

GaPc-Cl films of ca. 1.0  $\mu\text{m}$  thickness were vacuum deposited on optically transparent platinum substrates and placed in contact with the same aqueous ferri/ferrocyanide redox couple. Upon illumination (Figure 1b), the entire current-voltage curve is displaced *positively* from the true  $E^{\circ'}$  to the  $E_{\text{FB}}$  of the Pt/GaPc-Cl system, by an amount  $V_{\infty}(2) \approx +0.30$  V. The difference in the  $E_{\text{FB}}$  of the Au/GaPc-Cl and Pt/GaPc-Cl system is due to the difference in the *effective* work functions of the two metal substrates.<sup>8</sup> Tabulated values of the work function for clean Pt surfaces range from 5.65 to 5.75 eV (below the energy of an electron in vacuum) while those for Au are typically near 4.8 eV.<sup>9</sup> The predicted work function difference of 0.8 V or greater is not quite realized in the photoelectrochemical cells where  $|V_{\infty}(1)| + |V_{\infty}(2)| = V_{\infty}(3) \leq 0.65$  V. The first molecular layers of GaPc-Cl deposited from vacuum may be expected to lower the effective work function to the observed value as would other hydrocarbon constituents of the Pt-MPOTE surface.<sup>9</sup>

The Pt/GaPc-Cl films fabricated so far tend to have a higher porosity to solution reactants compared to the typical Au/GaPc-Cl films (as evidenced by the larger dark currents observed), which leads to some lowering of photopotential because of short-circuiting of the photoelectrochemical process at the exposed metal sites.<sup>10</sup> In photoelectrochemical cells using unstirred solutions, we have found that the dark current process is inhibited relative to that at photoactive sites. Reasonable photopotentials and photocurrents are still observed on films where the dark currents are up to 50% of those seen on the bare metals.<sup>10</sup>

Figure 2 shows a schematic of the Au/GaPc-Cl/ferri,ferrocyanide/GaPc-Cl/Pt photoelectrochemical cell as we hypothesize it exists prior to contact of any of the phases. This schematic is based upon our recent electrochemical and photoelectrochemical studies of band edges and work functions, vs. the ferri,ferrocyanide redox couple solution potential.<sup>2,3</sup> The relative band energies are those that are expected under strong illumination conditions, i.e., with the Au/Pc and Pt/Pc systems driven to their flatband condition. The expected open-circuit potentials for Au/Pc vs. R/Ox and Pt/Pc vs. R/Ox are shown as  $V_{\infty}(1)$  and  $V_{\infty}(2)$ , respectively. We have found that the  $E_{\text{F}}(\text{GaPc-Cl})$  can lie ca. 0.1 V positive of the  $E_{\text{F}}(\text{Au})$  and 0.3 V or more positive of the  $E^{\circ'}$  of  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ .<sup>3</sup> Upon contact of these phases in the dark, the Pc layer becomes charge depleted at both the Au/Pc and Pc/R,Ox interface. The *net* potential gradient in the Au/GaPc-Cl films at equilibrium, however, is such that photogenerated holes under strong illumination are still driven to the Pc/R,Ox interface. For the Pt/GaPc-Cl system, photogenerated electrons are driven to the Pc/R,Ox interface by the *net* electric field gradient within that film.

The photopotential was observed at various load currents for a Au/GaPc-Cl/ferri,ferrocyanide/GaPc-Cl/Pt electrochemical cell under ca. 100 mW/cm<sup>2</sup> polychromatic illumination (filtered to 470-900 nm) of *both* the photoelectrodes, in contact with 10<sup>-3</sup> M amounts of  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Fe}(\text{CN})_6^{3-}$ . The open-circuit photovoltage was ca. +0.55 V, the short-circuit current 0.1 mA/cm<sup>2</sup>, and the fill factor 0.55 for the most optimized cells. Using maximal power values, the power conversion efficiency was determined to be 0.03-0.05%. Since the cell was not optimized to minimize light losses, this efficiency may be low by a factor of 2-3. Cells with 10 mM redox electrolyte concentrations yielded higher short-circuit currents (by a factor of 3-4) but with lower fill factors (near 0.3). At higher electrolyte concentrations the  $i/V$  curves were nearly linear with a slope dictated by film resistance, thus leading to the poorer fill factors. The Pt/GaPc-Cl

films tend to exhibit lower photoconductivities than the counterpart Au/GaPc-Cl films. Even when the electrodes are produced simultaneously, such that the Pc films appear to be identical as determined by electron microscopy and spectroscopic assay,<sup>12</sup> the films formed on the Pt-MPOTE are more resistive and less stable than the films formed on the Au-MPOTE.

These cells demonstrate a *thin-film* photovoltaic system where the driving force for the photoelectrochemical response is provided solely by the work function difference between the two metals. The Pc films act as the charge-separating medium and the electrolyte acts as the third contacting phase, less likely to cause short-circuiting of the photoresponse than a metal contact.<sup>5</sup> The resulting cell gives a photopotential response ca. 20% of the theoretical maximum dictated by the sum of the apparent bandgaps (ca. 3.0 eV) of the two GaPc-Cl/metal systems.<sup>11</sup> This technology may lend itself to additional improvements in performance through miniaturization of both the photoactive surfaces and the electrolyte layer between them.

**Acknowledgment.** This research was supported by grants from the National Science Foundation, CHE83-17769, and IBM Corp. We also thank Len Raymond of the Microelectronics Laboratory at the University of Arizona for the fabrication of the Pt-MPOTE.

(11) Rieke, P. C. Ph.D. Dissertation, University of Arizona, Tucson, 1984.

(12) Visible transmission spectroscopy of thin films of GaPc-Cl ( $\leq 500$  nm) shows an absorbance band extending from ca. 500 to 850 nm with an absorptivity  $\beta$  of  $\geq 5 \times 10^4$  cm<sup>-1</sup>. Thicker films (1  $\mu\text{m}$ ) show similar absorbance spectra when examined by photoacoustic spectroscopy. Assay of GaPc-Cl surface coverage is made by dissolving the film in a small volume of pyridine and quantitating the resultant solution concentration from the absorbance spectrum (see ref 11).

### Size and Selectivity in Zeolite Chemistry. A Remarkable Effect of Additive on the Products Produced in the Photolyses of Ketones

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Received January 25, 1985

Photolyses of dibenzyl ketones adsorbed on zeolites have been reported to result in decarbonylation and coupling of the resulting radicals to produce diaryl ethanes as the major products.<sup>1</sup> We report that the products formed in the photolysis of dibenzyl ketones on certain zeolites can be extremely sensitive both to zeolite structure and to simple sorbed additives such as water, benzene, cyclohexane, and hexane.

The zeolites<sup>2</sup> investigated were NaA, NaX, NaY, and LZ-105. Dibenzyl ketone (DBK) and *p*-methylbenzyl benzyl ketone (*p*-MeDBK) were deposited on the zeolites<sup>2</sup> from pentane solutions,<sup>3</sup>

(1) (a) Turro, N. J.; Wan, P. *J. Am. Chem. Soc.* **1985**, *107*, 678. (b) For other publications dealing with photochemistry on zeolites, see: Casal, H. L.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 628. Suib, S. L.; Kostapapas, A. *J. Am. Chem. Soc.* **1984**, *106*, 7705. Baretz, B. H.; Turro, N. J. *J. Photochem.* **1984**, *24*, 201. Turro, N. J.; Wan, P. *Tetrahedron Lett.* **1984**, 3665.

(2) The zeolite samples were Linde Molecular Sieves obtained from the Union Carbide Corp. The zeolites employed were sodium exchanged with concentrated aqueous NaCl and subsequently baked at 550 °C for at least 6 h. A further baking at 550 °C for 1 h was employed just before sample preparation, with care being taken to minimize the time which the sample was exposed to the atmosphere.

(3) In a typical experimental 0.4 mg of ketone in 0.2 mL of pentane was added to a vial containing 40 mg of zeolite soaked in a minimum amount of pentane. The bulk of the solvent was rapidly removed by placing the sample in a warm (50 °C) stream of flowing air. The sample was then placed into a quartz photolysis cell, equipped with a side arm, which allowed vacuum ( $2 \times 10^{-4}$  torr) degassing.

(8) (a) Rose, A. *Phys. Status Solidi* **1979**, *56*, 11. (b) Rose, A. "Concepts in Photoconductivity and Allied Problem"; R. E. Krieger Pub. Co.; New York, 1978.

(9) (a) Riviere, J. C. In "Solid State Surface Science"; Green, M. Ed.; Marcel Dekker: New York, 1969; Vol. I, pp 179. (b) "CRC Handbook of Chemistry and Physics", 58th ed.; Weast, R. C., Ed.; Cleveland, 1977-78, p E-81.

(10) (a) Rieke, P. C.; Linkous, C. L.; Armstrong, N. R. *J. Phys. Chem.* **1984**, *88*, 1351. (b) Klofta, T. J.; Rieke, P. C.; Linkous, C. L.; Buttner, W. J.; Nanthakumar, A.; Mewborn, T.; Armstrong, N. R. *J. Electrochem. Soc.*, submitted for publication.



the lack of isomerization is not due simply to rapid diffusional separation of the radical pairs is supported by the generally lower efficiency of photolysis on LZ-105 relative to NaX or NaY and by the high cage efficiency for combination of benzyl radicals. Also consistent with this mechanism is the absence of any significant influence of additives on the course of the photolysis. None of the results appear to require cation-specific effects, although such factors may be involved in determining the differences observed with some of the additives.

The fact that the major products of reaction formed on NaY changes from *p,p'*-BZ for benzene as additive to *p*-I for cyclohexane as additive is remarkable and demonstrates the high sensitivity of radical pair rotational motion anisotropies to the

shape and size of the molecular species employed as a cavity filler. Further confirmation of this conclusion is provided by the observation that the major isomeric product from DBK in "empty" NaX is *p*-I, whereas the major isomeric product when benzene is added is *o*-I. These results attest to the high size and shape selectivity for adsorption of molecules on zeolites.

**Acknowledgment.** The authors at Columbia thank the National Science Foundation for their generous support of this research. They also thank Professor D. M. Ruthven, University of New Brunswick, Canada, for helpful discussions concerning diffusion and sorption in zeolites.

Registry No. DBK, 102-04-5; *p*-MeDBX, 35730-02-0.

## Additions and Corrections

**Zoanthamine: A Novel Alkaloid from a Marine Zoanthid** [*J. Am. Chem. Soc.* **1984**, *106*, 7983-7984]. C. BHEEMASANKARA RAO,\* A. S. R. ANJANEYULU, N. S. SARMA, Y. VENKATESWARLU, RICHARD M. ROSSER, D. JOHN FAULKNER,\* MARINE H. M. CHEN, and JON CLARDY\*

Page 7983: In the author listing, Anjaneyulu and Venkateswarlu are incorrectly spelled. In the second paragraph, the yield should read ( $9 \times 10^{-4}\%$  wet weight).

**Treatment of Electrostatic Effects within the Molecular Mechanics Method.** [*J. Am. Chem. Soc.* **1983**, *105*, 1716]. LJILJANA DOŠEN-MICOVIĆ, DRAGOSLAV JEREMIĆ, and NORMAN L. ALLINGER\*

Page 1718: Equation 6 should read:

$$\mu_{ix} = \sum_{j=1}^n (B_{3i-2,3j-2}\mu_{jx}^{\circ} + B_{3i-2,3j-1}\mu_{jy}^{\circ} + B_{3i-2,3j}\mu_{jz}^{\circ})$$

$$\mu_{iy} = \sum_{j=1}^n (B_{3i-1,3j-2}\mu_{jx}^{\circ} + B_{3i-1,3j-1}\mu_{jy}^{\circ} + B_{3i-1,3j}\mu_{jz}^{\circ})$$

$$\mu_{iz} = \sum_{j=1}^n (B_{3i,3j-2}\mu_{jx}^{\circ} + B_{3i,3j-1}\mu_{jy}^{\circ} + B_{3i,3j}\mu_{jz}^{\circ})$$

Page 1719: In eq 18 the first row should look as follows:

$$\gamma_{H(C)}\gamma_{C(H)} > \gamma_{C(C)}$$

Page 1720: The caption to Figure 1 should refer to ref 35 not ref 32.

Page 1722: In Table III columns 7, 8, and 9 are mixed up. They should look as follows:

Table III. The IDME Parameter Set

	bond (J-P)		
	...C—Cl	C—Br	C=O
$\nu_{JP}$	0.56	0.54	0.68
$\gamma_{J(P)}$	0.2	0.2	0.2
$\gamma_{J(P)}^0$	0.4	0.4	0.4
$\sigma_J^0$	0.07	0.07	0.07
$\sigma_P^0$	0.35	0.30	0.70
LP	3.8 (2.9) <sup>c</sup>	5.3 (3.1) <sup>c</sup>	2.3
TP	1.85 (2.2)	2.7 (3.1)	1.4
VP	1.85 (2.2)	2.7 (3.1)	0.46
CR(J)	0.771	0.771	0.771
CR(P)	0.99	1.14	0.638

The dipole field tensor  $T_{ij}$ , which has not been given explicitly in the paper looks as follows:

$$T_{ij} = -\frac{3}{\epsilon r^5} \begin{vmatrix} x^2-(r^2/3) & xy & xz \\ yx & y^2-(r^2/3) & yz \\ zx & zy & z^2-(r^2/3) \end{vmatrix}$$

where  $r$  is the distance between dipoles  $i$  and  $j$ ;  $x$ ,  $y$ ,  $z$  are the components of the vector from  $i$  to  $j$ ; and  $\epsilon$  is the medium dielectric constant, equal 1.5 for the vapor phase in our calculations.