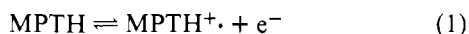


presence of 0.05 M LiClO₄ the cmc of SDS is approximately fivefold less than that determined in water alone.¹² The enhanced rates of decay of MPTH⁺ in the cationic and nonionic surfactant systems relative to those seen in the base electrolytes in the absence of surfactant are suggestive of micellar catalysis in these systems.¹³

The observed dependence of the DPV peak potential for the oxidation of MPTH at pre-cmc concentration levels of SDS lends itself to quantitation of both the stoichiometry and the formation constant of the cation radical-surfactant complex. For the oxidation of MPTH in the presence of SDS, the system may be represented as



At 25 °C, the dependence of the peak potential for the oxidation of MPTH on the concentration of SDS is given by^{9,14}

$$E_{p(a)'} = E_{p(a)}^\circ - 0.059 \log K - 0.059(p) \log [\text{SDS}] \quad (3)$$

where $E_{p(a)'}$ is the DPV peak potential in the presence of SDS and $E_{p(a)}^\circ$ is that observed in its absence. The data shown in Figure 1 affords a least-squares slope of $-53 (\pm 3)$ mV which corresponds to $p \approx 1$ indicating a stoichiometry of one dodecyl sulfate anion per 10-methylphenothiazine cation radical.^{14c} From the least-squares intercept of these data (303 (± 7) mV) and the value of $E_{p(a)}^\circ$ observed in 0.05 M LiClO₄,⁷ the formation constant for the (MPTH⁺)(DS⁻) complex evaluates as $2.0 \times 10^3 \text{ M}^{-1}$. It is important to note that this formation constant reflects interaction between MPTH⁺ and monomeric dodecyl sulfate entities, not between MPTH⁺ and micelles.¹⁵

This interaction between MPTH⁺ and dodecyl sulfate anion suggests the site of solubilization of MPTH⁺ in SDS micelles to be the Stern region wherein the charged head groups of the surfactant reside. Examination of the ultraviolet absorption maxima of MPTH⁺ in aqueous, micellar SDS, and hydrocarbon media provides insight concerning the site of solubilization of the cation radical. These data¹⁶ suggest that, in micellar SDS systems, MPTH⁺ resides in a highly polar environment rather than in the hydrocarbon "core" of the micelle.¹⁷ While models for micelle structure remain in question,¹⁸ the results reported here are consistent with an "open" structure which allows both MPTH⁺ and water to be interspersed among the aggregated surfactant molecules.^{18,19}

References and Notes

- (a) Seeman P. *Pharmacol. Rev.* **1972**, *24*, 583-655. (b) Roth, S.; Seeman, P. *Biochim. Biophys. Acta* **1972**, *255*, 207-219. (c) Beckett, A. H.; Hewick, D. S. *J. Pharm. Pharmacol.* **1967**, *19*, 134-136. (d) Coccia, P. F.; West-erfeld, W. W. *J. Pharmacol. Exp. Therap.* **1967**, *157*, 446-458. (e) Carr, C. J. *Adv. Biochem. Psychopharmacol.* **1974**, *9*. (f) Usdin, E.; Forrest, I. S., Eds. "Psychotherapeutic Drugs"; Marcel Dekker: New York, 1977; Part II, Chapters 1-3.
- (a) Alkaltis, S. A.; Beck, G.; Grätzel, M. *J. Am. Chem. Soc.* **1975**, *97*, 5723-5729. (b) Vanderkooi, J. M. *Biochem. Biophys. Res. Commun.* **1976**, *69*, 1043-1049. (c) Moroi, Y.; Braun, A. M.; Grätzel, M. *J. Am. Chem. Soc.* **1979**, *101*, 567-572. (d) Moroi, Y.; Infelta, P. P.; Grätzel, M. *Ibid.* **1979**, *101*, 573-579.
- Cheng, H. Y.; Sackett, P. H.; McCreery, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 962-967.
- (a) Blount, H. N.; Evans, J. F. In "Characterization of Solutes in Nonaqueous Solvents"; Mamantov, G., Ed.; Plenum Press: New York, 1978; pp 105-129. (b) Shine, H. J. *ACS Symp. Ser.* **1978**, No. 69, 359-375. (c) Bandlish, B. K.; Padilla, A. G.; Shine, H. J. *J. Org. Chem.* **1975**, *40*, 2590-2595. (d) Shine, H. J.; Kim, K. *Tetrahedron Lett.* **1974**, 99-101. (e) Hansen, P.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1973**, 264-271. (f) Cauquis, G.; Deronzier, A.; Serve, D. *J. Electroanal. Chem.* **1973**, *47*, 193-198.
- Anionic, cationic, and nonionic micelles were formed from sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), and Brij-35 (C₁₂H₂₅(OCH₂CH₂)₂₃OH), respectively.
- "Aqueous media" refers to SDS or Brij-35 in 0.05 M LiClO₄ and CTAB in 0.05 M KBr. CTAB is not soluble in LiClO₄ solution.
- At a platinum electrode at 25.0 °C. DPV peak potential (vs. SCE) for the MPTH/MPTH⁺ couple in 0.05 M LiClO₄ is 0.498 (± 0.004) and in 0.05 M KBr is 0.522 (± 0.003) V. DPV peak potentials for this couple in Brij-LiClO₄

and CTAB-KBr were 0.512 (± 0.023) and 0.535 (± 0.011) V, respectively, at surfactant concentrations spanning the critical micelle concentrations (cmc's).⁸

- (a) Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems"; Academic Press: New York, 1975. (b) The cmc's of the systems of interest to this work were determined by substrate (MPTH) solubilization (UV absorption) to be the following: SDS-LiClO₄, $1.6 (\pm 0.2) \times 10^{-3}$ M; Brij-LiClO₄, 120 (± 14) mg %; CTAB-KBr, $5.3 (\pm 0.7) \times 10^{-5}$ M.
- Galus, Z. "Fundamentals of Electrochemical Analysis"; Ellis Horwood, Ltd.: Chichester, England, 1976; Chapter 14.
- Such invariance of peak potential with concentration may well be due to comparable extents of MPTH-micelle and MPTH⁺-micelle interactions.
- Litt, M. H.; Radovic, J. *J. Phys. Chem.* **1974**, *78*, 1750-1754.
- Mukerjee, P.; Mysels, K. J. "Critical Micelle Concentrations of Aqueous Surfactant Systems"; National Bureau of Standards (NSRDS-NBS 36) U.S. Government Printing Office: Washington, D.C., 1971.
- (a) Cordes, E. H.; Dunlap, R. B. *Acc. Chem. Res.* **1969**, *2*, 329-337. (b) The decay kinetics of MPTH⁺ in all media examined in this work were found to be second order with respect to [MPTH⁺]. Residence of MPTH⁺ in a localized region of the aggregate (e.g., the Stern region) would markedly enhance the rate of decay of the cation radical in that its effective concentration is increased. In CTAB media the added presence of nucleophilic Br⁻, also localized in the cationic head group region, provides further enhancement of the rate of solvolysis of MPTH⁺.^{4a} Although such nucleophiles do not undergo addition reactions with substituted phenothiazine cation radical, they have been shown to catalyze the hydrolysis of these species: Evans, J. F.; Lenhard, J. R.; Blount, H. N. *J. Org. Chem.* **1977**, *42*, 983-988. This behavior of Br⁻ vis-à-vis that of the nonnucleophilic ClO₄⁻ is also evident from the half-lives shown in Table I.
- (a) Peover, M. E.; Davies, J. D. *J. Electroanal. Chem.* **1963**, *6*, 46-53. (b) DeFord, D. D.; Hume, D. N. *J. Am. Chem. Soc.* **1951**, *73*, 5321-5322. (c) Equation 3 is valid for [SDS] ≥ 10 [MPTH]. The lower limit of SDS concentration which could be examined was dictated by this requirement and the upper limit by the cmc of SDS in this medium.
- Evans, C. A.; Bolton, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 4502-4504 have shown strong interaction between *N*-methylphenazonium cation radical and SDS micelles ($K \approx 10^5 \text{ M}^{-1}$).
- In H₂O, $\lambda_{\text{max}}^{\text{MPTH}^+}$ 269 (± 1); in 0.05 M LiClO₄, 270 (± 1); in 20 mM SDS-0.05 M LiClO₄, 271 (± 1); in *n*-heptane, 254 (± 1); in *n*-pentane, 256 (± 1) nm.
- Evans and Bolton¹⁵ report the mean residence position of *N*-methylphenazonium cation radical to be "in the hydrocarbon region a few ångströms below the head groups".
- Menger, F. M. *Acc. Chem. Res.* **1979**, *12*, 111-117.
- This view is consistent with the findings of Yeh, P.; Kuwana, T. *J. Electrochem. Soc.* **1976**, *123*, 1334-1339.

Gregory L. McIntire, Henry N. Blount*

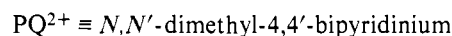
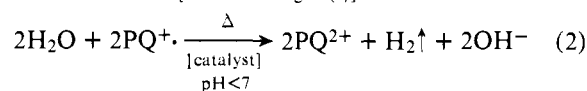
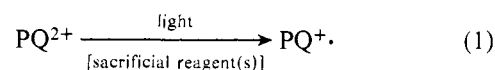
Brown Chemical Laboratory, The University of Delaware
Newark, Delaware 19711

Received July 9, 1979

Photoelectrochemical Reduction of *N,N'*-Dimethyl-4,4'-bipyridinium in Aqueous Media at p-Type Silicon: Sustained Photogeneration of a Species Capable of Evolving Hydrogen

Sir:

We report here a new approach to the energetically uphill generation of H₂ from H₂O. There have been numerous recent claims concerning chemical systems for the photoinduced evolution of H₂ from aqueous media, but in many of the systems reported there are sacrificial reducing agents used which cloud the overall thermodynamics and preclude sustained evolution of H₂.¹⁻⁶ However, these studies have resulted in several interesting procedures for manipulating charge-transfer kinetics such that generation of H₂ is possible by schemes such as that represented:⁶



We are prompted by these studies to report the sustained photogeneration (without sacrificial reagents) of PQ⁺ in aqueous solutions using a p-type Si photocathode in an electrochemical cell. p-type semiconductors are known to be capable of serving as photocathodes for direct H₂ production,⁷ but a survey of the literature reveals that p-type materials

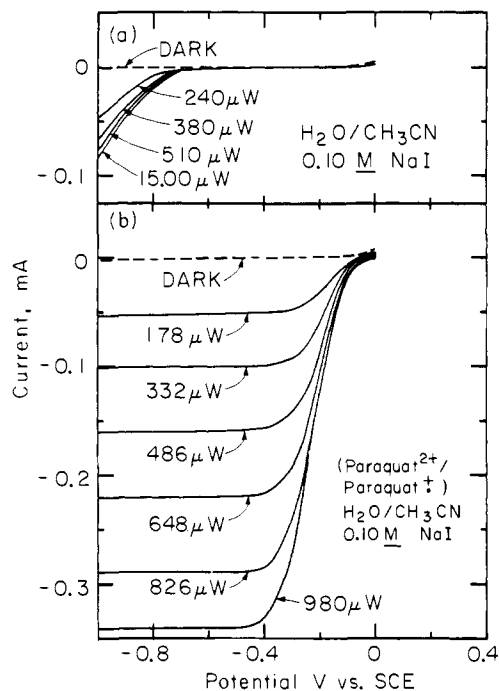


Figure 1. Current-voltage curves (10 mV/s) for p-Si photocathode. Illumination power, 514.5 nm, is given in microwatts. For power or current density, multiply values given by 13 cm^{-2} . Part a: stirred, Ar-purged solution of distilled H_2O (70%)/ CH_3CN (30%) with 0.10 M NaI at pH 5.5. Part b: same solution but with 0.025 M $\text{PQ}^{2+}/\text{PQ}^{+}$. $E_{\text{redox}} = -0.32 \text{ V}$ vs. SCE.

studied to date are poor photocathodes generally and poor H_2 photocathodes in particular. The reason for this is not clear, but the electrodes typically have low quantum efficiency, output voltages, and fill factors. We assert that the semiconductors studied to date have inherently slow H_2 evolution rates. We propose that a scheme where PQ^{2+} is reduced to PQ^{+} at a photocathode followed by chemistry according to eq 2 may represent an efficient uphill route to photochemical H_2 generation. The value of $E^\circ(\text{PQ}^{2+}/\text{PQ}^{+})$ in H_2O is -0.7 V vs. SCE;⁸ the efficiency of a p-type semiconductor photocathode is measured by the extent to which PQ^{+} can be produced with good quantum yield at a potential more positive than at a reversible electrode. The hope is that the one-electron photoreduction of PQ^{2+} at p-Si would be fast under conditions where

Table I. Output Parameters for p-Si-Based Photoelectrochemical Cells^a

input power, μW^b	Φ_e^c	max power out, $\mu\text{W} (\eta_{\text{max}}, \%)^d$	max V (V at η_{max}), mV ^e
A. $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ (70:30)/0.1 M NaI/0.025 M $\text{PQ}^{2+}/\text{PQ}^{+}$; $E_{\text{redox}} = -0.32 \text{ V}$ vs. SCE			
178	0.65	3.5 (2.0)	260 (130)
486	0.73	9.8 (2.0)	290 (130)
980	0.70	14.3 (1.5)	340 (130)
B. $\text{CH}_3\text{CN}/0.1 \text{ M } (n\text{-Bu}_4\text{N})\text{ClO}_4/0.01 \text{ M } \text{PQ}^{2+}/\text{PQ}^{+}$; $E_{\text{redox}} = -0.30 \text{ V}$ vs. SCE			
180	0.43	3.8 (2.1)	300 (180)
550	0.46	13.3 (2.4)	360 (170)
760	0.47	18.4 (2.4)	370 (180)

^a All cells employ a Pt counterelectrode; E_{redox} was established by in situ generation of PQ^{+} from PQ^{2+} . ^b Input power in microwatts at 514.5 nm (Ar ion laser); for power density multiply by 13 cm^{-2} . ^c Quantum yield for electron flow (electrons/photon incident) at E_{redox} corresponding to the short-circuit quantum yield. ^d For power density, multiply by 13 cm^{-2} ; η_{max} is the maximum efficiency for light to electricity (maximum power point). ^e Open-circuit photovoltage, max V, and voltage at the maximum power point.

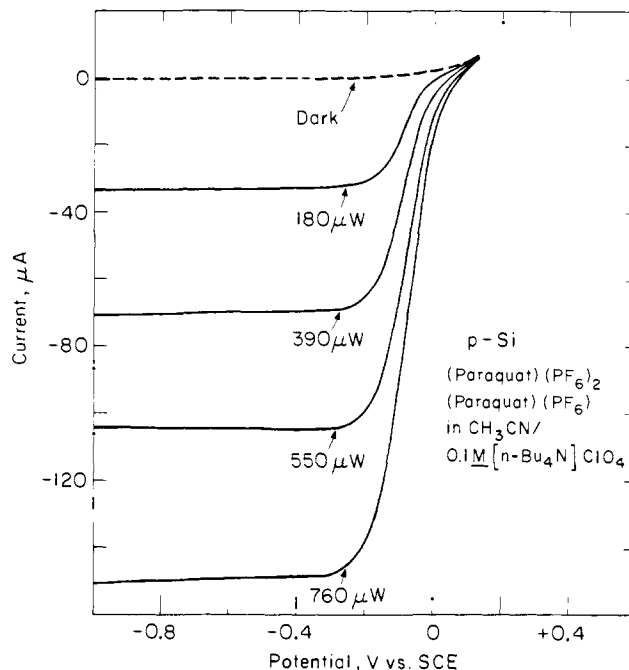
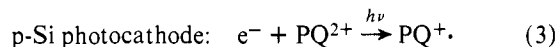


Figure 2. Current-voltage curves (10 mV/s) for p-Si photocathode illuminated with 514.5-nm light at indicated power. For power or current density, multiply values given by 13 cm^{-2} . Solution is stirred, Ar-purged $\text{CH}_3\text{CN}/0.10 \text{ M } (n\text{-Bu}_4\text{N})\text{ClO}_4/0.01 \text{ M } \text{PQ}^{2+}/\text{PQ}^{+}$; $E_{\text{redox}} = -0.30 \text{ V}$ vs. SCE.

H_2 evolution is found to be slow. We now describe our results.

Figure 1 shows the comparison of the photocurrent-voltage curves for illuminated p-type Si in aqueous solution, pH 5.5, with and without added PQ^{2+} , and Table I summarizes quantitative data culled from the Figures 1 and 2. The CH_3CN is used to improve the solubility of the $\text{PQ}^{2+}/\text{PQ}^{+}$ system, and the $E^\circ(\text{PQ}^{2+}/\text{PQ}^{+})$ is at -0.61 V vs. SCE in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (30:70). First, in the absence of PQ^{2+} , there is the expected light effect on the cathodic current, but the photocurrent onset is near the potential where the evolution of H_2 at a reversible electrode can be observed. This means that the p-Si requires light and electricity to effect H_2 evolution. These results accord well with those found earlier for p-type Si.⁹ Further, the achievable photocurrent density is low and the observed quantum yields for electron flow are very small. The dramatic effect of PQ^{2+} on the photocurrent-voltage curves in Figure 1a is obvious. Reduction of PQ^{2+} to PQ^{+} can be effected at potentials substantially more positive than at a reversible electrode; i.e. the onset of the photocathodic current is near 0 V vs. SCE. Quantum yields for electron flow are respectable at electrode potentials significantly positive of $E_{\text{redox}}(\text{PQ}^{2+}/\text{PQ}^{+})$. Further, the photocurrent-voltage curves have a good fill factor, even at the higher photocurrent densities. That PQ^{+} is the photoelectrochemical product is evidenced by the intensely blue-colored (air sensitive) material observed to stream from the photocathode upon illumination in solutions containing initially only PQ^{2+} (PQ^{+} , $\lambda_{\text{max}} 603 \text{ nm}$ ($\epsilon 12000$)).¹⁰

The operation of a photoelectrochemical cell where the cell chemistry is



has been sustained in the aqueous pH 5.5 solution for a 24-h period at 0.4 mA (4 mA/cm^2) without variation in the photocurrent or output parameters. In such a situation there is no net chemical change and the cell can be used to sustain the

conversion of light into electricity, as has been shown for other semiconductor-based photoelectrochemical cells.⁷ As indicated in Table I the efficiency for conversion of 514.5-nm light is ~2%.

Illuminated p-Si sustains the formation of PQ⁺ from PQ²⁺ under conditions where catalysts such as PtO₂, Pt/asbestos, Pd/asbestos, etc.,⁶ are known to effect chemistry according to eq 2. Furthermore, with p-Si the PQ²⁺ reduction is energetically uphill by up to 0.5 V at pH 5.5. This means that the H₂ evolution can be driven uphill by 0.5 V. In a two-compartment cell employing H₂O as the solvent (pH 5.5) we have been able to drive the PQ²⁺/PQ⁺ potential to -0.6 V vs SCE—a potential more negative than necessary to yield H₂ from the solution. Such can be accomplished when the electrode potential is held at -0.3 V vs. SCE. We are presently constructing two-compartment cells to measure the efficiency for H₂ generation, but the main points are as follows: (i) p-Si (band gap = 1.1 eV)¹¹ can be excited with visible light to contribute up to 0.5 V toward the 1.23 V needed to split H₂O; (ii) there are no sacrificial reagents involved; (iii) the p-Si/PQ²⁺/PQ⁺ is better than p-Si alone in that the PQ⁺ can be used to efficiently evolve H₂ once generated. Finally, we note that, in H₂O as the solvent, the photocathodic peak for the PQ²⁺ reduction in a cyclic voltammetry scan is ~0.5 V more positive than at a reversible electrode at pH 5.5. This shows that good quantum efficiency obtains for the uphill reduction process, a fact confirming the equilibrium current-voltage scans shown in the figures.

Our data show that the PQ²⁺/PQ⁺ system can be driven to an electrochemical potential >0.3 V more negative than the potential to which the p-Si is potentiostated. This means that the optical energy input is converted into chemical energy. Thus, assuming that the PQ⁺ can be efficiently catalyzed to yield H₂,⁶ and suitable separators can be found, the p-type Si photoelectrode can contribute >0.3 V toward the 1.23 V needed to split H₂O in a two-compartment cell. In such a situation the anode reaction would be O₂ evolution from H₂O, and H₂ would be evolved from the cathode compartment using the PQ²⁺/PQ⁺/catalyst system. Thus, the only sacrificial reagent would be the H₂O itself. However, since the p-Si only contributes a fraction of the 1.23 V needed to split H₂O, a power supply in series in the external circuit would be necessary to sustain the photoelectrolysis of H₂O, but, to the extent that the power supply provides <1.23 V, the input optical energy is converted into stored chemical energy in a sustained fashion.

Since the interface energetics for p-Si have been studied in CH₃CN solvent,¹² we investigated the output parameters for the p-Si/PQ²⁺/PQ⁺ system in CH₃CN where $E^{\circ}(\text{PQ}^{2+}/\text{PQ}^{+})$ is -0.45 V vs. SCE.⁸ Figure 2 shows the photocurrent onset to be a little more positive than in the aqueous pH 5.5 media, but the essentials are the same. The nonaqueous cell chemistry is as shown in eq 3 and 4, and the conversion of light into electricity can be sustained without net chemical change. The sustained efficiency of 2.4% for the 514.5-nm light appears to represent the most efficient p-type-based photoelectrochemical cell reported to date.¹³

Acknowledgments. We thank the National Aeronautics and Space Administration for support of this research. N.S.L. acknowledges support as a John and Fannie Hertz Fellow and M.S.W. acknowledges support as a Dreyfus Teacher-Scholar Grant recipient, 1975-1980. Support from the M.I.T. Cabot Solar Energy Fund is also gratefully acknowledged.

References and Notes

- Lehn, J.-M.; Sauvage, J.-P. *Nouv. J. Chim.* **1977**, *1*, 449.
- Mann, K. R.; Lewis, N. S.; Miskowski, V. M.; Erwin, D. K.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* **1977**, *99*, 5525.
- Brown, G. M.; Brunshwig, B. S.; Creutz, C.; Endicott, J. F.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 1298.
- Durham, B.; Dressick, W. J.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1979**, 381.
- Ford, W. E.; Otvos, J. W.; Calvin, M. *Nature (London)* **1978**, *274*, 507.
- Krasna, A. I. *Photochem. Photobiol.* **1979**, *29*, 267.
- Nozik, A. J. *Annu. Rev. Phys. Chem.* **1978**, *29*, 189.
- Hunig, S.; Gross, J.; Schenk, W. *Justus Liebig's Ann. Chem.* **1973**, *1*, 324.
- Candea, R. M.; Kastner, M.; Goodman, R.; Hickok, N. *J. Appl. Phys.* **1976**, *47*, 2724.
- Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133.
- Wolf, H. F. "Silicon Semiconductor Data"; Pergamon Press: Oxford, 1969; p 111.
- Laser, D.; Bard, A. J. *J. Phys. Chem.* **1976**, *80*, 459.
- Comparable efficiency would appear to obtain in the p-type GaAs/NH₃/e⁻ cell recently reported, but the solvated e⁻ system is relatively unstable compared with the PQ²⁺/PQ⁺ system: Malpas, R. E.; Itaya, K.; Bard, A. *J. Am. Chem. Soc.* **1979**, *101*, 2535.

Dana C. Bookbinder, Nathan S. Lewis, Mark G. Bradley
Andrew B. Bocarsly, Mark S. Wrighton*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received July 9, 1979

Aldol Addition = Cycloaddition without Cycloadduct Formation?

Sir:

In the reaction of preformed enolates with carbonyl compounds it has been repeatedly assumed that both driving force and stereochemical outcome are inherently connected with the formation of metal chelated aldol adducts.¹ We studied the addition of metalated carboxylic acids (**1**) to aldehydes (**2**) and found that—at least in the transition state—metal chelation is of no importance; by contrast, our experimental results (Tables I and II) are fully explained by merely electronic interactions between the two components which we assume to

Table I. Dependence of the Ratio of 3:4 on R¹ and R². Total Yields Are between 87 and 98%. The Carboxylic Acid Dianions Have Been Generated with Lithium Diisopropylamide in THF

run	R ¹	R ²	M	3:4
a	Ph	Me	Li	58:42
b	Ph	<i>i</i> -Pr	Li	66:34
c	Ph	<i>t</i> -Bu	Li	70:30
d	<i>t</i> -Bu	<i>t</i> -Bu	Li	80:20
e	mesityl	mesityl	Li	>98:2
f	1-adamantyl	<i>t</i> -Bu	Li	>98:2
g	1-adamantyl	1-adamantyl	Li	>98:2

Table II. Dependence of the Ratio of 3c (Threo):4c (Erythro) on the Counterion M. The Various M's Are in Order According to Falling Charge:Radius Ratios. Total Yields Are between 85 and 97%

run	M	3c:4c
a	Mg _{1/2} ^a	52:48
b	Zn _{1/2} ^a	55:45
c	Li ^b	66:34
d	Li ^c	70:30
e	Li ^b /cryptofix 2.1.1	70:30
f	Na ^b	79:21
g	Na ^b /cryptofix 2.2.1	82:28
h	K ^b	79:21
i	<i>n</i> -Bu ₄ N ^d	85:15
j	K ^b /cryptofix 2.2.2	90:10
k	K ^b /18-crown-6	>97:3

^a The dianion was prepared with sodium naphthalenide + subsequent addition of MgBr₂(ZnBr₂). ^b The dianion was prepared with metal naphthalenide. ^c The dianion was prepared with lithium diisopropylamide. ^d The lithium dianion was quenched with Me₃SiCl and then treated with N(Bu)₄F in THF.