# Medium Effects in the Electroreduction of Benzophenone in Aprotic Solvents

W. Ronald Fawcett\* and Milan Fedurco

Department of Chemistry, University of California, Davis, California 95616 Received: February 4, 1993; In Final Form: April 8, 1993

The kinetics of electroreduction of benzophenone have been studied at a mercury ultramicroelectrode in seven aprotic solvents. In addition, the temperature dependence of the standard rate constant was determined in three solvents, and the effect of tetraalkylammonium cations on the kinetic parameters was assessed in acetonitrile. On the basis of an analysis of the solvent effects, it is shown that this fast electron-transfer reaction is adiabatic. A model for solvation of the activated complex based on three contiguous spheres corresponding to the two phenyl rings and the carbonyl group is described and used to assess the outer-sphere contribution to the Gibbs activation energy for electron transfer.

## Introduction

The electrochemistry of benzophenone (Bzph) has been the subject of some interest, especially with respect to its relationship to the spectroscopy of this molecule.<sup>1</sup> Early work<sup>2-5</sup> showed that Bzph undergoes a one-electron reduction to form a stable anion radical in dimethylformamide (DMF) and acetonitrile (AN). These studies included ESR spectroscopic investigations of the anion radicals and determination of the dependence of the standard potential for this reaction on the nature of substituents on the phenyl ring. More recently, attention has been focused on the kinetics of electron transfer.<sup>6-9</sup> Studies at mercury electrodes<sup>7,8</sup> have shown that the reaction is fast, the rate constant in acetonitrile being greater than could be measured by cyclic voltammetry with scan rates up to 100 V s<sup>-1</sup> at a hanging drop electrode.<sup>7</sup>

Bzph is an interesting system for examination of solvent effects on electron-transfer reactions.<sup>10</sup> As pointed out by Petersen and Evans,<sup>7</sup> the inner-sphere reorganization energy associated with this process is expected to be small, so the outer-sphere reorganization energy, which depends on the dielectric properties of the solvent, is expected to dominate in determining the magnitude of the Gibbs activation energy. Since the charge in the anion radical is distributed over the whole anion radical, the effective radius of the reactant is large, and the rate constant is high. As a result, one needs an experimental technique which is capable of precisely determining heterogeneous rate constants greater than 1.0 cm s<sup>-1</sup>. One such technique is high-frequency ac admittance voltammetry at ultramicroelectrodes, which has been applied recently to studies of electron-transfer reactions involving ferrocene<sup>11</sup> and buckminsterfullerene.<sup>12</sup>

In this paper, we report kinetic data obtained by the highfrequency ac admittance technique for the electroreduction of Bzph in a variety of solvents and in the presence of different electrolytes. The data are analyzed to determine the role of the medium in electron transfer and also to examine the effect of reactant structure.

### **Experimental Section**

**Reagents.** The solvents acetonitrile (AN), acetone (AC), dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), hexamethylphosphoramide (HMPA), propionitrile (PN), and propylene carbonate (PC) were purchased as ACS certified chemicals and were further purified using techniques described in the literature.<sup>13</sup>

Benzophenone (Aldrich) was twice recrystallized from absolute ethanol and dried under reduced pressure at room temperature for 12 h. All tetraalkylammonium perchlorates (Fluka), namely, ethyl (TEAP), propyl (TPAP), butyl (TBAP), hexyl (THxAP), and octyl (TOAP), were prepared, purified, and dried as described previously.<sup>14</sup> Cobaltocenium hexafluorophosphate and silver perchlorate (both Strem) were used as received.

Apparatus and Procedures. A Solatron 1250 frequency response analyzer served as the source of dc potential and sinusoidal perturbation (10 mV peak to peak). The signal was fed into the external input of an EG&G/PAR 273 potentiostat through a low-impedance, purely resistive attenuator (10:1). The built-in current follower of the potentiostat was bypassed and replaced by a high-bandwidth (100 kHz) current preamplifier (EG&G Model 181). All instruments were connected to a common ground. The signal from the electrode was fed directly into this preamplifier. Its output and the reference signal from the potentiostat were fed into two channels of the frequency response analyzer to obtain the in- and out-of-phase components of the admittance.

Cyclic voltammetry was performed using the EG&G 273 potentiostat (see Figure 1). The peak separation was usually in the range 59-70 mV. The error in estimation of the standard potential,  $E_s$ , was less than 5 mV. Diffusion coefficients of Bzph were calculated from the peak current at a scan rate of 10 V s<sup>-1</sup> after correction for *i*R drop using the Randles-Sevcik equation. The solution resistance,  $R_s$ , was measured in the range 650-65000 Hz in the supporting electrolyte prior to the addition of Bzph. The value of  $R_s$  was taken from the higher frequency range 20-60 kHz, where  $R_s$  was approximately constant. The temperature of the cell was controlled to a precision  $\pm 0.5$  °C by circulating an ethylene glycol:water mixture (1:1) in a jacket surrounding the cell using a Brinkman circulator (RM6). All measurements were performed with a reactant concentration of 2 mM and with 0.1 M TEAP as electrolyte (if not stated otherwise) at 22 ± 0.5 °C.

A three-electrode system was employed with a Hg ultramicroelectrode, a working electrode, and a Pt counter electrode with an area of  $\sim 2 \text{ cm}^2$ . A Ag wire immersed in 0.01 M AgClO<sub>4</sub> and 0.09 M TBAP in acetonitrile and separated from the working solution by a ceramic tip (Bioanalytical Systems) served as reference electrode. The solution in the reference compartment was changed every day in order to maintain potential stability. Cobaltocenium (Cob<sup>+</sup>) hexafluorophosphate at a concentration of 2 mM served as internal potential standard, with all values of  $E_s$  being referred to that of the Cob<sup>+/0</sup> couple in order to eliminate the effect of changing liquid junction potentials in different solvents.

The Hg ultramicroelectrode was prepared on the end of a gold wire with a radius of 12.5  $\mu$ m (Goodfellow Metals) which was sealed in a soft glass capillary in a Bunsen flame. The tip of the capillary was polished with fine carborundum paper (Buehler), diamond paste (Beuhler, 3  $\mu$ m followed by 1  $\mu$ m), and finally



Figure 1. Cyclic voltammogram for the reduction of 2 mM benzophenone in DMA containing 0.1 M TEAP at a Hg ultramicroelectrode using a sweep rate of 10 V s<sup>-1</sup>. The potential scale is with respect to a  $Ag/Ag^+$ reference electrode.



Figure 2. Randles plot of impedance data obtained for the benzophenone system in AN containing 0.1 M TEAP at the standard potential using a Hg ultramicroelectrode with ac frequencies in the range 18-51 kHz.

alumina (0.3  $\mu$ m followed by 0.05  $\mu$ m) on a polishing wheel. The electrode was then placed in a sonicator containing nanopure water for 30 s and then in pure methanol, and finally it was dried in a strong stream of compressed air exiting from a disposable pipet. The electrode was then placed in a small volume of freshly distilled Hg (2-3 mL) for 20 s. The smoothness of the Au ultramicroelectrode and the hemispherical shape of the resulting Hg ultramicroelectrode were confirmed under an optical microscope (magnification 450×) before every experiment. The area of the Hg ultramicroelectrode was confirmed by determining the diffusion coefficient for the nitromesitylene system, which was also studied at a dropping mercury electrode<sup>14</sup> (DME). These parameters agreed to better than 1%, confirming that the Hg electrode is indeed a hemisphere whose area is known on the basis of the radius of the gold wire. Furthermore, capacitance measurements on the Hg ultramicroelectrode in PC with 0.1 M TEAP at potentials around  $E_s$  for Bzph were in very good agreement with capacity measurements on a DME.

Alternating current admittance was measured at potential intervals of 5 mV in a potential range of 0.7 V symmetrical with respect to  $E_s$ . The frequency range used was 18000–51000 Hz (seven frequencies). A Randles plot (Figure 2) was made to confirm the correctness of the equivalent circuit. At a given frequency, the non-faradaic in- and out-of-phase admittances in the regions preceding and following the faradaic peak were fitted to a third-degree polynomial by least squares.<sup>12</sup> After blank line correction and  $R_s$  correction at every frequency, the rate constants were determined in the vicinity of the standard potential using the deLevie–Husovsky method.<sup>15,16</sup> Finally,  $k_s$  and  $\alpha_{ex}$  were obtained from the slope and intercept of a plot of the logarithm of the rate constant against electrode potential (Figure 3). The



Figure 3. Potential dependence of the rate constant for reduction of benzophenone at a Hg ultramicroelectrode in AN containing 0.1 M TEAP for potentials in the range  $-0.04 \le E \le 0.04$  with respect to the standard potential.

TABLE I	: Kine	tic Para	meters fo	or the l	Electrore	duction	of
Benzophe	none in	Various	Aprotic	Solven	ts at 22 '	°C	

solvent	std potential <sup>a</sup> E <sub>s</sub> /V	diffusion coefficient 10 <sup>6</sup> D/cm <sup>2</sup> s <sup>-1</sup>	std rate constant k <sub>s</sub> /cm s <sup>-1</sup>	$\begin{array}{c} \text{exptl} \\ \text{transfer} \\ \text{coefficient}^b \\ \alpha_{\text{ex}} \end{array}$	exptl activation enthalpy <sup>c</sup> $\Delta H^*_{ex}/$ kJ mol <sup>-1</sup>
AC	0.925	20.9	2.00	0.58	-
AN	0.806	19.1	2.70	0.58	-
DMA	0.904	6.4	0.51	0.50	23.1
DMSO	0.803	3.3	0.31	0.53	24.0
HMPA	0.923	1.8	0.11	0.49	-
PC	0.843	2.3	0.18	0.50	27.1
PN	0.861	15.2	1.82	0.55	-

<sup>a</sup> Measured with respect to the standard potential for the COB<sup>+/0</sup> couple in the same solvent. The electrolyte was 0.1 M TEAP in all cases. <sup>b</sup> Defined as  $(-RT/F)((\partial \ln k_t)/2E)$ . <sup>c</sup> Defined as  $-R[(\partial \ln k_s)/\partial(1/T)]$ .

reproducibility of the standard rate constant was better than  $\pm 10\%$ .

#### Results

Kinetic data for the reaction

$$Bzph + e^- \to Bzph^- \tag{1}$$

were collected at 22 °C in seven aprotic solvents as a function of potential using 0.1 M TEAP as electrolyte. It is readily apparent from the data presented for the AN system in Figure 3 that the error level is low and that rate constants were measured up to 6 cm s<sup>-1</sup>. The temperature dependence of the kinetic parameters was determined in DMA, DMSO, and PC. A summary of the results is given in Table I.

Values of the standard potential on the Cob<sup>+/0</sup> scale are plotted against the Gutmann acceptor number AN<sup>17,18</sup> in Figure 4. A good linear relationship between these parameters is found with a correlation coefficient, r, equal to 0.968. Solvent acidity clearly plays the most important role in determining the variation in  $E_s$ in spite of the fact that the other solvent parameters are expected to be involved.<sup>20</sup>  $E_s$  should also depend on solvent basicity because the standard potential of the reference couple in which a cation participates is expected to be solvent dependent.<sup>21</sup> However, the anionic character of the benzophenone anion radical is apparently more important than the cationic character of the cobaltocenium cation.

It is also apparent from the data in Table I that the diffusion coefficient for Bzph varies considerably with solvent, being largest in the solvents of low viscosity. The value of D determined in solutions containing 0.1 M TEAP is plotted against the viscosity of the pure solvent on logarithm scales in Figure 5. An excellent linear relationship is obtained between the logarithms of these two quantities with a slope of -1. This demonstrates that the



Figure 4. Standard potential for the reduction of benzophenone in various solvents on the  $COB^{+/0}$  scale plotted against the Gutmann-Mayer acceptor number of the solvent.



Figure 5. Diffusion coefficient of benzophenone in various solvents plotted against the viscosity of the pure solvent using logarithmic scales.

activation processes for diffusion of the reactant and flow of the solvent vary in a similar way with solvent nature, as one would expect.

Considerable variation in the standard rate constant with solvent was also found. In order to demonstrate that solvent dynamics plays a role in the kinetics of reaction 1, the standard rate constant is plotted against the solvent's longitudinal relaxation time,  $\tau_L$ , on logarithmic scales in Figure 6. An excellent linear relationship with a slope equal to -0.91 is obtained. This suggests that the reaction is close to adiabatic. However, the result does not consider the fact that the outer-sphere contribution to the Gibbs activation energy also depends on the solvent. On the basis of the method used to separate the two solvent contributions described earlier,<sup>22</sup> one may fit the data to an equation of the form

$$\ln k_{\rm s} = \ln k_{\rm so} - \theta \ln \tau_{\rm L} - g\gamma \tag{2}$$

where  $k_{so}$  is the solvent-independent value of the standard rate constant,  $\theta$  a fraction between 0 and 1 describing the degree of reaction adiabaticity,  $\gamma$  the Pekar factor, and g a collection of constants divided by the effective radius,  $r_e$ , of the reactant. For a heterogeneous electron-transfer reaction in which the effects of imaging may be neglected, g is given according to the Marcus model<sup>23</sup> by

$$g = \frac{N_0 e^2}{32\pi\epsilon_0 RTr_e}$$
(3)

where  $N_0$  is the Avogadro constant, e the fundamental electron charge, and  $\epsilon_0$  the permittivity of free space. The Pekar factor is defined as the reciprocal of the optical dielectric constant  $\epsilon_{op}$ minus that of the static dielectric constant  $\epsilon_s$ :

$$\gamma = \frac{1}{\epsilon_{\rm op}} - \frac{1}{\epsilon_{\rm s}} \tag{4}$$

When eq 2 is fitted to the data shown in Figure 6 the resulting



Figure 6. Standard rate constant for reduction of benzophenone plotted against the longitudinal relaxation time of the solvent using logarithmic scales.

 TABLE II:
 Solvent Parameters Relevant to the Data

 Analysis
 Parameters

solvent	longitudinal relaxation time $\tau_L/ps$	longitudinal relaxation enthalpy ΔH <sub>L</sub> /kJ mol <sup>-1</sup>	MSA distance parameter $\delta_{sa}/pm$	Pekar factor $\gamma$
AC	0.3	3.7	45.4	0.495
AN	0.2	5.7	41.0	0.529
DMA	1.5	8.1	49.8	0.459
DMSO	2.1	10.7	39.1	0.437
HMPA	8.8	11.5	52.0	0.438
PC	3.3	13.5	41.9	0.480
PN	0.4	5.8	(43)	0.503

value of  $\theta$  is 0.96. However, for the solvents selected for the present study, there is a weak correlation between  $\ln \tau_L$  and  $\gamma$  (r = -0.856), so the analysis is not completely reliable. It was noted that correlation between  $\ln k_s$  and  $\ln \tau_L$  is very strong (r = -0.993), whereas that between  $\ln k_s$  and  $\gamma$  is quite weak (r = 0.833). The latter result suggests that the Marcus model for outer-sphere contribution to the Gibbs activation energy which leads to the final term in eq  $2^{23}$  may not be suitable for the present system and that a model which takes into account local reactant-solvent interactions may be more appropriate.<sup>24</sup> On the basis of the present analysis, one may conclude that the coefficient  $\theta$  is between 0.91 and 1.00, probably quite close to unity.

If one assumes that the reaction is adiabatic ( $\theta = 1$ ), then the standard rate constant may be written as<sup>22</sup>

$$k_{\rm s} = \kappa K_{\rm p} \tau_{\rm L}^{-1} \left(\frac{\Delta G^*}{4\pi RT}\right)^{1/2} \exp(-\Delta G^*/RT) \tag{5}$$

where  $\kappa$  is the electronic transmission coefficient,  $K_p$  the encounter pre-equilibrium constant, and  $\Delta G^*$  the Gibbs activation energy. On the basis of calculations carried out recently, using the mean spherical approximation (MSA),<sup>25</sup> values of the outer-sphere contributions to Gibbs energy,  $\Delta G^*_{os}$ , and enthalpy of activation,  $\Delta H^*_{os}$ , are equal within experimental error. Assuming that any contribution to the inner-sphere Gibbs energy of activation is also equal to the corresponding enthalpy, one may write

$$\Delta G^* \sim \Delta H^* = \Delta H^*_{ex} - \theta \Delta H_{L} \tag{6}$$

where  $\Delta H^*_{ex}$  is the experimentally observed enthalpy of activation and  $\Delta H_L$  the longitudinal relaxation enthalpy which is obtained from the temperature dependence of the solvent's dielectric parameters.<sup>25</sup> On the basis of the values of  $\Delta H_L$  estimated earlier<sup>25</sup> (Table II) and the data reported in Table I, the Gibbs activation energy for reaction 1 is between 13 and 15 kJ mol<sup>-1</sup> for the solvents studied. One may now estimate the parameter  $\kappa K_p$  using eq 5 and the values of  $\tau_L$  for these solvents (Table II). The resulting value is 3.1 ± 1.2 pm. This is considerably less than the value obtained from the analysis of kinetic data for the metallocenes<sup>11,25</sup>



Figure 7. Model for the solvation of benzophenone in which the molecule is represented as three contiguous spheres, two corresponding to the phenyl rings with radii equal to 232 pm and the third to the carbonyl group with a radius of 114 pm.

and suggests that there may be a steric factor for the present system such that a specific orientation of the molecule with respect to the electrode is required for electron transfer.

It is interesting to see if one may estimate the value of the outer-sphere Gibbs reorganization energy on the basis of a model for the solvation of the activated complex. Since the electrontransfer reaction is fast, the effective radius of the reacting system must be large. Loutfy and Loutfy<sup>1</sup> represented the molecule as three contiguous spheres to make this estimate, two large spheres corresponding to each of the phenyl rings and a smaller one corresponding to the carbonyl group. However, their model did not properly consider the effect of the adjacent spheres on the charging process, and they also chose unrealistically large radii for the spheres with respect to the actual dimensions of the benzophenone molecule (Figure 7). A more detailed model for the outer-sphere Gibbs activation energy with a reacting system modeled as two contiguous spheres was described by Fawcett and Kharkats<sup>26</sup> and is applied here to a system modeled as three contiguous spheres. Defining  $r_1$  to be the radius of the smaller sphere and  $r_2$  the radius of the two larger spheres, the effective radius of the reacting system  $r_e$  is given by

$$\frac{1}{r_{e}} = \frac{f_{1}^{2}}{r_{1}} + \frac{2f_{2}^{2}}{r_{2}} + \frac{2f_{1}f_{2}}{r_{12}} + \frac{2f_{2}^{2}}{r_{22}} - 2f_{1}^{2}F(r_{12},r_{2}) - 2f_{2}^{2}F(r_{12},r_{1}) - 2f_{2}^{2}F(r_{22},r_{2})$$
(7)

where

$$F(r_{xy}, r_x) = \frac{r_{xy}}{2(r_{xy}^{2} - r_x^{2})} \left[ \frac{r_x}{r_{xy}} - \left( 1 - \frac{r_x^{2}}{r_{xy}^{2}} \right) \ln \frac{r_{xy} + r_x}{(r_{xy}^{2} - r_x^{2})^{1/2}} \right]$$
(8)

 $f_1$  is the fraction of the charge on the carbonyl group in the anion radical and  $f_2$  that on either of the phenyl rings which are assumed to carry equal fractions. The distances  $r_{12}$  and  $r_{22}$  are between the centers of spheres 1 and 2 and of spheres 2 and 2, respectively. This relationship is only appropriate for the case that two of the spheres are of equal size with the same fraction of the charge density in the anion radical.

In order to apply this model to the benzophenone system, one must have reasonable values of the distance parameters required to estimate  $r_e$ . On the basis of published structural data,<sup>27</sup> the distance from the carbon atom of the carbonyl group to the center of a phenyl ring is 292 pm. Assuming that the angle made by the bonds between this carbon atom and the two phenyl rings is 120°, then the distance between the centers of the two rings ( $r_{22}$ ) is 465 pm. It follows that the maximum possible radius of the phenyl ring represented as a sphere is 232 pm. This is considerably less than the usually assumed value (350 pm) and reflects the fact that solvation of these systems cannot be as complete as it would be if the phenyl system were isolated. On the basis of the usual C=O distance (122 pm) and assuming that the angle formed by the C--C=O part of the Bzph molecule is 120°, the distance

TABLE III:Estimates of the Outer-Sphere GibbsReorganization Energy for the Reduction of Benzophenone in<br/>Various Solvents Assuming an Effective Reactant Radius<br/>Equal to 0.475 nm

	$\Delta G^*_{\mathrm{os}}/\mathrm{kJ} \mathrm{mol}^{-1}$			
solvent	Marcus model	MSA model	experiment <sup>a</sup>	
AC	18.1	16.5	-	
AN	19.3	17.8	-	
DMA	16.8	15.2	15.0	
DMSO	16.0	14.8	13.3	
HMPA	16.0	14.4	-	
PC	17.6	16.1	13.6	
PN	18.4	16.9	-	

<sup>a</sup> Estimated on the basis of eq 5 assuming that the inner-sphere Gibbs reorganization energy is negligible and that the reaction is perfectly adiabatic ( $\theta = 1$ ).

from the center of the phenyl ring to the O atom is 346 pm. Thus, the radius of a sphere centered on this atom and touching both of the spheres enclosing the phenyl groups is 114 pm  $(r_1)$ . Finally, the distance between the center of the small sphere and either of the larger ones  $(r_{12})$  is 346 pm. On the basis of ESR data,<sup>1</sup> the fraction,  $f_1$ , of charge on the carbonyl group in the anion radical is 0.215, and that on each phenyl ring,  $f_2$ , is 0.393.

When these parameters are substituted in eq 7, the resulting value of  $r_e$  is 475 pm. This result indicates that the estimate of  $\Delta G^*_{os}$  is small and the rate of reaction large. According to the Marcus model and neglecting the effect of images, the estimate of  $\Delta G^*_{os}$  is

$$\Delta G^*_{\rm os} = \frac{N_0 e^2 \gamma}{32\pi\epsilon_0 r_e} \tag{9}$$

On the basis of the MSA, the expression for  $\Delta G^*_{os}$  is

$$\Delta G^*_{\rm os} = \frac{N_0 {\rm e}^2 \gamma}{32\pi\epsilon_0} \frac{1}{r_{\rm e} + \delta_{\rm sa}} \tag{10}$$

where  $\delta_{sa}$  is the MSA distance parameter appropriate for anions.<sup>24</sup> Values of the parameters for the solvents considered in this study are summarized in Table II.

Estimates of  $\Delta G^*_{\infty}$  were obtained by both the Marcus and MSA models and are summarized together with the experimental estimates in Table III. The values of  $\Delta G^*_{\infty}$  according to the Marcus model are 1–2 kJ mol<sup>-1</sup> higher than those according to the MSA. The latter values are on the average 1 kJ mol<sup>-1</sup> higher than the experimental results. Considering the very approximate nature of the model used to describe the solvation of the activated complex for this reaction, the results are very satisfying. It should be noted that the MSA distance parameters were derived from data for simple spherical ions, namely, the alkali metal and halide ions, and therefore are not strictly applicable to the present system. However, since the model for estimating the effective radius of the activated state involves only spheres, one may expect the MSA model to work reasonably well.

The effect of tetraalkylammonium (TAA<sup>+</sup>) cation size on the rate constant for reduction of Bzph was also investigated in AN. From the kinetic parameters summarized in Table IV, it is clear that the standard rate constant drops markedly with increase in the size of the TAA<sup>+</sup> cation. This result is attributed to increased blocking of the electrode by these cations, which are attracted into the double layer at potentials negative of the pzc.<sup>14</sup> On the basis of the analysis presented earlier, the rate constant is assumed to decrease exponentially with increase in the thickness of the blocking layer, d, according to the relationship

$$k_{\rm s} = k_{\rm so} {\rm e}^{-\beta d} \tag{11}$$

where  $k_{so}$  is the standard rate constant on an uncovered electrode and  $\beta$  a parameter which depends on the barrier height for electron

TABLE IV: Kinetic Parameters for the Electroreduction of Benzophenone in Acetonitrile in the Presence of Various Tetraalkylammonium Perchlorates at 22 °C

		and a second sec		
electrolyte (0.1 M)	standard potential <sup>a</sup> E <sub>s</sub> /V	diffusion coefficient 10 <sup>6</sup> D/cm <sup>2</sup> s <sup>-1</sup>	standard rate constant $k_s/cm s^{-1}$	exptl transfer coefficient <sup>b</sup> $\alpha_{ex}$
TEAP	0.806	19.1	2.7	0.58
TPAP	0.800	18.7	1.03	0.57
TBAP	0.794	18.2	0.42	0.58
THxAP	0.794	17.5	0.21	0.59
TOAP	0.784	16.7	0.11	0.57

<sup>a</sup> Measured with respect to the standard potential of the COB<sup>+/0</sup> couple in the same solution. <sup>b</sup> Defined as  $(-RT/F)((d \ln k_f)/dE)$ .



Figure 8. Plot of the logarithm of the standard rate constant  $k_s$  against the estimated thickness of a layer of tetraalkylammonium ions of increasing size. The reactions studied are benzophenone reduction in acetonitrile (Bzph), nitromesitylene reduction in propylene carbonate (NM), and 2-methyl-2-nitropropane reduction in acetonitrile (NP).

tunneling. The thickness d was set equal to twice the radius of the TAA<sup>+</sup> ion in the case of TEA<sup>+</sup> and TPA<sup>+</sup> and to the radius of the ion plus 0.37 nm for the larger cations. This method of estimating d is based on the assumption that three of the tetrahedrally disposed alkyl arms of the TAA<sup>+</sup> cation are oriented toward the electrode and can bend in the attractive electrode field so that the nitrogen atom is a constant distance from the electrode in the case of the larger ions.<sup>14</sup> Plots of  $\ln k_s$  against d for the data reported here together with earlier results for nitromesitylene (NM) reduction in PC14 and 2-methyl-2-nitropropane (NP) reduction in AN<sup>28</sup> are shown in Figure 8. The slopes of these plots are different, corresponding to values of  $\beta$ equal to 16.1 nm<sup>-1</sup> for the case of Bzph, 21.8 nm<sup>-1</sup> for NP, and 12.3 nm<sup>-1</sup> for NM. These fall in the range normally observed for this quantity.<sup>29</sup> The standard potentials for reduction of Bzph and NP are close to one another,<sup>7</sup> so one may assume that the environment near the reaction site is approximately the same for these systems. Thus, the difference in the values of  $\beta$  must reflect properties of the molecules themselves and the manner in which they affect the shape of the energy barrier for electron tunneling. This is an interesting subject which is beginning to receive more attention in both theoretical and experimental studies.<sup>29,30</sup>

### Discussion

The rate constants for reduction of Bzph and related compounds were first reported by Loutfy and Loutfy.<sup>1</sup> Their value of the rate constant in AN (0.18 cm s<sup>-1</sup>) is 15 times smaller than that obtained in the present study. Since the diffusion coefficient reported by these authors  $(4.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})$  also disagrees with the present result, it would seem that systematic errors were involved in their data. On the other hand, Petersen and Evans<sup>30</sup> reported a diffusion coefficient for Bzph in AN which is essentially the same as the present result and noted that the standard rate constant was greater than  $1 \text{ cm s}^{-1}$  with 0.1 M TEAP as electrolyte. Finally, Arevalo et al.<sup>8</sup> found a standard rate constant in dimethylformamide equal to  $0.43 \,\mathrm{cm}\,\mathrm{s}^{-1}$ . Their result is consistent with those obtained here.

The interesting aspect of the present study is that the rate constants for electroreduction of Bzph are approximately the same as those for two other known fast electron-transfer reactions, namely, the electrooxidation of ferrocene<sup>11</sup> and cobaltocene.<sup>25</sup> On the other hand, the enthalpy of activation is slightly larger in spite of the fact that the Bzph system has a larger effective radius. These results are attributed to the fact that an electrontransfer reaction in which an anion is formed from a molecule is expected to be slower than the reaction involving the same molecule oxidized to form a cation. Thus, if one compares the present data with those for the electroreduction of cobaltocene to form the cobaltocenate anion,<sup>25</sup> one finds that the reduction of Bzph is 1 order of magnitude faster. On the other hand, the enthalpy of activation for the cobaltocene reduction is only slightly higher than that for the present system. These differences are clearly due to differences in the dynamic solvent effect for the cobaltocene reaction for which the fraction  $\theta$  is equal to 0.6. As a result, the contribution from the temperature dependence of the solvent's longitudinal relaxation time to the experimentally observed  $\Delta H^*_{ex}$  is smaller. It should be kept in mind that the estimates of  $\Delta G^*_{os}$  given in Table III were obtained assuming that the reaction is perfectly adiabatic. If one sets the coefficient  $\theta$  equal to 0.9 in eq 5, the estimates of  $\Delta G^*$  increase by about 1 kJ mol<sup>-1</sup>. This difference is quite small and not important with respect to assessing the model used to estimate  $\Delta G^*_{\infty}$ .

Some comment should also be made on a possible relationship between the degree of dependence of the pre-exponential factor on solvent dynamics and the effect of electron tunneling distance on the rate constant. The parameter  $\theta$  in eq 2 is related to the value of the electronic transmission coefficient, which depends in a complex way on the shape of the Gibbs activation energy barrier and the degree of orbital overlap in the electron-exchange reaction.<sup>31-33</sup> The fact that  $\theta$  is close to unity for the reduction of Bzph in the presence of TEAP suggests that the transmission coefficient  $\kappa$  is also close to unity. As the reactants are separated by increasing the size of the TAA<sup>+</sup> cation,  $\kappa$  decreases if the reaction is nonadiabatic.<sup>29</sup> Thus, it would be interesting to examine the relationship between the standard rate constant and the solvent's longitudinal relaxation time in a series of solvents using both small and large TAA+ ions. This experiment does not appear to have been carried out to date.

Although the model used to estimate the outer-sphere activation parameters is reasonably successful, it clearly underestimates the effective radius of the reactant. Since the radius of a benzene ring is approximately 340 pm, one should represent these parts of the molecule as ellipsoids with a longer axis along the line from the carbon atom of the carbonyl group through the center of the ring. Similarly, considering the fact that the van der Waal's radius of the oxygen atom is 140 pm, an ellipsoid with the long axis through the C=O bond would give a better representation of the solvation of this part of the molecule. Thus, a model consisting of three contiguous ellipsoids would result in a higher effective radius for the molecule and thus lower estimates of the activation parameters.

Finally, the high-frequency ac admittance technique used for the present study is ideally suited for studying fast electrontransfer reactions. Not only can the state of the electrode surface be monitored directly in the experiment, but also problems with iR drop are insignificant because ultramicroelectrodes are used. Data for other fast electron reactions are presently being obtained in this laboratory and will be presented in future papers.

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