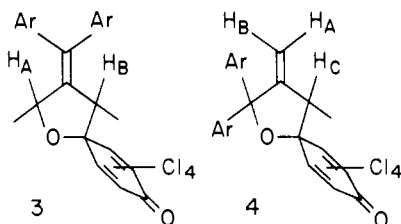


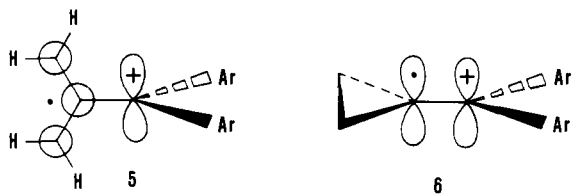
**Figure 1.**  $^1\text{H}$  NMR spectra (90 MHz) of an acetone- $d_6$  solution containing 0.02 M chloranil and 0.02 M 2,2-dianisyl-1-methylenecyclopropane (**1**, Ar =  $\text{C}_6\text{H}_4\text{OCH}_3$ ) in the dark (bottom) and during UV irradiation (top).



the two pairs of protons have the same signal direction and comparable enhancements. This finding suggests a common intermediate for the regeneration of **1** and for the formation of **3** and **4**. On the other hand, the fact that **1** shows emission, whereas **3** and **4** show enhanced absorption (Figure 1), suggests that two different pathways exist between this intermediate and the "products."

Two of the polarization-determining parameters,<sup>12</sup> the initial spin multiplicity of the radical ion pairs ( $\mu > 0$ ) and the relative magnitude of their  $g$  factors ( $\Delta g < 0$ ), can be assigned unambiguously. The observed rearrangement<sup>3</sup> and the polarization suggest that the methylene carbons bear positive spin density and that their protons have negative hyperfine coupling constants ( $a < 0$ ). Given these parameters, the signal direction of the adducts is compatible with singlet recombination ( $\epsilon > 0$ ) of the intermediate radical ion pairs, whereas the starting material most likely is regenerated after separation of the geminate radical ion pairs ( $\epsilon < 0$ ).

On the basis of these considerations, we propose a trimethylenemethane radical cation (**5**) in which the spin density



(11) The adducts are characterized by the following data. **3**: mp 153–155 °C (colorless needles);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.22 (2 H, dd), 3.80 (6 H, s), 4.98 (2 H, dd), 6.81–7.08 (8 H, m); mass spectrum,  $m/e$  (25 eV, 120 °C) 514 ( $\text{M}^+ + 2$ , 7.1%), 512 ( $\text{M}^+$ , 12.7%), 510 (11.6%), 267 (100%), 251 (17.8%), 235 (35.0%); IR (KBr) 1685, 1600, 1580, 1508, 1280, 1240  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{24}\text{H}_{18}\text{O}_4\text{Cl}_4$ : C, 56.28; H, 3.54. Found: C, 56.46; H, 3.64. **4**: mp 194–196 °C dec (colorless needles);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.40 (2 H, dd), 3.80 (6 H, s), 5.25 (1 H, td), 5.50 (1 H, td), 6.80–7.33 (8 H, m); mass spectrum,  $m/e$  (25 eV, 120 °C), 514 ( $\text{M}^+ + 2$ , 31.3%), 512 ( $\text{M}^+$ , 55.8%), 510 (49.1%), 405 (26.3%), 267 (100%), 235 (30.8%), 214 (45.9%), 135 (54.9%); IR (KBr) 1680, 1608, 1578, 1508, 1280, 1250  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{24}\text{H}_{18}\text{O}_4\text{Cl}_4$ : C 56.28; H, 3.54. Found: C, 56.25; H, 3.65.

(12) Kaptein, R. *J. Chem. Soc., Chem. Commun.* 1971, 732–733.

is primarily localized in an allyl moiety, whereas the charge is primarily localized in a diarylmethylene group attached in the 2-position.<sup>13</sup> The previously proposed perpendicular (bisected) arrangement<sup>3</sup> of the two  $\pi$  systems is consistent with the apparent localization of spin and charge. This type of intermediate is also favored as the least motion intermediate; its formation requires only rotation of the methylene group and not of the bulkier diphenylmethylene moiety.

Further insight into this system is provided by the photoreaction of chloranil with **2**, which gives rise to strong emission for the cyclopropane singlet but does not result in any phenyl polarization. Moreover, this reaction does not produce any evidence for rearrangement to **1**. For the analysis of this polarization,  $\mu$  ( $> 0$ ) and  $\Delta g$  ( $< 0$ ) once again are unambiguous. The signal direction is then compatible either with singlet recombination ( $\epsilon > 0$ ) and positive hfc's or with triplet recombination ( $\epsilon < 0$ ) and negative hfc's. The latter combination of parameters is unlikely, since negative hfc's are characteristic for the ring-opened trimethylenemethane radical cation **5**, which generates **1** as well as **3** and **4**, none of which are observed. Accordingly, we assign positive hfc's to the intermediate and identify it as belonging to a principally different structure type, **6**, which is in essence a diphenylethylene radical cation. The electron spin is localized principally on the tertiary cyclopropane carbon whereas the charge is localized in the diarylmethyl moiety. The cyclopropane bonds are not involved in delocalizing either charge or spin. This assignment is supported by photoreaction of chloranil with 1,1-diphenyl-2-methylpropene, formally a hydrogenolysis product of **2**. The CIDNP effects observed in this reaction are quite analogous to the results observed for **2**: the allylic (methyl) protons show strong emission, whereas no polarization is observed for the phenyl groups.

The results reported here provide yet another example of two different radical cation structures derived from the same carbon skeleton. The accessibility of the structures is governed by substituent effects. For the radical cation of **2** the geminal pair of aryl substituents restricts spin and charge to the  $\pi$  system, whereas the highly delocalized species **5** results from the interaction of the aromatic  $\pi$  system with the Walsh orbitals of the cyclopropane ring.

(13) This charge distribution shows a similar trend as that derived for the 1,1-diphenylallyl cation (Olah, G. A.; Spear, R. J. *J. Am. Chem. Soc.* 1975, 97, 1539–1546), but **5** shows an even stronger localization of the charge.

## Dependence of Rate Constants for Photoinduced Charge Separation and Dark Charge Recombination on the Free Energy of Reaction in Restricted-Distance Porphyrin–Quinone Molecules

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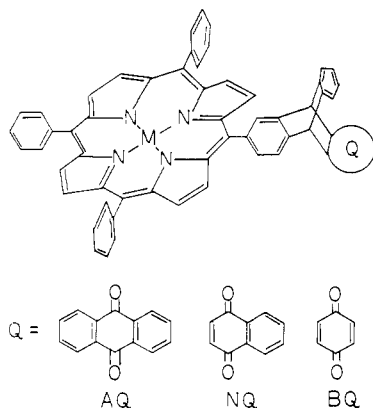
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The primary electron-transfer event of photosynthesis involves oxidation of the lowest excited singlet state of a chlorophyll electron donor by a nearby electron acceptor.<sup>1</sup> The distance between the donor and the acceptor is restricted by the surrounding reaction center protein. We recently prepared a series of restricted-distance porphyrin–quinone donor–acceptor molecules designed to study electron-transfer proceeding from the lowest excited singlet state of the porphyrin (Figure 1).<sup>2</sup> We now report that the rate constants for both radical ion pair formation and recombination in these molecules depend on the exothermicity of the respective

(1) Holten, D.; Hoganson, C.; Windsor, M. W.; Schenck, C. C.; Parson, W. W.; Migus, A.; Fork, R. L.; Shank, C. V. *Biochim. Biophys. Acta* 1980, 592, 461.

(2) Wasielewski, M. R.; Niemczyk, M. P. *J. Am. Chem. Soc.* 1984, 106, 5043.



**Figure 1.** Structures of the zinc,  $M = \text{Zn}$ , and free base,  $M = 2\text{H}$ , *meso*-triphenyltriptycenequinones: TPPAQ, TPPNQ, TPPBQ, ZnTPPAQ, ZnTPPNQ, and ZnTPPBQ, where the fused quinones are anthraquinone, AQ, naphthoquinone, NQ, or benzoquinone, BQ.

electron-transfer reaction in the manner originally proposed by Marcus and later modified and extended by others.<sup>3</sup>

The porphyrin-quinone molecules were excited with a 2-ps laser flash at 600 nm. The formation and decay of the porphyrin-quinone radical pair state was monitored at 460 and 650 nm with a 2-ps broad-band probe light pulse as described previously.<sup>2</sup> Measurements were performed at 21 °C in toluene ( $\epsilon = 2.4$ ) and in butyronitrile ( $\epsilon = 20$ ). Each transient was analyzed by using the treatment of Provencher and could be described by a single exponential rise or decay.<sup>4</sup> It is important to note that the radical ion pair state of each molecule decays cleanly to ground state with no evidence of excited-state formation.<sup>2</sup>

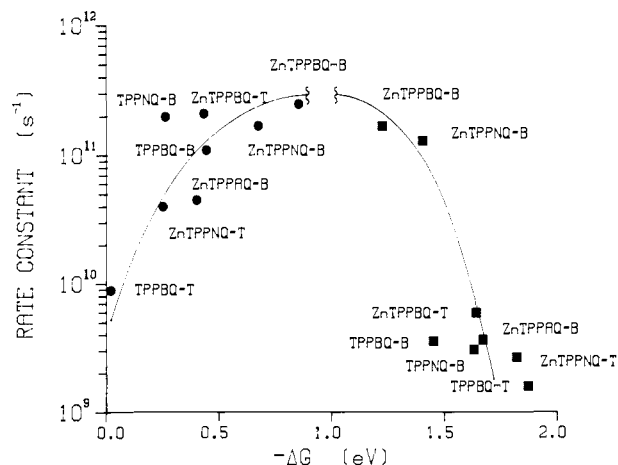
The exothermicity of the charge separation,  $-\Delta G_{\text{cs}}$ , and that of the charge recombination,  $-\Delta G_{\text{cr}}$ , were obtained from eq 1 and 2, respectively, where  $E(S_1)$  is the energy of the lowest excited

$$-\Delta G_{\text{cs}} = E(S_1) - E_{\text{D}}^{\text{ox}} + E_{\text{A}}^{\text{red}} + \Delta G(\epsilon) \quad (1)$$

$$-\Delta G_{\text{cr}} = E_{\text{D}}^{\text{ox}} - E_{\text{A}}^{\text{red}} - \Delta G(\epsilon) \quad (2)$$

singlet state of the molecule,  $E_{\text{D}}^{\text{ox}}$  and  $E_{\text{A}}^{\text{red}}$  are the measured  $E_{1/2}$  values for the one-electron oxidation and reduction of the porphyrin donor and quinone acceptor, respectively,<sup>2</sup>  $\epsilon$  is the solvent dielectric constant, and  $\Delta G(\epsilon)$  is a term that incorporates both the solvent-dependent Coulomb energy change upon ion pair formation or recombination and the free energy of solvation of the ions.  $\Delta G(\epsilon)$  was evaluated by using the recent treatment of Weller which is based upon application of the Born equation.<sup>5</sup> With reference to eq 16 in Weller's paper, an ionic distance  $a = 10.5 \text{ \AA}$  and an average ionic radius of  $5.2 \text{ \AA}$  were used to calculate  $\Delta G(\epsilon) = -0.45 \text{ eV}$  for toluene and  $-0.03 \text{ eV}$  for butyronitrile. The correction for toluene agrees well with the fact that we did not observe radical ion pair state formation whenever  $E(S_1) < E_{\text{D}}^{\text{ox}} - E_{\text{A}}^{\text{red}} + 0.4 \text{ eV}$ .<sup>2</sup>

Figure 2 is a plot of rate constant vs. reaction exothermicity for both radical ion pair formation from the lowest excited singlet state of the porphyrin and for radical ion pair recombination leading back to the ground states of the donor and the acceptor.<sup>6</sup> At the  $10.5 \pm 0.5 \text{ \AA}$  donor-acceptor distance<sup>7</sup> in these molecules the charge separation rate constants for  $-\Delta G > 0.4 \text{ eV}$  approach the  $(2\text{--}4) \times 10^{11} \text{ s}^{-1}$  rate constants observed for the primary charge



**Figure 2.** Plot of rate constant vs. exothermicity for the reaction  ${}^1\text{P}^* - \text{Q} \rightarrow \text{P}^+ - \text{Q}^-$  and for  $\text{P}^+ - \text{Q}^- \rightarrow \text{P} - \text{Q}$ , where P = porphyrin and Q = quinone. The B and T after the name of the compounds indicate data obtained in butyronitrile or in toluene, respectively. The maximum uncertainty in any given rate constant is  $\pm 20\%$ .

separation of photosynthesis.<sup>1</sup>

Plotted on the same graph are the rate constants for the subsequent radical ion pair recombination reaction. Since each of these reactions proceeds directly to the ground electronic state without intermediate excited-state formation, the charge recombination rate constants can be measured at high exothermicities. The rate constant for this process dramatically decreases over 2 orders of magnitude as the exothermicity of the recombination reaction increases.

This large decrease in rate is predicted by theory and results from increasingly unfavorable Franck-Condon factors between the radical ion pair state and the corresponding neutral ground state.<sup>3</sup> Miller et al. recently observed solvent-dependent 30–500-fold decreases in rate for highly exothermic electron transfer over a fixed  $15\text{-\AA}$  distance between aromatic radical anions and neutral molecules.<sup>8</sup> The electron-transfer rate constants observed in that work are about 1000 times smaller than those reported here presumably because the anion-neutral molecule distance is longer than the porphyrin-quinone distance, 15 vs.  $10.5 \text{ \AA}$ , respectively. Both of these fundamentally different experiments demonstrate that a key prerequisite for clear observation of the so-called inverted region in the rate vs.  $-\Delta G$  dependence is the elimination of diffusion control of the electron-transfer kinetics.<sup>3j</sup> This is highlighted by the fact that several of our measured rate constants are faster than the diffusion-control limit.

Although the charge separation and recombination reactions involve different electronic states of the porphyrin donor, the dependences of the rate constants for each reaction on exothermicity shown in Figure 2 reach a common maximum at about  $k = 2.5 \times 10^{11} \text{ s}^{-1}$  and  $-\Delta G = 0.9 \text{ eV}$ . This is reasonable because the nuclear configuration and hence the vibrational energy level structure of the lowest excited  $\pi^*$  singlet states of rigid molecules with extended  $\pi$  systems, e.g., porphyrins,<sup>9</sup> is often very similar to that of the ground singlet state. By use of this assumption the maximum of the curve at about  $-\Delta G = 0.9 \text{ eV}$  can be interpreted as the approximate total reorganization energy for both the charge separation and recombination reactions.<sup>3</sup>

The question remains as to what fraction of this energy change is due to relaxation processes involving the solvent vs. the porphyrin-quinone molecules. Interestingly, the measured reorganization energy is approximately solvent independent. The fastest electron transfers may be competing with dielectric relaxation of the solvent<sup>10</sup> and with vibrational relaxation<sup>11</sup> within the porphyrin-quinone molecules. These effects would tend to reduce

(3) (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966. (b) Levich, V. O. *Adv. Electrochem. Electrochem. Eng.* **1966**, *4*, 249. (c) Dogonodze, R. R. In "Reactions of Molecules at Electrodes"; Hush, N. S., Ed.; Wiley-Interscience: New York, 1971. (d) Van Duyne, R. P.; Fischer, S. F. *Chem. Phys.* **1974**, *5*, 183. (e) Kestner, N. R.; Logan, J.; Jortner, J. *J. Phys. Chem.* **1974**, *78*, 2148. (f) Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358. (g) DeVault, D. *Q. Rev. Biophys.* **1980**, *13*, 387. (h) Redi, M.; Hopfield, J. *J. Chem. Phys.* **1980**, *72*, 6651. (i) Brunschwig, B. S.; Logan, J.; Newton, M. D.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 5798. (j) Marcus, R. A.; Siders, P. *J. Phys. Chem.* **1982**, *86*, 622.

(4) Provencher, S. W. *J. Chem. Phys.* **1976**, *64*, 2772.

(5) Weller, A. *Z. Phys. Chem. (Wiesbaden)* **1982**, *133*, 93.

(6) The curves drawn in Figure 2 for both the charge separation and the charge recombination data are each the best fit to a quadratic function.<sup>3a</sup>

(7) The donor-acceptor distances were estimated by using Corey-Pauling-Koltun molecular models.

(8) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047.

(9) Seybold, P. G.; Goutermann, M. *J. Mol. Spectrosc.* **1969**, *31*, 1.

(10) Huppert, D.; Kanety, H.; Kosower, E. M. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 161.

the solvent dependence. However, this is not a complete explanation. Comparisons between X-ray structural data of porphyrins and porphyrin radical cations show that oxidation results in little change in nuclear configuration.<sup>10</sup> Similarly, IR and Raman spectroscopic evidence suggests that reduction of quinones to their radical anions principally results in changes in the C-O distance.<sup>11</sup> These data point back to the solvent as a principal contributor to the reorganization energy. Current work is focusing on these problems.

In conclusion, two principal features of these molecules allow us to clearly observe inverted rate vs.  $-\Delta G$  behavior at high exothermicities. First, the donor-acceptor distance is restricted, and, second, the highly exothermic charge recombination reactions do not produce electronically excited states of the donor or acceptor.

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- (11) Bixon, M.; Jortner, J. *Faraday Discuss. Chem. Soc.* 1982, 74, 17.  
 (12) Spaulding, L. D.; Eller, P. G.; Bertrand, J. A.; Felton, R. H. *J. Am. Chem. Soc.* 1974, 96, 982.  
 (13) (a) Clark, B. R.; Evans, D. H. *J. Electroanal. Chem. Interfacial Electrochem.* 1976, 69, 181. (b) Tripathi, G. N. R. *J. Chem. Phys.* 1981, 74, 6044.

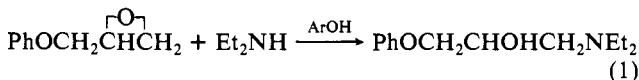
### 1,8-Biphenylenediol Is a Double-Hydrogen-Bonding Catalyst for Reaction of an Epoxide with a Nucleophile

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The reaction of phenyl glycidyl ether with diethylamine in butanone solution is catalyzed by hydroxyl compounds, with the

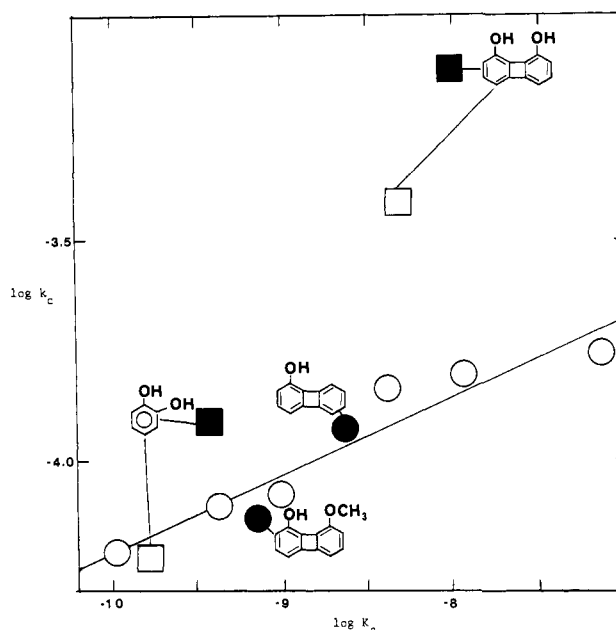


catalytic activity of meta- and para-substituted phenols increasing with their increasing acidity.<sup>1</sup> We have found that 1,8-biphenylenediol, which is known from X-ray crystal structures of its adducts to be capable of forming two strong hydrogen bonds simultaneously to the same oxygen atom,<sup>2</sup> is a significantly better catalyst for this reaction than would be expected from data on meta- and para-substituted phenols, 1-biphenylenol, and 8-methoxy-1-biphenylenol. As shown by the Brønsted plot of slope 0.18 in Figure 1 (based on data in Table I), 1,8-biphenylenediol is 3 times as good a catalyst, per hydroxyl group, as it would be if its point fell on the Brønsted line; its catalytic activity is that expected for a phenol that is about 600 times as acidic. The other derivatives of 1-biphenylenol are no better catalysts than would be expected from the Brønsted plot. Neither is the diol catechol, whose hydroxy groups are not well placed for simultaneous hydrogen bonding with a common oxygen atom.

The kinetics of reaction 1 at 30 °C were followed by VPC measurements on the concentration of the epoxide relative to that of naphthalene, present as an internal standard ( $\sim 0.08$  M). The rate follows kinetic eq 2, in which E, N, and A are the epoxide,

$$-dE/dt = (k_c[\text{ArOH}] + k_a[\text{A}] + k_u)[\text{E}][\text{N}] \quad (2)$$

amine, and alcohol product. The values of  $k_a$  ( $9.4 \times 10^{-6} \text{ M}^{-2} \text{ s}^{-1}$ ) and  $k_u$  ( $3.5 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ ) were obtained from runs in which



**Figure 1.** log-log plot of catalysis constants in the reaction of diethylamine with phenyl glycidyl ether vs. ionization constants for the catalyst. (O) meta- and para-substituted phenols, (●) monohydroxy derivative of biphenylene, (■) uncorrected data for a diol, (□) statistically corrected data for a diol.

**Table I.** Catalysis Constants for Reaction of Diethylamine with Phenyl Glycidyl Ether<sup>a</sup>

catalyst	$10^5 k_c$ , $\text{M}^{-2} \text{ s}^{-1}$	$\text{p}K_a^b$
phenol	6.0	9.98 <sup>c</sup>
<i>p</i> -chlorophenol	7.7	9.38 <sup>c</sup>
<i>m</i> -chlorophenol	8.2	9.02 <sup>c</sup>
<i>m</i> -nitrophenol	14.3	8.40 <sup>c</sup>
<i>p</i> -cyanophenol	15.3	7.95 <sup>c</sup>
<i>p</i> -nitrophenol	17.0	7.15 <sup>c</sup>
catechol	11.9	9.49 <sup>c</sup>
1-biphenylenol	11.5	8.64 <sup>d</sup>
8-methoxy-1-biphenylenol	7.3	9.15 <sup>d</sup>
1,8-biphenylenediol	75	8.00 <sup>e</sup>

<sup>a</sup> In butanone solution at 30 °C. Calculated by using eq 2. <sup>b</sup> In water at 25 °C. Obtained from the source noted. <sup>c</sup> Körtum, G.; Vogel, W.; Andrussov, K. "Dissociation Constants of Organic Acids in Aqueous Solution"; Butterworths: London, 1961. <sup>d</sup> Hahn, S., The Ohio State University, personal communication, 1984. <sup>e</sup> Miles, D. E. Ph.D. Dissertation, The Ohio State University, Columbus, OH, 1982.

no catalyst was added.<sup>3</sup> The extent of the background reaction, defined as the value of  $(k_a[\text{A}] + k_u)/(k_c[\text{ArOH}] + k_a[\text{A}] + k_u)$  at half-reaction, ranged from 13% to 40% of the total reaction. Concentrations used were around 0.2 M phenyl glycidyl ether, 0.3 M diethylamine, and 0.03–0.15 M catalyst.

The reaction mechanism presumably involves protonation, by the acid catalyst, of the epoxide oxygen atom as it is displaced from carbon by the attacking amine. The relatively small Brønsted  $\alpha$  of 0.18 suggests that the extent of proton transfer in the transition state is not very large. By itself, however, it does not tell whether cleavage of the C-O bond runs ahead of formation of the O-H bond, so that the epoxide oxygen atom has become more negative in the transition state than it was in the reactant or not. The observation of double-hydrogen-bonding catalysts shows the oxygen probably has become more negative and hence

(3) The values of  $k_a$  and  $k_u$  varied by as much as  $\pm 44\%$  and  $\pm 7\%$ , respectively, in different runs, but high values of  $k_a$  were obtained with low values of  $k_u$ . Hence the first-order rate constant  $(k_a[\text{A}] + k_u)$  for that part of the reaction not resulting from catalysis by ArOH is much less uncertain. In a run using 0.0578 M *p*-nitrophenol, where there was a relatively large amount of background reaction (31%), replacement of  $k_a$  and  $k_u$  by values 44% larger and 7% smaller, respectively, decreased the calculated value of  $k_c$  by less than 0.6%.

(1) Partansky, A. M. *Adv. Chem. Ser.* 1970, 92, 29-47.

(2) Hine, J.; Ahn, K.; Gallucci, J. C.; Linden, S.-M. *J. Am. Chem. Soc.* 1984, 106, 7980-7981.