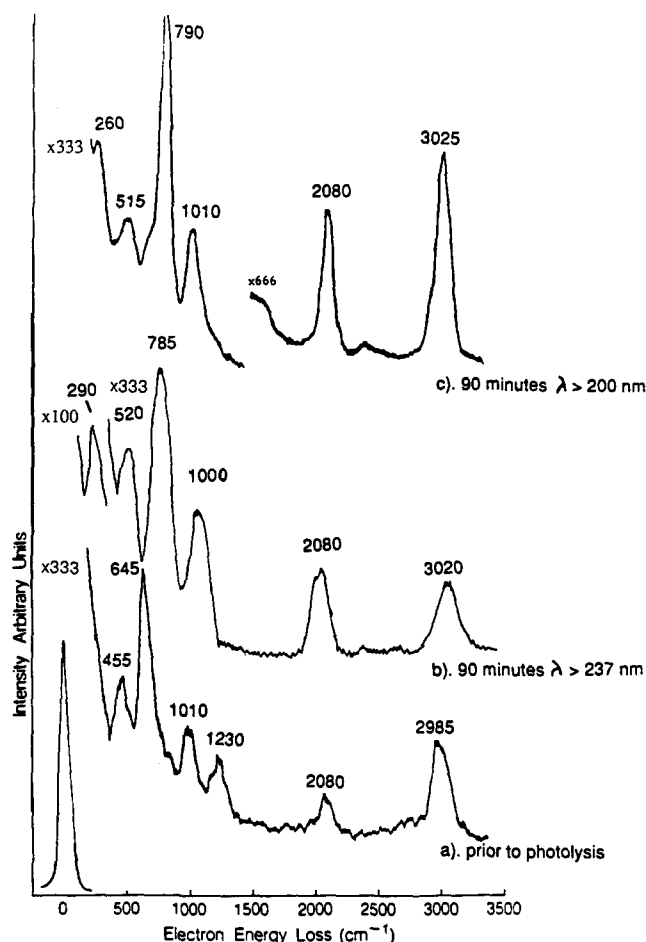


FIG. 5. EEL spectra (specular angle) of monolayer coverages of *cis*-DCE on Pt(111) at 110 K. (a) Before photolysis; (b) after 90 min photolysis with CsI filter ($\lambda > 237$ nm); (c) after 90 min photolysis without filter ($\lambda > 200$ nm). Spectra (b) and (c) are of different samples.

was observed if the sample was photolyzed with the CsI filter ($\lambda > 237$ nm) but not when the sample was photolyzed without the filter ($\lambda > 20$ nm).

Figure 6 shows similar experiments with *trans*-DCE. These samples were prepared by warming a multilayer sample to 158 K and then recooling to 110 K . Again during photolysis, the temperature of the platinum substrate was monitored and its temperature never rose more than 1° . All of the features seen in Figs. 5(b) and 5(c) are reproduced, this time beginning with the *trans*-DCE monolayer. This close similarity includes the behavior of the peak at 300 cm^{-1} .

Spectrum 5(c) is remarkably close in its major features to the spectrum displayed in Fig. 3(c) of I, obtained by heating to 270 K a monolayer sample of *cis*-DCE on Pt(111). Evidently the same chemical change has occurred on photolysis with $\lambda > 237$ as is produced by warming to 270 K . With the same arguments presented in I, we identify the common parts of spectra 5(b) and 5(c) with the EEL spectrum of acetylene adsorbed on Pt(111), as first reported by Ibach and Lehwald.¹⁵ Again as in I, we assign the intense peak at 300 cm^{-1} to the Cl-Pt stretch of chlorine adsorbed on Pt(111). Evidently photolytic dehalogenation has taken place.

To provide evidence about the presence of the EEL peak

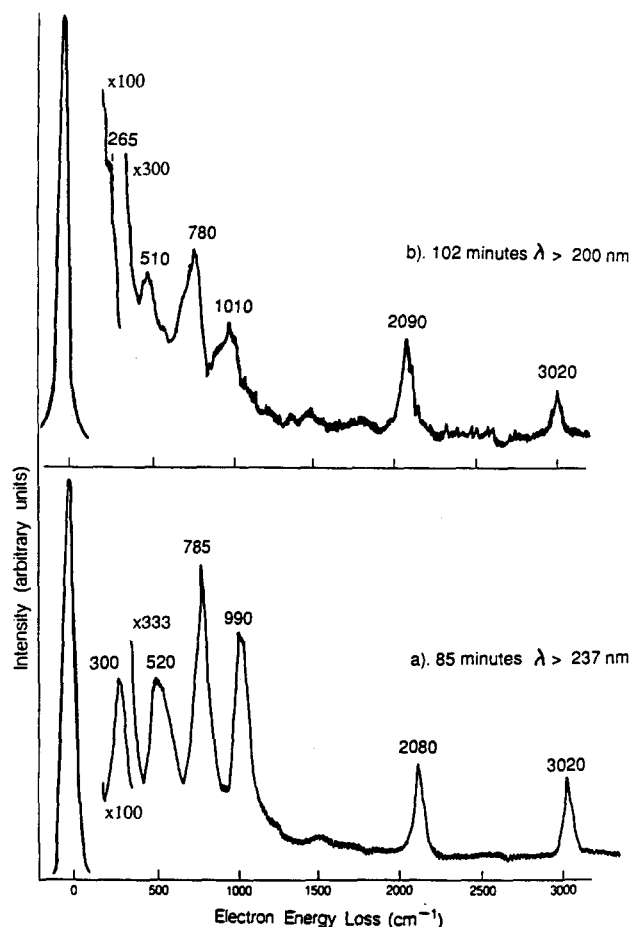


FIG. 6. EEL spectra (specular angle) of monolayer coverages of *trans*-DCE on Pt(111) at 110 K. (a) After 85 min photolysis with CsI filter ($\lambda > 237$ nm); (b) after 102 min photolysis without filter ($\lambda > 200$ nm). Spectra (a) and (b) are of different samples.

at 300 cm^{-1} in spectrum 5(b) and its absence in 5(c), an experiment was performed in which a sample of *cis*-DCE on Pt(111) was warmed to 270 K, recooled to 110 K, and then the sample was photolyzed for 90 min using the unfiltered mercury lamp. The intensity of the 300 cm^{-1} loss peak was not affected by this photolysis (nor were the intensities of any other peaks). This indicates that the chromophore responsible for the 300 cm^{-1} loss peak, presumably the Cl-Pt stretch, is not removed by secondary photolysis at $200 < \lambda < 237$ nm.

DISCUSSION

Multilayer photolysis on Pd(111) and Pt(111) at 110 K

Whether photolysis begins with *trans*-DCE (Figs. 1 and 4) or *cis*-DCE (Fig. 2) the major outcome is the production of the other isomer. Furthermore, the relative amounts of the two isomers on prolonged photolysis are independent of the starting point; the steady state ratio is about 0.4 ± 0.1 *cis*- and 0.6 ± 0.1 *trans*-DCE (see Fig. 3), and apparently the same on Pt(111) as on Pd(111). The steady state behavior indicates, as well, that photodesorption is not an important process.

This result can be compared to the photochemistry observed in the liquid state¹² and in solid krypton.¹³ (The gas phase photochemistry is much more complex, presumably because of free radical chains.) The matrix results are most relevant. Cartland and Pimentel¹³ found that radiation of *trans*-DCE with $\lambda > 200$ nm for 1 h caused some isomerization to *cis*-DCE. Irradiation of *cis*-DCE in krypton for a 3 h period also caused isomerization to the *trans*-DCE but an estimated 8% of the photolyzed *cis*-DCE caused elimination to give the products HCl and monochloroacetylene. The most intense peaks of C_2HCl fall, in Kr matrix, at 3309 and 2100 cm^{-1} . Close inspection of spectrum 2(b) reveals possible loss peaks at 2178 and 3347 cm^{-1} with intensity just above the noise level. These bands, if real, might be evidence for photoproduction of C_2HCl in the multilayer sample.

The liquid state photolysis studies of Grabowski and Bylina¹² are also of interest. They found that photolysis with the full spectrum of a high pressure Hg lamp caused isomerization, some polymerization, and also the production of HCl. When the lamp was filtered to restrict photolysis to $\lambda > 290$ nm, no photolysis occurred. However, after the liquid was saturated with O_2 at a pressure of 30 atm or greater, isomerization was again observed and now without either polymerization or HCl elimination. Grabowski and Bylina concluded¹² that photolysis in the range 400–300 nm in the presence of the paramagnetism of triplet O_2 caused excitation of the triplet $T_1 \leftarrow S_0$ transition. Quantum yield studies were consistent with the model that such triplet excitation of either *cis*- or *trans*-DCE causes isomerization through a single intermediate state. The quantum yields led to steady state fractions of 0.55 ± 0.07 *cis* and 0.39 ± 0.05 *trans*. This gives a ratio, *cis/trans* = 1.4 ± 0.3 , noticeably larger than our value, 0.7 ± 0.2 . This difference, which seems to be outside the combined experimental uncertainties, may reflect the different excited state surfaces being accessed upon photolysis, S_1 for the multilayer and T_1 for the liquid phase. Excited state geometries of the triplet and singlet states will certainly differ as well as the relative UV extinction coefficients of the two isomers. Both excited state geometries and UV extinction coefficients will of course have an influence on the quantum yields of the two isomers and therefore the steady state ratios.

Thus, the results of photoysis of either *cis*- or *trans*-DCE in multilayer coverages on either Pd(111) or Pt(111) are remarkably like those obtained for photolysis of the DCE's isolated in Kr matrix and for the pure liquid. Furthermore, the matrix studies offer an interesting contrast in apparent photolysis efficiency. In the matrix study, only a modest fraction of the DCE was isomerized after 3 h of photolysis using a 1000 W high pressure Xe lamp. The present study indicates that on Pd(111) a steady state is reached in less than 1 h using the somewhat less intense AH-4 Hg lamp (see Fig. 1). On Pt(111), this steady state may be approached in less than 30 min [see Fig. 4(c)]. This difference could be entirely due to inefficient photolysis in the matrix case because of scattering, a notorious matrix problem at the shorter wavelengths. In addition, it is difficult to assess the relative effectiveness of the focusing optics used in the various experiments. Nevertheless, our data suggest that the

multilayer surface photochemistry is comparable to or perhaps even more efficient than matrix photolysis.

Monolayer photolysis on Pt(111) at 110 K

Figures 5 and 6 show that with $\lambda > 237$ nm, photolysis of either *cis*- or *trans*-DCE gives the same product spectrum. This spectrum, identified in I as that of acetylene chemisorbed on Pt(111), plus an intense loss peak at 300 cm^{-1} due to the Cl–Pt stretch, was obtained in I by warming monolayer DCE samples on Pt(111) to above 210 K.

Of course, our first concern is that the results shown in Figs. 5 and 6 are not merely due to heating the sample above 210 K, where thermal processes could cause the observed changes. There are three data that rule out this possibility. First, the substrate temperature was continuously monitored during irradiation with a thermocouple spot welded to the bottom of the crystal and its temperature never rose more than 1° or 2° s when the photolysis lamp was turned on. Thus, a temperature gradient above 100° across the 2 mm Pt sample thickness would be needed for the front surface temperature to exceed 210 K. This thermal gradient could not be reached since it would imply a thermal conduction exceeding the entire energy dissipation of the AH-4 lamp. This conclusion is corroborated by the experimental observation that irradiation of the multilayer samples (which are optically thin) does not cause desorption, which occurs at about 160 K. The third piece of evidence is that the EEL spectrum recorded after photolysis without the CsI filter does not include the 300 cm^{-1} peak which is present after pyrolytic decomposition.

It is still worth considering whether a single photon, locally absorbed, could give a momentary local heating (a "hot spot") sufficient in magnitude and duration to decompose the adsorbate by thermal processes. Suppose that a single photon of wavelength exceeding 200 nm is absorbed by a platinum cluster whose temperature is raised by 100° and that the cluster has heat capacity near that of bulk platinum (which averages at 5.5 cal/mol deg between 110 and 210 K). Then the cluster contains less than 260 atoms. This would be equivalent to a cube 6.4 atoms on a side, with side dimension less than 18 \AA or a monolayer 16 atoms on a side, with side dimension less than 44 \AA . We believe that a photon of wavelength exceeding 2000 \AA could not be absorbed in a conducting, single crystal of Pt by a region this small. The only alternative is that the absorption is localized by the adsorbate chromophore which, then, rapidly transfers its electronic excitation into phonon vibrational motion restricted to a volume of the dimensions given above. There is a large body of experience in matrix isolation photochemistry that shows that as an excited guest molecule relaxes through the host lattice phonon modes, the local temperature rises by no more than a few degrees. These considerations strongly disfavor an interpretation of the present results based on thermal decomposition induced by a local hot spot.

Thus, we conclude that dehalogenation of the chemisorbed DCE has been induced photolytically on the Pt(111) surface at 110 K. With photolysis wavelengths exceeding 237 nm, an EEL peak at 300 cm^{-1} indicates the production of adsorbed chlorine atoms whereas, with $\lambda > 200$ nm, this

loss peak is not observed. Instead there is revealed a weaker feature at 260 cm^{-1} which we assign to a Pt–C stretch due to the acetylene product.

Photochemical pathways

Molecular states accessible

Since we have identified the chemical structure of the adsorbed DCE as that of a dihalogenated ethane, we will investigate first whether this molecule is a suitable prototype that helps us understand the observed surface photochemistry. The halogenated ethanes are known to undergo photoelimination at vacuum UV wavelengths and C–X bond rupture at longer wavelengths, extending above 200 nm. Figure 7 shows the UV absorption of 1,2-dichloroethane in octane solution at room temperature. This absorption, which extends to about 220 nm, is attributed to an $n \rightarrow \sigma^*$ excitation of chlorine atom electrons. By inference, an analogous triplet state is expected at somewhat longer wavelengths. For surface adsorbed DCE, the absorptions will no doubt be perturbed because two of the alkane bonds are made to surface platinum atoms. Nevertheless, this absorption of dichloroethane provides a basis for assuming that the adsorbed DCE absorbs in the spectral region under investigation. In addition, the photochemistry of the haloethanes points to carbon–chlorine bond rupture and bimolecular elimination reactions as possible reaction channels.

Figures 8 and 9 show a variety of possible reactions, with energetics based upon our best estimates of the bond energies of the Pt–Cl, Pt–H, and Pt–C bonds, respectively,

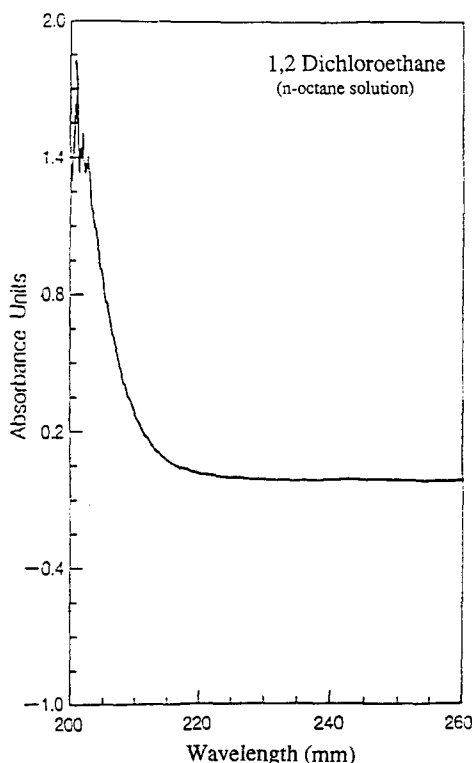


FIG. 7. UV absorption spectrum of 1,2-dichloroethane in *n*-octane solution at 300 K.

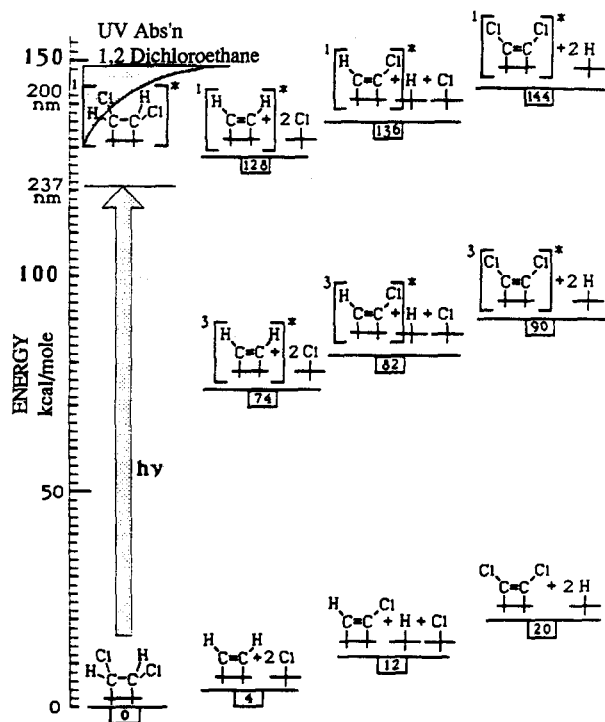


FIG. 8. Energetics of the photochemistry of surface-bound DCE: Possible diatomic elimination reactions to give surface-bound products.

taken to be 47.5,¹⁶ 56.9,¹⁷ and 35 ± 5 ¹⁸ kcal/mol. All of the other estimated quantities are based upon conventional bond additivity, with bond energies as follows: C–C, 83; C=C, 146, C–H, 99, C–Cl, 81 kcal/mol. Notice that if we

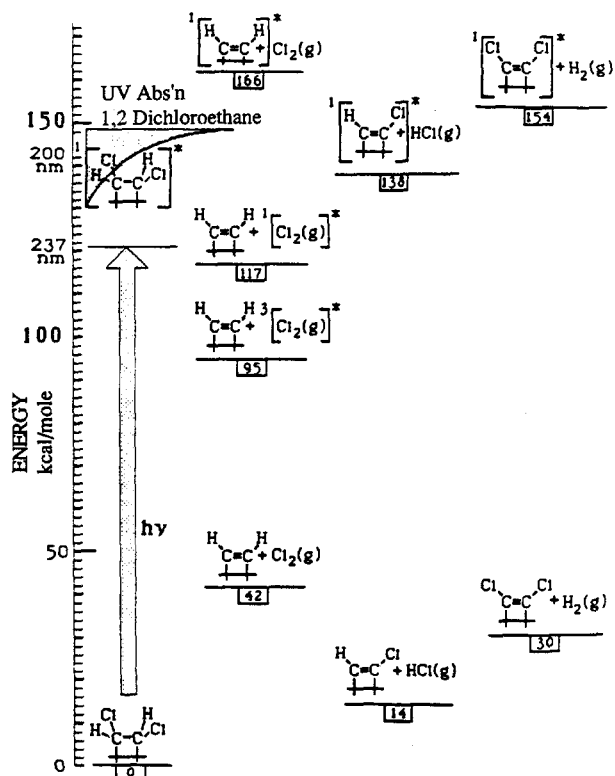


FIG. 9. Energetics of the photochemistry of surface-bound DCE: Possible reactions to give gaseous diatomic elimination products.

assume that the carbon–platinum bond is the same for all of the structures shown, the heat of adsorption (-4 kcal/mol, see I), is the only reaction heat that is affected by the value used for the Pt–C bond energy.

Figures 8 and 9 show that if we consider only the ground state energies of the various possible products, there is ample energy to produce gaseous, diatomic products HCl, H₂, or Cl₂ and monatomic products Cl, H, 2Cl, H + Cl, or 2H. When we turn to reactions in which all products remain bound to the platinum ("surface-only" reactions), again the ground states suggest that there is enough energy to produce one or two bound Cl atoms, one or two bound H atoms, or a bound Cl atom. Thus, if all of the energy associated with photon absorption were immediately available, several reaction products would be expected rather than only the one product actually observed.

Diatomic elimination channels

This simplistic view of the accessible reaction channels ignores the fact that the chemistry is initiated on an electronically excited surface that undoubtedly correlates with excited states of the final products rather than with the ground states. Figure 8 shows the energetic implications for three of the surface-only reaction channels. We have assumed that the olefinic chromophore has its excited state about 124 kcal/mol above the ground state, as suggested by the onset of UV absorption by dichloroethene.¹³ Then we have placed the triplet states about 70 kcal/mol above the ground state, as estimated for ethylene by Lee and Pimentel.¹⁹ Figure 8 suggests that with 200 nm excitation, there is not enough energy to produce two surface-bound H atoms and that only a modest activation energy would be needed to inhibit formation of one H and one Cl atom, each surface bound. Thus, these energy estimates favor elimination of two chlorine atoms, both of which remain on the platinum surface.

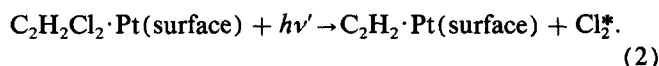
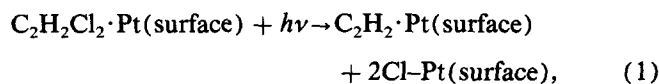
Since platinum is low in the Periodic Table, it is conceivable that its spin–orbit coupling could facilitate crossover from the initially excited singlet state to the corresponding triplet state. The placement of the product triplet states (see Fig. 8) suggests, however, that if this were to occur, the available energy would be ample to open all three reaction channels. Since we observe only one product, the evidence disfavors the involvement of the triplet reaction surface.

If we apply these same considerations to the reaction channels producing gaseous products HCl, H₂, or Cl₂, the singlet excited states require, respectively, 138, 154, and 166 kcal/mol (see Fig. 9). These estimates place only the first reaction product, HCl, within energy reach. Since an activation energy barrier might be expected for molecular elimination, even this reaction is an unlikely one. Turning to the triplet states, again there is enough energy to open all three channels (HCl, 84; H₂, 100, and Cl₂, 112 kcal/mol) and, since we identify only one product, we conclude again that the triplet surface is not involved.

The reaction channel producing gaseous Cl₂ is unique in that the gaseous product itself has low-lying singlet and triplet states. The singlet state is revealed by continuous absorption due to a ¹Π_g state²⁰ with indistinct onset at about 380 nm (75 kcal/mol) and maximum absorption at 328 nm (87

kcal/mol). This gives an excited singlet product state (probably dissociative) at energies exceeding 117 kcal/mol. The lowest triplet state²⁰ of Cl₂(*A* ³Π), lies at 539 nm (53 kcal), to provide a triplet channel for energies above 95 kcal/mol (see Fig. 9).

Figures 8 and 9 offer, then, two favored excited singlet reaction channels, each involving loss of two chlorine atoms, one occurring entirely on the Pt surface at about 128 kcal/mol and one involving the gaseous product Cl₂ at about 117 kcal/mol. In each case, the remaining product is chemisorbed acetylene, as observed:



To rationalize the wavelength dependence, we postulate that there is virtually no activation energy for the surface-only reaction (1) but that there is a modest activation energy (10–20 kcal/mol) for loss of the gaseous product. The implication would be that at longer wavelengths, only reaction (1) can occur but as photon energy rises, reaction (2) becomes dominant. We feel that the energy discrepancy between the CsI cutoff, 121 kcal/mol, and the energy estimated for reaction (1), 128 kcal/mol, is easily within the uncertainty in our estimate of the singlet excitation of the adsorbed carbon–carbon double bond.

Bond rupture channels

As mentioned earlier, ground state energetics do not preclude single atom bond rupture reaction to produce gaseous Cl or H atoms or surface-bound Cl and H requiring, respectively, 81, 99, 34, and 42 kcal/mol. The remaining product would be a halogen-substituted, platinum-bound ethyl radical with unknown excited state energies. We have no spectral nor thermal desorption evidence for the formation of such a radical surface species, so these possible reaction channels will be put aside.

Surface excitations

Alternate explanations of the observed photochemistry might be sought in terms of a more collective excitation of the metal (e.g., surface plasmons or interband transitions) or some sort of charge–transfer excitation. While such excitations may occur, they seem more likely to delocalize the photon energy and interfere with rather than facilitate surface photochemistry. Furthermore, these hypothetical excitations offer no guidance on the specific chemistry to be expected. Insofar as such excitations involving the metal surface takes place, we picture them as relaxation channels that would serve to lower the photochemical quantum yield.

Comparison to other work

Thus, we find that the observed photochemistry can be attributed to the adsorbed molecular chromophore. There has been a great deal of theoretical work devoted to clarifying the excited states of adsorbates on metals, notably by

Avouris and co-workers.²¹ Effects considered include metallic screening (surface plasmons)^{22,23} and resonance electron tunneling to the metal.^{24,25} There has been little experimental success in observing intramolecular electronic transitions for chemisorbed molecules. Robota *et al.*,²⁶ using a sensitive ellipsometry optical technique, found no evidence of intramolecular electronic transitions for aromatics and azoaromatics chemisorbed on Ni(111) (benzene, naphthalene, pyridine, and pyrazine). They did, however, find a broad absorption near 290 nm for every one of these adsorbates, which they attribute to enhancement of a nickel interband transition. There has been more success with electron energy loss spectroscopy.²⁷ Energy loss peaks in the spectra of a pyridine monolayer adsorbed on Ag(111)²⁸ and on Ni(001)²⁹ have been assigned as intramolecular Π→Π* transitions with only small energy shifts from gas phase transitions. For NO chemisorbed on Ni(100),²⁷ loss features were related to gas phase transitions with only modest energy changes (Δ*E*~0.5 eV). Gluck *et al.*³⁰ summarize their own work and that of others on the photodecomposition of Mo(CO)₆, W(CO)₆, and Fe(CO)₅ physisorbed on Si(111) at 90 K. Of course, the semiconductor surface presents a photolysis environment quite different from that of a conducting metal.

Transition metal complexes offer another avenue since there is a wealth of information published on the electronic absorption spectra of transition metal complexes. Of course, metal atom *d*–*d* transitions are not relevant. Metal atom–ligand charge transfer transitions tend to be more intense and they have at best indirect relevance to metal surface–adsorbate charge–transfer bands. There is much less information concerning the effect on intramolecular transitions of ligands bonded to a metal atom, possibly because the ligand electronic transitions tend to be weaker and at shorter wavelengths than charge–transfer bands.

In view of the paucity of data about electronic excitation of chemisorbed molecules, the present work may encourage further studies based upon photochemistry rather than on optical techniques. Even low quantum yields become amenable to study because of cumulative effects over prolonged photolysis periods.

CONCLUSIONS

The most important general conclusion to be drawn from this study is that photoinduced chemistry of adsorbed molecules can be competitive with energy decay mechanisms involving a metal surface. This is initially demonstrated in the photolytic *cis*–*trans* isomerization of multilayer samples of the DCE's on either Pd(111) or Pt(111). The behavior is like that of room temperature liquid samples and of the matrix-isolated DCE's, undoubtedly based upon excitation of the ethylenic chromophore of the physisorbed molecules. The photochemistry is taking place within 10–25 Å of the metal surface since these multilayer samples are no more than two to five layers thick. The photolysis times for substantial isomerization, about 30–60 min, are comparable to those found with the same photolysis source but for the DCE isolated in a cryogenic, inert gas matrix. Hence, the

proximity of the metal surface has, at most, only a modest effect on quantum yield for this unimolecular process.

Photolysis at monolayer coverage is even more interesting since the DCE is clearly chemisorbed in an alkane-like structure (see I). The EEL spectrum clearly shows that the photochemistry gives the same products as obtained thermally: two chlorine atoms are lost, leaving surface-bound acetylene. The chlorine atoms seem to remain surface bound if photolysis wavelengths exceeding 237 nm are used, whereas they are lost completely for wavelengths extending to 200 nm.

The monolayer photochemistry proves to be amenable to interpretation based upon the intramolecular absorption expected for an alkane-like adsorbate. The fact that a single hydrocarbon product is obtained leads to rejection of triplet reaction channels and it focuses attention upon the importance of recognizing that the chemistry has been initiated on an electronically excited singlet reaction surface. The interpretation implies that the gas phase alkane transitions leading to diatomic elimination are shifted about 8000 cm^{-1} to longer wavelengths (i.e., λ 237 nm). Furthermore, we infer that the barrier to forming two surface-bound chlorine atoms is small, less than 10 kcal/mol, whereas the barrier to elimination of Cl_2^* (leading to two gaseous chlorine atoms) must be larger, perhaps in the range 10–20 kcal/mol.

This study dispels, then, some of the pessimism about metal–surface photochemistry that has been engendered by expectations that deactivation would be prohibitively rapid. This study points, we feel, to a promising field of photochemistry of molecules chemisorbed on a metal surface.

ACKNOWLEDGMENTS

This work was supported by the Office of Energy Sciences, Chemical Division of the U. S. Department of Energy, under Contract No. DE-AC03-76SF00098.

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