

same order in the ($E_2 - E_1$) values, by which the dication state of **1a** is shown to be most stable among them.

X-ray diffraction analysis of **1b**¹¹ indicates that the molecule belongs to the approximate D_{2d} symmetry (excluding eight carbomethoxy groups with flexible conformations) and has the puckered structure of the central four-membered ring. Figure 1 shows a unique stacking structure of molecules of **1b** related by the crystallographic 2_1 symmetry along the c axis resulting in a one-dimensional column in the crystal lattice. Some van der Waals contacts are found between the sulfur atoms of interdonor molecules, the shortest one being 3.608 Å (twice the van der Waals radius of sulfur is 3.70 Å).

These results suggest that the [4]radialenes, in particular **1a**, should be useful electron-donor candidates for organic metals. In fact, **1a** forms a 1:2 charge-transfer salt (black needle crystals, mp > 300 °C) with TCNQ, and the room temperature electrical conductivity on the compressed pellet is fairly high ($0.032 \Omega^{-1} \text{cm}^{-1}$). Furthermore, the E_a value (0.057 eV) is very small. The preparation and electrical characterization of **1a**-TCNQ single crystals are currently under active investigation.

Acknowledgment. Partial support from the Ministry Education, Science and Culture, Japan (the Grant-in-Aid for Developmental Scientific Research, Project 59850140 and for Scientific Research, Project 59430017) is greatly acknowledged. We are deeply thankful to Prof. H. Inokuchi, Dr. T. Enoki, and K. Imaeda (Institute for Molecular Science) for measurement of electrical conductivities.

Supplementary Material Available: ORTEP drawing and full tables of fractional atomic coordinates and interatomic bond distances and angles in **1b** (5 pages). Ordering information is given on any current masthead page.

(11) Crystal data of **1b**: $\text{C}_{32}\text{H}_{24}\text{O}_{16}\text{S}_8$, FW = 921.1, orthorhombic, space group $P2_12_12_1$, $a = 17.9317$ (1) Å, $b = 25.757$ (2) Å, $c = 8.539$ (1) Å, $U = 3808.7$ (4) Å³, $D_x = 1.606 \text{ g cm}^{-3}$, $Z = 4$. X-Ray diffraction data were measured on a Rigaku four-circle diffractometer using nickel-filtered $\text{Cu K}\alpha$ radiation. A total of 3217 reflections were collected up to $2\theta = 120^\circ$ by the θ - 2θ scan technique. The structure was solved by the direct method (MULTAN-78) and refined by the full-matrix least squares (XRAY-76) by using the 3073 observed reflections [$|F_0| \geq 3\sigma(F_0)$] to the R index of 0.052 including non-hydrogen atoms with anisotropic thermal parameters.

Measurement of the Activation Barrier for Carrier Transport at n-GaAs Semiconductor/Liquid Junctions

Louis G. Casagrande and Nathan S. Lewis*

Department of Chemistry, Stanford University
Stanford, California 94305

Received July 1, 1985

The mechanism of carrier transport at semiconductor/liquid interfaces is an important and controversial topic in photoelectrochemistry. Of particular concern is the transport kinetics for interfaces whose open-circuit voltage, V_{oc} , is constant over some range of solution redox potential.^{1,2} Fermi level pinning has been postulated to apply to n-GaAs, p-GaAs, and p-InP interfaces in both aqueous and nonaqueous solvents.^{2,3} However, direct identification of the various recombination mechanisms has been acknowledged to be difficult,³ and to date, few experimental

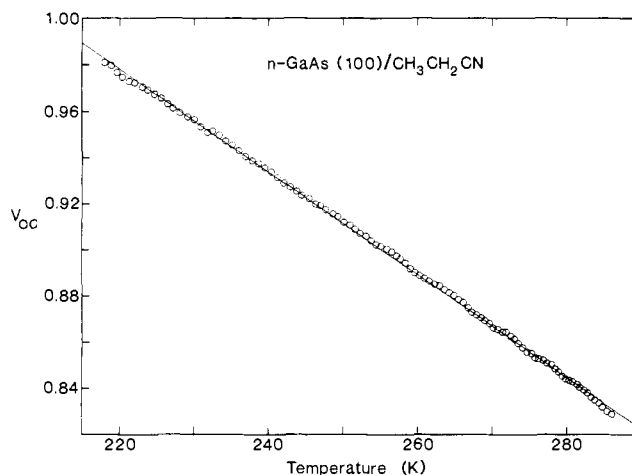


Figure 1. V_{oc} vs. T for the n-GaAs/ $\text{FeCp}_2^{+/0}$ - LiClO_4 - $\text{CH}_3\text{CH}_2\text{CN}$ system. Voltages were measured between an n-GaAs working electrode (0.05–0.2 cm^2) and a Pt wire poised at the solution potential. The cell is immersed in an ethanol solution in a strip-silvered Dewar Flask, and the cooling rate is typically 5 K/min.

techniques have been reported which allow correlation of the key photostationary state observable, the open circuit voltage, to the transport mechanism of these interfaces. We report here measurements of the temperature dependence of the open-circuit voltage for the n-GaAs semiconductor/liquid junction system.

For surface barrier systems, activation energies can be obtained from plots of V_{oc} as a function of temperature.⁴ Thermionic emission of majority carriers over a low surface barrier would yield an activation energy equal to the effective barrier height. In contrast, the characteristic activation energies of other transport mechanisms differ from this value and can be predicted by conventional kinetic treatments of semiconductor junction transport.⁴

Figure 1 indicates the temperature dependence of V_{oc} for the n-GaAs/0.05 M FeCp_2 -0.5 mM $\text{FeCp}_2^{+/0}$ -0.2 M LiClO_4 - $\text{CH}_3\text{C}-\text{H}_2\text{CN}$ junction^{1b} (ELH type tungsten-halogen bulb; (100) oriented, $2 \times 10^{17} \text{ cm}^{-3}$ Se doped, n-GaAs; 2-s etch in 4:1:1 $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2/\text{H}_2\text{O}$) at an illumination intensity of 100 mW/cm^2 . We observe a slope for V_{oc} vs. T of $-2.1 \pm 0.2 \text{ mV/K}$ and an extrapolated intercept of $1.45 \pm 0.1 \text{ V}$ at 0 K. The band gap (E_g) of GaAs is 1.42 eV at 300 K and 1.52 eV at 0 K;⁴ thus, the intercept of V_{oc} vs. T , determined over the range of 300–200 K, is very close to E_g . Association of this intercept with the transport activation energy indicates that thermionic emission of majority carriers over a Fermi level pinned barrier is not the dominant transport mechanism at this interface.

Other factors which might complicate the interpretation of V_{oc} vs. T plots for these junctions have been considered in detail. Variation of the bulk semiconductor properties which produce changes in short-circuit photocurrent density (J_{sc}) with temperature, such as the carrier mobilities, the absorption coefficient, and the minority carrier lifetime, will lead to changes in J_{sc} of 2 mA/cm^2 over the entire temperature range.⁵ This will produce a change of only 3 mV in V_{oc} . Variation in the barrier height as a result of changes in $E(A^+/A)$ with temperature is another possible source of complication. Determination of the temperature dependence of $E^{0'}(\text{FeCp}_2^{+/0})$ in 0.2 M LiClO_4 - $\text{CH}_3\text{CH}_2\text{CN}$ by nonisothermal reference electrode technique yields a temperature coefficient of 0.6 mV/K, in accord with the measurements of Weaver for $E^{0'}(\text{FeCp}_2^{+/0})$ in CH_3CN solvent.⁶ The negative shift in $E(A^+/A)$ with decreasing T might decrease the barrier height; thus, for the n-GaAs/ $\text{FeCp}_2^{+/0}$ - $\text{CH}_3\text{CH}_2\text{CN}$ system, the intercept

(1) (a) Lewis, N. S. *Ann. Rev. Mater. Sci.* **1984**, *14*, 95. (b) Gronet, C. M.; Lewis, N. S. *Appl. Phys. Lett.* **1983**, *43*, 115.

(2) Bard, A. J.; Bocarsly, A. B.; Fan, F.-R. F.; Walton, E. G.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 3671.

(3) (a) Bard, A. J.; Fan, F.-R. F.; Gioda, A. S.; Nagasubramanian, G.; White, H. S. *Discuss. Faraday Soc.* **1980**, *70*, 19. (b) Fan, F.-R. F.; Bard, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 3677. (c) Dominey, R. N.; Lewis, N. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 1261. (d) Baglio, J. A.; Calabrese, G. S.; Harrison, D. J.; Kamieniecki, E.; Ricco, A. J.; Wrighton, M. S.; Zoski, G. D. *J. Am. Chem. Soc.* **1983**, *105*, 2246. (f) Nagasubramanian, G.; Wheeler, B. L.; Bard, A. J. *J. Electrochem. Soc.* **1983**, *130*, 1680.

(4) (a) Fahrenbruch, A. L.; Bube, R. H. "Fundamentals of Solar Cells"; Academic Press: New York, 1983. (b) Sze, S. M. "Physics of Semiconductor Devices", 2nd ed.; Wiley: New York, 1981.

(5) Stuerke, C. *Conf. Rec. IEEE Photovoltaic Spec. Conf.* **1978**, *13th*, 551.

(6) (a) Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 1131. (b) Hupp, J. T.; Weaver, M. J. *Inorg. Chem.* **1984**, *23*, 3639.

of the V_{oc} vs. T plot would only establish a lower limit for the barrier height. However, we rule out a significant change in V_{oc} from the 60-mV thermal shift in $E(A^+/A)$ because V_{oc} for n-GaAs/Fe(MeCp)₂⁺⁰ ($E^0(Fe(MeCp)_2^{+/0}) = +0.19$ V vs. SCE) at 300 K is equal to V_{oc} for n-GaAs/FeCp₂^{+0/0} ($E^0(FeCp_2^{+/0}) = +0.30$ V vs. SCE). Finally, changes in J_{sc} yield different slopes of V_{oc} vs. T plots but produce little change in the extrapolated intercepts (1.38 ± 0.06 eV for J_{sc} 0.1–20 mA/cm²), strongly supporting the interpretation of Figure 1 as yielding the effective activation energy for carrier transport in the n-GaAs/CH₃CH₂CN junction.

Several other processes can be excluded from consideration based on current-voltage-temperature data. Bulk recombination/diffusion in these n-GaAs samples is excluded due both to the high minority carrier diffusion length, L_p ($>4 \mu\text{m}$), and to the lack of dependence of V_{oc} on the product of the two bulk crystal parameters, L_p and majority carrier density.^{1,4} Suppression of thermal majority carrier injection due to the low concentration of solution acceptor or due to slow electrode kinetics⁷ is ruled out by the insensitivity of V_{oc} to the concentration of FeCp₂ and FeCp₂⁺ at a fixed solution potential. Also, recombination/generation processes inherent to the material can be excluded in our system because n-p⁺ junctions made with identical n-GaAs material yield V_{oc} values of >1.0 V under AM1 conditions at 300 K.

The recombination mechanism which is most consistent with the complete transport data on this interface is recombination/generation through surface trapping levels. Application of Schockley-Read-Hall statistics to surface recombination processes indicates that this mechanism can produce intercepts of E_g for V_{oc} vs. T plots.⁴ Furthermore, we have observed $V_{oc} > 1.05$ V for the n-GaAs/CH₃CH₂CN-FeCp₂⁺⁰ system at 200 K and 10 suns light intensity, indicating that the barrier height in the n-GaAs/CH₃CH₂CN-FeCp₂⁺⁰ system is, conservatively, in excess of 1.1 V. Our data thus indicate that the thermal barrier to majority carrier injection is extremely high. This is incompatible with a simple thermal process activated by a 0.7–0.9-V pinned barrier.

Finally, our results also bear on important aspects of solid-state Schottky junction theories and their relation to semiconductor/liquid junction behavior. Excess As at the GaAs surface has been postulated to be responsible for surface recombination processes.⁸ Alternatively, the unified defect model for III-V materials proposed by Spicer et al. indicates that defects intrinsic to the (110) face of n-GaAs form with exposure of the clean surface to various metals or to oxygen. These defects pin the Fermi level at either 0.7 or 0.9 eV from the conduction band at the surface.⁹ Exposure of our n-GaAs (100) samples to oxidizing etches and to air before immersion in the cell implies that similar surface chemistry should apply to our liquid junction systems. Furthermore, Bard et al. have suggested correlations of the behavior of III-V Schottky junction systems to liquid junctions.² Our kinetic transport data do not directly locate the equilibrium position of the n-GaAs Fermi level; however, we clearly observe V_{oc} values and activation barriers for transport which are much greater than would be predicted based on the solid-state junction models. Importantly, this implies that chemical treatments which affect surface recombination processes at the n-GaAs/CH₃CH₂CN system can, in principle, yield V_{oc} values that approach the bulk diffusion/recombination limited performance for GaAs homojunctions. Our data also indicate that V_{oc} vs. T measurements can be useful in elucidating the dominant recombination mechanism and in distinguishing carrier inversion limited liquid junction systems from Fermi level

pinned junction behavior. Efforts to identify the chemical nature of the surface recombination sites at these n-GaAs interfaces and to modify their kinetic transport behavior are in progress.

Acknowledgment. We acknowledge helpful discussions with W. Spicer, R. Bube, A. Fahrenbruch, and R. Swanson regarding this research. Funding for this work was provided by the Department of Energy, Office of Basic Energy Sciences. We also thank C.L.R. Lewis of Varian Associates for a generous supply of epitaxial n-GaAs samples, and N.S.L. acknowledges support for the Exxon Education Foundation and Monsanto Corp. under the Presidential Young Investigator Program.

Registry No. GaAs, 1303-00-0; LiClO₄, 7791-03-9; CH₃CH₂CN, 107-12-0; ferrocene, 102-54-5.

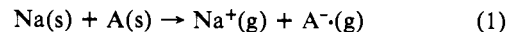
Calorimetric Solution Electron Affinities

Gerald R. Stevenson* and Ramli Tamby Hashim

Department of Chemistry, Illinois State University
Normal, Illinois 61761

Received May 20, 1985

The very endothermic nature of reaction 1 is independent of



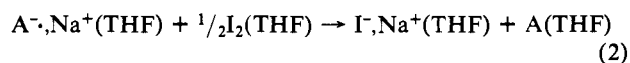
$$\Delta H^\circ = +158.3 \text{ kcal/mol for A = naphthalene}$$

$$\Delta H^\circ = +152.4 \text{ kcal/mol for A = benzophenone}$$

the organic substrate. Even the benzophenone ketyl (BZO⁻), which is one of the most persistent anion radicals and is commonly used to dry solvents in the laboratory,¹ has an electron affinity of 14.7 kcal/mol and an enthalpy of reaction 1 of 152.4 kcal/mol.

The persistence of the benzophenone ketyl in solvents like THF is clearly due to the solvation thermodynamics of the anion radical cation ion pair. More exothermic solvation of a ketyl over a hydrocarbon anion radical is expected due to the very electronegative oxygen that contains much of the charge density of the benzophenone anion radical. Despite the importance of solvation enthalpies in controlling the stabilities and chemistry of organic anion radicals, no experimental solvation enthalpies for anything other than hydrocarbon anion radicals have been reported.^{2,3} This is the case, because the only method for obtaining anion radical solvation enthalpies involves reacting the anion radical with water in a calorimeter.⁴ However, the enthalpy of this reaction can only be converted to the anion radical solvation enthalpy if the reaction produces only one hydrogenated species, the heat of hydrogenation of the substrate to form this species is known, and the reaction of the anion radical with water is exothermic enough to be observed over the heat of the aequation of the anion radical solvent. These conditions have restricted our knowledge of anion radical solvation energies to just those of the polyacenes. Here we wish to report a new technique that can be used for the direct measurement of relative solution electron affinities, which can be utilized for the determination of solvation enthalpies for any persistent anion radical system.

When bulbs containing the anion radical of either naphthalene or benzophenone in THF are broken under 100 mL of THF containing 0.6 g of I₂ in a solution calorimeter, the change in the temperature of the calorimeter is due to only one reaction, reaction 2. Since reaction 2 simply involves the subtraction of an electron



(7) Morrison, S. R., "Electrochemistry at Semiconductor and Oxidized Metal Electrodes"; Plenum Press: New York, 1980.

(8) (a) Freeouf, J. L.; Woodall, J. M. *Appl. Phys. Lett.* **1981**, *39*, 727. (b) Thurmond, C. D.; Schwartz, G. P.; Kammlott, G. W.; Schwartz, B. J. *Electrochem. Soc.* **1980**, *127*, 1366. (c) Heller, A.; Miller, B.; Lewerenz, H. J.; Bachmann, K. J. *J. Am. Chem. Soc.* **1980**, *102*, 6555. (d) Chang, C. C.; Citrin, P. H.; Schwartz, B. J. *Vac. Sci. Technol.* **1977**, *14*, 943.

(9) Spicer, W. E.; Lindau, I.; Skeath, P.; Su, C. Y. *J. Vac. Sci. Technol.* **1980**, *17*, 1019.

(1) Riddick, J. A.; Bunger, W. B. "Organic Solvents"; Weissberger, A., Ed.; Wiley-Interscience: New York, 1970.

(2) Stevenson, G. R.; Schock, L. E.; Reiter, R. C. *J. Phys. Chem.* **1983**, *87*, 4004.

(3) Stevenson, G. R.; Chang, Y. *J. Phys. Chem.* **1980**, *84*, 2265.

(4) Stevenson, G. R.; Schock, L. E.; Reiter, R. C. *J. Phys. Chem.* **1984**, *88*, 5417.