

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 PQ^{2+} under conditions where catalysts such as PtO_2 , Pt/asbestos, Pd/asbestos, etc.,⁶ are known to effect chemistry according to eq 2. Furthermore, with p-Si the PQ^{2+} reduction is energetically uphill by up to 0.5 V at pH 5.5. This means that the H_2 evolution can be driven uphill by 0.5 V. In a two-compartment cell employing H_2O as the solvent (pH 5.5) we have been able to drive the PQ^{2+}/PQ^{+} potential to -0.6 V vs SCE—a potential more negative than necessary to yield H_2 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 H_2 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 H_2O ; (ii) there are no sacrificial reagents involved; (iii) the p-Si/ PQ^{2+}/PQ^{+} is better than p-Si alone in that the PQ^{+} can be used to efficiently evolve H_2 once generated. Finally, we note that, in H_2O as the solvent, the photocathodic peak for the PQ^{2+} 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 PQ^{2+}/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 H_2 ,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 H_2O in a two-compartment cell. In such a situation the anode reaction would be O_2 evolution from H_2O , and H_2 would be evolved from the cathode compartment using the PQ^{2+}/PQ^{+} /catalyst system. Thus, the only sacrificial reagent would be the H_2O itself. However, since the p-Si only contributes a fraction of the 1.23 V needed to split H_2O , a power supply in series in the external circuit would be necessary to sustain the photoelectrolysis of H_2O , 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 CH_3CN solvent,¹² we investigated the output parameters for the p-Si/ PQ^{2+}/PQ^{+} system in CH_3CN where $E^{\circ}(PQ^{2+}/PQ^{+})$ 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.

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- Comparable efficiency would appear to obtain in the p-type GaAs/ NH_3/e^- cell recently reported, but the solvated e^- system is relatively unstable compared with the PQ^{2+}/PQ^{+} system: Malpas, R. E.; Itaya, K.; Bard, A. *J. Am. Chem. Soc.* **1979**, *101*, 2535.

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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 R^1 and R^2 . Total Yields Are between 87 and 98%. The Carboxylic Acid Dianions Have Been Generated with Lithium Diisopropylamide in THF

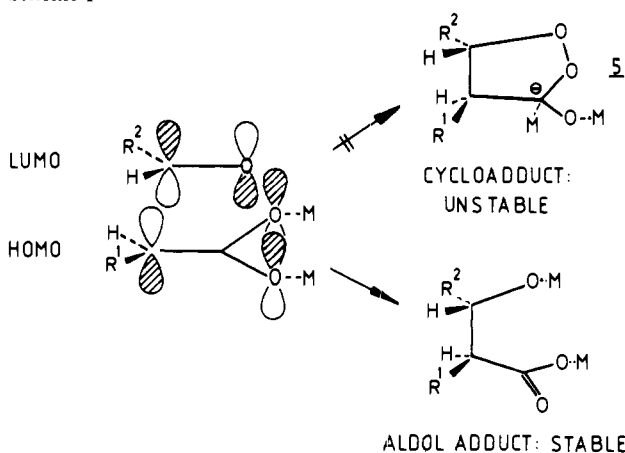
run	R^1	R^2	M	3:4
a	Ph	Me	Li	58:42
b	Ph	<i>i</i> -Pr	Li	66:34
c	Ph	<i>t</i> -Bu	Li	70:30
d	<i>t</i> -Bu	<i>t</i> -Bu	Li	80:20
e	mesityl	mesityl	Li	>98:2
f	1-adamantyl	<i>t</i> -Bu	Li	>98:2
g	1-adamantyl	1-adamantyl	Li	>98:2

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>m</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 $MgBr_2$ ($ZnBr_2$). ^b The dianion was prepared with metal naphthalenide. ^c The dianion was prepared with lithium diisopropylamide. ^d The lithium dianion was quenched with Me_3SiCl and then treated with $N(Bu)_4F$ in THF.

Scheme I

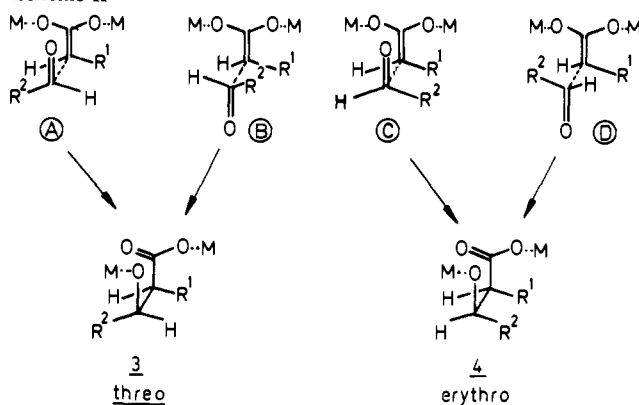


form a two-plane complex similar to that of a 1,3-dipolar cycloaddition³ (Scheme I).

Under the conditions applied (THF, -50°C , 10 min), the reaction of **1** and **2** is entirely irreversible.⁴ For the transition states leading to the diastereomeric adducts **3** (threo) and **4** (erythro), four distinguishable geometries have to be considered (Scheme II): two with a syn (A and C) and two with an anti (B and D) arrangement of the oxygens. A simple decision of whether the syn or the anti transition state is more favorable can be made by employing bulky R^1 and R^2 substituents. In this case, B and C can be neglected in favor of A and D, and, thus, one should obtain preferentially **3** if the syn geometry or **4** if the anti geometry is the better one. As Table I shows, the syn mechanism is clearly favored. To explain this preference, chelate formation between the counterion M and the oxygens—which of course is only possible if syn geometry obtains—might be postulated. That this interpretation cannot be correct is demonstrated by the variation of M for a given R^1 - R^2 pair ($\text{R}^1 = \text{Ph}$, $\text{R}^2 = t\text{-Bu}$, Table II). In case of chelation the transition-state complexes would be tightened with increasing ability of M to bind oxygen ligands (for which the charge:radius ratio⁵ of M may be taken as an estimate); hence, A should gain over C and the ratio of **3**:**4** should be increased. Amazingly, the data of Table II show that the very opposite is true! The highest values for **3**:**4** are found for K^+ /cryptofix 2.2.2 (run j) and K^+ /18-crown-6 (run k), whereas the highly polarizing metal ions Mg^{2+} and Zn^{2+} (runs a and b) lead to almost total stereoselectivity; K^+ , NBu_4^+ , Na^+ , and Li^+ are in between. Scheme I illustrates how we interpret this unexpected result: the syn transition state owes its stability to a 1,3-dipolar-cycloaddition-like³ interaction between the allyl anion-type HOMO and the π^* orbital of the $\text{C}=\text{O}$ group which serves as the LUMO. The metal ions are located in the plane of the carboxylic acid dianion and lower the HOMO energy by detracting electron density. This effect goes parallel to the charge:radius ratio of M and weakens the HOMO-LUMO interaction. So we have the loosest complex (and consequently the lowest **3**:**4** ratio) for Mg^{2+} and the tightest complex (and hence the highest stereoselectivity) for K^+ /18-crown-6.⁶ Na^+ /cryptofix 2.2.1 (run g) and Li^+ /cryptofix 2.1.1 (run e) show about the same effect as Na^+ and Li^+ themselves, indicating that the cryptand M-interaction is not very high in these cases.⁷ Despite the cycloaddition-like transition state the corresponding cycloadduct (**5**) is unlikely to be generated, because this would imply the formation of a weak O—O bond and two negative charges on adjacent atoms.⁸

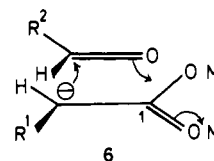
It appears remarkable that the HOMO-LUMO interaction in Scheme I should be strong enough to outbalance the electrostatic repulsion between the oxygens of the dianion and the carbonyl compound. However, an analogous situation occurs in the addition of diazoalkanes to carbonyl compounds, where

Scheme II



the interaction of two electronegative termini (N and O) does not prevent the formation of the 1,3-dipolar-cycloaddition complex.⁹

As an alternative to Scheme I a [2 + 2]-cycloaddition-like transition state¹⁰ (**6**) might be considered in which the devel-



oping negative charge at the carbonyl O interacts with the vacant p_z orbital at C-1. However, one would expect for such a mechanism that the threo selectivity should grow with the polarizing power of M, because this would increase the electrophilicity of C-1 and tighten the complex.

Why has our HOMO-LUMO effect not been observed in the aldol additions of ref 1? Two reasons may be held responsible: (1) in these aldol additions, equilibration regularly is very fast, and so the stereochemical outcome may correspond to thermodynamic rather than to kinetic control; (2) in comparison with the normal enolate system the carboxylic acid dianion has an additional oxygen which enhances the postulated HOMO-LUMO interaction.

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- The irreversibility of the addition, which is a crucial point in our argumentation, was secured by a number of control experiments. (a) $\text{M} = \text{Li}$: samples were taken from various reaction mixtures (e.g., runs a-c in Table I) at -50°C and, after hydrolysis, analyzed by ^1H NMR; in all cases it was found that, under these conditions, the **3**:**4** ratios remain constant for several hours; equilibration of dilithium **3** and **4** requires 1-3 days at room temperature. (b) The same experiments were performed for $\text{M} = \text{Na}$ and K and gave similar results. (c) Additionally, erythro-3-hydroxy-4,4-dimethyl-2-phenylpentanoic acid (i.e., the parent acid of **4** in Table II) was treated with 2 mol equiv of K^+ /18-crown-6 naphthalene in THF at -50°C for 10 min; after hydrolytic workup the acid was recovered unchanged; the same result was obtained with K^+ /naphthalene and K^+ /cryptofix 2.2.2 naphthalene as bases.
- E.g., Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Interscience: New York, San Francisco, London, 1962; p 321.
- This mechanistic picture, however, is true only for the transition state; in later stages of the addition, metal chelation of course occurs and is responsible for the product distribution under thermodynamic control.
- This is surprising, as cryptofix 2.1.1., 2.2.1, and 2.2.2 have been recommended as particularly effective in the selective complexation of Li^+ , Na^+ , and K^+ , respectively (e.g., Pierre, J.-L.; le Goallier, R.; Handel, H. *J. Am. Chem. Soc.* **1978**, *100*, 8021). However, in analogy to our results, it has been reported (Evans, D. A.; Golob, A. M. *Ibid.* **1975**, *97*, 4765) that complexation, at least by crown ethers, is negligible in the case of Na^+ , but highly effective for K^+ .
- A rough estimate of the relative stability of **5** vs. **3-4** (at least in their protonated forms) can be obtained from thermochemical data: Benson, S. W.

"Thermochemical Kinetics"; Wiley: New York, 1968; pp 178-181. It is found that **5** (+ 2H⁺) is ~68 kcal mol⁻¹ less stable than **3-4** (+ 2H⁺). However, the energy difference between **5** and **3-4** should be considerably larger, because **5** has to accommodate the two negative charges in the vicinal position, whereas in **3-4** they are four bonds apart.

- (9) We thank Professor Huisgen, Munich, for communicating these unpublished results to us.
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Isotopomer Differentiation by Means of Inclusion

Sir:

Tetra(4-methylpyridine)nickel(II) thiocyanate (**1**) forms inclusion compounds with a variety of guest molecules, including *p*-xylene and naphthalene.¹ Sorption isotherms for many analogous systems have been studied,² the crystal structure of some inclusion compounds has been determined,^{3,4} and the cavity shape has been discussed.⁴ The competition between guests such as *p*-xylene and ethylbenzene for sites in the host lattice has been investigated quantitatively.⁵ A similar, less marked, but potentially useful, competition is reported here for isotopomers with the same host. After **1** is shaken with an excess of a mixture of *p*-(CH₃)₂C₆H₄ (A) and *p*-(CD₃)₂C₆D₄ (B), of A and (CD₃)₂C₆H₄ (C), or of C₁₀H₈ (D) and C₁₀D₈ (E), dissolved in *n*-pentane, the inclusion compound forms which is shown below to have a higher D/H ratio; the mother liquor has a lower D/H ratio than that of the original mixture.

The host material, **1**, was prepared as described elsewhere.⁶ Its composition corresponded closely to theoretical. The purities of the deuterated compounds were quoted by the manufacturer as follows: B, 98+; C, 99+; E, 99+ at. % deuterium. A was reagent grade material, purified further by stirring for several days with **1**, filtering off the resulting solid, and recovering A by dissolving the solid in dilute HCl, extracting it with *n*-pentane, and distillation over a 2 °C range. This procedure is intended to reduce the amounts of possible impurities such as ethylbenzene or other isomers which are far less included than A. D was reagent grade product recrystallized from ethanol.

Although the inclusion compound with *p*-xylene can be made in the absence of a diluent, the latter was used to increase the quantity of liquid phase (and thus the fluidity of the system) without excessive use of the deuterated compound, and pentane was chosen for the diluent to eliminate interference in the mass spectral range of interest.

Mixtures of A and B, of A and C, and of D and E, all in pentane, were prepared as indicated in Table I using a syringe, and a small portion was set aside in a sealed tube for subsequent

analysis. This is referred to below as the original mixture. The remainder of the mixture was added to a 10-mm Pyrex tube containing **1**, and the tube cooled in dry ice and sealed. The quantities were chosen such that the resulting liquid phase (L) weighed 4-10 times that of the solid phase (S) and such that an excess of guest was always present. This ensured that all of **1** had been saturated with guest. For *p*-xylene and naphthalene, saturation occurs when the molar host/guest ratio is unity. The tubes were tumbled slowly at room temperature for several days to equilibrate, during which time the guests distributed themselves between liquid and solid phases. The tubes were then centrifuged, L was withdrawn and set aside, and S was air dried briefly. S was decomposed with 6 N HCl, and the liberated guests were extracted with pentane. A small portion of **1** was stirred with L, HCl was added to decompose it, and the guests were extracted with pentane, similar to the decomposition of S. (The addition of **1** to L was merely to provide a similar history for both L and S apart from the inclusion step.) The HCl, in addition to causing decomposition and dissolution of all of the products except the guests, prevents the 4-methylpyridine from being extracted.

The original solution and the pentane extracts from L and S were then analyzed with a CEC 21-104 analytical mass spectrometer in order to compare the areas of the parent peaks: A, 106; B, 116; C, 112; D, 128; E, 136 amu. After the background was checked, the instrument parameters including chart speed were adjusted so that the peaks in the range of interest were as large and as smooth as possible. The area of the larger of the two parent peaks was usually ~30 cm³. After the sample had been admitted, time was allowed for the pressure within the spectrometer to stabilize. At least four spectra were then taken consecutively for a given sample and the areas under the parent peaks measured with a high quality planimeter. The average ratio of the areas was taken as a measure of the relative amounts of the two isotomeric guests. With the limitations of the spectrometer included it is estimated that these ratios are accurate to ~1%. Compound **1**, alone, decomposed with HCl and then extracted with pentane, gave no peaks in the region of interest. There is no isotope exchange between B and C and the other substances used; this is doubtless true also for E.

The mole ratios, determined as described, are given in Table I. For all of the experiments, the values for L, original solution, and S differ by considerably more than the experimental error. In all instances the deuterated isotopomer is included to a slightly greater extent than the protonated. The fact that the ratios for the original mixture lie between those of L and S shows that the results are internally consistent. The fractions given in the second last column were estimated by assuming the total absence of host in L, absence of pentane in S, and a guest/host ratio in S of unity. If one defines a separation factor for the deuterated species, *s_d*, as the mole ratio in S divided by the mole ratio in L, the values in the last column are obtained. Its magnitude, at least in the system A-B, appears to be the

Table I. Distribution of Isotopomers between Liquid and Solid Phases

guest mixture	quantities used			mole ratio (B/A, C/A, or E/D)			fraction of total guest pptd	<i>s_d</i>
	mixture mL	pentane, mL	host, g	L		S		
				orig	S			
A + B	0.45	2.0	0.15	0.808	0.863	0.899	0.08	1.11
	0.10	2.0	0.16	1.05	1.12	1.30	0.36	1.24
	0.20	2.0	0.17	1.17	1.22	1.30	0.10	1.11
	0.85	1.5	0.30	1.43	1.46	1.49	0.08	1.04
A + C	0.40	2.0	0.17	0.937	1.02	1.13	0.09	1.21
	0.40	2.0	0.15	0.933	1.04	1.13	0.08	1.21
	0.36	2.0	0.16	1.27	1.31	1.40	0.10	1.10
D + E	0.15 ^a	2.1	0.10	1.96	2.02	2.04	0.17	1.04

^a Gram.