

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)<sub>2</sub><sup>+0</sup> ( $E^0(Fe(MeCp)_2^{+0}) = +0.19$  V vs. SCE) at 300 K is equal to  $V_{oc}$  for n-GaAs/FeCp<sub>2</sub><sup>+0</sup> ( $E^0(FeCp_2^{+0}) = +0.30$  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 ( $1.38 \pm 0.06$  eV for  $J_{sc}$  0.1–20 mA/cm<sup>2</sup>), strongly supporting the interpretation of Figure 1 as yielding the effective activation energy for carrier transport in the n-GaAs/CH<sub>3</sub>CH<sub>2</sub>CN 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.<sup>1,4</sup> Suppression of thermal majority carrier injection due to the low concentration of solution acceptor or due to slow electrode kinetics<sup>7</sup> is ruled out by the insensitivity of  $V_{oc}$  to the concentration of FeCp<sub>2</sub> and FeCp<sub>2</sub><sup>+</sup> at a fixed solution potential. Also, recombination/generation processes inherent to the material can be excluded in our system because n-p<sup>+</sup> 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.<sup>4</sup> Furthermore, we have observed  $V_{oc} > 1.05$  V for the n-GaAs/CH<sub>3</sub>CH<sub>2</sub>CN-FeCp<sub>2</sub><sup>+0</sup> system at 200 K and 10 suns light intensity, indicating that the barrier height in the n-GaAs/CH<sub>3</sub>CH<sub>2</sub>CN-FeCp<sub>2</sub><sup>+0</sup> 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.<sup>8</sup> 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.<sup>9</sup> 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.<sup>2</sup> 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/CH<sub>3</sub>CH<sub>2</sub>CN 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.

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**Registry No.** GaAs, 1303-00-0; LiClO<sub>4</sub>, 7791-03-9; CH<sub>3</sub>CH<sub>2</sub>CN, 107-12-0; ferrocene, 102-54-5.

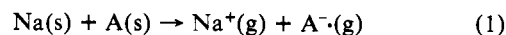
## Calorimetric Solution Electron Affinities

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The very endothermic nature of reaction 1 is independent of



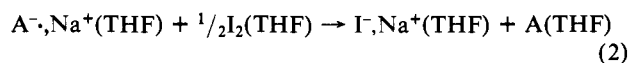
$$\Delta H^\circ = +158.3 \text{ kcal/mol for A = naphthalene}$$

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

the organic substrate. Even the benzophenone ketyl (BZO<sup>-</sup>), which is one of the most persistent anion radicals and is commonly used to dry solvents in the laboratory,<sup>1</sup> 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 electro-negative 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.<sup>2,3</sup> This is the case, because the only method for obtaining anion radical solvation enthalpies involves reacting the anion radical with water in a calorimeter.<sup>4</sup> 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 I<sub>2</sub> 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



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Table I<sup>a</sup>

reaction	$\Delta H^\circ$ , kcal/mol, at 25 °C		
	NP,Na	BZO,Na	BZO,K
$A(\text{THF}) + \text{I}^-, \text{M}^+(\text{THF}) \rightarrow \text{A}^-, \text{M}^+(\text{THF}) + \frac{1}{2}\text{I}_2(\text{THF})$	$+59.1 \pm 1.4$	$+51.2 \pm 1.2$	$+49.3 \pm 0.7$
$\frac{1}{2}\text{I}_2(\text{THF}) + \text{M}(\text{s}) \rightarrow \text{I}^-, \text{M}^+(\text{THF})$	$-75.3 \pm 0.3^b$	$-75.3 \pm 0.3$	$-85.2 \pm 0.3$
$\text{A}(\text{s}) \rightarrow \text{A}(\text{THF})$	$+2.7 \pm 0.1^c$	$+2.1 \pm 0.1$	$+2.1 \pm 0.1$
$\text{A}(\text{s}) + \text{M}(\text{s}) \rightarrow \text{A}^-, \text{M}^+(\text{THF})$	$-13.5 \pm 1.8$	$-22.01 \pm 1.6$	$-33.8 \pm 0.8$
$\text{A}(\text{g}) \rightarrow \text{A}(\text{s})$	$-17.4^d$	$-22.7$	$-22.7$
$\text{A}^-(\text{g}) \rightarrow \text{A}(\text{g}) + \text{e}^-(\text{g})$	$+3.5$	$+14.7^e$	$+14.7$
$\text{M}(\text{g}) \rightarrow \text{M}(\text{s})$	$-25.9$	$-25.9$	$-21.4$
$\text{M}^+(\text{g}) + \text{e}^-(\text{g}) \rightarrow \text{M}(\text{g})$	$-118.5$	$-118.5$	$-100.1$
$\text{A}^-(\text{g}) + \text{M}^+(\text{g}) \rightarrow \text{A}^-, \text{M}^+(\text{THF})$	$-171.8 \pm 1.9$	$-174.4 \pm 1.7$	$-163.3 \pm 1.4$

<sup>a</sup>The enthalpy for reaction 1 can be obtained by summing the reactions 5-8 in this table. <sup>b</sup>These enthalpies were obtained by subtracting the heat of solution of I<sub>2</sub> from that of MI in THF and adding the heat of formation of MI. <sup>c</sup>These values are simple heats of solution and were measured in our laboratory using previously published techniques.<sup>8</sup> <sup>d</sup>The best literature values for these four reactions have been recently compiled.<sup>2</sup> <sup>e</sup>The EA of BZO is taken from ref 9.

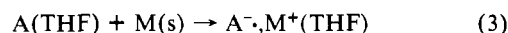
from the anion radical and its addition to iodine, it is a direct measurement of the relative solution EA, and the solution electron affinity of A can be very simply obtained as shown in Table I.

Crushing glass bulbs containing the sodium salt of either the naphthalene anion radical [NP<sup>-</sup>, Na<sup>+</sup>(THF)] or benzophenone ketyl [BZO<sup>-</sup>, Na<sup>+</sup>(THF)] under 100 mL of dry THF containing 0.6 g of I<sub>2</sub> results in a rise in the temperature of the calorimeter due to reaction 2, where A = NP or BZO. The change in the heat content of the calorimeter varies linearly with the amount of anion radical salt in the bulbs, and the slopes of the lines are  $-59.1 \pm 1.4$  and  $-51.2 \pm 1.2$  kcal/mol for A = NP and BZO, respectively. This means that the ketone has a solution electron affinity that is about 8 kcal/mol more than that of naphthalene. In the gas phase, on the other hand, BZO has an EA that is 11.2 kcal/mol greater than that for NP. It was expected that the benzophenone would have a larger solution EA than does naphthalene. However, it is very surprising that the difference in the EA's of benzophenone and naphthalene is not augmented but is attenuated by the solvent.

Utilizing Table I the solvation enthalpy of BZO<sup>-</sup> + Na<sup>+</sup> was found to be  $-174.4 \pm 1.7$  kcal/mol. To be certain that this new technique is operating correctly, it was applied to the NP system yielding a solvation enthalpy for NP<sup>-</sup> + Na<sup>+</sup> of  $-171.8 \pm 1.7$  kcal/mol, which is in excellent agreement with that previously reported<sup>5</sup> of  $-172.5 \pm 4.0$  kcal/mol. The heat of generation of the BZO anion radical from the neutral molecule and the metal in their standard states in THF (solvated neutral molecule and solid metal), reaction 3, is more negative than that for the naphthalene system by about 8 kcal/mol.

The solvation enthalpy of BZO<sup>-</sup>(g) + K<sup>+</sup>(g) was found to be  $-163.3 \pm 1.4$  kcal/mol,<sup>6</sup> which is considerably lower than that for the sodium system. This is consistent with the earlier observation by M. Szwarc<sup>7</sup> that the smaller cations involved in ion association are better solvated than are the larger cations involved in ion association. That is, the solvent has better cation contact with BZO<sup>-</sup>, Na<sup>+</sup> than with BZO<sup>-</sup>, K<sup>+</sup>. It is, however, surprising that a change in the cation from Na<sup>+</sup> to K<sup>+</sup> yields a much more dramatic change in the thermodynamics of solvation of the anion radical than does the alteration of the anion from a ketyl to a hydrocarbon anion radical. It should be noted that the more

exothermic generation of the K-BZO ion pair than that of the Na-BZO ion pair, reaction 3, is due to the smaller ionization



$$\text{M} = \text{Na}; \text{A} = \text{benzophenone}; \Delta H^\circ = -24 \text{ kcal/mol}$$

$$\text{M} = \text{K}; \text{A} = \text{benzophenone}; \Delta H^\circ = -35 \text{ kcal/mol}$$

$$\text{M} = \text{Na}; \text{A} = \text{naphthalene}; \Delta H^\circ = -16 \text{ kcal/mol}$$

potential of K. Thus, BZO<sup>-</sup>, K<sup>+</sup>(THF) is lower in energy relative to the metal and BZO in their standard states in THF than is BZO<sup>-</sup>, Na<sup>+</sup>(THF), despite the poorer solvation of the former system.

We have described the only calorimetric technique for the direct measurement of relative solution electron affinities of neutral molecules, and this technique will be applicable to all persistent anion radicals.

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### Preparation, Structure, and Coordination Chemistry of Mo[S-2,4,6-C<sub>6</sub>H<sub>2</sub>(CHMe<sub>2</sub>)<sub>3</sub>]<sub>4</sub>

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The coordination chemistry of monomeric MoX<sub>4</sub> complexes (X = a monodentate anion) is relevant to the reduction of molecular nitrogen by nitrogenase, since it is generally agreed that at least one end of dinitrogen binds to molybdenum and that the molybdenum is in a relatively high oxidation state, perhaps Mo(IV).<sup>1</sup> There are only two well-characterized examples of MX<sub>4</sub> species, Mo(SCMe<sub>3</sub>)<sub>4</sub><sup>2</sup> and Mo(NMe<sub>2</sub>)<sub>4</sub>.<sup>3,4</sup> The former is the more

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(6) A plot of the change in the heat content of the calorimeter vs. the millimoles of BZO<sup>-</sup>, K<sup>+</sup>(THF) is linear and has a slope of  $-49.4 \pm 0.7$  kcal/mol. All three such plots described in this paper represent at least seven separate experiments (points), and the errors reported in the enthalpy of reaction 2 represent the standard deviations of the slopes of these lines. All three plots have intercepts of 0.0. Any water or other protic impurity in the THF containing the I<sub>2</sub> in the calorimeter would yield Birch reduction products. NMR analysis of the calorimeter contents did not yield detectable amounts of dihydro materials.

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