Surface-Molecule Proton Transfer: A Demonstration of the Eley-Rideal Mechanism

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Hyperthermal molecular DABCO [$N(C_2H_4)_3N$] is scattered from hydrogen-covered Pt(111). Some of the scattered molecules are protonated at the surface and leave with a kinetic energy which is strongly dependent on the incident energy. This means that proton abstraction is occurring immediately on collision and it serves as a clear demonstration of an Eley-Rideal mechanism. No isotope effect was observed, excluding a tunneling mechanism. The proton transfer shows a threshold energy equal to the difference between the surface work function and the molecular ionization potential. The reaction therefore proceeds via a molecule-surface electron transfer and a subsequent H-atom abstraction.

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Molecular-beam scattering (MBS) from surfaces has been extensively used to determine surface structure and to probe the dynamics of many gas-surface processes. The ability to select the state of the incident beam allows determination of the role of such variables as translational energy,[1] orientation,[2] and internal energy.[3]

The increase of the molecular kinetic energy to the hyperthermal energy range (1–20 eV) can expose many new phenomena and observations since this energy range contains activation energies for chemical and charge-transfer processes.[4] Hyperthermal surface ionization was studied in organic molecules and both molecule-surface[5–8] and surface-molecule[5–9] electron-transfer processes were observed. Dissociative ionization was also studied[5,6,8–13] and its relevance to collision-induced dissociation was discussed.[5,10]

Heterogeneous catalytic reactions can be classified as proceeding via the Eley-Rideal (ER) or the Langmuir-Hinshelwood (LH) mechanism.[14] In the ER mechanism molecules from the gas react with surface chemisorbed reagents,[15] whereas in the LH mechanism both reagents are chemisorbed and equilibrated at the catalyst's surface prior to reaction.[16] However, intermediate situations can occur as well.[17,18] The two mechanisms can be distinguished by the reaction-rate dependence upon the pressures of the reagents.[14] Although in this way the ER mechanism is determined for many reactions, until now a direct transfer of an adsorbed atom to an impinging gas molecule has not been found in MBS experiments.

In MBS studies chemical reactions on surfaces have only been observed to proceed through adsorbed precursors, and differential information could only be obtained about the adsorption and dissociation processes.[19] Study of the state dependence of the actual reaction step would be possible if this reaction occurs immediately. For many scattering events, a potential-energy barrier to further surface interactions (chemisorption, reaction, dissociation, and ionization) exists.[20–22] Recent experiments have shown that at hyperthermal incident energies a molecule from the gas phase can overcome these bar-

riers.[4,23] In the particular case of surface ionization, the barrier given by the difference between the surface work function and the ionization potential is quite large and cannot be bridged by the average thermal energy. However, ionization can occur if the incident energy is high enough.[5–13]

Although surface ionization occurs primarily by electron transfer, it can also occur by proton transfer at Brønsted acid sites if the incident molecule has a high proton affinity.[5,21,24] Surface-molecule proton transfer is one of the most important catalytic reactions. This catalytic reaction is also easy to study experimentally since its product is an ion and can be detected efficiently.

In this paper we present experimental results on the proton abstraction of hyperthermal DABCO [$N(C_2H_4)_3N$ or 1,4 diazabicyclo-222-octane] from H-covered Pt(111) to show the possibility of immediate atom pick-up reactions at hyperthermal incident energies. DABCO was chosen because of its high proton affinity[25,26] and molecular mass (112 amu) allowing hyperthermal energies up to 9 eV to be obtained by seeding in He or H_2. As a substrate Pt(111) was chosen since its work function is relatively high,[27] and the Pt/H_2 interaction has been extensively studied.[28,29] We note, however, that this system is not a typical example for a heterogeneous catalytic reaction as it involves with a light-particle (ion) transfer to a heavy molecule. However, its mere existence at low surface temperature suggests its ER nature.

The experimental setup is described in detail elsewhere.[5] DABCO molecules were seeded in a hydrogen or a helium supersonic beam and accelerated to kinetic energies between 1 and 9 eV. DABCO was placed behind the nozzle in a sampling chamber at room temperature. The nozzle has an 80-μm-diam hole in a small ruby disk mounted on a 2-mm alumina tube. It can be differentially heated with a heated volume of 10^{-3} cm^3.[30] The beam was skimmed and collimated through two differentially pumped chambers into an ultrahigh-vacuum chamber (UHV) (base pressure of 1×10^{-9}

mbar). Using a mechanical chopper the beam was either square-wave modulated for phase-sensitive detection or chopped for time-of-flight (TOF) measurements. The Pt(111) surface was initially prepared by fast-argon-atom bombardment (10 keV), thermal annealing (900 K), and oxygen treatments ($P \simeq 2 \times 10^{-6}$ mbar, 600 K). The surface was cleaned between all the measurements with alternating O_2 and H_2 treatments and the DABCO flux was limited to $\sim 10^{-4}$ monolayer/sec. The surface cleanliness was checked with Auger electron spectroscopy and specular He scattering. Two quadrupole-mass-spectrometer (QMS) heads (UTI 100C) served as detectors: one for the direct beam and the second one mounted at 45° to the molecular-beam axis for the scattered beam 2.5 cm from the surface. The Auger electron spectrometer (VG-CLAM 100 hemispherical analyzer) was also used for ion energy analysis. The surface was positively biased to repel positive ions and the zero ion energy was calibrated by thermal alkali impurities desorption from the heated Pt(111) crystal.

When the molecular beam of DABCO seeded in He or H_2 is scattered from Pt(111) positive ions are formed. Three different types of characteristic mass spectra (MS) were found and are shown in Fig. 1. If the surface is clean and the incident energy E_i is larger than 7 eV, we observed the MS of Fig. 1(b) which consists of two
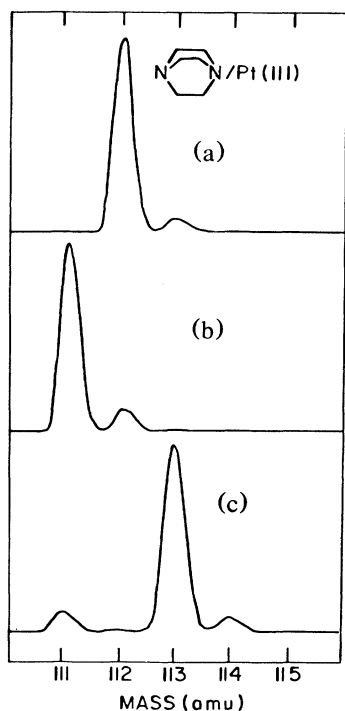
peaks. The main peak corresponds to $m/e = 111$, which is 1 amu less than the molecular weight of DABCO. This indicates that the incident molecule lost an H^- to the surface. Because of the ^{13}C and ^{15}N natural abundance in DABCO, 8% of the dehydrogenated DABCO will appear at $m/e = 112$. This explains the smaller second peak in the MS. Therefore, on clean Pt(111) at $E_i > 7$ eV the ionization process is dominated by dissociative ionization. If we lowered E_i (by seeding in He) to below 4 eV, we obtained the ion MS of Fig. 1(a). Now all scattered ions are undissociated, which causes the main peaks at $m/e = 112$ and the ^{13}C-isotope peak at $m/e = 113$. Similarly, on oxygen-covered Pt(111) at this kinetic energy, we observe the molecular ion exclusively. Once the surface is completely covered with hydrogen atoms the MS will be dominated by a peak at $m/e = 113$ for both energies, as shown in Fig. 1(c). So for H-covered Pt(111) the hyperthermal surface ionization proceeds via a proton abstraction from the surface. The proton abstraction increases linearly, whereas the other ion peaks decrease linearly with the H coverage at the (111) terraces.[31] Various mixtures of these spectra can also be observed depending on the experimental conditions.

Once Pt(111) is completely H covered, practically all ions leaving the surface are protonated. In order to demonstrate the impulsive nature of this process we show in Fig. 2 TOF spectra of protonated DABCO which was detected through the quadrupole mass spectrometer. The QMS was tuned to 113 amu and thus possible interference with molecular ions (when the surface is not fully covered with H_2) was practically eliminated. In these experiments a cw beam was used and the surface bias voltage was pulsed with 8-μsec pulses of 4.0 V and the flight distance from the surface is approximately 25 cm. It is clearly observed that the protonated molecular ions generated from the scattering of 8.5-eV DABCO molecules are considerably faster than those generated

FIG. 1. Mass spectra of the positive ions produced by the scattering of hyperthermal DABCO from Pt(111), $\theta_i = 20°$. (a) $E_i = 4$ eV, clean Pt(111). (b) $E_i = 8$ eV, clean Pt(111). (c) $E_i = 8$ eV, highly H-covered Pt(111).
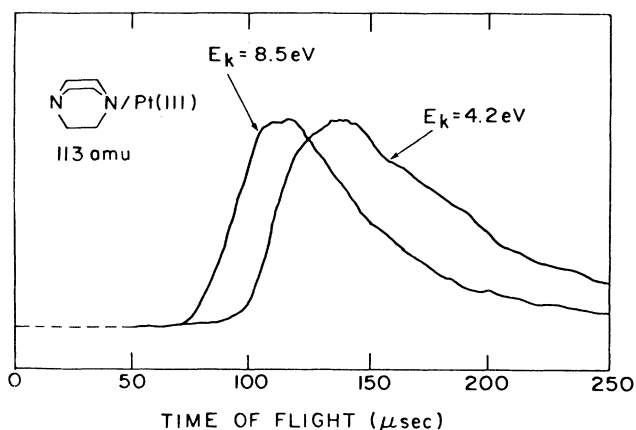

FIG. 2. TOF of protonated DABCO (113 amu) ions leaving the surface.

from molecules having 4.2-eV incident kinetic energy. We claim that the differences between the two TOF traces constitute an unequivocal proof that the protonated DABCO did not equilibrate at the surface; i.e., DABCO molecules pick up protons from the surface during a direct scattering without adsorption and thermalization. Thus a direct pickup of an absorbate by an incident molecule (an ER mechanism) is shown to be possible in MBS. No accurate calibration of the TOF has been made, but similar differences were observed in the incident-energy dependence of the scattered ion energy distributions measured with our energy analyzer.[31] In these measurements (which did not separate the small contribution of the molecular ions) we have measured scattered ion energy of ~1.0 eV at 4.2-eV incident molecular kinetic energy. Thus most of the incident kinetic energy was converted into surface phonons and intramolecular vibrational energy.[32] At least 1.5 eV of the kinetic-energy loss was initially converted into surface electronic energy due to the image potential (surface ionization potential). We also note that the mere observation of protonated DABCO from H-covered "cold" Pt(111) suggests that an ER mechanism is involved. At 373-K surface temperature the expected thermal surface ionization yield (with or without proton transfer) is
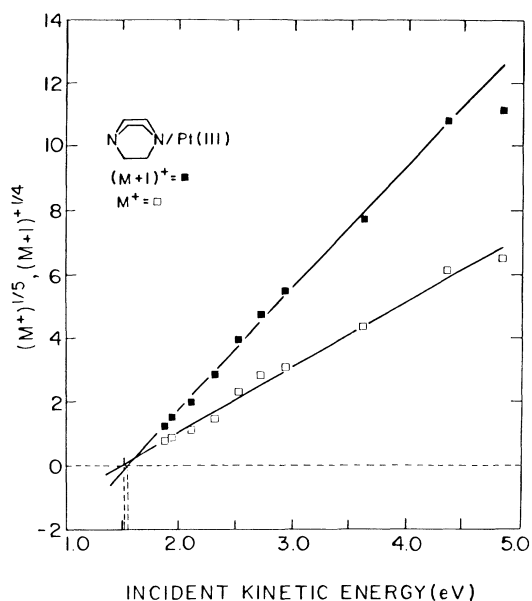

INCIDENT KINETIC ENERGY (eV)

FIG. 3. Measured ion yield for DABCO scattered from Pt(111) as a function of E_i for both protonation (■) and ionization by electron transfer (□). In order to linearize the results and to show the fit obtained $(M^+)^{1/5}$ and $[(M+1)^+]^{1/4}$ are plotted vs the incident kinetic energy. Measurements are performed at a partly H-covered surface (T_s =386 K, P_{H_2} =5×10⁻⁶ mbar, $\Theta \simeq 0.20$). Drawn through the experimental points are fits of the form $k(E_i - E_{th})^n$, yielding k =223, E_{th} =1.55 eV, n =4 for protonation and k =38.2, E_{th} =1.52 eV, n =5 for electron transfer.

anticipated to be extremely small.[23] We have measured the relative ionization probabilities of DABCO at partly H-covered Pt(111) ($\Theta \simeq 0.20$) by both electron and proton transfer by measuring the heights of the corresponding peaks in the MS. The kinetic-energy dependence of these ionization processes was studied at different He seeded-beam conditions. The experimental data are shown in Fig. 3. The lines drawn through the measurements are fits of the form $Y=k(E_i-E_{th})^n$, where E_i is the incident energy and E_{th} is the threshold energy.[33]

It is clearly observed in Fig. 3 that for both processes the threshold energies are practically identical with a value of 1.55 eV, which is exactly the threshold one would expect for the electron-transfer process, since 1.55 eV is the difference between the ionization potential of DABCO (7.25 eV)[26,34] and the surface work function of Pt(111) with H coverage of 20% (5.7 eV).[27,28] For proton abstraction a different threshold is expected. By using the activation energy for the desorption of H_2, the dissociation energy of H_2, the ionization energy of an H atom, the surface work function, and the proton affinity[25] of DABCO one finds that the proton abstraction will be endothermic by approximately 0.5 eV. Obtaining this value by using the (DABCO-H)⁺ homolytic bond strength[25] gives the same result. This is 1 eV lower than the threshold determined experimentally, which strongly suggests that proton abstraction proceeds via an electron transfer with a subsequent abstraction of an H atom. This proposed mechanism is further supported by a comparison with ion-scattering experiments. When positive nitrogen-containing organic ions with an incident energy of ~25 eV are scattered from contaminated surfaces, up to 75% of the reflected ions have an H atom attached.[35] The emerging picture is that hyperthermal surface-molecule proton transfer proceeds by an electron transfer and subsequently an exothermic H-atom transfer with close to unit probability. The ratio of this ion transfer at a D-covered to a H-covered surface was measured to be 1.0 ± 0.2. This also confirms, that atom/ion transfer is not the rate-limiting step since a tunneling mechanism would show a strong isotope effect. Since the H atom is too light to change the momentum of the DABCO ion appreciably, the 1-eV potential energy gained by transferring the H atom from the surface to the DABCO ion will not result in a gain of translational energy. The DABCO ion will be a spectator during the attachment of the H atom.[36] The excess energy will be distributed in the internal degrees of freedom of the product.

Finally, we note that the process of H^+/D^+ transfer may serve both for the detection of the scattered molecule[5,8,13] as well as for the detection of hydrogen atoms on surfaces. The detection sensitivity is estimated to be 10⁻⁴ monolayer of hydrogen and 10⁻⁵ monolayer of deuterium (lower interference from ¹³C or ¹⁵N isotopes).

With this study we have shown for the first time that atoms can be abstracted from a surface by incident mol-

ecules during direct scattering. We found that surface-molecule proton transfer takes place by an initial electron transfer and a subsequent transfer of an H atom to the ion; so, although in the integral process the molecule is protonated, a real proton actually never has been transferred.

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