J. Am. Chem. Soc. **1994,** *116,* 10399–10402

Simulated Tribochemistry: An Atomic-Scale View of the Wear of Diamond

Judith A. Harrison*,† and Donald W. Brenner‡

Contribution from the Chemistry Department, U.S. Naval Academy, Annapolis, Maryland 21402-5026, and Naval Research Laboratory, Code 6179, Washington, DC 20375-5342

Received June 13, 1994⊗

Abstract: Molecular dynamics simulations are used to explore the atomic-scale chemistry and associated wear that occurs when diamond surfaces are placed in sliding contact. The simulations predict complex radical chemistry initiated by the shearing of hydrogen atoms from chemisorbed molecules. Observed chemical mechanisms include hydrogen abstraction from the surfaces, radical recombination, transient surface adhesion, and formation of debris at the interface. These simulations provide the first glimpse into the rich, nonequilibrium tribochemistry that occurs at diamond and related covalently-bonded interfaces.

Placing two solid bodies in sliding contact usually results in wear of one or both of the bodies, often with the formation of debris.[1,2] The nascent particles that form the debris can further interact, either physically or chemically, with the solid bodies or with other nascent particles. This interaction of chemistry and friction is known as tribochemistry,[2,3] the results of which are well-known in everyday life—combustion engines break down, cutting tools become dull, and bearings fail. Despite the obvious importance of these consequences, and the long history of the field of tribology, much of the atomic-scale dynamics responsible for friction-induced wear remain elusive.

There have been numerous experimental attempts to characterize tribochemical reactions and resulting wear. For example, Heinicke and co-workers[4] have examined the tribochemical reactions which take place in ball mills; Singer[5] has developed a thermochemical analysis to describe the reactions which take place during the wear of MoS_2 films, TiN and TiC coatings, and steel implanted with Ti^+; and Fisher[6] has examined the kinetics of tribochemical reactions. However, charcterization of these reactions has proven difficult because traditional analysis methods such as optical microscopy, electron microscopy, cathodoluminescence, and infrared spectroscopy[7-9] are restricted to examination of the contact region subsequent to sliding. This limitation has led to a historic lack of information regarding the mechanisms of tribochemical reactions. Even new atomic-scale proximal probe techniques, such as atomic-force[10] and friction-force microscopies,[11] have yet to characterize specific, atomic-scale, tribochemical reaction mechanisms.

Macroscopic experiments have shown that, for diamond sliding on diamond in ultrahigh vacuum, friction is initially low. As sliding progresses, however, friction increases dramatically.[8,9] It has been asserted that the friction is low initially due to saturation of surface radical sites by hydrogen and perhaps oxygen. Sliding is thought to wear away particles from the surfaces, creating radical sites. Once these radical sites have been formed, the surfaces adhere through the formation of chemical bonds. The formation of wear debris is then thought to result from the shearing of these bonds during continued sliding. This debris appears opaque and powdery and is composed of mostly amorphous or unsaturated carbon with little hydrocarbon and graphite.[8,9] Wear rates associated with this process have been observed to depend on the direction of abrasion.[8,9]

Ideally, one would like to be able to monitor reactants and the formation of the various intermediates as sliding progresses. Theoretical techniques such as molecular dynamics, where the precise positions of all atoms are known as a function of time, are uniquely suited to this task.[12,13] Indeed, in this work, we report specific examples of tribochemical reaction sequences that can occur when two diamond surfaces are placed in sliding contact. These simulations provide the first glimpse into the rich, nonequilibrium tribochemistry that is possible in this and related covalently-bonded systems.

The molecular dynamics friction experiment was carried out in the following way. Two diamond lattices consisting of 10 carbon atom layers, each layer containing 16 atoms, were placed in contact. The contacting surfaces of both lattices were the (111) surfaces of the diamond lattices. Two series of simulations were carried out. In the first series, the (111) contacting surfaces of both lattices were terminated with hydrogen only. In the second series, two hydrogen atoms from the upper surface were removed and replaced with ethyl ($-CH_2CH_3$ or R) groups

---

* To whom correspondence should be addressed.

† U.S. Naval Academy.

‡ Naval Research Laboratory.

⊗ Abstract published in *Advance ACS Abstracts,* October 1, 1994.

(1) Bowden, F. P.; Tabor, D. *Friction: An Introduction to Tribology*; Anchor Books, Anchor Press/Doubleday: Garden City, NY, 1973; pp 9–24.

(2) Rabinowitz, E. *Friction and Wear of Materials*; John Wiley & Sons: New York, 1965; pp 52–167.

(3) Granick, S. *Mater. Res. Bull.* **1991**, *16*, 33–35.

(4) Heinicke, G. *Tribochemistry*; Carl Hanser Verlag: Munich, 1984.

(5) Singer, I. L. *Surf. Coatings Technol.* **1991**, *49*, 474–481.

(6) Fisher, T. E. *Fundamentals of Friction: Macroscopic and Microscopic Processes*; Singer, I. L., Pollack, H. M., Eds.; H. M. Kluwer Academic Publishers: Dordrect, The Netherlands, 1992; pp 299–310.

(7) Tabor, D.; Field, J. E. *The Properties of Natural and Synthetic Diamond*; Field, J. E., Ed.; Academic Press: London, 1992; pp 547–571 and references therein.

(8) Feng, Z.; Field, J. E. *Surf. Coatings Technol.* **1991**, *47*, 631–645.

(9) Wilks, J.; Wilks, E. M. *The Properties of Diamond*; Field, J. E., Ed.; Academic Press: London, 1979; pp 351–381.

(10) Binnig, G.; Quate, C. F.; Gerber, Ch. *Phys. Rev. Lett.* **1986**, *56*, 930–933. Burnham, N. A.; Colton, R. J. *Scanning Tunneling Microscopy and Spectroscopy*; Bonnell, D. A., Ed.; VCH: New York, 1993; pp 191–249 and references therein.

(11) Mate, C. M.; McClelland, G. M.; Erlandsson, R.; Chiang, S. *Phys. Rev. Lett.* **1987**, *59*, 1942–1945. Meyer, E.; et al. *Thin Solid Films* **1992**, *220*, 132–137. German, G. J.; Cohen, S. R.; Neubauer, G.; McClelland, G. M.; Seki, H.; Coulman, D. *J. Appl. Phys.* **1993**, *73*, 163–167.

(12) For reviews of simulations related to friction, see: *Mater. Res. Soc. Bull.* **1993**, 18. See also: Glosli, J. N.; McClelland, G. M. *Phys. Rev. Lett.* **1993**, *70*, 1960–1963.

(13) Harrison, J. A.; White, C. T.; Colton, R. J.; Brenner, D. W. *J. Phys. Chem.* **1993**, *97*, 6573–6576.

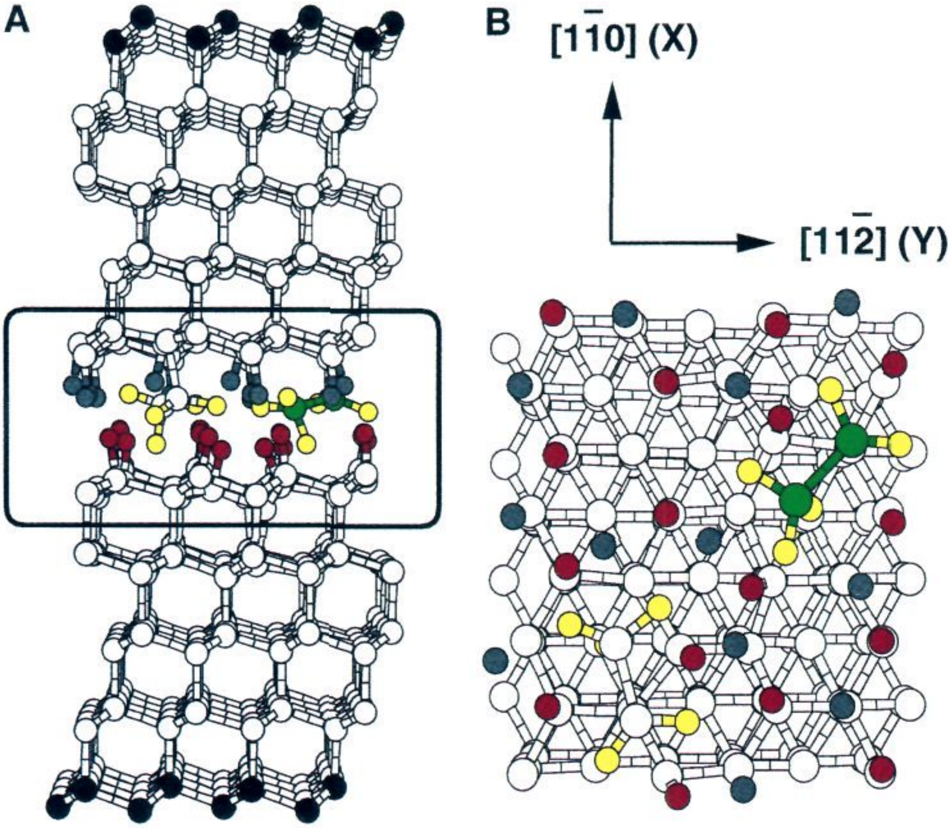

Figure 1. Typical starting configuration for the system with chemisorbed ethyl ($-CH_2CH_3$ or R) groups at the interface. Large white and green circles represent carbon atoms, and small circles represent hydrogen atoms. Hydrogen atoms are color coded according to their original attachment site. Red atoms were originally attached to the lower surface, grey atoms to the upper surface, and yellow atoms to the R groups. To differentiate between the two R groups, the carbon atoms of one of the groups are colored green. The system is viewed along the $[1\bar{1}0]$ direction and the [111] direction in A and B, respectively. The two layers of carbon atoms which are held rigid throughout the course of the simulation have been indicated by coloring the atoms of each row closest to the viewer black in A. The box in A denotes the region of interface illustrated in Figure 2. In B, the carbon atoms of the upper lattice are not shown.

(Figure 1). This configuration may model the atomic-scale residue on terraces that would likely remain after a diamond film was produced by the gas phase deposition of hydrocarbon molecules. In the following discussion, these chemisorbed groups will be denoted D_u-R (D_l-R), where D_u represents attachment to the upper (lower) diamond surface. The outermost two layers of each lattice (filled circles in Figure 1A) are held rigid throughout the course of the simulation to define the separation between the lattices and to use as a holder when sliding the surfaces. Each series of simulations was composed of three sliding runs whose starting orientations span the unit cell perpendicular to the sliding direction. In this way, approximate averages over the unit cell were obtained.[13]

Sliding was achieved by moving the rigid layers of the upper surface at a constant velocity in a given sliding direction. In these simulations, both the $[1\bar{1}0]$ and the $[11\bar{2}]$ crystallographic directions were investigated and the sliding velocity was 1 Å/ps. All nonrigid atoms were allowed to dynamically evolve in time according to classical equations of motion. The forces governing their motion were derived from an empirical hydrocarbon potential that is unique among hydrocarbon potentials in its ability to model chemical reactions, including appropriate atomic rehybridization.[14] The temperature of the system was maintained by applying a thermostat to the middle five layers of each lattice.[15] The simulations reported here were performed at 70 K; additional simulations at 300 K showed similar results. Periodic boundary conditions were applied in the plane of the surfaces, simulating an infinite interface. The simulations were performed for 30 ps at an average normal load that corresponded to a pressure of approximately 33 GPa. We note that this pressure is well below that which causes plastic deformation on the macroscopic scale (100 GPa).[16] In addition, this pressure is comparable to the pressures (up to 30 GPa) achieved in macroscopic friction experiments on diamond[7,8] in which wear has been observed.

Sliding did not result in the shearing of hydrogen atoms from the lattices or in any chemical reactions at any of the loads examined[13] when the flat, hydrogen-terminated surfaces were examined. In contrast, when the ethyl groups were present, the simulations show wear that is, in the majority of cases, initiated by the shearing of hydrogen atoms from the tails of these groups. The resulting free hydrogen atoms are able to react at the interface in a number of ways. For example, they can recombine with an existing radical site (including the site from which they were abstracted), they can abstract a hydrogen atom from either surface, or they can abstract a hydrogen atom from another chain to produce an H_2 molecule which is trapped at the interface. After initiation, the reactive radicals left on the tails of the adsorbed molecules can also react in a number of ways. For example, they can be eliminated by recombination with hydrogen atoms, they can abstract hydrogen atoms from the

---

(14) Brenner, D. W. *Phys. Rev. B* **1990**, *42*, 9458–9471. Brenner, D. W.; Harrison, J. A.; White, C. T.; Colton, R. J. *Thin Solid Films* **1991**, *206*, 220–223.

(15) Berendsen, H. J. C.; Postma, J. P. M; van Gunsteren, W. F.; DiNola, A.; Haak, J. R. *J. Chem. Phys.* **1984**, *81*, 3684–3690.

(16) Brooks, C. A. *The Properties of Diamond*; Field, J. E., Ed.; Academic Press: London, 1979; pp 383–402.

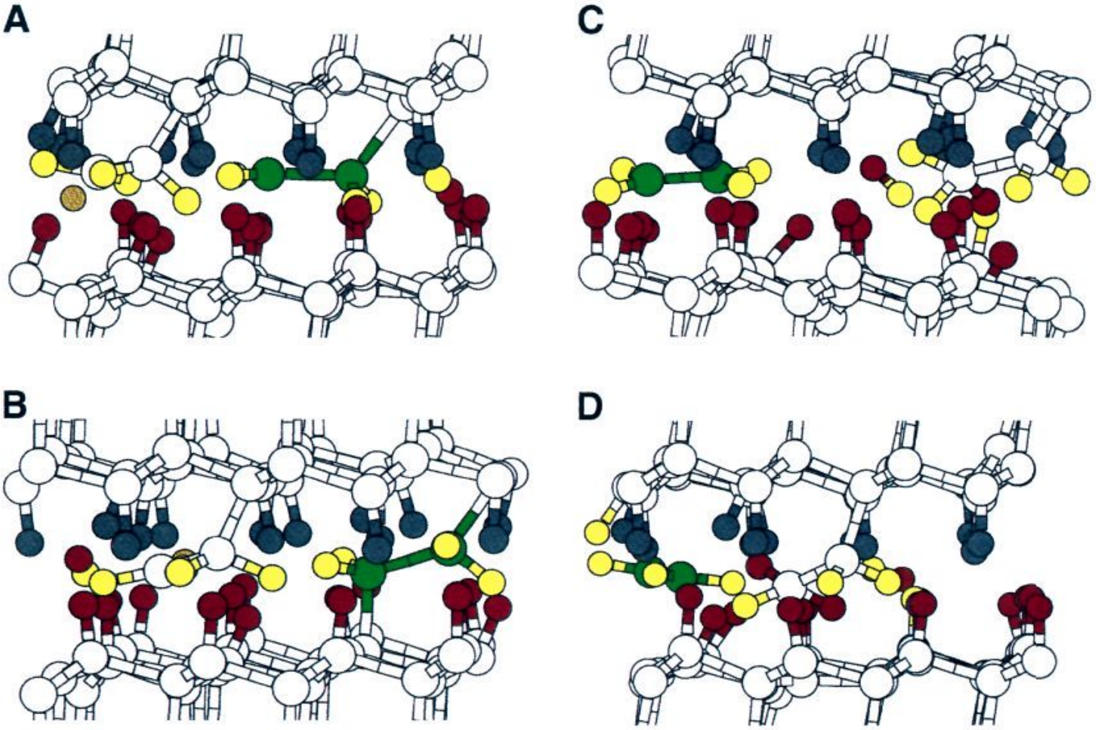

Figure 2. Simulation configurations at different times for sliding the upper surface in the $[11\bar{2}]$ direction with the same color coding as in Figure 1. (A) System after hydrogen atoms have been sheared from the ends of both R groups. These free hydrogen atoms are colored dark yellow to help distinguish them from bound atoms. (B) Adhesion of the two surfaces via the formation of a carbon−carbon bond from the R group at the right (colored green) to the lower surface. A hydrogen molecule (red−yellow) is visible at the left of the figure. (C) Simulation after the adhesive bonds between the surfaces have broken. The resulting ethylene molecule (green) is visible at the left of the panel. A hydrogen molecule is also visible in the center of the panel. (D) Ethylene and hydrogen molecules are still present at the interface. Hydrogen atoms which originated from the R groups have added to the upper (at the left) and lower (at the right) diamond surfaces. One of the R groups has abstracted two hydrogen atoms from the lower diamond surface.

opposing surface, or they can form bonds with existing radical sites on the opposing surface. The latter configuration results in adhesion between the two surfaces. With continued sliding, the simulations show that the bonds to each surface may simultaneously break, leaving molecular wear debris trapped at the interface.

The aforementioned set of complex chemical reactions occurred only *after* hydrogen atoms were shorn from the ethyl groups during the sliding. These reactions are, therefore, the first set of chemical reactions observed in molecular dynamics simulations which were initiated by the sliding process, i.e., tribochemical reactions. We note that molecular dynamcis simulations using this empirical hydrocarbon potential have shown it is possible to initiate chemical reactions in other ways. For instance, bombardment of diamond surfaces with hydrogen and C_{60} molecules can lead to hydrogen addition or abstraction and to the destruction of the C_{60} molecule due to chemical reactions with the diamond surface.[17,18] Indentation of a diamond surface with a diamond tip can lead, under certain conditions, to adhesion between the tip and the surface. In that case, adhesion was shown to be the result of the formation of chemical bonds between the tip and the surface.[19]

In addition to initiation by the shearing of hydrogen atoms, we also observed that for sliding in the $[1\bar{1}0]$ direction the tails of the ethyl groups may become "caught" between hydrogen atoms on the lower surface. Continued sliding shears the entire tail from the rest of the ethyl group, leaving a chemisorbed $CH_2^{\bullet}$ group and a free $CH_3^{\bullet}$ species. The simulations show that the latter species can form a bond with an existing radical site, it can shear a hydrogen from a chemisorbed ethyl group, or it can recombine with the chemisorbed $CH_2^{\bullet}$.

Comparison of the tribochemical reactions for sliding in both crystallographic directions examined here reveals that the sequence of reactions, and the products of these reactions, can differ depending on the sliding direction. This can be traced to the different arrangement of hydrogen atoms in the two directions. For sliding in the $[1\bar{1}0]$ direction, the hydrogen atoms along the rows perpendicular to the sliding direction are closer than in the rows perpendicular to the $[11\bar{2}]$ sliding direction (Figure 1B). This causes the tail groups of the ethyl chains to become more tightly lodged during sliding and results in breakage of the carbon−carbon bond in the ethyl chain. These different reaction mechanisms imply different wear rates for each direction, consistent with the experimental observation that wear rates are dependent on the direction of abrasion.[8,9]

The complex tribochemistry is best illustrated by describing in detail events that were observed for a typical simulation of the system shown in Figure 1 sliding in the $[11\bar{2}]$ crystallographic direction. As sliding is started, each of the ethyl groups has a hydrogen atom sheared from the $-CH_3$ portion of the group (Figure 2A). This shearing of the hydrogen atoms creates two radical sites, one on each ethyl group, and two free hydrogen atoms. The tail portions of these groups are then smaller and "flatter" than the tail of the original ethyl groups; therefore, they are able to slide over the lower diamond surface with less distortion of the other chemisorbed atoms and less vibrational excitation at the interface.

---

(17) Page, M.; Brenner, D. W. *J. Am. Chem. Soc.* **1991**, *113*, 3270−3274.

(18) Mowrey, R. C.; Brenner, D. W.; Dunlap, B. I.; Mintmire, J. W.; White, C. T. *J. Phys. Chem.* **1991**, *95*, 7138−7142.

(19) Harrison, J. A.; White, C. T.; Colton, R. J.; Brenner, D. W. *Surf. Sci.* **1992**, *271*, 57−67.

The free hydrogen atoms, which originated from the tails of the ethyl groups, become trapped at the sliding interface.[20] One of these hydrogen atoms abstracts a hydrogen atom from the lower diamond surface to form a hydrogen molecule, H_2 (Figure 2C). This molecule does not undergo any further reaction during the simulation.

As the sliding continues, one of the radical-containing ethyl groups passes over the radical site on the lower surface that was created by the abstraction of hydrogen by a free hydrogen atom. These two radicals combine to form a carbon–carbon bond. As a result, the upper and lower surfaces become chemically joined by a $D_u-CH_2CH_2-D_l$ linkage (green entity in Figure 2B). The upper and lower surfaces remain adhered until the shear stress from continued sliding becomes too great for the carbon–carbon bonds that connect the two surfaces. At that point, the carbon–carbon bonds to the upper and lower surfaces break at approximately the same time, creating an ethylene molecule, CH_2CH_2 (Figure 2C), and leaving radical sites on both the upper and lower surfaces. The flat ethylene molecule (the carbon–carbon double bond requires that ethylene be planar) remains trapped at the interface for the remainder of the simulation undergoing no further chemical reactions (Figure 2D). The nascent radical site on the lower surface is filled via the addition of a free hydrogen atom which originated from the tail of an ethyl group (Figure 2D).

The two original chemisorbed ethyl groups do not undergo the same sequence of reactions. After the shearing of the hydrogen atom from the tail of the second ethyl group, the resulting radical abstracts a hydrogen atom from the lower surface (Figure 2C). This yields a radical on the lower surface and a fully-saturated ethyl group on the upper surface. Continued sliding results in the "wearing" of another hydrogen atom from the tail of the ethyl group, creating a new radical site. This free hydrogen atom becomes trapped at the interface and eventually adds to the radical site on the upper surface that was created by the shearing of the $D_u-CH_2CH_2-D_l$ connection (Figure 2D). Upon continued sliding, the radical on this ethyl group abstracts a second hydrogen atom from the lower surface to again become saturated (Figure 2d). This group does not undergo any additional reactions by the end of the 30 ps simulation.

In summary, we report the first observation of specific tribochemical reactions when two diamond surfaces are placed in sliding contact. We find complex, nonequilibrium radical chemistry that is initiated by the loss of hydrogen from chemisorbed molecules. This chemistry consists of the abstraction of hydrogen from each surface, radical recombination, transient adhesion of the sliding surfaces, and formation of molecular wear debris. Each of these observations is consistent with conclusions inferred (but not directly measured) from experimental studies of the friction and wear of diamond surfaces. In addition, the observation that sliding the two hydrogen-terminated diamond surfaces without chemisorbed molecules did not result in shearing of hydrogen and the production of wear debris implies that surface roughness plays a critical role in initiating wear and subsequent formation of debris.

Acknowledgment. This work was supported by the Office of Naval Research (ONR) under Contracts No. N00014-94-WR-23017 and No. N00014-94-WX-23024. D.W.B. is supported by the Advanced Research Projects Agency and by ONR through the Naval Research Laboratory. J.A.H. is supported by ONR through the U.S. Naval Academy. James Butler, Richard Colton, Barbara Garrison, Irwin Singer, Susan Sinnott, and Carter White are thanked for many helpful discussions. Carter White is also thanked for technical assistance. The figures were generated with the program XMol (XMol, version 1.3.1, Minnesota Supercomputer Center, Inc., Minneapolis, MN, 1993).

---

(20) The simulation geometry keeps the free molecules trapped at the interface for the duration of the simulation. However, if the geometry was different, e.g. a tip and a surface, it would be possible for a molecule to escape the interface region at some point during the sliding.