The situation is different in AcOH and in 1:1 AcOH–Ac_2O. The high k_α/k_t values would usually be ascribed to ≥99% return with racemization of intermediate ion pairs,[2c] but this is in contrast with the results in TFE and in 80% EtOH and with the lower extent of ion-pair return (31% in 1:1 AcOH–Ac_2O and 47% in AcOH) in the solvolysis of (*Z*)-1,2-dianisyl-2-phenylvinyl bromide.[10] On the other hand, route b, with a rate-determining formation of **10**, accounts for the fact that formation of **11** precedes that of **4** with the ~3-fold higher k_α in AcOH compared with that in the much more ionizing TFE,[9] but it raises two problems: (a) it postulates racemization via capture of the hybrid ion **10a–b**[11] at C-10 rather than at C_α, although capture at C_α gives an aromatic system; (b) it has to explain the very high $k_{rcar}(\mathbf{2})/k_\alpha(\mathbf{1})$ ratio which indicates that the ionization **2** ⟶ **16** is favored over the ionization **1** ⟶ **10**, although in the solvolytic generation of an sp^2-hybridized ion an α halogen is activating compared with an α hydrogen.[12] We ascribe the two phenomena to a steric interaction of the 1 and 8 hydrogens of the 9-anthryl group of the 9-anthrylmethyl cations **10** and **16** with the other α substituents.[13] A consequent loss of planarity, e.g., by rotation of the anthryl and/or the anisyl groups, results in destabilization of the ions which is higher for **16** (α-Br) than for **10** (α-H). The outcome is a higher k_{rcar} for **2**, reduced importance of **10b** compared with **10a** and a lower rate of route b, steric hindrance to capture of C_α of **10**, and preferred capture by AcOH or AcO^- at C-10[5] to give **11**. Capture at C_α first gives **14** (S = Ac) which solvolyzes rapidly to give **4**, probably via **8** (S = Ac). Since the titrimetric k_t remains constant during a run and is identical with the values measured by UV, **4** is probably formed via the modified route b, $\mathbf{1} \rightarrow \mathbf{9} \rightarrow \mathbf{10}\ (\rightarrow \mathbf{11} \rightarrow \mathbf{10}) \rightarrow \mathbf{14} \rightarrow \mathbf{8} \rightarrow \mathbf{4}$, and not via $\mathbf{1} \rightarrow \mathbf{9} \rightarrow \mathbf{10} \rightarrow \mathbf{11} \rightarrow \mathbf{12} \rightarrow \mathbf{13} \rightarrow \mathbf{7} \rightarrow \mathbf{8} \rightarrow \mathbf{4}$.

In conclusion, the solvolytic site of **1** in good-ionizing relatively nonacidic solvents (80% EtOH, TFE) is C_α, and C–Br bond cleavage is rate determining. In AcOH, the initial solvolytic site is C-10 and C–$^+OH_2$ and C–OAc bond cleavages are rate determining for the loss of optical activity and for the solvolysis, respectively. The mechanistic consequences are (i) the availability of an additional competing route to the several ones known for vinylic solvolysis,[14] and (ii) that the k_α/k_t probe for ion-pair return should not be used indiscriminately for vinylic systems.

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(5) A minor product, which becomes the main product in wet AcOH/NaOAc, is 7-(9-anthryl)-7-bromoquinone methide, formed probably by attack of AcO^- on the methoxy group of **10.** This product was not formed in 1:1 AcOH–Ac_2O. Z. Rappoport, J. Greenblatt, and Y. Apeloig, *J. Org. Chem.*, in press.

(6) The product[5] and both k_α and k_t are sensitive to small amounts of water in the AcOH. The values given are for a single batch of AcOH.

(7) From Table I, the *uncorrected* $k_t°/k_d = 2.64$ and ≥62% of **4** are derived from the free ion **5.** By correction for the normal salt effect, $k_t = 3.33 \times 10^{-4}\ s^{-1}$ with 0.1 M Bu_4NBr; i.e., $k_t°/k_d = 7.8$ and ≥87% of **4** are derived from **5.**

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Transient Photocurrents and Conversion Losses in Polysulfide-Based Photoelectrochemical Cells

Sir:

The development of a practical photoelectrochemical cell (PEC) for solar energy conversion into electricity requires long-term output stability and reasonable conversion efficiency. Treatments have been presented which can predict the thermodynamic stability of a certain semiconductor/electrolyte combination,[1] but, even if a system is thermodynamically unstable, kinetic factors may still lead to long-term stability.[2] Transient photocurrents, as reported by us recently,[3] can be useful in certain cases, to evaluate PEC performance by way of the, somewhat neglected, effect of the cell's solution kinetics.

We describe here how such transients yield information on long-term stability and conversion efficiency losses in PEC's using polychalcogenide redox electrolytes. Figure 1 illustrates the time dependence of the photocurrent (at close to short circuit conditions) in a PEC comprising a thin-layer, polycrystalline CdSe photoelectrode and polysulfide redox electrolyte.[4] The transient photocurrent can be analyzed by considering the difference between the peak-current density (I_p) and the steady-state one (I_s), and by defining a normalized ratio (NR) ≡ $(I_p - I_s)/I_p$. As $(I_p - I_s)$ expresses conversion losses in the cell, NR = 0 represents zero loss and NR = 1 total loss, i.e., a situation with no steady-state output.

To gain insight in the cause of these transients, the NR was investigated as a function of several solution parameters (Figure 2). (Not shown are effects of temperature or peak-

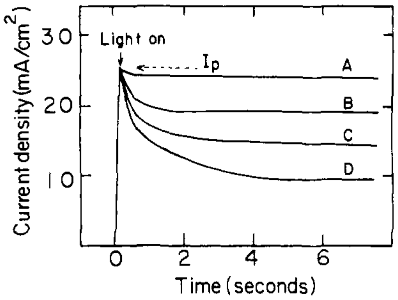

Figure 1. Scheme of photocurrent density vs. time in *n*-CdSe/polysulfide/CoS PEC. Electrolyte composition: A, 0.9 M [S^{2-}], no OH^-, 6.10^{-3} M [Se^{2-}], temp, 34 °C, NR, 0.05 (the same behavior is obtained in 2 M [S^{2-}], 2 M [S], 2 M [OH^-], no Se^{2-}); B, 0.9 M [S^{2-}], 1 M [S], no OH^-, no Se^{2-}, temp, 34 °C, NR, 0.2; C, 0.25 [S^{2-}], 0.2 M [S] no OH^-, no Se^{2-}, temp, 44 °C, NR, 0.4; D, as C but at 24 °C, NR, 0.6. Identical peak current densities (I_p) were obtained in all cases by adjusting the incident light intensity; a 2-cm^2 area of polycrystalline thin layer of CdSe on Ti was exposed to light and solution. Light source: filtered 250-W quartz–iodine lamp (λ >610 nm only). Care was taken to ensure that the counter electrode[3a] was negligibly polarized, so that no part of the transient response ascribed to the CdSe could be due to such polarization.

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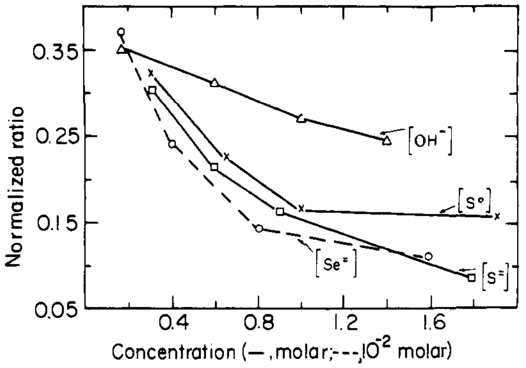

Figure 2. Equal peak current density ("*isorheic*") plots of the dependence of the normalized ratio on electrolyte composition (each point is derived from measurements such as those shown in Figure 1) (I_p = 20 mA/cm², temp, 34 °C): △, 0.25 M [S^{2-}], 0.2 M [S], no Se; X, 0.9 M [S^{2-}], no Se, no OH^-; □, 1 M [S], no Se, no OH^-; ○, 0.25 M [S^{2-}], 0.2 M [OH^-], no S (note 100X lower concentration scale for Se).

current density, the latter of which can be controlled by the light intensity and/or load resistance. The NR decreases with increasing temperature as well as with decreasing I_p.)

Interestingly, those changes in parameters which lower NR also increase PEC output stability,[2b,5] suggesting a connection between the two phenomena.

Transient phenomena (such as the one described here) have been reported for other systems as well. Charge-trapping and back-reactions were suggested to explain transients with n-TiO_2[6] and n-Fe_2O_3[7] electrodes, respectively. In the polyiodide system, apparently similar transients to those observed here occur,[8] but these are probably caused by counterelectrode limitations.

Upon illumination of a (n-type) photoelectrode, electronic oxidizing species (holes) move to the semiconductor-electrolyte interface, where they meet reduced ionic species from the solution. Ideally, all the photoproduced holes reaching the interface react rapidly with the solution species. This reaction can continue unimpeded only if the, now oxidized, solution species are removed (at a sufficient rate) from the electrode surface, thus allowing fresh, reduced species to reach it. If the last process is not fast enough, the rate of the electrochemical reaction drops after a short initial period. Side reactions, such as photodecomposition of the semiconductor and electron-hole recombination, may now become more important.

This general description can be expressed for the n-CdSe/polysulfide electrolyte system as follows. The reactions at the photoelectrode surface are

$$S_x^{2-} + 2h^+ \rightarrow xS \text{ (photoelectrochemical)} \quad (1)$$

$$S_x^{2-} + S \rightarrow S_{x+1}^{2-} \text{ (sulfur dissolution)} \quad (2)$$

When (1) is faster than (2), S accummulates at the electrode surface hindering the approach of S_x^{2-} to the surface. The probability of photocorrosion (= self-oxidation) of the semiconductor, which is small as long as all the holes reaching the surface have an ample supply of S_x^{2-} with which to react, can increase now as an alternative way of consuming holes arriving at the surface. Concomitantly, there will be increased electron-hole recombination in the semiconductor, manifested by an increase in $I_p - I_s$. The rate of (1) is controlled by the real current density which depends on the incident light intensity and on the real electrode surface area, while that of (2), on the other hand, depends on solution parameters such as the concentrations of S,S^{2-} and OH^-, as well as on the temperature. I_p, then, represents the maximal current that can be drawn from the system, namely the current through the unblocked electrode, while ($I_p - I_s$), and thus NR, describes the extent of blocking at the electrode surface.

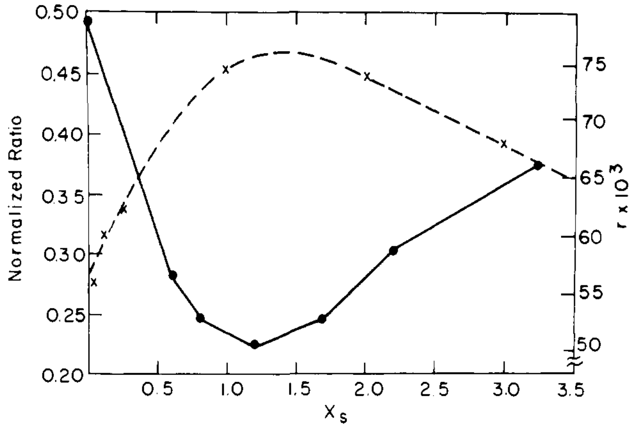

Figure 3. Comparison between rate of dissolution of S in polysulfide solution[10b] (in min⁻¹; dashed line; 0.5 M [OH^-], 0.25 M [S^{2-}], 80 °C) and NR (solid line, 0.2 M [OH^-], 0.25 M [S^{2-}], 34 °C) as a function of X_s = [added S^0]/[added S^{2-}]). The data from ref 10b are for a stirred solution; decreasing the temperature shifts the maximal rate of S dissolution to somewhat lower X_s values.[10b]

Comparing our results with those obtained for the solubility of sulfur in polysulfide solutions,[10] we see that all conditions that favor fast sulfur dissolution lead to a low NR in our case. Hartler et al.[10b] define a variable, X_s, the ratio between the zerovalent and divalent sulfur in polysulfide solutions, and find that the rate of sulfur dissolution is maximal at $X_s \sim 1.4$. We find NR to pass through a minimum at a similar value of X_s (Figure 3).

Transients similar to those obtained with CdSe photoelectrodes are observed also using metal (Pt, Au) electrodes in polysulfide solution, which are connected to a step function generator giving anodic pulses. With these metal electrodes, the NR dependence on parameters such as electrolyte composition and current density is similar to that observed with intermittent light on CdSe photoelectrodes. The role of S dissolution in these transients is illustrated further by experiments using Se^{2-}-containing solutions. The presence of Se^{2-} was shown to have a dramatic stabilizing effect on CdSe/polysulfide PEC's.[5] This effect is related to a decrease in the amount of S/Se exchange in the electrode top layer, keeping it Se richer and leading to increased stability. (Also, from the arguments in ref 2b, the effect of Se^{2-} on S dissolution will counteract the decrease in crystallite size in the top layer, thus exerting a parallel stabilizing effect.)

Figure 2 shows that even small amounts of Se^{2-} lower the NR considerably, something that is found also using metal electrodes as described above. Clearly then, we are dealing here with a solution phenomenon and the effects of adding Se^{2-} to polysulfide solutions, on CdSe stability are, at least in part, kinetic ones. (The experiments on metal electrodes also show that the transient response is not due to a reverse reaction since the anodic voltage pulses were typically several hundred millivolts positive of the equilibrium potential, and at such potentials the reverse reaction will be vanishingly small.) Following our previous reasoning, this suggests that the addition of selenide leads to an increase in the rate of sulfur dissolution in polysulfide solution. This we confirmed by independent dissolution experiments.

The effect of the kinetics of sulfur dissolution in polysulfide solutions on the stability of illuminated CdSe photoelectrodes can be summarized as follows. A buildup of sulfur at the CdSe surface leads to a reduced supply of S_x^{2-} to the CdSe. The photodecomposition reaction can now increase in rate as an alternative mode of consumption for holes at the surface. This leads to increased exchange between CdSe and sulfur from the electrolyte, leading to a thicker, and probably more polycrystalline, CdS layer on top of the CdSe, which results in irreversible degradation of the CdSe.[2b] This effect is alleviated by any factor which increases the rate of sulfur dissolution in polysulfide solution, such as an increase in [S^{2-}] or addition of Se^{2-} to the electrolyte. Thus, in the CdSe/polysulfide system, NR can be looked upon as a measure of the stabilizing influence of the electrolyte on the photoelectrode. In the course of several accelerated output stability experiments (corresponding to at least a month under day-night AM1 conditions), the NR of the PEC was checked. It was found that the most stable PEC (as judged by remaining output after passing a fixed number of coulombs) also gave the lowest NR.[11] The earlier reported difference in stability between single-crystal and thin layer polycrystalline CdSe photoelectrode PEC's[2b] is also reflected in lower NR's for the latter, more stable system. The cause for this lies probably in lower real current densities on the high surface area, polycrystalline electrodes.

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Preparation of a Porphyrin–Iron–Carbene Model for the Cytochrome P 450 Complexes Obtained upon Metabolic Oxidation of the Insecticide Synergists of the 1,3-Benzodioxole Series

Sir:

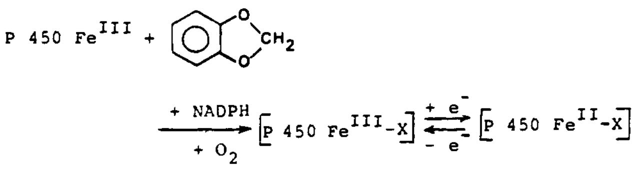
Evidences have been presented in favor of the formation of cytochrome P 450-iron-carbene complexes during reductive metabolism of polyhalogenated compounds.[1-3] These compounds do react with ferroporphyrins, in the presence of an excess of reducing agent, leading to stable iron(porphyrin)-(carbene) complexes.[4-7] (eq 1). The iron-carbene structure of one of them has been definitely established by an X-ray analysis.[8]

$$\mathrm{Fe^{II}(P) + RR'CX_2 \xrightarrow[-2\,X^-]{+2\,e^-} Fe^{II}(P)(CRR')} \qquad (1)$$

P = porphyrin or cytochrome P 450

Various derivatives of 1,3-benzodioxole are well-known insecticide synergists. Their use in combination with an insecticide results in a marked increase in toxicity, presumably because of their ability to inhibit the enzymes responsible for insecticide detoxication.[9] The benzodioxole derivatives are oxidatively metabolized in vivo and in vitro by cytochrome P 450 dependent monooxygenases with formation of very stable complexes of this cytochrome in the ferrous state, characterized by a Soret peak at 455 nm.[10] After aerobic removal of the reducing agent (NADPH), the Soret band shifts to 438 nm which has been explained by the formation of the corresponding ferric complexes.[10c-d] The latter are also obtained by reaction of cytochrome P 450 with benzodioxole derivatives in the presence of cumene hydroperoxide.[10d]

Scheme I



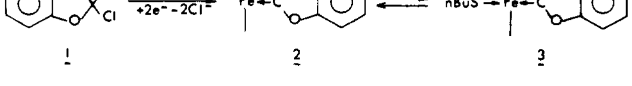
The great stability of the iron-metabolite (X) bond in these complexes is probably at the origin of the synergistic action of the benzodioxole derivatives (Scheme I). It has been proposed[11] that the iron ligand present in these complexes is the 1,3-benzodioxole-2-carbene[12] formed by oxidation of the methylene group of 1,3-benzodioxole.

The present paper describes the isolation and characterization of an iron(II)(porphyrin)(1,3-benzodioxol-2-carbene) complex, obtained by reduction of 2,2-dichloro-1,3-benzodioxole according to eq 1, and brings indirect evidence for the presence of this carbene as ligand in the benzodioxole-derived cytochrome P 450-iron(II) complexes (Scheme I).

Addition of deaerated 2,2-dichloro-1,3-benzodioxole (**1**)[13a] to an NMP[14] solution of Fe^{II}(TPP) results in an immediate oxidation of the iron, giving Fe^{III}(TPP)(Cl). Progressive addition of 2 equiv of compound **1**[13b] to a CH_2Cl_2–NMP (20/1) solution of Fe(TPP) vigorously stirred in the presence of an excess of iron powder as a reducing agent leads to the formation of a new species characterized in visible spectroscopy (in benzene) by peaks at 412 and 516 nm. After filtration and two crystallizations from CH_2Cl_2–CH_3OH, purple crystals of complex **2** are obtained (yield, ≃50%). Its following characteristics—λ 412 nm (ϵ 2 × 10^5), 516 (18 × 10^3), 540 (sh), in benzene; ^1H NMR (C_6D_6, Me_4Si) 8.82 (s, 8 H), 8.02 (m, 8 H), 7.27 ppm (m, 12 H), for the protons of the porphyrin ring; ^{13}C NMR (C_6D_6, Me_4Si) 148.3, 143.7, 134.5, 133.8, 128.1, 126.8, 122.3 ppm, for the carbons of the porphyrin ring—are indicative of a low-spin iron(II)–porphyrin complex with an axial symmetry. They are similar to those which have been reported for the pentacoordinated Fe(TPP)(CS)[6] and Fe(TPP)(carbene)[4,5,7] complexes. The presence of the axial 1,3-benzodioxole-2-carbene ligand in complex **2** is indicated by its mass spectrum which exhibits two intense peaks at *m/e* 120 and 240 corresponding to the $C_7H_4O_2$ carbene and to the olefin obtained by its dimerization.[15a] Moreover, the only signals which appear in addition to those of the porphyrin in the ^1H and ^{13}C NMR spectra of complex **2**—^1H NMR δ 5.23 (m, 2 H), 4.8 ppm (m, 2 H); ^{13}C NMR 107.2, 122.5, 147.4 ppm—are those which are expected for a benzodioxole-derived carbene[15c] bound to iron and held in a close proximity to the porphyrin ring[15b] (Scheme II). Complex **2** is stable in deaerated solution, but slowly oxidized to the μ-oxo[Fe^{III}(TPP)]$_2$O complex in the presence of oxygen ($t_{1/2}$ in benzene at 27 °C, ≃0.5 h).

In the cytochrome P 450 complex where the iron(II) is

Scheme II



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