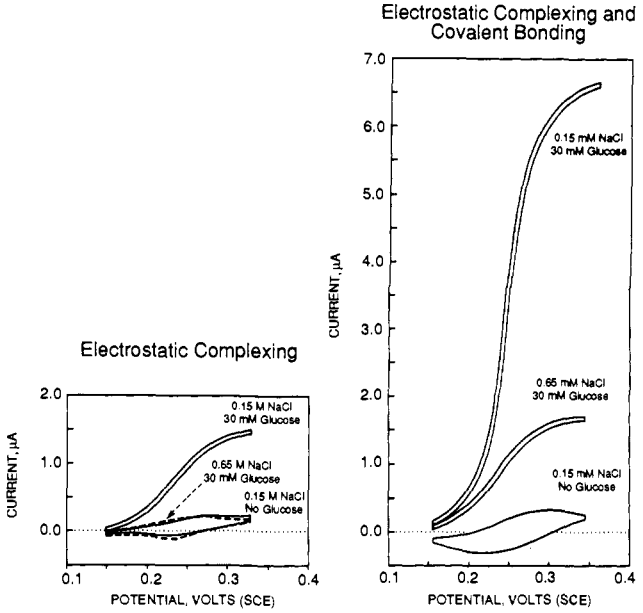

Figure 2. Cyclic voltammograms for glucose oxidase enzyme electrodes: Without glucose, 0.15 M NaCl; with 30 mM glucose, 0.15 M NaCl; and with 30 mM glucose, 0.65 M NaCl. Left: enzyme electrodes made with the copolymer of poly(vinylpyridine $Os(bpy)_2Cl$) and poly(vinyl-*N*-methylpyridinium chloride). Right: enzyme electrode made with the same polycationic redox polymer but covalently bound to the enzyme's tyrosine functions through azo links. 3 mm diameter glassy carbon electrodes; scan rates 2 mV/s.

zation of the copolymerized aminostyrene followed by reacting the diazonium salt with tyrosine functions of the enzyme allows covalent bonding of the redox polymer to hydrophilic channels in the enzyme's protein.

Cyclic voltammograms of the resulting enzyme electrodes are shown in Figure 2. Glucose is electrooxidized at moderate ionic strength (0.15 M NaCl), where the first (i.e., not covalently bound) redox polymer is electrostatically complexed to the enzyme but not at high ionic strength (0.65 M NaCl) where the electrostatic complex dissociates (Figure 2, left). When the redox polymer is covalently bound to the enzyme (Figure 2, right), a high glucose oxidation current is observed at low ionic strength that persists at high ionic strength. At 0.65 M NaCl the glucose electrooxidation current for the covalently bound system is as high as for the electrostatic complex at 0.15 M NaCl.

Because glucose oxidase is itself a polyelectrolyte, the loss of current at 0.65 M NaCl could be caused simply by structural changes in the enzyme. We find, however, that enzyme-related changes account only for a minor fraction of the loss. To test for these changes we measured the output of glucose electrodes made with glucose oxidase and low-molecular weight redox mediators, either neutral (ferricinium carboxylate) or positively charged (protonated dimethylaminomethylferricinium chloride) at different NaCl concentrations. Upon increasing the NaCl concentration from 0.15 to 0.65 M the currents of the two electrodes (at +0.45 V vs SCE) declined only by 20% and 30%, respectively, in contrast with the current of the electrode made with the polycationic redox polymer that dropped by a factor of >50 essentially to nil (Figure 2, left). We conclude that it is primarily the breakup of the electrostatic complex between the redox polymer and the enzyme, not a structural change in the enzyme, that causes the drastic decline in the glucose-dependent current at high ionic strength.

Electrostatic complexing of oxidoreductases and redox proteins, whereby electron transfer becomes possible, is known for the cytochrome *c* peroxidase/cytochrome *c* system, for the cytochrome *c* oxidase/cytochrome *c* system, and for the ferredoxin $NADP^+$ oxidase/ferredoxin system. These natural electron-transfer complexes, like the synthetic ones described here, are sensitive to ionic strength before, but not after, covalent attachment of the redox proteins to their complexing enzymes.[4]

The significance of low molecular weight organic nitrogen compounds in promoting electron transfer between electrodes and the smaller redox proteins, like cytochrome *c* (but not between electrodes and the larger redox enzymes) is well documented.[5] We see here that adsorption of a polycationic redox polymer on an electrode and its interaction with glucose oxidase also enhance electron transfer and form the basis of a glucose electrode.

In summary, we find that the natural process of electron transfer in electrostatic complexes between polyanionic enzymes and polycationic redox proteins can be mimicked: electron transfer takes place in a complex between polyanionic glucose oxidase and a polycationic redox polymer. The complex decomposes, and the electron-transfer rate becomes vanishingly small, at high ionic strengths. The rate of electron transfer remains, however, fast even at high ionic strengths if the redox polymer and the enzyme are covalently bound.

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Confinement Control in Solid-State Photochemistry[1]

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For three decades our research group has been investigating unusual photochemical organic reactions in solution. In recent years we have returned to these reactions and studied their counterpart crystalline photochemical reactivity. In view of the increasing interest[2] in this area, we wish to report our preliminary findings.

We report (1) three striking examples of control of photochemical rearrangements by crystalline environment, (2) quantum

(1) We have used "Photochemistry in a Box" informally to describe these studies.

(2) (a) Ariel, S.; Evans, S. V.; Garcia-Garabay, M.; Hwang, C.; Harkness, B. R.; Omkaram, n.; Scheffer, J. R. *J. Am. Chem. Soc.* **1988**, *110*, 5591-5592. (b) Scheffer, J. R.; Garcia-Garabay, M.; Nalamasu, O. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1987; Vol. 8, Chapter 4. (c) Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433-481. (d) *Organic Solid State Chemistry*; Desiraju, G. R., Ed.; Elsevier: Amsterdam, 1987. (e) In zeolites note: Turro, N. J.; Zhang, Z. *Tetrahedron Lett.* **1987**, 5637-5640.

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Table I. Solid-State Quantum Yields and Corresponding Solution Values

reactant	total ϕ_{soln}[a,b]	total ϕ_{solid}[a]
dicyanotriene **1**[c]	0.17	0.0008
triphenyl enone **6**[c]	0.16[e]	0.00003[f]
tetraphenyl diene **12**[d]	0.13[g]	0.016

[a] Error of ±10%. [b] In Benzene. [c] Irradiated at 313 nm. [d] Irradiated at 302 nm. [e] Data from ref 6. [f] Only endo bicyclic **7** was detected at low conversion. [g] 0.058 for vinylcyclopropane **17** and 0.074 for vinylcyclopropane **18**.

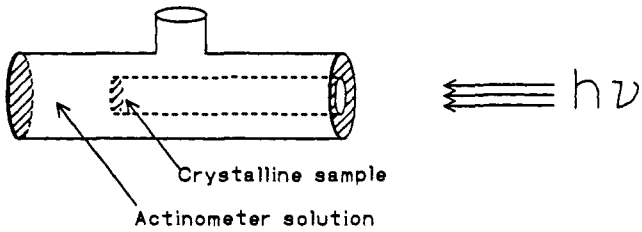


Figure 1. Solid-state quantum yield photolysis cell.

yield observations, and (3) three quantitative predictors of photochemical behavior in crystals.

The first case is the rearrangement of tetraphenyldicyanooctatriene (**1**). For many years we have sought without success to divert the di-π-methane rearrangement[3] to afford cyclopentenes by substitution of a vinyl moiety on the central, "methane" carbon.[4] For example, in benzene tetraphenyldicyanotriene (**1**) afforded only di-π-methane photoproducts.[5] This is understood by the preferred formation of transoid a–b diradical **3T** in solution (Scheme I).

In contrast, irradiation[6] of crystalline dicyanotriene **1** gave only dicyanocyclopentene **4**. Clearly, this is understood as formation of diradical **3C** in a cisoid a–b conformation in the crystal.

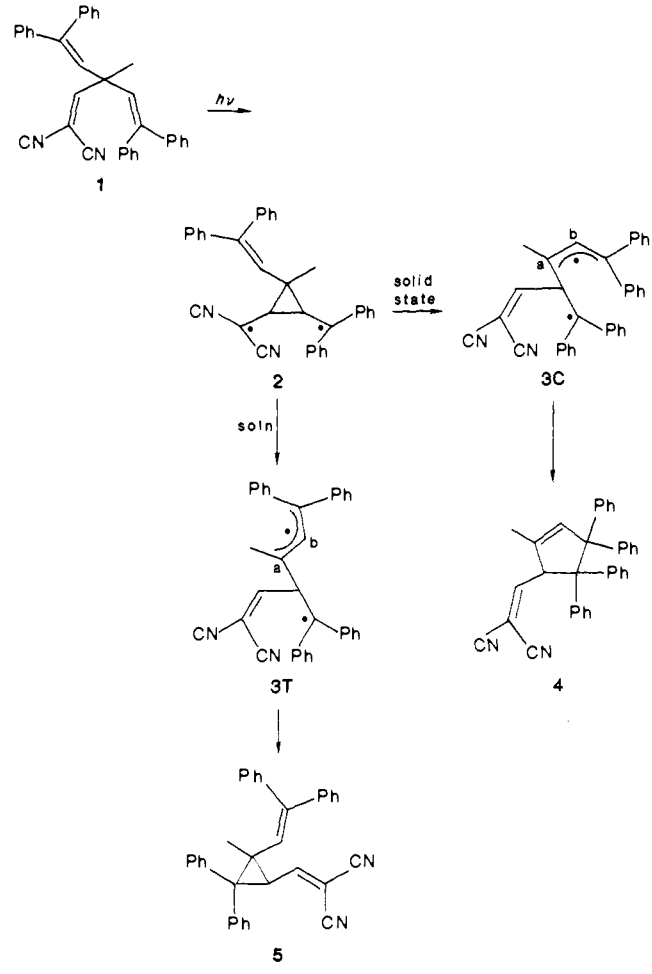
In a second example 4,5,5-triphenyl-2-cyclohexenone (**6**) in solution gave[7] the exo stereoisomer of bicyclic ketone **7**, 3,5,5-triphenyl-2-cyclohexenone (**8**), and vinylcyclobutanone **9**. Remarkably, photolysis of the crystalline material led to the endo stereoisomer of bicyclic ketone **7** and benzobicyclic ketone **10** in a 4:1 ratio. Thus, the formation of the bicyclo[3.1.0] structure **7** proceeds with inverted stereochemistry in the crystal compared with solution.

In the third example 1,1,3,3-tetraphenyl-1,4-pentadiene (**16**) afforded two photoproducts **17** and **18** in solution in a 1:1.3 ratio. But irradiation in the crystal proved completely selective yielding only vinylcyclopropane **17** (Scheme III), illustrating the utilization of solid-state photochemistry to simplify reactions. We also note the reversal of regioselectivity in the solid.

Quantum yields (Table I) were determined with the Micro-optical bench[8] equipped with the quartz cell depicted in Figure 1. Since the sample was largely surrounded by ferrioxalate actinometer,[9] scattered light could be subtracted.

We find that solid-state quantum yields are lower than in solution. This accords with the idea that in the crystal, the reaction

Scheme I. Tri-π-methane Reaction Course in Crystalline vs Solution Medium



energetically preferred by an isolated molecule often cannot take place for spatial reasons and one observes the "second or third best" reaction, which by definition[10] has lower efficiency. Reactions which are of interest but are energetically inaccessible in solution become accessible in solid-state photochemistry. Further, the restricted environment seems to lead to lower efficiencies as well.

In considering factors directing solid-state photochemistry, we find two inherently different modes of control. Many known solid-state photochemical reactions seem to derive from conformational fixation, in which two potentially reacting groups are held in proximity in the crystal but not in solution.[2]

The second type of selectivity in solid-state photochemistry might be termed confinement control. Thus, often the photochemical reaction favored kinetically in solution proceeds via a geometry not able to fit in the space allotted in the crystal lattice. This is particularly common in deep-seated photorearrangements and seems involved in our solid-state photochemistry.

We propose three quantitative ways of dealing with confinement control. First, least motion has been considered[11a] controlling in solid-state photochemistry. A second useful measure is volume

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(5) (a) Also, 1,1-dicyano-2,3-bis(diphenylvinyl)-2-methylcyclopropane and *cis*- and *trans*-1,1-diphenyl-2-(dicyanovinyl)-2-methyl-3-(diphenylvinyl)-cyclopropane were formed. (b) Details of the characterization of all reactants and photoproducts will be presented in a full paper. All compounds were properly analyzed.

(6) Preparative photolysis of crystalline material deposited on the inner wall of a cylindrical flask was under deoxygenated nitrogen with a 450 W medium pressure mercury lamp with parallel results at −78°, 0° and room temperature.

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(10) This is not strictly correct: excited state lifetimes in a rigid solid are likely to be longer with a tendency to raise quantum yields. Nevertheless, the efficiences are seen to be lower in the solid.

(11) (a) Least motion as a factor in crystal photochemistry was first suggested by Cohen and Schmidt (Cohen, M. G.; Schmidt, G. *J. Chem. Soc.* **1964**, 1996–2000). (b) Volume around a reactant has been considered by Gavezzotti (Gavezzotti, A. *J. Am. Chem. Soc.* **1983**, *105*, 5220–5225) in contrast to the present study which focuses attention on volume increases in the reactant. (c) The suggestion was made by Cohen (Cohen, M. D. *Angew Chem., Int. Ed. Engl.* **1975**, *14*, 386–393) that reaction must take place with minimal distortion of the reaction cavity.

Scheme II. 4,5,5-Triphenylcyclohexenone Rearrangement in Solid and Solution

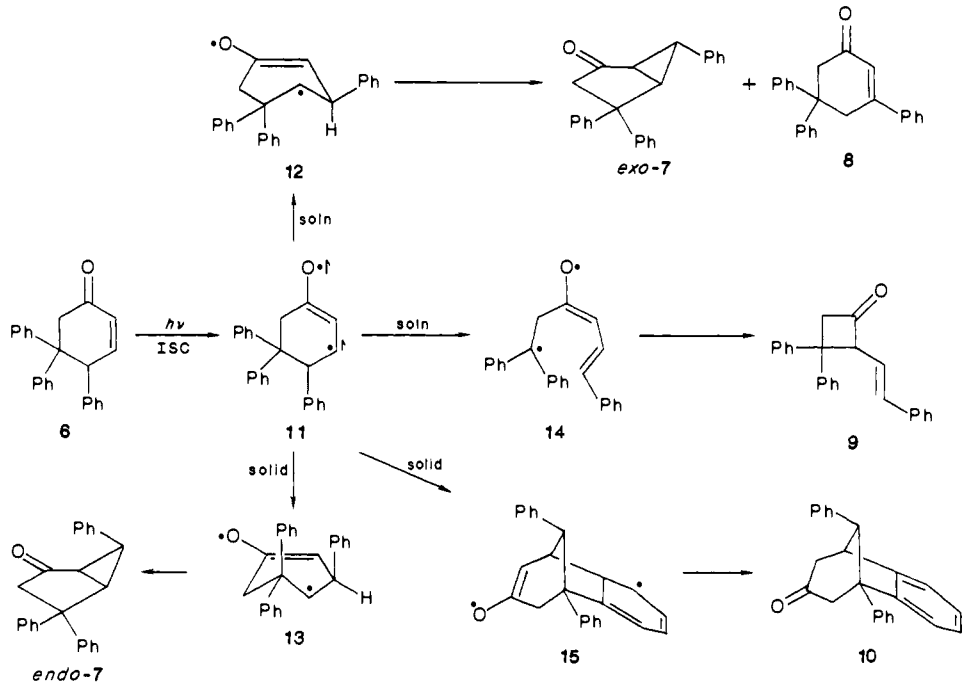


Table II. Correlation of Calculated Reactivity Parameters with Observation

		to photoproduct			to diradical species				
reactant	photoproduct	motion,[a] Å/atom	ΔV,[b] %	ΔS,[c] %	diradical	motion,[a] Å/atom	ΔV,[b] %	ΔS,[c] %	state[d]
dicyanotriene **1**	cyclopentene **4**	1.37	35	6	**3C**	0.24	6	1	solid
	cyclopropane **5**	2.20	41	11	**3T**	1.87	26	10	soln
triphenyl enone **6**	*endo* bicyclic **7**	0.72	24	1	**13**	1.15	25	4	solid
	benzobicyclic **10**	0.64	21	3	**15**	0.65	18	1	solid
	exo bicyclic **7**	1.49	32	12	**12**	1.18	27	9	soln
	triphenyl enone **8**	1.27	29	17	**12**	1.18	27	9	soln
	cyclobutanone **9**	1.24	38	11	**14**	(0.55)	16	4	soln
diene **16**	cyclopropane **17**	0.98	28	7	**19**	0.81	25	2	both
	cyclopropane **18**	1.19	34	2	**20**	0.86	27	7	soln

[a] Average straight line atomic movement from reactant to photoproduct or diradical. [b] Volume of superimposed species not in common with reactant. [c] Overlap with neighboring molecules. [d] State of reactant photolyzed resulting in the formation of the photoproduct. [e] Artificially compressed conformer.

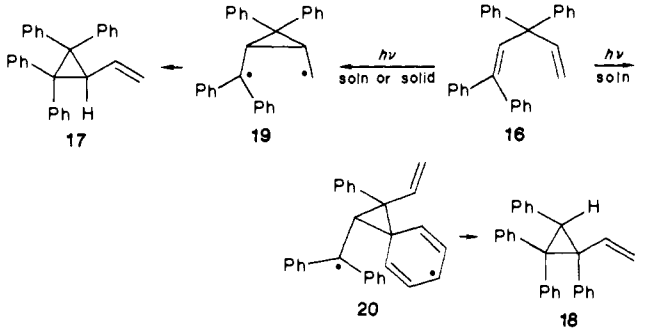
increase during a reaction. However, these two are really manifestations of a third, more basic factor, namely the extent to which the reacting molecule can deform itself toward product in the confines of the crystal lattice.

The three methods use reactant X-ray structures. Intermediates and products were constructed by using modified molecular mechanics in which torsional angles were varied to maximize congruence with reactants.[12,13]

(A) Least motion was quantified by summing the normalized displacements of atoms in reactant in proceeding past the "branch point" of the reaction, where the branch point is defined as that point along the reaction coordinate where the pathways to alternative products diverge. (B) Volume increments were obtained similarly. (C) In reactant X-ray lattices, computational replacement of one molecule with a photoproduct or diradical species permitted determination of the interference (i.e., overlap) with the surrounding lattice.[13]

Inspection of Table II reveals, in comparing crystal and solution reactivity of a given compound, that those reactions with small values of "motion", ΔV, and "overlap" (ΔS) are preferred in the crystal.

Scheme III. Di-π-methane Reaction Course in Crystalline vs Solution Medium



(12) (a) We find one quantitative consideration of least motion as the root-mean-square sum of atomic displacements[12b] and one cited comparison differing by 4% of solid vs solution.[12c] (b) Theocharis, C. R.; Jones, W. in Ref 2d. (c) Thomas, N. W. cited in ref 12b. (d) We find one example of the repulsion energy of a reactant methyl group on deformation toward product with an adjacent methyl of the crystal lattice.[2b,12e] (e) Scheffer, J. R.; Trotter, J., et al. *J. Am. Chem. Soc.* **1984**, *106*, 5726–5728. (f) Note Scheffer et al. (Scheffer, J. R., Trotter, J. et. al. *Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt.* **1988**, *156*, 63–64) report a root-mean-square least motion for a single reactant using product crystal structure.

(13) (a) Product and branch point structures were obtained with molecular mechanics structures and the MACROMODEL[13b] flexibile superimposition routine which afforded that structure with maximum congruence to reactant. Volumes and overlaps were obtained using TRIBBLE.[13c] (b) Still, W. C.; Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Caufield, C.; Liskamp, R.; Hendrickson, T.; Chang, G. MACROMODEL V1.5, Columbia University, New York, NY, 10027, (c) Pensak, D. *Ind. Res. Dev.* 1983, *25*, 74–78.

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Electrochemical Fixation of Carbon Dioxide in Oxoglutaric Acid Using an Enzyme as an Electrocatalyst

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We report the first electrochemical fixation of CO_2 in oxoglutaric acid using an enzyme (isocitrate dehydrogenase, ICDH) as an electrocatalyst and methylviologen (MV^{2+}) as a mediator. The product is isocitric acid. The reaction occurs selectively with current efficiencies approaching 100% at −0.95 V vs SCE in a 0.2 M tris buffer (pH 7). These conditions are the mildest reported to date for efficient reduction of CO_2. Enzymes have previously been used as electrocatalysts for the direct reduction of CO_2 to formic acid but not for the fixation of organic compounds.[1] The principle applied here is to reverse the in vivo metabolic pathway of isocitric acid oxidation to yield oxoglutaric acid and CO_2. These are catalyzed by ICDH in the presence of nicotinamide adenine dinucleotide phosphate ($NADP^+$). Uniquely, this electrolytic system does not require the use of $NADP^+$.

To date, most studies on the electrochemical reduction of CO_2 have focused on the direct reduction of CO_2 to carbon monoxide, formic acid, formaldehyde, etc. Enhanced reaction selectivity and/or creation of milder electrolysis conditions have been reported.[2] In addition, direct reduction to methane has recently attracted much attention.[3] The efficient reduction of bicarbonate to formate has been reported[4] as CO_2-related electrochemistry. Only one example of the fixation of organic compounds has been published: the electrolysis of 1,4-benzoquinone, in the presence of CO_2, yielded 2,5-dihydrobenzoic acid.[5]

The present reaction system was constructed by postulating that when CO_2 is reductively fixed in an organic molecule, the enzyme is oxidized; the oxidized enzyme is to ultimately be reduced back to its original form by methylviologen cation radicals. The latter are produced at a glassy carbon cathode. Cyclic voltammograms taken in the presence and absence of CO_2 are shown in Figure 1. Solution conditions include 0.2 M tris buffer (pH 7.7, 0.2 M $NaHCO_3$), 1.0×10^{-4} M MV^{2+}, 1 unit of ICDH, and 1.0×10^{-2} M oxoglutaric acid. It is well-known that the cathodic current peaks at −0.75 and at −1.05 V are due to the reduction of MV^{2+} to $MV^{\bullet+}$ and $MV^{\bullet+}$ to MV^0, respectively. When CO_2 was introduced, these cathodic waves increased slightly, while the anodic waves were slightly suppressed. This suggests that CO_2 fixation could be accomplished with the above-postulated reaction scheme. The electrolysis experiments were carried out in a two compartment cell separated by a Nafion membrane at potentials sufficiently negative to reduce MV^{2+} to $MV^{\bullet+}$. One compartment contained 25 mL of the above described CO_2-saturated electrolyte solution to which selected concentrations of MV^{2+} were added. The other cell contained only the tris buffer. Reaction product analysis was carried out with liquid chromatography.

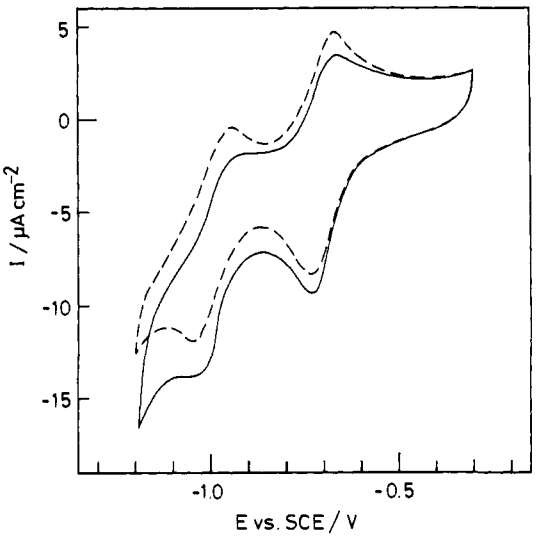

Figure 1. Cyclic voltammograms taken in 0.2 M tris buffer solutions (pH 7.7, 25 mL) containing 0.2 M $NaHCO_3$, 1.0×10^{-4} M MV^{2+}, 1 unit of ICDH, and 1.0×10^{-2} M oxoglutaric acid saturated with N_2 (−−) and CO_2 (—). Sweep rate was 10 mV s^{-1}. A glassy carbon electrode was used.

Table I. Electrochemical Fixation of Carbon Dioxide in Oxoglutaric Acid To Yield Isocitric Acid[a]

E (V vs SCE)	charge (C)	C (MV^{2+}) (M)	amount produced (μmol)	current efficiency (%) apparent	net
−0.75	0.88	1.0×10^{-4}	2.77	60.6	82.8
−0.85	1.53	1.0×10^{-4}	6.65	83.9	99.2
−0.95	1.65	1.0×10^{-4}	7.33	85.7	100
−0.95	1.60	5.0×10^{-5}	7.16	86.4	93.2
−0.95	1.45	2.0×10^{-5}	6.43	85.5	88.4
−0.95	0.96	1.0×10^{-5}	3.79	76.3	78.0

[a] The CO_2-saturated electrolyte (25 mL) was 0.2 M tris buffer containing 0.2 M $NaHCO_3$, 1 unit of ICDH, and 1×10^{-2} M oxoglutaric acid. Selected concentrations of MV^{2+} are given in the table.

Results obtained are shown in Table I. Both apparent and net current efficiencies are reported. The former was obtained by applying the coulombs consumed in the electrolysis to the amount of isocitric acid produced assuming that two electrons were involved in the fixation reaction. Current efficiencies >80% were achieved in each case. In the present reaction system, not MV^{2+} but $MV^{\bullet+}$ must be used to regenerate ICDH. Thus, a fraction of the total quantity of electricity consumed in the electrolysis can be attributed to the initial reduction of MV^{2+} to $MV^{\bullet+}$. This quantity (0.24 C for the case of 1×10^{-4} M MV^{2+}) is subtracted from the total numbers of coulombs to give net values. Net current efficiencies were then obtained as shown in Table I. Note that 100% net current efficiency is observed for the electrolysis at −0.95 V vs SCE in the presence of 1×10^{-4} M MV^{2+}. Decreases in MV^{2+} concentration reduce current efficiencies for CO_2 fixation. No fixation products were observed in the absence of MV^{2+}, indicating that MV^{2+} worked as an efficient mediator to recycle ICDH. Isocitric acid was produced in proportion to the electrolysis charge, judging from electrolysis results at −0.95 V vs SCE. If it is assumed that 1 unit of ICDH contains 1.5×10^{-9} mol of redox centers,[6] the turnover number of ICDH in the CO_2 fixation process amounts to more than 5500 for the case of electrolysis of 2.8 C.

The results shown here are significant for several reasons. Firstly, the electrolytic system does not require the use of $NADP^+$. $NADP^+$ normally plays an important role in vivo metabolic

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