

## Dependence of rate constants of heterogeneous electron transfer reactions on viscosity

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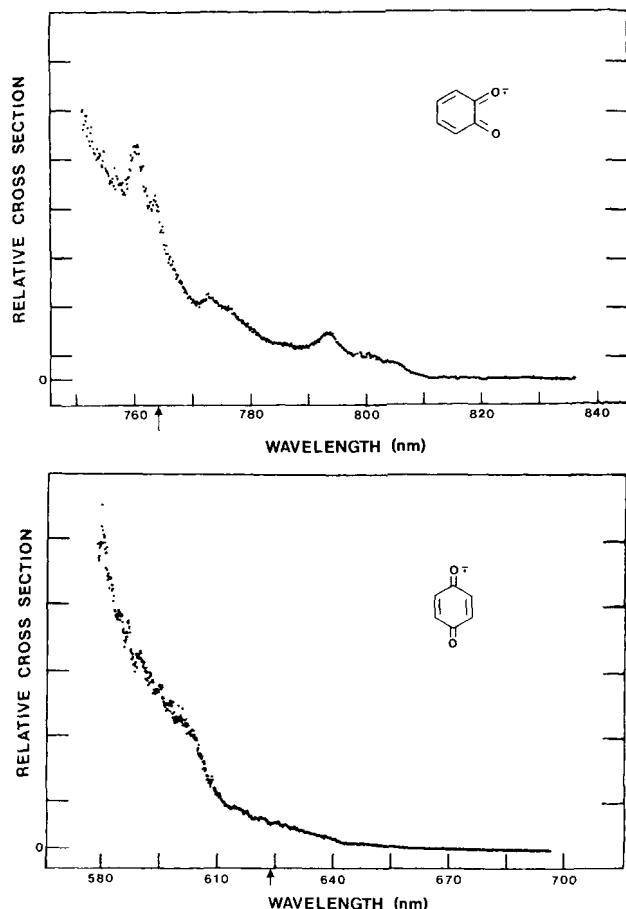
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**Figure 1.** Electron photodetachment spectra of *o*-benzoquinone (upper) and *p*-benzoquinone (lower) obtained with a 1-cm<sup>-1</sup> resolution. The arrows indicate threshold assignments for adiabatic electron affinities.

To determine if any threshold states exist in these anions we recorded the electron photodetachment spectrum of the two radical anions. These experiments were carried out in an ion cyclotron resonance spectrometer, using a Coherent 590 dye laser with a 1-cm<sup>-1</sup> line width as a light source. Details of the experimental apparatus have been reported.<sup>4,11</sup> The anion of PBQ was generated from electron capture by PBQ and the anion of OBQ was formed by dissociative electron impact on the cyclic sulfite of catechol. In Figure 1 we present the laser photodetachment spectra of OBQ<sup>-</sup> and PBQ<sup>-</sup>. The adiabatic electron affinities were assigned to threshold values of approximately 1.99 and 1.62 eV for PBQ and OBQ, respectively.<sup>12</sup>

Several resonances appear in the photodetachment spectrum of OBQ, the most intense of which are at 793, 764, and 761 nm. The threshold assignment for the adiabatic electron affinity of OBQ is at 764 nm, the position of one of the sharp resonances. A Fano line-shape analysis using the location of the resonance with respect to the continuum threshold as an adjustable parameter<sup>4</sup> places the threshold assignment at the position of the resonance corresponding to the 0-0 vibronic transition. The 0-0 transition has been found to occur at the assigned threshold energy for many structurally different enolate anions.<sup>4,5</sup> The small relative cross section for photodetachment at energies below the assigned threshold suggests photodetachment from vibrationally excited anion states (hot bands). The resonances lower in energy than the threshold are presumably due to hot band transitions to the dipole-supported state.

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(11) Details of the modification of the experimental apparatus will be reported in a future manuscript.

(12) Comita, P. B.; Marks, J.; McPeters, H. L.; Brauman, J. I., manuscript in preparation.

The two threshold resonances are separated by 55 cm<sup>-1</sup> and may be due to different vibrational modes or possibly different rotational branches of one vibration. The width of the resonances is about 45 cm<sup>-1</sup> and is governed by a manifold of rotational transitions. The hot band resonance at 793 nm is separated from the threshold resonances by 541 and 486 cm<sup>-1</sup>, corresponding to a low-frequency vibrational mode.

No fine structure at threshold was observed in the spectrum of the PBQ anion. Broad resonances due to valence excited states appear at much shorter wavelengths than the threshold region shown here. Similar valence excited-state resonances appear at shorter wavelengths in the OBQ<sup>-</sup> spectrum, verifying that the valence excited states in these anions are very similar.<sup>12</sup> The observation of threshold resonances occurring only for the dipolar molecule is consistent with the picture that a large dipole is required for a quasi-bound state to exist.

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**Registry No.** OBQ radical anion, 20526-43-6; PBQ radical anion, 3225-29-4.

### Dependence of Rate Constants of Heterogeneous Electron Transfer Reactions on Viscosity

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Studies presented here of the electrochemical behavior of the Fc(CN)<sub>6</sub><sup>3-/4-</sup> couple in aqueous and the Fc<sup>0/+</sup> couple (Fc is ferrocene) in dimethyl sulfoxide (Me<sub>2</sub>SO) solutions of different viscosities demonstrate that even for reactions that are far from the diffusion-controlled limit, the heterogeneous electron transfer (et) rate constant, *k*<sup>0</sup>, strongly depends upon viscosity. The effect of the solvent on rate constants of et reactions has been considered in a number of papers,<sup>1-4</sup> although explicit experimental studies of the effect of solvent viscosity on heterogeneous or homogeneous et are uncommon. Our interest in this topic was initiated during studies of the et kinetics at polymer-modified electrodes.<sup>5</sup> The rate constants for the reactants bound in polymer layers on an electrode surface were 2-3 orders of magnitude smaller than those for the same reactants dissolved in solution. The diffusion processes were also generally 10<sup>2</sup> to 10<sup>5</sup> times slower in the polymer matrix than in solution.<sup>5</sup> This apparent correlation between the observed rate constant, *k*<sup>0</sup>, and the diffusion coefficient, *D*, for reactants confined in polymer films is also evident in other studies of polymer-modified electrodes.<sup>6</sup> To assure that these reactions were far from the diffusion-controlled limit (where a dependence of *k*<sub>obs</sub> on *D* is clearly expected) and to make comparisons in less complicated media, we studied two different electrode reactions in solutions in which viscosities were varied by additives thought to have a minor effect on other variables (e.g., dielectric constant or electrode surface properties).

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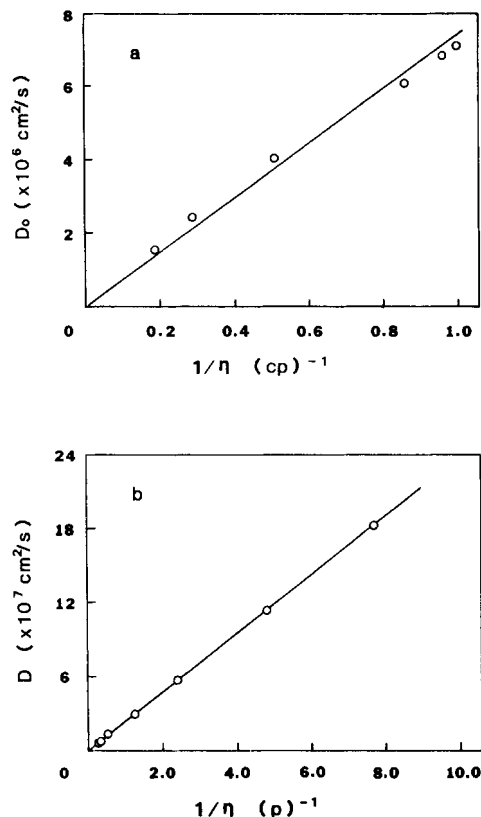
(2) (a) Hupp, J. T.; Weaver, T.; Weaver, M. J. *J. Electroanal. Chem.* **1983**, *152*, 1. (b) Weaver, M. J.; Gennett, T. *Chem. Phys. Lett.* **1985**, *113*, 213. (c) Gennett, T.; Milner, D. F.; Weaver, M. J. *J. Phys. Chem.*, submitted for publication.

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(4) Aleksandrov, I. V.; Gol'danskii, V. I. *J. Chem. Phys.* **1984**, *87*, 455.

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(6) Oyama, W.; Ohsaka, T.; Ushirogouchi, T. *J. Phys. Chem.* **1984**, *88*, 5274. (b) Oyama, N.; Ohsaka, T. *J. Am. Chem. Soc.* **1983**, *105*, 6003.



**Figure 1.** Plots of the diffusion coefficient,  $D$ , as a function of the reciprocal viscosity,  $1/\eta$ , for (a)  $\text{Fe}(\text{CN})_6^{3-/4-}$  in aqueous 0.5 M  $\text{K}_2\text{SO}_4$  solutions containing dextrose and (b) ferrocene in  $\text{Me}_2\text{SO}$  with 0.5 M  $\text{TBABF}_4$  and sucrose at 22.5 °C.

Standard solutions with the same supporting electrolyte concentrations but different viscosities were prepared by dissolving electrochemically inactive materials in the solvents (dextrose in water and sucrose in  $\text{Me}_2\text{SO}$ ). The values of  $k^0$  and  $D$  were obtained by rotating-ring electrode voltammetry for the  $\text{Fe}(\text{CN})_6^{3-/4-}$  aqueous system and convolution cyclic voltammetry for the  $\text{Fc}^{0/+}(\text{Me}_2\text{SO})$  system. Care was taken to correct for any uncompensated solution resistance in the determination of  $k^0$  in both techniques; experimental details will be presented elsewhere.<sup>7</sup>

The diffusion coefficients of the reactants,  $D$ , varied with the solution viscosity,  $\eta$ , as predicted by the Stokes-Einstein equation:<sup>9</sup>

$$D = kT/6\pi r\eta$$

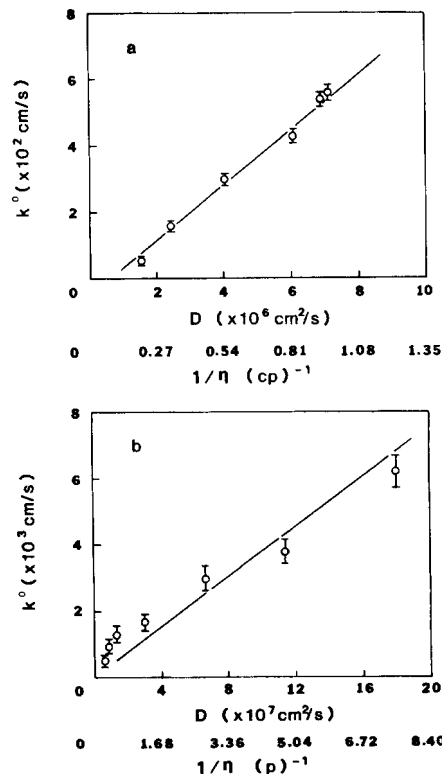
where  $k$  is Boltzmann's constant and  $r$  is the hydrodynamic radius of the diffusing species. This equation is applicable when the diffusing species is large with respect to the solvent molecules. Plots of  $D$  vs.  $1/\eta$  measured at room temperature (ca. 22.5 °C) are straight lines that intercept the origin (Figure 1); thus, relating  $k^0$  to  $D$  is macroscopically equivalent to relating  $k^0$  to  $1/\eta$ .

Kinetic data for the Pt/ $\text{Fe}(\text{CN})_6^{3-/4-}$  ( $\text{H}_2\text{O}$ ) system are shown in Table IA and plotted in Figure 2a. Comparing the values in the first row with those in the second row of Table IA, we found that  $k^0$  was not changed by the addition of small amounts of dextrose. This suggests that changes in the double-layer structure of the electrode by the introduction of dextrose do not have significant effect on  $k^0$ . The change of the solution dielectric constant with dextrose concentration is also small compared to the change in  $\eta$ . The plot in Figure 2a suggests  $k^0 \propto D$  (or  $1/\eta$ ). When the

**Table I.** Effect of Solution Viscosity ( $\eta$ ) on Diffusion Coefficient ( $D$ ) and Heterogeneous Electron Transfer Rate Constant ( $k^0$ )

dextrose conc, g/100 mL of $\text{H}_2\text{O}$	$\eta$ , cP	$\epsilon$	$D_0$ , $10^6$ $\text{cm}^2/\text{s}$	$D_R$ , $10^6$ $\text{cm}^2/\text{s}$	$k^0$ , $10^2$ $\text{cm}/\text{s}$	$\alpha$
A. $\text{Fe}(\text{CN})_6^{3-/4-}$ (5.00 mM) in Aqueous 0.5 M $\text{K}_2\text{SO}_4^a$						
0	1.00	79	7.14	6.23	5.6	0.53
0.2	1.00	79	7.11	6.23	5.6	0.53
1.0	1.04	79	6.86	5.98	5.4	0.53
5.0	1.16	78.5	6.07	5.23	4.3	0.50
20	1.97	75	4.03	3.36	3.0	0.52
40	3.47	71.5	2.41	2.00	1.6	0.54
55	5.31	69.5	1.54	1.29	0.55	0.50
sucrose conc, g/10 mL of $\text{Me}_2\text{SO}$						
g/10 mL of $\text{Me}_2\text{SO}$	$\eta$ , cP	$D$ , $10^7$ $\text{cm}^2/\text{s}$	$k^0$ , $10^3$ $\text{cm}/\text{s}$	$\alpha$		
B. Ferrocene in 0.5 M Tetra- <i>n</i> -butylammonium Tetrafluoroborate in $\text{Me}_2\text{SO}^b$						
2.32	13	18.3	6.2	0.82		
2.78	21	11.4	3.8	0.76		
3.47	42	5.67	3.0	0.74		
3.78	81	2.97	1.7	0.71		
3.96	183	1.31	1.3	0.72		
4.06	203	1.18	1.1	0.66		
4.10	210	1.14	0.88	0.65		
4.14	290	0.83	0.89	0.67		
4.16	325	0.74	0.78	0.72		
4.18	350	0.69	0.47	0.62		

<sup>a</sup>Pt rotating ring electrode, 22.5 °C. <sup>b</sup>Pt disk electrode, room temperature. Abbreviations:  $\epsilon$  dielectric constant,  $\alpha$  heterogeneous et coefficient.



**Figure 2.** Plots of the observed rate constants of the heterogeneous electron transfer reaction,  $k^0$ , as a function of the diffusion coefficient,  $D$  (and the reciprocal viscosity of the solution,  $1/\eta$ ): (a) Pt/ $\text{Fe}(\text{CN})_6^{3-/4-}$  in aqueous 0.5 M  $\text{K}_2\text{SO}_4$ -dextrose, (b) Pt/ferrocene in  $\text{Me}_2\text{SO}$  with 0.5 M  $\text{TBABF}_4$  and sucrose. The temperature was 22.5 °C ( $\pm 1$  °C).

(7) Steady-state current ( $i$ )-potential ( $E$ ) curves were taken at a rotating Pt ring electrode (geometric area, 0.311  $\text{cm}^2$ ) at different rotation rates ( $\omega$ ).  $D$  was determined from the limiting current and  $k^0$  from plots of  $1/i$  vs.  $\omega^{-1/2}$  at different potentials near  $E^0$ .<sup>5</sup> Convolution voltammetry was carried out at a Pt disk electrode (geometric area, 0.022  $\text{cm}^2$ ) for scan rates of 0.2–5.0 V/s. Experimental details and data treatment have been previously described.<sup>5a</sup>

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(9) Smoluchowski, M. Z. *Phys. Chem.* 1917, 92, 129.

viscosity of the solution was increased from 1.0 to 5.3 cP (ca. 5 times),  $k^0$  value decreased by approximately 10 times (from  $5.6 \times 10^{-2}$  to  $0.55 \times 10^{-2}$   $\text{cm s}^{-1}$ ). Data for Pt/ferrocene ( $\text{Me}_2\text{SO}$ ) system are given in Table IB and plotted in Figure 2. In this case the solution viscosity was varied over a much larger range. Values of  $k^0$  were proportional to  $D$  (or  $1/\eta$ ) up to  $\eta$  values of about 80

cP and fell off at higher viscosities. A plot of  $\log k^0$  vs.  $\log D$  had a slope of 0.7 over the whole range of  $\eta$ .

Although the classical et reaction theories, e.g., that of Marcus,<sup>10</sup> do not suggest a solvent viscosity dependence for outer-shell et, more recent theoretical treatments<sup>1-4</sup> emphasize the role of solvent dynamics. For example, Calef and Wolynes<sup>1</sup> stress the importance of the dielectric relaxation and thermal reorientation times of the solvent (which depend upon viscosity) in determining the pre-exponential factor in the rate expression. Rotational reorientation dynamics of the molecule undergoing the et reaction may also be important.

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**Registry No.**  $\text{Fe}(\text{CN})_6^{3-}$ , 13408-62-3;  $\text{Fe}(\text{CN})_6^{4-}$ , 13408-63-4;  $\text{K}_2\text{SO}_4$ , 7778-80-5;  $\text{TBABF}_4$ , 429-42-5; dextrose, 50-99-7; ferrocene, 102-54-5; ferrocenium, 12125-80-3; sucrose, 57-50-1.

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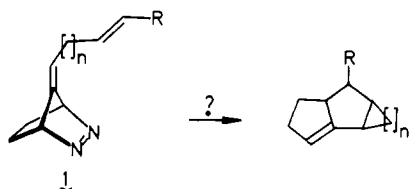
### Evidence for Hydrogen Atom Abstraction and Loss of Dilyophile Stereochemistry in an Intramolecular 1,3-Diyl Trapping Reaction

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Of the many unexplored questions concerning the factors that govern the outcome of intramolecular 1,3-diyl trapping reactions, one that is very easy to formulate focuses upon the course of the reaction as a function of the length of the tether that links the diyl and dilyophile. Until now, the tether length has been restricted to cases where  $n = 3$  (see 1), and in all but one recorded instance, linearly fused cycloadducts (viz., those with a tricyclo[6.3.0.0<sup>2,6</sup>]undecane skeleton) have corresponded to the major products.<sup>1</sup> Is this a general result? That is, will linearly fused products be formed regardless of the length of the tether? In this manuscript, we examine the chemistry of the diyl derived from 1 where  $n = 2$  and  $R = \text{CO}_2\text{CH}_3$ .



The diazene required to initiate this investigation was prepared from 4-hydroxybutanal, cyclopentadiene, and bis[(2,2,2-trichloroethoxy)carbonyl] azodicarboxylate by following a sequence analogous to that which we have published previously.<sup>2</sup>

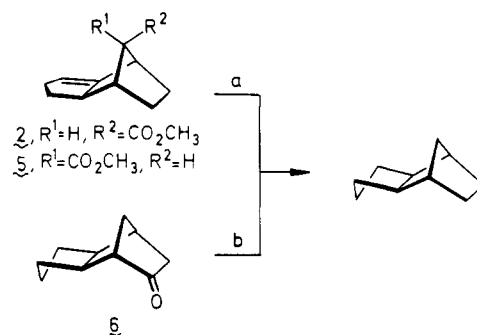
<sup>†</sup>UCSB.

<sup>‡</sup>WVU.

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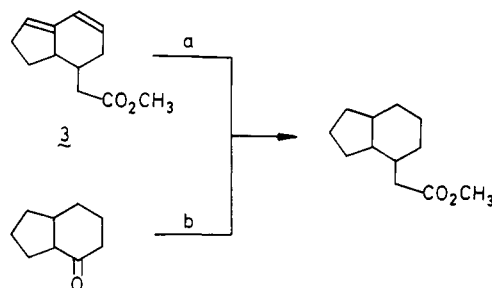
(2) See, for example: (a) Little, R. D.; Carroll, G. L. *J. Org. Chem.* 1979, 44, 4720. (b) Little, R. D.; Muller, G. W. *J. Am. Chem. Soc.* 1981, 103, 2744. (c) Stone, K. J.; Little, R. D. *J. Org. Chem.* 1984, 49, 1849. (d) Little, R. D.; Muller, G. W.; Venegas, M. G.; Carroll, G. L.; Bukhari, A.; Patton, L.; Stone, K. J. *Tetrahedron* 1981, 37, 4371.

Scheme I<sup>a</sup>



<sup>a</sup> (a) (1) KOH, MeOH; (2)  $\text{H}_2$ , 10% Pd/C; (3) ref 3. (b) (1)  $\text{HSCH}_2\text{CH}_2\text{SH}$ ,  $\text{BF}_3$ ; (2) Raney nickel.

Scheme II<sup>a</sup>



<sup>a</sup> (a)  $\text{H}_2$ , 10% Pd/C; (b)  $[(\text{MeO})_2\text{POCHCO}_2\text{CH}_3] \text{Na}$ , DME, then  $\text{BH}_3\text{-THF}$  and MeOH.

A 5 mM solution of 1 dissolved in THF was heated at reflux until the starting material disappeared as evidenced by TLC. After removal of the solvent, careful analysis of the reaction mixture by capillary column GC and 300-MHz  $^1\text{H}$  NMR (PMR) revealed the presence of four components 2-5 (83% isolated yield), formed in a ratio of 16:5:1.5:1. The two major products 2 and 3 were separated from each other and the remaining materials. Mass spectral and elemental analysis indicated that they were isomeric, each having a structural formulation corresponding to  $\text{C}_{12}\text{H}_{16}\text{O}_2$ . Catalytic hydrogenation of the major product 2 followed by inspection of the fully decoupled  $^{13}\text{C}$  NMR spectrum of the resulting product revealed only 8 rather than 12 lines anticipated for a linearly fused product, i.e., one with a tricyclo[6.2.0.0<sup>2,6</sup>]decane skeleton. This result suggests either that several of the resonances of a linearly fused cycloadduct are accidentally degenerate or that the molecule is not linearly fused and instead possesses an element of symmetry.

The gross structural features of this material were determined by following the sequence outlined in Scheme I. That is, 2 was saponified, the carbon-carbon  $\pi$  bond was reduced, and the carboxylic acid unit was removed using a Barton decarboxylation sequence.<sup>3</sup> The resulting hydrocarbon proved to be identical with that derived from the commercially available 8-ketotricyclo[5.2.1.0<sup>2,6</sup>]decane (6)<sup>4</sup> after removal of the carbonyl. The stereochemical disposition of the ester unit was established unambiguously through a single-crystal X-ray structural analysis of the carboxylic acid derived from 2.<sup>5</sup> As illustrated, the carboxylic acid unit is oriented anti to the endocyclic five-membered ring. In other words, the stereochemistry about the dilyophile  $\pi$  bond has been lost. Such a result is unprecedented; all previous intramolecular diyl trapping reactions wherein dilyophile stereochemistry has been an issue have proceeded stereospecifically and

(3) Barton, D. H. R.; Crich, D.; Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* 1983, 939.

(4) This material is available from the Aldrich Chemical Co.

(5) (a) To be certain that epimerization did not occur during the saponification of ester 2, the carboxylic acid was reesterified and was shown to be identical with 2. (b) Full X-ray data is available as supplementary material.