Measurement of the Binding Energy for Di-σ C_2H_4/Pt{111}: Does a Radical Intermediate Form During Thermal Desorption?

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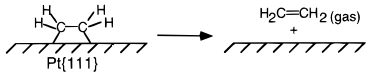
The thermal desorption of an intact molecule from a well-defined surface represents one of the simplest surface chemical reactions available for investigation. For adsorbate systems where several reaction channels are accessed, determining the mechanism of desorption is virtually impossible from the analysis of final state products. In this paper we address the mechanism of thermal desorption of di-σ C_2H_4 from Pt{111}, as shown in Scheme 1, using an impulsive (femtosecond time scale) scattering probe of the initial state of the reactant. Many aspects of the surface chemistry of the C_2H_4/Pt{111} system have been studied intensively over the last 20 years,[1] and the understanding of this multichannel reactivity has evolved considerably[2] with the application of new, time-resolved surface analysis probes. The specific reaction shown in Scheme 1 is of interest because the mechanism of desorption, involving rehybridization of the carbon atoms, remains almost totally unknown. The reaction is of technological interest because the rate of ethylene desorption competes effectively with the rate of hydrogenation. Furthermore, the mechanism of olefin hydrogenation in general remains uncertain,[3] and our measurements suggest that a radical intermediate may be available for hydrogen addition during the thermal desorption reaction.

We report the first measurement of the well depth of the di-σ C_2H_4/Pt{111} potential energy surface. This well depth, or binding energy, is determined by measuring the threshold for impulsive desorption. Combining the binding energy for this state, 2.1 ± 0.1 eV, with the thermally determined activation energy for desorption of 0.7 ± 0.2 eV leads us to conclude that at least two steps (and probably three) are involved in the mechanism of di-σ C_2H_4 thermal desorption from Pt{111}. A plausible mechanism would involve a radical intermediate formed by cleavage of one σ bond along the reaction pathway. A weakly bound precursor state, a "π state" also appears to be accessed during the thermal desorption reaction.

At low temperature a di-σ bonding configuration has been proposed for the C_2H_4/Pt{111} adsorbate−surface complex on the basis of electron energy loss[4], ultraviolet photoelectron,[5] and near edge X-ray absorption fine structure[6] spectra. These studies suggest that in this geometry the carbon−carbon double bond is converted to a single bond (parallel to the surface) as each carbon atom forms a σ-type bond to adjacent Pt atoms. As a result, the carbon atoms rehybridize from sp^2 (π state) to sp^3 (di-σ state) upon adsorption at 90 K. Using temperature-programmed desorption, both C_2H_4 and C_2H_6 are observed to desorb at roughly 300 K.[7] The activation energy for thermal desorption from the di-σ adsorption state has been previously measured[7] to be 0.73 eV (assuming a preexponential factor of 10^{13}). It is important to note that temperature-programmed desorption involves a nonequilibrium measurement; thus, the activation energy for desorption need not equal the binding energy, especially if there are local minima along the potential energy surface. A classic example is desorption from a chemisorption state through a precursor state wherein the binding energy is not equal to the measured activation energy.[8]

Scheme 1



We determine the binding energy of di-σ C_2H_4/Pt{111} by measuring the threshold (minimum) translational energy required to collisionally eject C_2H_4 from the surface. The collision is produced using a seeded, hyperthermal beam of Xe atoms having energy resolution of ~25% ($\Delta E/E$, full width at half-maximum). The atomic beam was produced by seeding Xe ($^1/_2$−1%) in H_2 and expanding the mixture through a heated nozzle. The apparatus used to conduct this experiment has been described previously.[9] Briefly, the atomic beam is directed onto a Pt{111} crystal housed in an ultrahigh vacuum surface analysis chamber with base pressure of 10^{-10} Torr. The Pt crystal is mounted on an (x, y, z, ϕ) translation stage and is electron-beam heated to 1200 K and liquid nitrogen cooled to 90 K. Ethylene is dosed onto the crystal using a variable leak valve. We use quantitative X-ray photoelectron spectroscopy (XPS) to measure the C(1s) concentration before and after collision-induced desorption (CID)[10] in order to measure the quantity of C_2H_4 removed from the surface.

In each experiment a clean crystal was cooled to 90 K and 11% of a saturated surface of C_2H_4 was adsorbed. Next, the adsorbate-covered surface was bombarded with Xe atoms for incident angles of 0, 30, or 45°. The kinetic energy of the Xe atoms ranged between 4 and 6 eV. The decrease in the C_2H_4 surface coverage as measured by XPS was then converted into a cross section, σ_{CID}, using

$$\sigma_{CID}(E_i,\phi_i) = \ln(\Theta^i_{C_2H_4}/\Theta^f_{C_2H_4})/F_{xe}t\cos(\phi_i) \qquad (1)$$

where F_{xe} is the instantaneous flux of incident Xe atoms, ϕ_i is the incident polar angle, E_i is the incident kinetic energy, t is the time of the desorption experiment, and $\Theta^i_{C_2H_4}$ and $\Theta^f_{C_2H_4}$ represent the initial and final ethylene surface coverages measured by XPS, respectively. The CID cross sections are plotted as a function of Xe energy and angle of incidence in Figure 1. The solid line in Figure 1 was determined by a numerical convolution procedure to account for the finite spread in the Xe beam energy. As a result, the measured cross sections reflect this energy dependence. To extract the true energy dependence of the desorption cross section, the Xe beam energy distribution was convoluted with a trial excitation function and compared to the measured cross sections.[11] The excitation function used to extract the true dependance was

$$\sigma_{CID}(E) = s(E - E_{thrs})^N/E \qquad (2)$$

where s is a scalar, E corresponds to the incident energy of the atomic beam, E_{thrs} is the threshold for CID, and N is a fitting parameter. Using a computer program, the Xe energy distribution was convoluted with eq 2. The resulting model cross sections were then compared to the experimental data, and the parameters s, E_{thrs}, and N were optimized to yield the best fit to the measured cross sections. The threshold energy obtained from this procedure was 5.2 ± 0.1 eV with $s = 0.021 \pm 0.02$ and $N = 2.1 \pm 0.1$. This threshold, then, must be exceeded for collision-induced desorption of di-σ C_2H_4 to occur.

The C_2H_4/Pt{111} di-σ binding energy can be calculated[9] from the measured energetic threshold by accounting for the two energy transfer steps which must occur before C_2H_4 desorbs from the surface in the collision-induced desorption experiment. The first energy transfer step is between the incident Xe and the adsorbed C_2H_4, and the second occurs between the trans-

(1) Carter, E. A.; Koel, B. E. *Surf. Sci.* **1990**, *226*, 339 and references.
(2) Land, T. A.; Michely, T.; Behm, R. J.; Hemminger, J. C.; Comsa, G. *J. Chem. Phys.* **1992**, *9*, 6774. Erley, W.; Li, Y.; Land, D. P.; Hemminger, J. C. *Surf. Sci.* **1994**, *301*, 177.
(3) Goodbey, D.; Zaera, F.; Yeates, R.; Somorjai, G. A. *Surf. Sci.* **1986**, *167*, 150. Beebe, T. P., Jr.; Yates, J. T., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 663. Bowker, M.; Gland, J. L.; Joyner, R. W.; Li, Y.; Slin'ko, M. M.; Whyman, R. *Catal. Lett.* **1994**, *25*, 293.
(4) Steininger, H.; Ibach, H.; Lehwald, S. *Surf. Sci.* **1982**, *117*, 685.
(5) Felter, T. E.; Weinberg, W. H. *Surf. Sci.* **1981**, *103*, 265.
(6) Horsey, J. A.; Stohr, J.; Koestner, R. J. *J. Chem. Phys.* **1985**, *83*, 3146.
(7) Windham, R. G.; Bartram, M. E.; Koel, B. E. *J. Phys. Chem.* **1988**, *92*, 2862.
(8) King, D. A. *Surf. Sci.* **1977**, *64*, 43.
(9) Szulczewski, G.; Levis, R. J. *J. Chem. Phys.* **1994**, *101*, 11070.
(10) Beckerle, J. D.; Johnson, A. D.; Ceyer, S. T. *J. Chem. Phys.* **1990**, *93*, 4047.
(11) Hales, D. A.; Su, C. X.; Lian, L.; Armentrout, P. B. *J. Chem. Phys.* **1994**, *100*, 1049.

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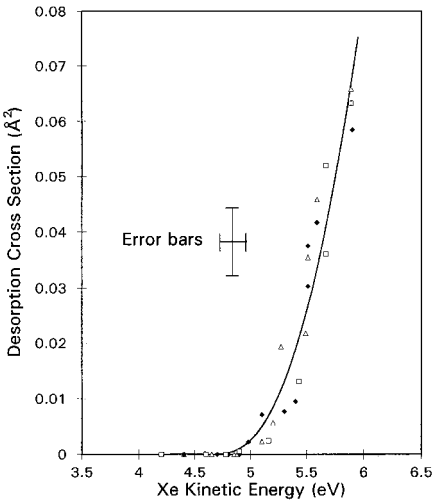

Figure 1. Measured collision-induced desorption cross section σ_{CID} for a 0.11 ML C_2H_4/Pt{111} surface at 90 K as a function of total incident Xe kinetic energy and angle of incidence with respect to the surface normal: □, 0°; ◆, 30°; △, 45°. The solid line is fit to the function $\sigma_{CID}(E_i) = s(E_i - E_{thrs})^N/E_i$, where E_i = Xe kinetic energy, $s = 0.024 \pm 0.002$, $N = 2.1 \pm 0.1$, and $E_{thrs} = 5.2 \pm 0.1$ after convolution for the Xe beam kinetic energy function. Error bars correspond to absolute error in the measurement; relative error bars are 25% of absolute.

lationally energetic C_2H_4 and the surface lattice. To account for energy transfer[13] in these events, we treat the particles as rigid spheres and use classical mechanics. The equation[9,12] to calculate the binding energy, E_b, from the threshold is then

$$E_b = E_{thrs}\frac{4M_{C_2H_4}M_{Xe}}{(M_{C_2H_4}+M_{Xe})^2}\left[1-\frac{4M_{C_2H_4}M_{eff}}{(M_{C_2H_4}+M_{eff})^2}\right] \quad (3)$$

where $M_{C_2H_4}$, M_{Xe}, and M_{eff} are the atomic masses of ethylene and Xe and the effective surface mass, respectively. The effective mass of the surface atom results from the strong interactions between atoms in a metal lattice, and the effective mass changes with collision energy. The approximations are valid because the interaction time is short (∼30 fs), the velocities are high (3−5 km/s), and the masses of the particles involved correspond to a heavy−light−heavy energy transfer system. Using the empirical result of Winters et al.,[14] M_{eff} is equal to 1.5 Pt atoms at the threshold (for a 5 eV collision energy). Substituting the appropriate masses into eq 1, we calculate an upper limit for the binding energy of the di-σ state to be 2.1 ± 0.1 eV. Binding energies calculated theoretically range from 2.04[15] to 0.7 eV.[16] A di-σ binding energy of 2.1 eV is reasonable in comparison with a single Pt−C_2H_3 σ-bond energy of 1.3 eV determined from thermodynamic arguments.[17]

Note that our binding energy determination represents an upper limit for a given effective mass. The true binding energy could be less if the C_2H_4 ejects with internal excitation at the threshold. For instance, each quanta of CH vibrational excitation would lower the binding energy by ∼0.35 eV. However, the adiabaticity model[13] suggests that the relative probability of translational to vibrational energy transfer in a Xe−C_2H_4 collision is .001 when compared with kinetic energy transfer. In addition, high rotational excitation, i.e., $J = 13$, would be required to reduce the binding energy by ∼0.1 eV. Previous simulations[18] for collision-induced desorption of N_2 from W{100} reveal negligible internal excitation (∼0.02 eV) near the threshold. Also, in the well-calibrated CH_4/Ni{111} system,[12] we found no evidence for internal excitation during the impulsive ejection event. We conclude, then, that internal excitation lowers the calculated binding energy by less than the reported error bar. Note that the lowest possible binding energy results when M_{eff} is equal to one Pt atom, corresponding to a "lower limit" binding energy of 1.7 eV.

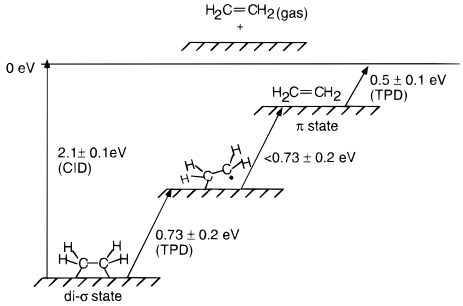

Figure 2. A partial reaction diagram showing the proposed ground and intermediate states involved in the thermal desorption process. The values for the activation barriers for the first (0.73 eV) and third (0.5 eV) thermal desorption reaction steps are found in ref 7. The value for the impulsive desorption energy (2.1 eV) is determined from the threshold for collision-induced desorption as shown in Figure 1.

We are now in a position to construct a partial reaction diagram for the thermal desorption chemistry of C_2H_4 on Pt{111}. The di-σ well depth determined in this work of 2.1 eV reveals the minimum quantity of energy required to transfer the adsorbate from the bottom of the potential energy well into the gas phase. The activation energy measured for thermal desorption, 0.73 eV,[7] does not correspond to the binding energy. From this we conclude that the mechanism for thermal desorption is not simply one step with an activation energy of 0.73 eV. Thus, the heat of adsorption is not equal to the heat of desorption. To what does the activation energy for thermal desorption then correspond? The simplest explanation would invoke a precursor state during thermal desorption.[8] The principle of microscopic reversibility suggests that the precursor state to di-σ bonding is a weakly bonded C_2H_4 wherein the hybridization of the C atoms is sp^2. The activation energy for desorption[7] of the π state has been measured on several transition metal surfaces and ranges between 0.2 and 0.5 eV. A simple precursor model would result in a maximum binding energy (0.73 + 0.5 eV) which is still substantially less than the binding energy measured in the collision-induced desorption experiment. We propose, then, that the temperature-programmed desorption experiment actually probes the energy required to sever one of the two di-σ bonds, presumably producing a surface-bound radical intermediate. The radical would have a bond energy near 0.73 eV. (We note that this is less than the bond determined for Pt−C_2H_3 of 1.3 eV. The bond energy for the Pt radical species should be less than that for the Pt−alkyl because a C_2H_4 π bond is forming as the Pt−C_2H_4· bond is breaking). An equal or lower quantity of energy is then required to cleave the second Pt−C σ bond, leaving the adsorbate in a weakly bound "precursor" state. The precursor state, having the lowest barrier to reaction, simply desorbs. The reaction diagram of Figure 2 summarizes the simplest thermal desorption model consistent with the measured reaction energies for di-σ C_2H_4/Pt{111}. We have performed simulations of the thermal desorption reaction on the basis of the model proposed in Figure 2 and find excellent agreement with the published TPD spectra,[7] and we have performed CID measurements for the C_2H_4/O/Pt{111} system which has no di-σ bonding character and find no evidence for the radical intermediate.[19] Also, we note that the radical intermediate provides a simple mechanism for self-hydrogenation[20] of C_2H_4 on Pt{111}.

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(12) Szulczewski, G.; Levis, R. J. *J. Chem. Phys.* **1993**, *98*, 5974.
(13) Levine, R. D.; Bernstein, R. B. *Molecular Reaction Dynamics and Chemical Reactivity*; Oxford University Press: New York, 1987.
(14) Winters, H.; Coufal, H.; Rettner, C. T.; Bethune, D. S. *Phys. Rev.* **1989**, *B41*, 240.
(15) Kang, D. B.; Anderson, A. B. *Surf. Sci.* **1985**, *155*, 639.
(16) Sautet, P.; Paul, J. F. *Catal. Lett.* **1991**, *9*, 245.
(17) Zaera, F. *J. Phys. Chem.* **1990**, *94*, 5090.
(18) Zeiri, Y. *Surf. Sci.* **1990**, *231*, 404.
(19) Velic, D.; Szulczewski, G.; Levis, R. *J. Chem. Phys.*, in press.
(20) Berlowitz, P.; Megiris, C.; Butt, J. B.; Kung, H. H. *Langmuir* **1985**, *1*, 206.