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Kinetics of the Permanganate Oxidation of *endo*-Dicyclopentadiene in Nonaqueous Organic Solution. Formation and Detection of the Manganate(V) Ester Intermediate[1]

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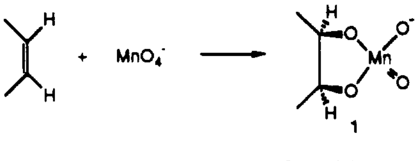
The kinetics of the formation process of the cyclic manganate(V) diester intermediate 1 observed during the permanganate ion oxidation of *endo*-dicyclopentadiene in dichloromethane with a quaternary ammonium salt was studied. The spectrophotometric behavior and the kinetic results of the intermediate formation are strikingly similar to those of the manganese species reported before as soluble (colloidal) manganese dioxide in other permanganate oxidations of double bonds. The manganate(V) ester intermediate is formed in first-order dependence on the concentration of the alkene at a rate faster than that of its decomposition into colloidal manganese dioxide which is also first-order dependent on the concentration of the alkene. It was pointed out that manganate(V) ester intermediates tend to be confused with soluble (colloidal) manganese dioxide because of the resemblance of UV-visible spectrum. The criteria to distinguish a manganate(V) ester from soluble (colloidal) manganese dioxide are proposed.

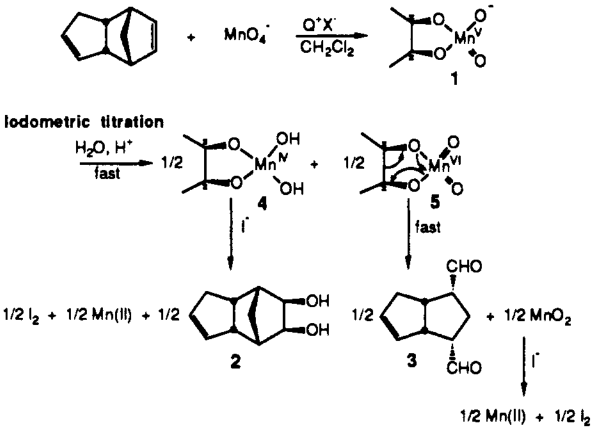
While it has been believed for nearly one century[2] that permanganate oxidation of carbon-carbon double bonds proceeds via the formation of cyclic manganate(V) diester intermediates 1 (eq 1), only recent reports have focused attention on their detection and real intermediacy.[3-5] In particular, considerable discussion has taken place on the oxidation state of the relatively stable manganese species which had been spectrophotometrically observed during the permanganate ion oxidation of carbon-carbon double bonds in phosphate-buffered solution[6,7] and in nonaqueous organic solution with quaternary ammonium salts.[8,9] More recently, it has been concluded by two groups,[10,11] on the basis of the fact that only 1.5-2.0 molar equiv of iodide ion was consumed by the intermediate during the iodometric titration, that the observed species is soluble (colloidal) manganese dioxide but not the cyclic manganate(V) intermediate 1 as originally thought.[6,9]



(1)

On the contrary, noting that the 1,2-diol 2 and the dialdehyde 3 were formed in a 1:1 ratio after the iodometric titration of the manganese intermediate obtained during the permanganate oxidation of *endo*-dicyclopentadiene (DCPD) in dichloromethane, we proposed in the previous paper[1] a mechanism in which the detected intermediate is still the cyclic manganate(V) ester 1 even though only 2.0 molar equiv of iodide were consumed by the intermediate (Scheme I). This result and the disagreement about the nature of the "detectable intermediate" with other reports prompted us to report the details of the spectrophotometric and kinetic features of the formation of our intermediate which are strikingly similar to those of the manganese species reported as soluble (colloidal) manganese dioxide.[7,9-11]

Scheme I



Experimental Section

The solvent (dichloromethane) was purified before use by refluxing with potassium permanganate and benzyltriethylammonium chloride followed by distillation from the solution. *endo*-Dicyclopentadiene (DCPD) was purified by distillation using a 20-cm Vigreux column. The quaternary ammonium halides (Q^+X^-) and potassium permanganate (analytical grade) were obtained from Tokyo Kasei Kogyo Co. and Wako Junyaku Co., respectively, and used without purification.

Solutions were prepared as follows. Powdered potassium permanganate (1 mmol) and a quaternary ammonium halide (2 mmol) were dissolved in dichloromethane (10 mL), and the solution was allowed to stand overnight in a refrigerator. The concentration of permanganate ion was adjusted by dilution and determined accurately by iodometric titration or spectrophotometric method immediately before use.

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(1) Homogeneous Permanganate Oxidation in Nonaqueous Organic Solution. 5. Part 4: Ogino, T.; Kikuiri, N. *J. Am. Chem. Soc.* **1989**, *111*, 6174.

(2) G. Wagner, J. *Russ. Phys. Chem. Soc.* **1895**, *27*, 219.

(3) Wiberg, K. B.; Deutsch, C. J.; Roček, J. *J. Am. Chem. Soc.* **1973**, *95*, 3034.

(4) Lee, D. G.; Brownridge, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 3033; **1974**, *96*, 5517.

(5) Simándi, L. I.; Jáky, M. *J. Am. Chem. Soc.* **1976**, *98*, 1955.

(6) (a) Freeman, F.; Fuselier, C. O.; Karchefski, E. M. *Tetrahedron Lett.* **1975**, 2133. (b) Freeman, F.; Karchefski, E. M. *Biochim. Biophys. Acta* **1976**, *447*, 238.

(7) (a) Simándi, L. I.; Jáky, M.; Freeman, F.; Karchefski, E. M. *Inorg. Chim. Acta* **1978**, *31*, L457. (b) Freeman, F.; Fuselier, C. O.; Armstead, C. R.; Dalton, C. E.; Davidson, P. A.; Karchefski, E. M.; Krochman, D. E.; Johnson, M. N.; Jones, N. K. *J. Am. Chem. Soc.* **1981**, *103*, 1154.

(8) (a) Ogino, T.; Mochizuki, K. *Chem. Lett.* **1979**, 443. (b) Ogino, T. *Tetrahedron Lett.* **1980**, *21*, 177.

(9) Lee, D. G.; Brown, K. C. *J. Am. Chem. Soc.* **1982**, *104*, 5076.

(10) (a) Freeman, F.; Kappos, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6628. (b) Freeman, F.; Kappos, J. C. *J. Org. Chem.* **1986**, *51*, 1654. (c) Freeman, F.; Chang, L. Y. *J. Am. Chem. Soc.* **1986**, *108*, 4504. (d) Freeman, F.; Chang, L. Y.; Kappos, J. C.; Sumarta, L. J. *J. Org. Chem.* **1987**, *52*, 1460.

(11) (a) Lee, D. G.; Perez-Benito, J. F. *Can. J. Chem.* **1985**, *63*, 1275. (b) Perez-Benito, J. F.; Lee, D. G. *Can. J. Chem.* **1985**, *63*, 3545. (c) Lee, D. G.; Brown, K. C.; Karaman, H. *Can. J. Chem.* **1986**, *64*, 1054.

0022-3263/90/1955-2653$02.50/0

Table I. Kinetic Data for the Oxidation of DCPD by Permanganate Ion in CH_2Cl_2 with $PhCH_2(Et)_3NCl$ at 25 °C

no.	[DCPD] × 10^3, M	[$KMnO_4^-$] × 10^4, M	k_ψ × 10, s^{-1}		k_2, M^{-1} s^{-1}	
			420 nm	525 nm	420 nm	525 nm
	3.82	2.45	1.04	1.07		
1	5.09	2.45	1.35	1.36	26.2	26.9
	7.65	2.45	1.90	1.98		
	3.82	2.45	1.05	1.06		
2	5.09	2.45	1.34	1.34	26.5	27.1
	7.65	2.45	1.96	2.08		
	3.82	2.44	1.03	1.05		
3	5.09	2.44	1.34	1.34	26.1	26.8
	6.37	2.44	1.59	1.69		
	4.30	2.91	1.20	1.19		
4	5.83	2.91	1.61	1.61	27.6	27.9
	6.80	2.91	1.86	1.93		
	3.55	2.49	0.972	0.988		
5	4.88	2.49	1.38	1.39	27.7	27.9
	6.01	2.49	1.65	1.64		
average					26.8 ± 0.7	27.3 ± 0.5

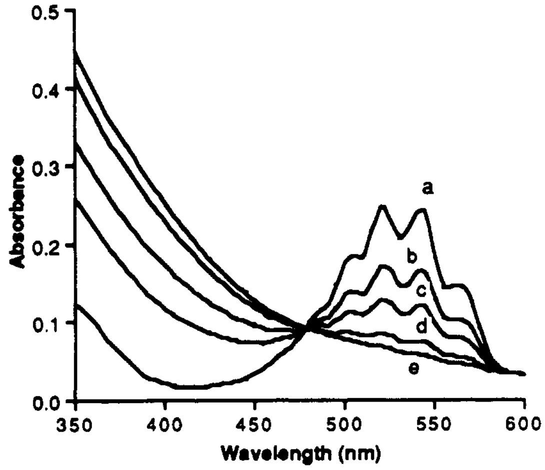


Figure 1. Repetitive scan of absorbance for the reaction of permanganate ion with DCPD in CH_2Cl_2 at 25 °C: (a) 0 s; (b) 16 s; (c) 32 s; (d) 65 s; (e) 97 s. $[KMnO_4]_0 = 0.90 \times 10^{-4}$ M, $[DCPD]_0 = 1.63 \times 10^{-3}$ M, $Q^+X^- = Et_4NBr$.

The ultraviolet–visible spectra were determined by continuous scanning on a modified Union Giken MCPD-350PC multichannel spectrophotometer.

The kinetics were determined with a Union Giken MX-7-01 stopped-flow reactor in a Hitachi Model 210 spectrophotometer which was connected to a Sharp MZ-80B personal computer and its peripherals. The temperature was maintained with a refrigerated and heated bath circulator.

The reactions were performed under pseudo-first-order conditions by use of a large excess of DCPD and monitored by the measurement of absorbance at 420 nm (formation of the intermediate) and 525 nm (disappearance of permanganate ion). The observed values of the absorbance were taken into the computer (8 or 16 data/s) and then recorded on a X/Y plotter as plots against time after required corrections and/or conversions into logarithms (Figure 2 and Figure 3).

Results and Discussion

Figure 1 shows the spectral changes monitored for the reaction of permanganate ion with DCPD by repetitive scanning during the period of 0–97 s. An isosbestic point was observed at 480 nm, and these changes are remarkably similar to those reported for the oxidation of uracils in phosphate buffered solution[7] and the oxidation of methyl cinnamate in dichloromethane solution.[9] Despite the instability of the intermediate noted previously, the isosbestic point could be observed irrespective of the rate of the intermediate formation, which can be controlled by changing the concentration of the alkene as described below. A simple interpretation for this is obtained if one assumes that both the rates of the formation and the decomposition are dependent on the concentration of the alkene, i.e., the slower formation then the slower decomposition. First-order dependence of the decay of the intermediate on the alkene concentration has been shown previously.[1]

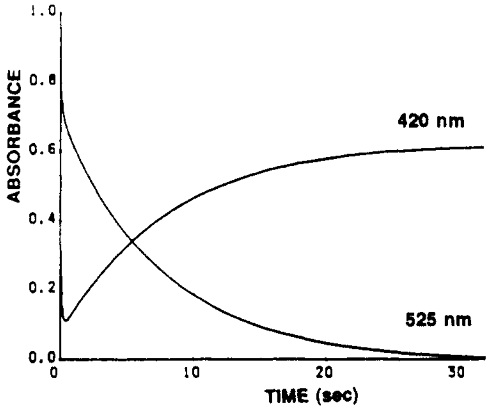


Figure 2. Plots of absorbance vs time showing the appearance of the manganate(V) ester intermediate (420 nm) and the disappearance of permanganate ion (525 nm) at 25 °C. The 525-nm plot is corrected by reducing the contribution of the forming intermediate to the absorbance at this wavelength. $[KMnO_4]_0 = 2.49 \times 10^{-4}$ M, $[DCPD]_0 = 4.88 \times 10^{-3}$ M, $Q^+X^- = PhCH_2(Et)_3NCl$.

Figure 2 shows the disappearance of permanganate ion monitored at 525 nm and the formation of the manganate(V) ester intermediate measured 420 nm by the stopped-flow technique. The plots at 525 nm were corrected in the computer by subtracting the contribution of the growing intermediate to the absorbance at this wavelength so that the curve represents the decrease of net absorbance of permanganate ion. The reactions were carried out under pseudo-first-order conditions, and the corresponding rate plots were obtained by converting the ordinates to log A or log $(A_\infty - A)$ as shown in Figure 3. Both the plots at 420 nm and at 525 nm showed good linearity until 85–90% conversion and agreement of the slopes. The pseudo-first-order rate constants (k_ψ) calculated from the slope of the plots were found to be proportional to the concentration of DCPD, indicating that the reaction is also first-order dependent on the alkene concentration (Figure 4). A second-order rate constant

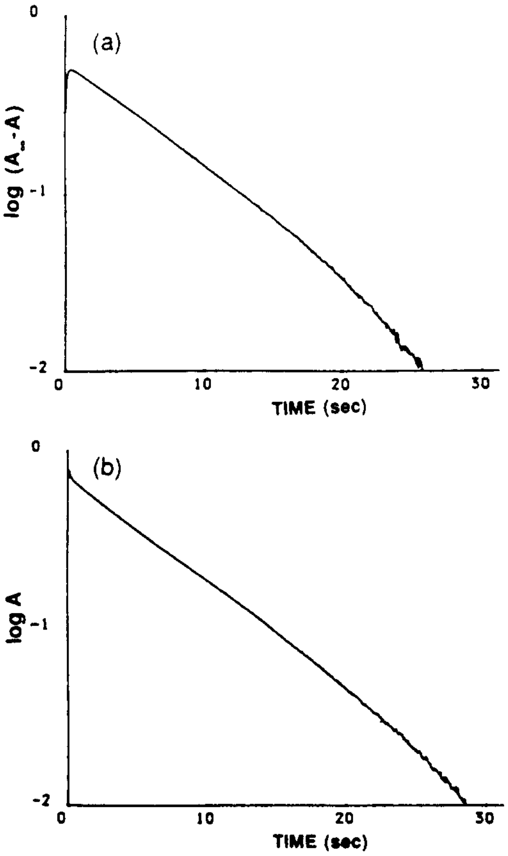


Figure 3. Typical pseudo-first-order rate plots for the reaction of permanganate ion with DCPD in CH_2Cl_2 at 25 °C: (a) at 420 nm; (b) at 525 nm. $[KMnO_4]_0 = 2.49 \times 10^{-4}$ M, $[DCPD]_0 = 4.88 \times 10^{-3}$ M.

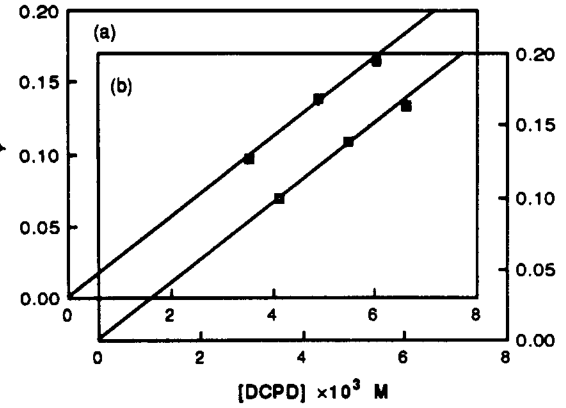


Figure 4. Dependence of the pseudo-first-order rate constants (k_ψ) for the formation of the manganate(V) ester intermediate on DCPD concentration in CH_2Cl_2 at 25 °C: (a) at 420 nm, slope = 27.7; (b) at 525 nm, slope = 27.9 $[KMnO_4]_0 = 2.49 \times 10^{-4}$ M, $Q^+X^- = PhCH_2(Et)_3NCl$.

(k_2) was obtained as the slope of a plot of k_ψ vs [DCPD], which passes through the origin. The final values of k_2 were determined as the average of five experiments, each of which is consist of three kinetic measurements with varied concentration of DCPD (Table I). It is noted that the values of k_2 obtained at 420 and 525 nm are also in good agreement with each other.

Table II summarizes the second-order rate constants thus obtained at various temperature. Two sets of the activation parameters of the reaction were obtained from the plots of ln (k_2/T) vs $1/T$ at 420 and 525 nm (Figure 5) in good agreement, and the results are summarized in Table III with those reported by other workers for the permanganate oxidation of double bonds under various conditions. A comparison of these data, when combined with the resemblance of the spectrophotometric behaviors, suggests that these reactions proceed in the same manner and the manganese species detected in these reactions are all similar to each other. Since our previous studies on the oxidation state and kinetics for the decay reaction of the intermediate[1,12] strongly suggested that the initially observed manganese species is the cyclic manganate(V) diester ion intermediate 1, it also appeared that those observed in the other permanganate ion oxidations[7,9-11] are the manganate(V) intermediates, but not manganese dioxide. The oxidation state of these manganese species should be reexamined by analysis of the organic products formed after iodometry.

Table II. Rate Constants at Various Temperatures

temp, K	k_2 420 nm	k_2 525 nm
290.2	22.1 ± 1.1	22.3 ± 1.0
293.2	23.5 ± 1.2	24.0 ± 1.1
298.2	26.8 ± 0.7	27.3 ± 0.5
301.2	29.1 ± 0.6	29.4 ± 0.3

Table III. Activation Parameters for the Formation of the Spectrophotometrically Detectable Intermediate in the Permanganate Oxidation of Double Bonds

alkene	media	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, eu
endo-dicyclopentadiene[a] (420 nm)	CH_2Cl_2, Q^+X^-	3.8 ± 0.5	−39.3 ± 1.5
endo-dicyclopentadiene[a] (525 nm)		3.78 ± 0.03	−39.3 ± 0.1
methyl cinnamate[b]	CH_2Cl_2, Q^+X^-	5.6 ± 0.8	−38 ± 3
uracil[c]	H_2O, pH 6.7	5.3 ± 0.8	−40 ± 3
cinnamic acid[d]	H_2O, acidic	4.2 ± 0.5	−30 ± 2

[a] This work. [b] Reference 9. [c] Reference 7. [d] Reference 4.

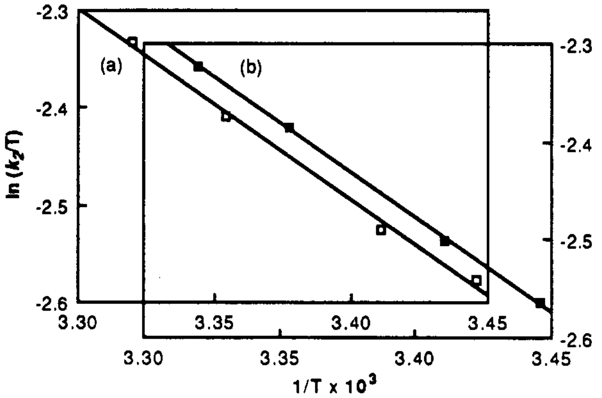
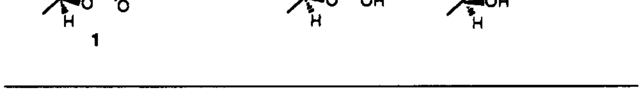


Figure 5. Plots for determining the activation parameters for the intermediate formation: (a) at 420 nm, slope = −1.90 ± 0.23, intercept = 3.98 ± 0.78, correlation coefficient = 0.998; (b) at 525 nm, slope = −1.900 ± 0.014, intercept = 3.98 ± 0.05, correlation coefficient = 1.

Soluble (colloidal) manganese dioxide is actually formed after the decomposition of the manganate(V) intermediate 1 via abstraction of a hydrogen or an electron from excess alkene in dichloromethane at a rate slower than that of the intermediate formation (eq 2).[1] One must be careful



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(12) Ogino, T.; Kazama, T.; Kobayashi, T. *Chem. Lett.* **1985**, 1863.

so as not to confuse the manganate(V) ester intermediate with soluble (colloidal) manganese dioxide since the UV–visible spectrum of soluble (colloidal) manganese dioxide appears similar to those of the manganate(V) intermediate 1 if compared at $\lambda > 300$ nm. The manganate(V) intermediate can be distinguished from soluble (colloidal) manganese dioxide by the following criteria: (1) spectra of the manganate(V) esters have a clear absorption maximum at ca. 280 nm[6–8] while soluble (colloidal) manganese dioxide shows no maximum in its spectrum;[1] (2) plots of log A vs log λ ($\lambda > 300$ nm) for colloidal manganese dioxide give a straight line with a slope near to -4 as expected from Raileigh's Law ($A = C/\lambda^4$)[13] for colloidal solutions,[14] while the plots for the manganate(V) ester intermediates give the line with a slope steeper than -5;[10,11] (3) soluble (colloidal) manganese dioxide often shows an increase in absorbance at all wavelength on standing due to flocculation, while the manganate(V) intermediate shows decrease in absorbance due to the decomposition reaction.[1,12]

From these criteria, it appears that the manganese species observed during the reaction of permanganate ion with alkynes in dichloromethane[15] or with trimethylamine[16] in aqueous phosphate buffers are mainly colloidal manganese dioxide. In those cases, the decomposition rates of initially formed manganate(V) intermediates may be faster than those of the formation because of the instability of the intermediate itself or the high reducing power of the reductant used in excess. However, the manganese species observed during the permanganate oxidation of alcohols in dichloromethane with a quaternary ammonium salt appears to be also a manganate(V) compound.[17]

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[13] Barrow, G. M. *Physical Chemistry*, 2nd ed.; McGraw-Hill: New York, 1966; p 803.

[14] See footnote 22 in ref 1.

[15] Lee, D. G.; Lee, E. J.; Chandler, W. D. *J. Org. Chem.* **1985**, *50*, 4306.

[16] Mata-Perez, F.; Perez-Benito, J. F. *Can. J. Chem.* **1985**, *63*, 988.

[17] Ogino, T.; Kikuiri, N. Unpublished observations.

Photocatalyzed and Electrocatalyzed Reduction of *vic*-Dibromides and Activated Ketones Using Ruthenium(I) Tris(bipyridine) as Electron-Transfer Mediator

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Effective photosensitized reduction of *vic*-dibromo and keto compounds occurs in acetonitrile solutions that include ruthenium(II) tris(bipyridine) (Ru(bpy)$_3^{2+}$) as photosensitizer and triethylamine (TEA) as electron donor. (*R*,*S*)-1,1′-(1,2-Dibromo-1,2-ethanediyl)bis(benzene) (**1**) and (*R*,*R*:*S*,*S*)-1,1′-(1,2-dibromo-1,2-ethanediyl)bis(benzene) (**2**) are debrominated to a mixture of (*E*)- (**5**) and (*Z*)-1,1′-(1,2-ethenediyl)bis(benzene) (**6**); $\phi = 0.34$ for **1** and $\phi = 0.24$ for **2**. Ethyl α,β-dibromobenzenepropionate (**3**) and (α,β-dibromo-α,β-dihydro-1-propenyl)benzene (**4**) are debrominated to (*E*)-ethyl α,β-didehydrobenzenepropionic acid (**7**), $\phi = 1.87$, and (*E*)-1-propenylbenzene (**8**), $\phi = 0.08$. The mixture of **5** and **6** formed upon debromination of **1** and **2** undergoes isomerization in the reaction medium to **6** through an energy-transfer mechanism. Debromination of the substrates occurs through the photosensitized formation of Ru(bpy)$_3^+$ ($E° = -1.33$ V vs SCE), which acts as an electron-transfer mediator in the process. The rates of the debromination processes are controlled by the primary reduction of the dibromo compounds by Ru(bpy)$_3^+$, except for **3** as substrate, where a radical chain mechanism is suggested. Cyclic voltammetry measurements reveal that Ru(bpy)$_3^+$ acts as catalyst in the debromination processes. Similarly, activated ketones, i.e., diphenylethanedione (**9**) and ethyl α-oxobenzeneacetate (**10**) are reduced by photogenerated Ru(bpy)$_3^+$ to 2-hydroxy-1,2-diphenylethanone (**11**), $\phi = 0.025$, and ethyl α-hydroxybenzeneacetate (**12**), $\phi = 0.049$.

Organic transformations catalyzed by photochemically and electrochemically induced electron-transfer reactions are a subject of extensive recent research efforts.[1–3] Photosensitized electron-transfer reactions using sacrificial electron donors were mainly examined in aqueous media.[4,5] The resulting photoproducts were applied in H_2 evolution,[6,7] CO_2 reduction,[8,9] and hydrogenation of gaseous unsaturated organic substrates.[10] Application of photosensitized electron-transfer reactions in organic transformations is limited due to the poor solubility properties of the organic substrates in water. Several approaches that

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[1] Julliard, M.; Chanon, M. *Chem. Rev.* **1983**, *83*, 425.

[2] (a) Fox, M. A. *Acc. Chem. Res.* **1983**, *16*, 314. (b) Fox, M. A. *Top. Curr. Chem.* **1988**, *71*, 142.

[3] Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, 403.

[4] (a) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. (b) Darwent, J. R.; Douglas, P.; Harriman, A.; Porter, G.; Richoux, M.-C. *Coord. Chem. Rev.* **1982**, *44*, 83.

[5] (a) Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717. (b) Sutin, N. *J. Photochem.* **1979**, *10*, 19.

[6] (a) Willner, I.; Steinberger-Willner, B. *Int. J. Hydrogen Energy* **1988**, *13*, 593. (b) *Photogeneration of Hydrogen*; Harriman, A., West, M. E., Eds.; Academic Press: London, 1983. (c) *Energy Resources through Photochemistry and Catalysis*; Grätzel, M., Ed.; Academic Press: New York, 1983.

[7] Gray, H. B.; Maverick, A. W. *Science* **1981**, *214*, 1201.

[8] (a) Willner, I.; Mandler, D. *J. Am. Chem. Soc.* **1989**, *111*, 1330. (b) Maidan, R.; Willner, I. *J. Am. Chem. Soc.* **1986**, *108*, 8100. (c) Willner, I.; Maidan, R.; Mandler, D.; Dürr, H.; Dörr, G.; Zengerle, K. *J. Am. Chem. Soc.* **1987**, *109*, 6080.

[9] Mandler, D.; Willner, I. *J. Chem. Soc., Perkin Trans. 2* **1988**, 997.

[10] (a) Degani, Y.; Willner, I. *J. Chem. Soc., Perkin Trans. 2* **1986**, 37. (b) Mandler, D.; Willner, I. *J. Phys. Chem.* **1987**, *91*, 3600. (c) Willner, I.; Maidan, R. *J. Chem. Soc., Chem. Commun.* **1988**, 876.

0022-3263/90/1955-2656$02.50/0