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Hydrogen Abstraction Reactions in the Kiloelectronvolt Particle Bombardment of Organic Films

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The bombardment of molecular solids with high-energy (500–25 000 eV) particles is an effective method of placing these molecules, as both ions and neutrals, into the gas phase for subsequent analysis via mass spectrometry (MS) techniques such as secondary ion MS (SIMS),[1] fast atom bomardment MS (FAB),[1e,h] and laser postionization MS.[1a,b] In addition to that of the intact parent molecule, peaks corresponding to fragments of the molecule, the molecule plus or minus a proton, and even various aggregates of the molecule are often found in the mass spectrum.[1–4] A number of mechanisms have been proposed for the formation of these detected species. Clusters smaller than the parent molecule are believed to result either from the direct ejection of a portion of the intact molecule[2,3,5,6] or from the unimolecular dissociation of larger transitory clusters during their flight to the detector.[5] Clusters larger than the parent molecule are proposed to result from either the near-surface reaction of two previously ejected entities,[4–7] the direct ejection of a large precursor ion created prior to the bombardment event,[1d,1f] or an oxidation or reduction reaction among escaping molecules within the selvage area, the solid–gas interfacial region most distorted by the bombarding particle.[1d–f,8] In this communication, we propose a new mechanism for molecule formation during the kiloelectronvolt (keV) particle bombardment of an organic film. Molecular dynamics computer simulations using a many-body interaction potential to describe the hydrocarbon interactions show a novel H abstraction mechanism whereby a free H atom formed during the collision event within ~100 fs abstracts another H atom from a stationary neighboring surface molecule to form gaseous H_2. Recombination type mechanisms involving lone H atoms have previously been proposed as unlikely because hydrogen's light mass usually results in a high ejection velocity.[9] Consequently, within a very short time, the atom is beyond the interaction range of the other heavier moving particles. The mechanism proposed here occurs on a short time scale and is a direct consequence of collisional motion. This is in contrast to previously proposed reactions for H transfer in which the reactions are extensions of thermal energy processes. The prediction here that free H atoms can react with stationary molecules before leaving the interaction area suggests new directions for explaining chemical reactions in organic films exposed to keV particle bombardment.

Molecular dynamics (MD) simulations have been successful in yielding insight into ejection processes ranging from energy and angular distributions to mechanisms of molecular emission that occur in the keV particle bombardment of solids.[5–7,9–14] Although previous MD simulations of the keV particle bombardment of organic films explained some of the ejection mechanisms in these systems, the potential energy functions used to model the adsorbates warranted only the exploration of molecular ejection and fragmentation, and not that of any chemical reactions which might occur among atoms originating from different adsorbate molecules.[5,6] Recently, a many-body interaction potential for hydrocarbons was developed that describes reactions among all atoms including those from different adsorbate molecules.[15] Thus, the possibility now exists to explore the importance of intermolecular reactions.

As a prototypical system for the keV bombardment of an organic film, the bombardment of a p(2×2) overlayer of ethylidyne (C_2H_3) adsorbed on the {111} face of Pt with a 500-eV Ar beam was chosen for investigation. C_2H_3, a stable intermediate in the Pt-catalyzed dehydrogenation of ethylene and acetylene,[2,16] adsorbs in a 3-fold hollow site through three Pt–C bonds with its C–C bond axis perpendicular to the Pt surface.[16] The molecular dynamics scheme being used has been described in great detail elsewhere.[10,11] Here, we include many-body potential energy functions which allow for chemical reactions among all of the constituents of the target. Thus, as the collision cascade evolves, reactions occurring among the substrate atoms, the substrate and adsorbate atoms, and the individual adsorbate atoms can be followed in time. The Pt–Pt interactions are described with a potential function based upon the embedded atom method (EAM).[11,17] The C–C, C–H, and H–H interactions are described with a Tersoff-like potential function fitted to the energetics of bulk diamond, graphite, and a wide array of small hydrocarbons, such as C_2H_4, C_2H_6, C_6H_6, and the radicals $^{\bullet}CH_3$ and $^{\bullet}C_2H_5$.[15] This potential has been successfully applied in MD simulations of a variety of chemical reactions,[15,18,19] including hydrogen abstraction from hydrogen-terminated diamond surfaces.[18] The Pt–C and Pt–H interactions are described by short-range Lennard-Jones 6/12 pair potentials,[20] which have been fitted to give bond distances and bond energies of 2.20 Å and 2.30 eV for Pt–C,[21,22]

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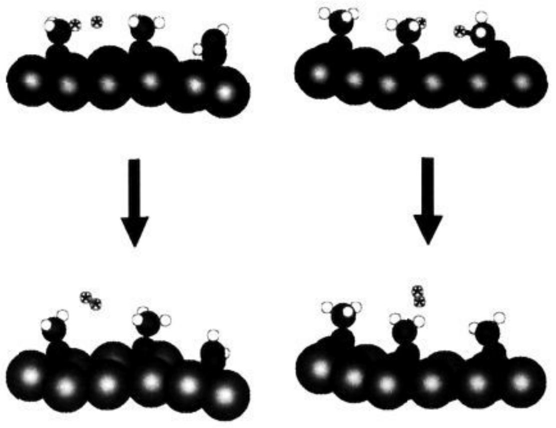

SCHEME 1 SCHEME 2

Figure 1. Two pathways found for H abstraction. The light gray, black, and white spheres represent the Pt, C, and H atoms, respectively. The H atoms that eventually form the H_2 molecule are marked with stars. In Scheme 1, the middle C_2H_3 is out of the plane of the reacting C_2H_3 molecules and does not enter into the H abstraction reaction. See the text for a description of the collision events.

and of 1.90 Å and 2.64 eV (in the 3-fold hollow) for Pt–H.[23,24] The Ar–Pt, Ar–C, and Ar–H interactions are modeled by a screened Molière potential that allows only repulsive interactions.[25] A complete description of the calculational details including the merging of the Pt and C potentials and the hydrocarbon repulsive interactions will be given in full later.[26]

Clusters varying in type from H_2 to $Pt_xC_yH_z$ result from the collision events. In this communication, however, only the formation of H_2 will be highlighted. Unexpectedly, 66% of the H_2 predicted by these simulations is created via a hydrogen abstraction type mechanism. Although many variations exist, the two main abstraction mechanisms seen for the formation of H_2 are shown in Figure 1. In the predominant mechanism, Scheme 1, a H atom is emitted when the C_2H_3 molecule on the right is hit by either an energetic Pt atom, an Ar atom, or a CH_x (x = 0–3) fragment. Once emitted, this H atom is propelled in the direction of a H atom on an undisturbed C_2H_3 molecule. This results in the formation of a H–H bond and the breaking of a C–H bond. In the particular trajectory shown in Scheme 1, the H atom has 0.77 eV of kinetic energy when it enters (40 fs later) the neighbor shell of the undisturbed C_2H_3 molecule. Since the barrier to hydrogen abstraction for small hydrocarbons is between 0.2 and 0.45 eV,[27] sufficient energy is available to overcome this barrier. Scheme 2 shows an intriguing mechanism in which a C_2H_3 molecule is bumped such that one of its H atoms interacts with a H atom on the neighboring C_2H_3 molecule. H_2 is formed, and two C–H bonds are broken. The C–H bond on the energetically excited C_2H_3 molecule is stretched to 1.37 Å, and the H atom has 0.98 eV of kinetic energy when it interacts with the neighboring C_2H_3 molecule. Each of the H abstraction reactions shown in Figure 1 is completed within 100 fs after the initial H atom is emitted; thus these are collisionally induced and not thermally induced reactions. Both of these pathways result in the same products: a free H_2 molecule and a C_2H_2 radical which remains adsorbed on the Pt surface. The H_2 molecules created are both vibrationally and rotationally hot, but out of the 90 formed, none have sufficient internal energy to dissociate. Although no experimental reports of H_2^+ in the SIMS of C_2H_3 are available,[2] H_2^+ has been observed in high-resolution time-of-flight SIMS images of polystyrene beads.[28]

The identification of how molecular reactions proceed during keV particle bombardment should help simplify the complex relationship which exists between the structure of the molecular solid and the peaks observed in the mass spectra. In particular, several mechanisms have been ventured for the origin of the molecular ions, $(M + H)^+$ and $(M - H)^-$, as these peaks are often quite intense.[1c–h,4,8] The "preformed ion" mechanism postulates that the $(M \pm H)^\pm$ ions are created prior to the ion bombardment event in which they are ejected.[1d,f] In the particular example of an organic film such as C_2H_3 adsorbed on a transition metal, it is not easy to imagine what chemical events would be necessary to give the adsorbed preformed $(C_2H_3 + H)^+$ ion.[29] Perhaps instead, the formation of these ions proceeds by a mechanism analogous to that seen here for the formation of H_2. If the free H atom abstracts a H^+ ion instead of a neutral H atom, then the $(H + H)^\circ$ molecule can be seen as a neutral comparable to the $(H + H)^+$ ion. Moreover, the abstraction process leaves an (M – H) entity, C_2H_2, on the surface which may later desorb. In addition to the "preformed ion" mechanism, reduction reactions of organic molecules have also been proposed to yield $(M \pm H)^\pm$ ions.[1d–f,8] These reduction reactions are proposed to proceed through either electron transfer alone or electron transfer with hydrogen attachment to the molecular ion.[1d,8] Until now, it was believed that the H atoms emanated either from the substrate matrix, which in FAB is often glycerol, or from the decomposition of the molecular ion itself.[1d,8] Although classical dynamics simulations do not take into account the presence of electrons, these simulations do suggest an alternate source of hydrogen.

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