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Quantum Chemical Approach to Redox Reactions Including Potential Dependence: Application to a Model for Hydrogen Evolution from Diamond

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The evolution of H_2 from diamond cathodes according to the proposed mechanism $H^+(aq) + \geqslant C-H + e^- \rightarrow H_2 + \geqslant C^\bullet$ is treated with ab initio quantum mechanics. The solvated proton and diamond surface C−H bond are modeled with molecular clusters, and the electron is introduced at selected potentials by using a remote donor molecule. The reduction occurs when the electron affinity, EA, of the surface complex increases to the ionization potential, IP, of the donor as the complex traverses its reaction coordinate. When they are equal, equilibrium is assumed and electron transfer occurs. The electrochemical potential, U, is given by $U = (\mathrm{IP/eV} - 4.6)$ V. For the H_2 generation reaction studied, the electron transfer coincides with the transition-state structure, and the activation energy is found to decrease as the potential becomes more negative. It is shown that surface C−H bonds will re-form by $H^+(aq)$ discharge on the surface carbon radicals. The potential-dependent reduction of $H^+(aq)$ to $H^\bullet$ is examined, too. Comparison is made with the gas-phase generation of hydrogen and surface carbon radicals. The present model employs the hydronium ion for $H^+(aq)$, methane and isobutane for surface C−H, and the self-consistent HF/STO-3G method. In general, use of an electron donor is not required. This approach should find application to many other electrochemical reactions.

Introduction

Boron-doped diamond films can have sufficient conductivity to function as practical electrodes. When the surface concentration of defects is low, such electrodes exhibit extraordinarily wide potential windows of inactivity toward redox reactions within the inner Helmholtz plane.[1−3] When the potential is driven positive enough, noticeable current begins to flow (on the mA/cm^2 scale) at +2.3 V (SHE), which is the onset of oxygen evolution on high-quality diamond polycrystalline electrodes.[2] Similar results were reported recently for (111) and (100) diamond electrodes.[4] This is an overpotential of 1.1 V (the reversible potential is 1.23 V[5]). At the other end of the window of inactivity, hydrogen evolution finally commences (on the mA/cm^2 scale) at −1.25 V potential, which, for this reaction, is an overpotential of 1.25 V. Platinum, a widely used electrode metal, shows a much narrower potential window of inactivity within the inner Helmholtz plane, extending from about 0.3 to 0.8 V. Oxidation of this surface commences at 0.8 V potential and oxygen evolution begins at 1.6 V, representing an overpotential of 0.4 V. In the other direction, atomic hydrogen is reduced on to the surface by reduction of solvated protons at potentials of 0.3 V and less. The overpotential for hydrogen evolution (on the mA/cm^2 scale) is very close to 0 V; platinum is an excellent hydrogen evolution catalyst.

The reduction of $H^+(aq)$ and evolution of H_2 on Pt can be explained easily. From thermodynamic data, the reduction potential for forming $H^\bullet(aq)$ is −2.1 V:[6]

$$H^+(aq) + e^-\ (-2.1\ \mathrm{V}) \rightleftharpoons H^\bullet(aq) \qquad (1)$$

The $H^\bullet$ is weakly stabilized, a few tenths of an electronvolt at most, by solvation. However, coupling the proton reduction with adsorption on a Pt electrode surface stabilizes $H^\bullet$ in the form of H(ads). At 0 V this stability is about 2.1 eV, and at the onset potential, 0.3 V, the stability is about 2.4 eV. The reaction

$$2H(ads) \rightarrow H_2 \qquad (2)$$

can occur when the strength of two H−surface bonds is about equal to the strength of the H_2 bond, which is 4.48 eV. A precise statement would be in terms of Gibbs energies, but we limit the discussion simply to energy. On this basis we see that, from energies alone, the potential at which eq 2 would be at equilibrium would be about 0.14 V. The fact that the overpotential is close to zero at room temperature indicates that the activation energy for H atom combination on Pt electrodes to form H_2 is small. Essentially, the Pt electrode is making reactive, though adsorbed, hydrogen atoms at 0 V potential.

What makes the diamond electrode so different for H_2 evolution? The H_2 reduction step probably requires some interaction with the surface; otherwise, H_2 evolution would be expected to commence at −2.1 V potential from the formation and recombination of $H^\bullet$, not at the more positive value of −1.25 V as observed.[2] A high-quality diamond film surface terminates in C−H bonds and small quantities of as yet to be characterized defects. The C−H terminated surface would react with H atoms if present because the diamond (111) surface C−H bond strength is, from thermal desorption kinetic studies,[7] 3.7 ± 0.1 eV, which is about 0.3 eV[5] less than the tertiary C−H bond strength in isobutane, a possible model molecule for this surface. Therefore, since the H_2 bond strength is 4.48 eV, the reaction

$$H^\bullet + \geqslant C-H \rightarrow \geqslant C^\bullet + H_2 \qquad (3)$$

would be exothermic by 0.78 ± 0.1 eV on the diamond (111) surface. Reaction 3 would have ~0.3 eV smaller exothermicity

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for isobutane, and ab initio calculations have produced a reaction energy 0.36 eV.[8] More interestingly, the isobutane calculations yielded values of 0.32[8] and 0.36 eV[9] activation energy for reaction 3. Furthermore, calculations employing good-sized cluster models yield 0.36 and 0.48 eV activation energies for the (111) and (100) surfaces, respectively.[9] From this is may be concluded that H atoms would react without much hindrance at room temperature with the diamond surface, if they could form.

What is the nature of the H^+(aq) interaction with the C−H terminated surface, and what is the mechanism for hydrogen evolution? A weak hydrogen bond may form between them, and hydrogen evolution might proceed according to[10]

$$H^+(aq) + \geqslant C{-}H + e^-(U) \rightarrow H_2 + \geqslant C^\bullet \qquad (4)$$

This mechanism has been verified for other p-type semiconductors, including germanium.[11] The surface would be regenerated as follows:

$$H^+(aq) + \geqslant C^\bullet + e^-(U) \rightarrow \geqslant C{-}H \qquad (5)$$

As the reaction coordinate is traversed, a transition state will be reached, and because of the nature of the bonding in this case, it is probable that the reacting system will be reduced by an electron from the cathode at this point:

$$\begin{aligned} &H_2O{:}H^+(aq) + \geqslant C{-}H + e^-(U) \rightarrow \\ &\qquad H_2O{:}\cdots H\cdots H\cdots C\leqslant \rightarrow H_2O + H_2 + \geqslant C^\bullet \qquad (6) \end{aligned}$$

As the O:H^+ and H−C approach one another, the occupied σ orbitals will give a closed-shell repulsion and the empty σ* orbitals will also interact, the bonding one becoming more stabilized as the transition state is approached. When this orbital is occupied by the electron transfer, the reacting system enters a new Born−Oppenheimer potential surface for the reduced state, and the energy decreases and the product ultimately forms. As the H_2 internuclear distance becomes shorter and the C−H and O−H becomes simultaneously longer, the C−H σ and O−H σ bonding counterparts are expected to evolve into the H_2 σ orbital and the antibonding counterparts into the O lone-pair orbital while the σ* bonding counterpart evolves into the C radical orbital.

The purpose of this paper is to show the results of an ab initio calculational approach to modeling the potential dependence of hydrogen evolution from diamond cathodes according to the mechanism outlined above. To define a tractable model, two simplifying approximations are made: (i) that during the bond rearrangements the bonds that are changing are satisfactorily modeled by small molecules, and the surrounding environment, including the extended carbon lattice of the diamond surface and the electrolyte, is a perturbation to the picture that will be studied separately; (ii) that an electron of controlled potential introduced into the reacting system allows a satisfactory description of the redox process, and the perturbation on the potential by the double-layer field will be studied separately. That is, the zeroth-order model focuses on the explicit components of equations such as (6).

Computational Approach

The simplest approach to hydrogen evolution, eq 6, according to the above prescription, would be to use the H_3O^+ molecule to represent H^+(aq) and the CH_4 molecule to represent a C−H bond terminating the diamond surface, in accordance with the above assumptions. Simply adding an electron with 0 eV energy on the physical (vacuum) scale to a quantum calculation of eq 6 would mean that its potential is approximately −4.6 V on the standard hydrogen electrochemical scale.[12] In this work we model other potentials by placing a donor molecule in the system about 10 Å away from the CH_4 molecule. At the moment of electron transfer equilibrium is assumed so that the electrochemical potential of the donor, *U*, is

$$U = (\mathrm{IP/eV} - 4.6)\ \mathrm{V} \qquad (7)$$

Longer distances such as 20 and 50 Å were explored, and the results were negligibly different. For results reported in this paper a Li atom with one or two H_2O molecules coordinated to it, which allows the selection of a range of ionization potentials, and hence electrochemical potentials, was chosen for the donor system when the reduction center had singlet spin. For a Li atom by itself, the ionization potential is 4.90 eV, which corresponds to 0.30 V potential. Other donor potentials used in this study were −1.40, −2.90, and −4.68 V. For doublet reduction centers Li_2 was used, with a potential of −0.91 V. This ensured that the reaction center was always in the proper state. The Gaussian 94[13] program package was drawn upon for the calculations.

Other aspects of our model are as follows. The $H_3C{-}H$ bond has, in calculations with the HF/STO-3G basis set, a calculated D_e of 4.99 eV, and so D_o would be about 4.8 eV, close to the experimental value of 4.56 eV. For isobutane, the D_e for $R_3C{-}H$ is 4.61 eV, so D_o would be about 4.4 eV, close to the experimental 4.0 eV. The proton solvation energy, forming H_3O^+(aq), is about 11.3 eV,[12] and for our HF/STO-3G calculation we obtain a D_e of 9.91 eV. This would correspond to a D_o of about 9.7 eV. This value is well below the proton solvation energy, but for proton transfer in this environment this may not be so bad. Using MP2/6-31G** calculations, the $H_2O{-}H^+$ bond strength is even less, with a D_e of 7.83 eV. Coordinating two water molecules stabilizes this H_3O^+ by 2.55 eV so that the bond strength of H^+ to $OH_2(H_2O)_2$ is 10.38 eV,[14] only 0.5 eV away from the HF/STO-3G value for H^+ bonding to H_2O. Thus, higher quality wave functions, inclusion of zero-point energies, and inclusion of hydronium solvation should not have a qualitative influence. In fact, the theoretical literature for H abstraction from isobutane[8] and diamond surface cluster models[9] indicate reductions of <0.1 eV in the activation energies due to inclusion of zero-point energies. Regarding effects of wave function quality for H abstraction from methane [reaction 3] the activation energy calculated by HF/STO-3G was 1.03 eV, while UMP4(SDQ)6-311G** calculations yield a 0.75 eV activation energy, which we regard as accurate. Similar ∼0.3 eV reductions should apply to the other transition states in our work, which for the most part are based on STO-3G calculations, since the orbital interactions at the transition states are all similar.

Results

The hydronium ion is calculated to form a weak, 0.06 eV, collinear hydrogen bond of length 1.65 Å with a methane C−H bond. It forms a hydrogen bond to the tertiary C−H bond of isobutane with a length of 1.5 Å and a strength of 0.16 eV. This weak attractive interaction will facilitate orienting the hydronium ion for H_2 formation. We have evaluated energies using 0.1 Å step sizes for the O···C, O···H, and H···C internuclear distances using CH_4 and $HC(CH_3)_3$ to find transition-state structures and activation energies at three potentials. As may be seen in Figure 1, the activation barriers decrease rapidly as the voltage becomes more negative, and the tertiary

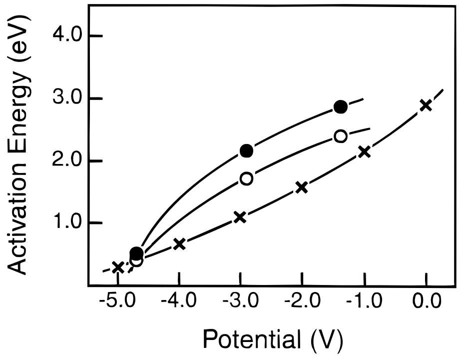

Figure 1. Calculated activation energies as functions of electrochemical potential, V (SHE), for H_2 formation by eq 6: (●) for CH_4 model, (○) for $HC(CH_3)_3$ model; and (×) for $H^\bullet$ generation by eq 10.

TABLE 1: Calculated Transition-State Structures Activation Energies, E_a (eV), and Reaction Energies, ΔE_r (eV), for CH_4 and $HC(CH_3)_3$ Models (Distances, d, in Å; Electrochemical Potentials, V, on the H_2 Scale)

model	potential	d_{CO}	d_{OH}	d_{CH}	d_{HH}	E_a	ΔE_r
CH_4	−1.40	3.5	1.2	1.4	0.9	2.9	0.39
	−2.90	3.6	1.1	1.5	1.0	2.2	−1.11
	−4.68	3.5	1.1	1.3	1.1	0.5	−2.89
$HC(CH_3)_3$	−1.40	3.6	1.3	1.3	1.0	2.4	0.02
	−2.90	3.6	1.1	1.5	1.0	1.7	−1.49
	−4.68	3.5	1.1	1.3	1.1	0.4	−3.27

C−H bond of isobutane has a uniformly lower barrier for the reaction than a primary C−H bond in methane.

Transition-state structure parameters are in Table 1. For these calculations only the structure of the hydronium ion was fully optimized; the methane and isobutane surface CH models were partially optimized by allowing the C atom to move along the C−H axis, representing relaxations normal to the surface, approaching planarity for $(CH_3)C^\bullet$ as in the previous ab initio work.[8,9] It may be seen that at the transition states the O···C distance is 3.5−3.6 Å, the H···H distance is around 1.0 Å, and the O−H and H−C bonds both are stretched.

Regeneration of the C−H bond, eq 5, is calculated to have no activation barrier at −0.9 V potential for the methane model when H_3O^+ is used to model $H^+(aq)$, so the original surface can be regenerated. Based on calculated HF/STO-3G energies, the reaction energy for hydrogen evolution

$$2H_3O^+ + 2e^- \ (0\ V) \rightarrow H_2 + 2H_2O \qquad (8)$$

is −1.4 eV, which corresponds to a predicted reversible potential of 0.7 V. Bond strength corrections and enthalpic and entropic contributions added to the reaction energy will yield $\Delta G°$ values from which the reversible potential can be calculated very accurately.[14] For potential-dependent trends in activation energies such contributions are less of an issue. The overall reaction energy including a diamond surface model, eq 5 plus eq 6, is the same as for eq 8.

Another approach to redox problems omits the donor function. In this case, for each unreduced reactant structure along the reaction coordinate an electron would be added and the system energy recalculated to yield the energy of the reduced system. The activation energy, E_a, would be found as follows: Let $E_{M+}(\mathbf{R})$ be the energy of the unreduced molecular system, M^+ in structure $\mathbf{R}$, and let $E_M(\mathbf{R})$ be the energy of M for this structure. Then for potential U, M^+ and M will be in equilibrium when

$$E_M(\mathbf{R}^*) - E_{M+}(\mathbf{R}^*) + 4.6\ \text{eV} + U(\text{eV/V}) = 0 \qquad (9)$$

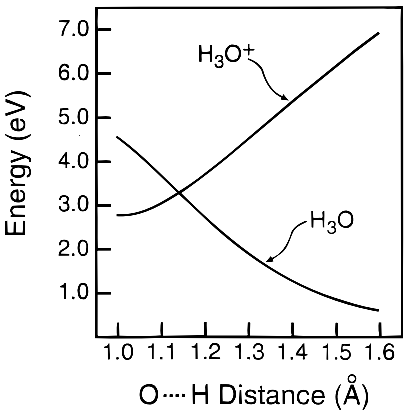

Figure 2. Energy of H_3O^+ (M^+) as a function of stretching one of the O−H bonds including relaxation of the H_2O structure, along with the self-consistent energy of H_3O (M) without structure relaxation.

which is the condition for charge transfer where $\mathbf{R}^*$ stands for the transition-state structure. Let $E_{M+}(\mathbf{R}_o)$ be the energy of the reactant that is to be reduced. Then $E_a(U)$, the activation energy at potential U, is given by

$$E_a(U) = E_M(\mathbf{R}^*) - E_{M+}(\mathbf{R}_o) + (4.6 + U/V)\ \text{eV} \qquad (10)$$

Equation 10 can be easily solved graphically when $\mathbf{R}$ is of dimension 1, which is not the case for hydrogen evolution.

Finally, our calculations yield for the reduction of a hydronium ion, eq 1,

$$H_3O^+ + e^-(U) \rightleftharpoons H^\bullet + H_2O \qquad (11)$$

an equilibrium potential of −1.8 V, close enough to the −2.1 V experimental value to provide another supportive check of the simple model. The activation energy for $H^\bullet$ formation by eq 11 can be obtained as a function of potential by graphical means. Figure 2 shows the energy of structurally optimized H_3O^+ as one of the O−H bonds is stretched along with the energy of H_3O in the same structure. Applying eq 9 and eq 10 to these curves yields $E_a(U)$ as shown by the lowest curve in Figure 1. The activation barrier is 1.7 eV at the −1.8 V calculated reversible potential. Since the electron transfer can occur only when the structure-dependent electron affinity of the reaction center matches the ionization potential of the donor center, enhancing the electron affinity should lower all the barriers in Figure 1. This would be expected to be achieved by using larger basis sets for the reaction center and through enlarging the system by solvating the hydronium ion and adding more carbon atoms to the surface model. Future studies will probe these effects.

Concluding Comments

A model has been developed and applied to understanding the overpotential to hydrogen evolution on semiconducting diamond electrodes which are themselves modeled by small clusters. The model has also recently been applied to outer Helmholtz plane reduction of dioxygen to water.[14] The general approach should find additional applications to the understanding of electrocatalysis and overpotentials at the molecular level. The reacting center at the electrode surface is a species of variable electron affinity and ionization potential, depending on its structure. The electrode is a donor or acceptor of electrons, and this capability is modeled by including a remote molecule with adjustable ionization potential, for reduction reactions or adjustable electron affinity for oxidation reactions. As the surface reacting complex is distorted in structure along the reaction path, the energy in general rises and its electron affinity or ionization potential changes, and when a match with donor or acceptor function of the electrode is reached, a momentary equilibrium is assumed, charge transfer occurs, and the surface reacting complex transfers to a new Born−Oppenheimer potential surface that leads to redox products. This model could be enhanced by increasing the size of the reacting surface complex and by adding double-layer molecules. The flat-band potential is about 0.7 V or more,[15] so in the potential range of hydrogen evolution the potential at the electrode surface will be affected by the space charge in the diamond and by electrolyte polarization at the interface. These effects need to be addressed in refining this approach. Tunneling corrections could also be incorporated. An alternative but approximate theory relies on electrode surface band shifting within the framework of the semiempirical atom superposition and electron delocalization molecular orbital theory. The potential of the surface model is thus changed parametrically in the absence of explicit inclusion of surface charging and double-layer molecules. This theory may be used to predict some trends with potential changes, such as variations in adsorbed CO bond vibrational energies[16] and activation energies for the decomposition of adsorbed H_2O.[17]

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