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Kinetics and Thermodynamics of the Electroreduction of Buckminsterfullerene in Benzonitrile

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Abstract: The kinetics and thermodynamics of the reduction of buckminsterfullerene (C_{60}) have been studied in benzonitrile solutions containing tetraalkylammonium salts as electrolytes. On the basis of the observed shifts in half-wave potential with electrolyte concentration, it is shown that the resulting anions from the first and second reduction steps, namely C_{60}^- and C_{60}^{2-} are associated with two or more tetraalkylammonium cations, the strength of the resulting association increasing with increasing cation size. The rate constants for both reactions and the activation enthalpy for the first step are also reported. Electron transfer is fast, as one would expect for a large spherical reactant. The kinetic data obtained are compared with data for other fast electron-transfer reactions.

Introduction

The chemistry of buckminsterfullerene (C_{60}), the new allotropic form of carbon,[1] has been investigated intensively in recent years. An important reaction of this molecule in solution is its reduction to the corresponding anion radical and dianion.[2] In fact, at low temperature it has been shown[2g,h] that up to six electrons may be transferred to the molecule in single electron-transfer steps.

Although C_{60} can be dissolved in only a few polar solvents, determination of the kinetic and thermodynamic aspects of its redox chemistry is an important part of characterizing this system in solution. On one hand, since the molecule is essentially spherical,[1] it represents an ideal system for testing the predictions of electron-transfer theory.[3] The relative role of ion–ion and ion–solvent interactions in determining the solution properties of the anionic species formed from C_{60} are also of interest from the point of view of solution structure. In fact, Greaney and Gorun[4] suggested that ion pairing between the anion radical C_{60}^- and tetrabutylammonium cations (TBA^+) occurs in methylene chloride–toluene solutions on the basis of the presence of both sharp and broad EPR signals obtained at room temperature. Careful examination of the electrochemical parameters obtained in solutions of varying ionic strengths can provide useful macroscopic information regarding these interactions.

In the present paper, we report a study of the thermodynamics and kinetics of the formation of C_{60}^- and C_{60}^{2-} in benzonitrile (BzN). The choice of solvent was based on the solubility of C_{60} and the resistivity of BzN solutions containing tetraalkylammonium perchlorates (TAAP) as electrolyte. Because of the polarizable range available in BzN, the present study was limited to the first two reduction steps. Considering the resistivity of the medium, we chose to use the ac admittance technique developed recently by Baranski[5] to determine kinetic parameters at ul-

tramicroelectrodes. In such an experiment, one may determine the equilibrium rate constant k_e and the experimental transfer coefficient α_{ex} under conditions for which one may simultaneously monitor the state of the electrode surface. Thermodynamic parameters were determined in cyclic voltammetric experiments which provide easy confirmation of reaction reversibility. We also report kinetic data for the oxidation of ferrocene (Fc) and related systems in BzN so that the present kinetic results may be compared with a growing body of data for fast heterogeneous electron-transfer reactions.[6]

Experimental Section

Reagents. A mixture of fullerenes was produced by a modification of the resistive-arc vaporization method.[7] Extraction of the resulting soot followed by chromatographic separation on alumina yielded pure C_{60} and C_{70}.[8] The electrolytes tetraethylammonium perchlorate (TEAP) and tetrabutylammonium perchlorate (TBAP) were obtained by metathesis of the corresponding bromides with perchloric acid in water. They were recrystallized twice from a water–ethanol mixture and dried under reduced pressure at 70 °C for 24 h. $AgClO_4$, cobaltacinium hexafluorophosphate ($CbPF_6$), and Fc were used as received from Strem. BzN (Kodak) was purified by distillation twice under reduced pressure. The first distillation was performed over P_2O_5, whereas the second was done over NaOH pellets.

Apparatus. Cyclic voltammetry was performed using the EG&G/ PAR 273 potentiostat. The error in estimation of the $E_{1/2}$ potential was less than 5 mV. The apparatus for ac voltammetry was similar to that built by Baranski.[5] The Solartron 1250 frequency response analyzer served as the source of dc potential and sinusoidal perturbation (10 mV peak-to-peak). This signal was fed into the external input of the 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 directly fed 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-phase and out-of-phase components of the admittance. The experimental parameters and data acquisition were controlled by a dedicated microcomputer.

The ac measurements were performed in a three-electrode cell. The working electrode was a Pt ultramicroelectrode made of wire with a diameter of 25 μm (Goodfellow Metal, Ltd.) sealed into a soft glass capillary in a Bunsen flame. The tip of the capillary was polished with fine carborundum paper and a 0.3-μm alumina slurry, in sequence. An Ag wire immersed in 0.01 M $AgClO_4$ and 0.09 M TBAP in acetonitrile and separated from the working solution by a ceramic tip (Bioanalytical Systems) served as the reference electrode. The solution in the reference electrode compartment was changed every day in order to maintain

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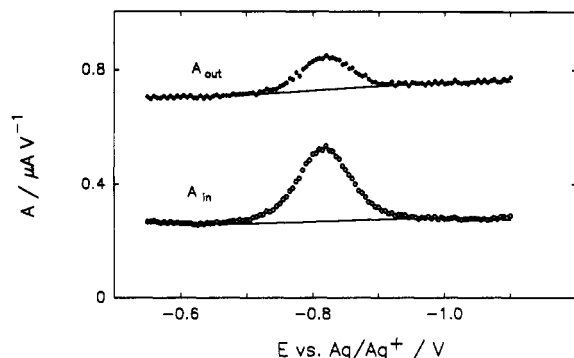
Figure 1. Plots of the in-phase and out-of-phase admittance as a function of dc potential at a frequency of 2 kHz observed for the reduction of 0.2 mM C_{60} in benzonitrile containing 0.1 M TEAP.
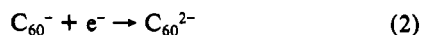

Figure 2. Plot of the rate constant for reduction of C_{60} in benzonitrile as a function of electrode potential measured with respect to the peak potential $E_{1/2}$. The kinetic data were obtained from the admittance data presented in Figure 1.

potential stability. The counter electrode was a Pt tab with an area of ~ 0.5 cm^2.

Procedures. All cyclic voltammetric experiments were performed in the presence of 0.5–1 mM Fc in the same solution. All ac experiments were performed with a C_{60} concentration in the range of 0.15–0.2 mM with 0.1 M electrolyte, the concentration of C_{60} being verified spectroscopically. The appropriate frequency range was estimated using a simulation program written by Baranski.[5c] The frequency range used was from 1.5 to 3.4 kHz. At lower frequencies, the signal-to-noise ratio was too small to obtain reasonable results. The admittance was measured at potential intervals of 5 mV in a potential range of 0.6 V around the standard potential of a given system. Since stray capacitance (2–3 pF in the present case, as estimated from open circuit admittance measurements) represents a negligible fraction of the electrode capacitance (400–1000 pF), no correction for it was necessary. The value of the solution resistance, estimated from the high-frequency admittance, was found to be 410 $\pm$ 30 Ω cm for 0.1 M TEAP and 490 $\pm$ 30 Ω cm for 0.1 M TBAP. The latter value is similar to that reported in the literature earlier (477 Ω cm).[9] The resistance and capacitance values served as a test that the cross sectional area of the wire was exposed to solution. The frequency dependence of the current follower response was found to be negligible using a RC circuit consisting of an 80-kΩ resistor and 400-pF capacitor in series.

At a given frequency, the nonfaradaic in-phase and out-of-phase admittances in the region preceding and following the faradaic peak were fitted to a third-degree polynomial by least squares (Figure 1). After blank line correction, the rate constants were determined in the vicinity of the standard potential using the de Levie–Husovsky method[10] as modified by Fawcett and Lasia.[11] This procedure is especially convenient because it does not require knowledge of the surface concentrations of the oxidized and reduced forms involved in the electrode reaction. In addition, linear diffusion is maintained for the ac frequency range used as demonstrated both by theoretical analysis[5c] and experimental verification.[5b] Finally, the equilibrium rate constant k_e and the experimental transfer coefficient α_{ex} were obtained from the slope and zero intercept of a plot of the logarithm of the rate constant against electrode potential (Figure 2). The reproducibility of the standard rate constant was $\pm 10\%$.

Results and Discussion

Thermodynamics. Two reversible reduction waves were observed by cyclic voltammetry at a scan rate of 10 mV s^{-1} in all electrolytes studied in the potential range from -0.8 to -1.5 V versus the Ag/Ag$^+$ reference electrode. They correspond to reactions 1 and 2. The position of these waves depends on electrolyte

$$C_{60} + e^- \rightarrow C_{60}^- \qquad (1)$$

$$C_{60}^- + e^- \rightarrow C_{60}^{2-} \qquad (2)$$

concentration, shifting in the positive direction when the concentration of the electrolyte c_s was increased. These changes can be attributed to changes in activity of the components of the reaction, to changes in the liquid junction potential between the reference electrode compartment and the main body of the cell,
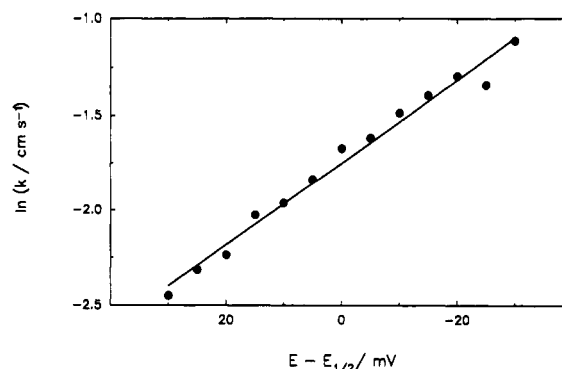
and to possible ion pairing between the anions involved in the above reactions and the TAA$^+$ cations of the electrolyte. The latter effect has been observed previously in the case of electroreduction of aromatic nitro compounds in the presence of TEA$^+$[12,13] and TBA$^+$ cations.[14]

In order to assess the observed potential shifts more carefully, they were compared to those for the electrooxidation of Fc.

$$\text{Fc} \rightarrow \text{Fc}^+ + e^- \qquad (3)$$

In this case, the shift was much smaller ($\lesssim 10$ mV) but also in the same direction. For a system in which the diffusion coefficients of the reactant and product are equal and the ion pairing is absent, the relationship between the peak or half-wave potential $E_{1/2}$ and the standard potential for the reduction reaction

$$A + e \rightleftharpoons B \qquad (4)$$

is as follows:

$$E_{1/2} = E_s + \frac{RT}{F} \ln \frac{\gamma_A}{\gamma_B} \qquad (5)$$

where γ_A and γ_B are the activity coefficients of species A and B, respectively. The change in half-wave potential of reaction 3 with change in ionic strength is then

$$\Delta E_{1/2} = \frac{RT}{F} \Delta \ln \gamma_{Fc^+} \qquad (6)$$

where the activity coefficient of the ferrocene molecule is assumed to be independent of ionic strength. On the basis of the limiting Debye–Hückel law, the value of $\Delta E_{1/2}$ expected for a change in ionic strength from 0.01 to 0.05 in BzN solutions containing a 1–1 electrolyte is -20 mV. Considering the fact that changes in the activity coefficient of the anion radical are expected to be much less than predicted by the limiting Debye–Hückel law, considering the ion's size and the ionic strength range, the corresponding value of $\Delta E_{1/2}$ is probably less than 10 mV. Since there is no independent means of estimating salt activity, this complication is ignored in the following analysis. With respect to possible ion pairing, if this occurred between the Fc$^+$ cation and perchlorate ions, one would observe an additional shift of $E_{1/2}$ in the negative direction. The fact that the observed change in $E_{1/2}$ amounts to no more than 10 mV in the positive direction suggests that ion pairing is negligible for the Fc$^+$ cation. Thus, we conclude that the observed change in $\Delta E_{1/2}$ is largely due to a change in liquid junction potential. In the following analysis, the half-wave potential of the Fc$^+$/Fc system is used as an internal standard.

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Table I. Kinetic and Thermodynamic Parameters for the Electroreduction of C_{60} in Benzonitrile at 25 °C

	$C_{60} + e \rightarrow C_{60}^-$		$C_{60}^- + e \rightarrow C_{60}^{2-}$	
	TEAP	TBAP	TEAP	TBAP
peak potential,[a] $E_{1/2}/V$	−0.889	−0.896	−1.344	−1.325
peak potential in absence of ion aggregation,[b] $E_{1/2}^0/V$	−0.962 ± 0.001	−0.988 ± 0.008	−1.391 ± 0.004	−1.396 ⬤ 0.008
no. of cations associated with product anion, n	2	2	3	3.4
association constant,[b] K_{an}	1670 ± 80	3500 ± 1100	$(1.1 ± 0.2) \times 10^5$	$(1.4 ± 0.5) \times 10^6$
rate constant at $E_{1/2}/$cm s^{-1}	0.18	0.10	0.09	0.04
rate constant at $E_{1/2}^0$,[c] $k_s/$cm s^{-1}	0.7	0.5	0.2	0.2
diffusion coefficient, $D/$cm^2 s^{-1}	2.6×10^6		2.5×10^{-6}	

[a] Measured with respect to the internal ferrocene/ferrocinium couple. [b] Estimated by analyzing the data using eq 9 (first step) or eq 11 (second step). [c] Obtained using the experimental linear relation between the logarithm of the rate constant and electrode potential.
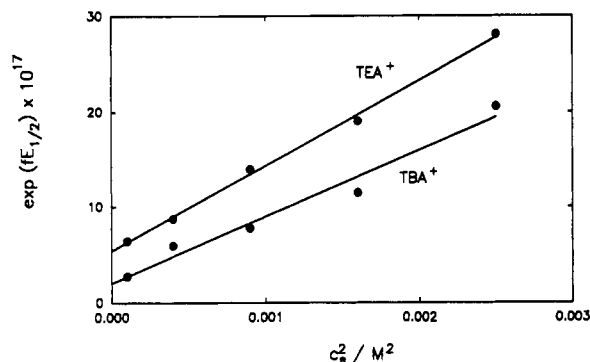
Figure 3. Plot of the function $\exp(fE_{1/2}) \times 10^{17}$ for the first reduction step against electrolyte concentration squared c_s^2, where $E_{1/2}$ is the peak potential and $f = F/RT$. The electrolytes were TEAP or TBAP as indicated.

The values of $E_{1/2}$ for the reduction of C_{60} and C_{60}^- were observed to shift in the positive direction with increase in TAAP concentration by more than 50 mV in both electrolytes. For the first reaction, some of this shift is due to a decrease in the activity coefficient for C_{60}^- and is given by the expression

$$\Delta E_{1/2} = \frac{-RT}{F} \Delta \ln \gamma C_{60}^- \tag{7}$$

Since there is no way of assessing this contribution, it is ignored in the following analysis. Activity effects are obviously larger for the second reduction step, so quantitative results for this reaction are less reliable.
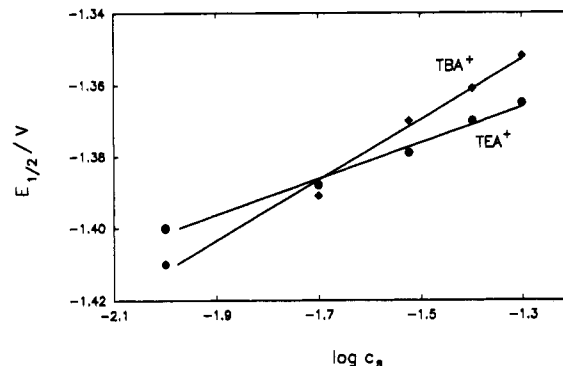
Association constants for the first reduction step may be extracted from the peak potential data obtained using the relationship[12–15]

$$\Delta E_{1/2} = E_{1/2} - E_{1/2}^0 = \frac{RT}{F} \ln (1 + K_{a1}a_s^n) \tag{8}$$

where $E_{1/2}^0$ is the half-wave potential estimated in the absence of ion association ($c_s = 0$), a_s is the mean salt activity, n is the number of cations associated with one anion, and K_{a1} is the association constant. When ion association is strong and $K_{a1}a_s^n \gg 1$, it follows that a plot of $E_{1/2}$ against $\ln a_s$ has a slope equal to nRT/F and permits one to determine the number of cations associated with each anion radical. For the present system, assuming that the mean activity is equal to electrolyte concentration, these plots show that n is equal to 2 in the limit of higher electrolyte concentrations. It follows that eq 8 can be rewritten as

$$\exp(fE_{1/2}) = \exp(fE_{1/2}^0) + \exp(fE_{1/2}^0)K_{a1}c_s^2 \tag{9}$$

where $f = F/RT$, so that a plot of $\exp(fE_{1/2})$ against c_s^2 should be linear and yield $E_{1/2}^0$ and K_{a1} from the intercept and slope. The present data plotted according to eq 9 are shown in Figure 3. The resulting values of $E_{1/2}^0$ and K_{a1} together with estimated errors are recorded in Table I. As one would expect, association between C_{60}^- and the TAA$^+$ cation is stronger for TBA$^+$ than for TEA$^+$.

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Figure 4. Plot of the peak potential for the second step against the logarithm of electrolyte concentration using data obtained in the presence of TEAP or TBAP as indicated.

Scheme I
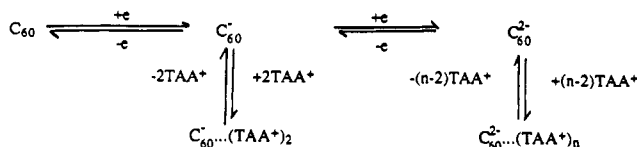
In the case of the second reduction step, the relationship between the half-wave potential and electrolyte concentration for the case of strong ion association is given by[15]

$$\exp(f\Delta E_{1/2}) = \frac{1 + K_{a\infty}c_s^n}{1 + K_{a1}c_s^2} \tag{10}$$

where n is the number of cations associated with the dianion C_{60}^{2-} and K_{a2} is the corresponding association constant. Assuming that ion association is strong so that 1 may be neglected in both the numerator and denominator, eq 10 simplifies so that the value of $n - 2$ can be determined from a plot of the peak potential against $\ln c_s$. Such a plot is shown in Figure 4, from which one finds that $n - 2$ is 1 in the case of the TEA$^+$ electrolyte and 1.4 in the case of the TBA$^+$ electrolyte. It follows that three TEA$^+$ cations and an average of 3.4 TBA$^+$ cations are associated with the dianion C_{60}^{2-}. Further analysis of the data requires rearranging eq 10 in the form

$$\exp(fE_{1/2}) (1 + K_{a1}c_s^2) = \exp(fE_{1/2}^0) + \exp(fE_{1/2}^0)K_{a2}c_s^n \tag{11}$$

The function on the left-hand side is easily calculated from the experimental data using the association constant determined earlier for the first step. Plots of the function on the left-hand side of eq 11 against c_s^n resulted in excellent straight lines, from which the values of K_{a2} and $E_{1/2}^0$ reported in Table I were estimated. The analysis of ion pairing for the second step is obviously less rigorous than that for the first. Since both monovalent and divalent ions are involved in reaction 2, the effects of nonideality are more important. Moreover, eq 10 should not be used with a fractional value of n but, strictly speaking, should consider the individual ion association steps so that a sum of terms relating to ion associates with three and four coordinated cations should appear in the numerator of eq 10. This refinement of the analysis is not

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Table II. Standard Rate Constants for the Electroreduction of Typically Fast Reactions in Benzonitrile Containing 0.1 M TBAP

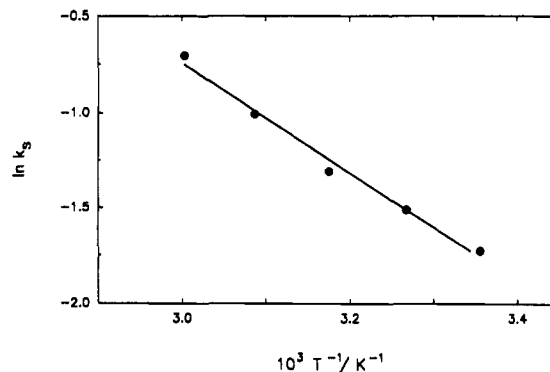| reaction	standard rate constant, k_s/cm s^{-1}
$Fc^+ + e \rightarrow Fc$	0.20
$Cb^+ + e \rightarrow Cb$	0.11
$C_{60} + e \rightarrow C_{60}^-$	0.30
$C_{70} + e \rightarrow C_{70}^-$ [a]	0.09

[a] Uncorrected for possible ion pairing effects.

warranted without proper consideration of ionic strength (activity coefficient) effects and, therefore, is not pursued here. However, the values of K_{a2} recorded in Table I give qualitative evidence that ion association is strong and an important feature of the solution chemistry of the ions formed from C_{60}.

On the basis of the above analysis, Scheme I is proposed for the electroreduction of C_{60} in BzN. The fact that two cations are associated with C_{60}^- undoubtedly reflects the charge distribution in this anion and may indicate that the anion radical no longer maintains the spherical shape of the parent molecule. It is also interesting that the number of ions associated with the reduced form of C_{60} increases with increases in anion charge and always results in a positively charged aggregate. This undoubtedly reflects a predominance of solvophobic interactions over electrostatic ones. Finally, the association constants are large when one compares them with those reported for other organic systems in the literature.[12-14]

Kinetics. Typical admittance data for the first reduction step are shown in Figure 1. Despite the fact that the concentration of C_{60} is quite low, the signal-to-noise ratio is excellent, so very good plots of the rate constant against potential can be obtained from the data in the region around the admittance maxima (see Figure 2). In all cases, the maxima on the admittance plots corresponded to $E_{1/2}$ within experimental error. Kinetic data obtained for both the first and second reduction steps in the two electrolyte solutions studied are recorded in Table I. The transfer coefficient was close to 0.5 in all systems, as one would expect for a simple electron-transfer reaction. In general, the rate constant is smaller in the presence of the larger cation in keeping with results for a number of systems studied at potentials negative of the point of zero charge in the presence of TAA$^+$ cations of varying size.[16] In addition, the rate constant for the second step is slower than that for the first. Since electron-transfer theory[3] predicts that the value of these rate constants should be the same when the reactants have the same size, the fact that the second process is slower is due to a repulsive double layer effect which is greater for the negatively charged reactant than for the neutral reactant. Since the ion association step following electron transfer shifts the peak potential in the positive direction, the experimental rate constants at the peak potential are smaller than those at the standard potential in the absence of ion pairing. The true standard rate constants were estimated by extrapolation, using the observed linear relations between the logarithm of the rate constant and electrode potential (Figure 2).

In order to assess the accuracy of the present results, kinetic data were obtained for other typically fast redox systems in the same solvent (See Table II). In the case of the Fc/Fc$^+$ system, the standard rate constant is 0.2 cm s^{-1}, a result that seems reasonable when compared to data obtained in other solvents.[17-20] Using results obtained by the same technique in other solvents[5a] the present result in BzN falls on the same linear correlation between the logarithm of the standard rate constant and the logarithm of the solvent's longitudinal relaxation time.[6] Furthermore, the results obtained recently[17] in two faster solvents, proprionitrile and butyronitrile, using a quite different experimental

Figure 5. Plot of the logarithm of the standard rate constant for reduction of C_{60} in benzonitrile solutions containing 0.1 M TEAP against reciprocal temperature.

technique confirm the earlier work. The present results for the Cb$^+$/Cb system is also consistent with data obtained for this reaction in other solvents.[5b] Thus, we are quite confident that the ac admittance technique used provides accurate kinetic data with none of the problems often encountered when using slower relaxation methods.

It is interesting to assess the kinetic data obtained here within the context of contemporary electron-transfer theory with consideration of dynamical solvent effects.[21] One may obtain an estimate of the lower limit of the Gibbs activation energy by assuming that the reaction is adiabatic. Then the standard rate constant is given by

$$k_s = \kappa K_p \tau_L^{-1} \left(\frac{\Delta G^*}{4\pi RT} \right)^{1/2} e^{-\Delta G*/RT} \tag{12}$$

where κK_p is the encounter preequilibrium term, which is approximately 20 pm for adiabatic reactions,[5a,22] τ_L is the longitudinal solvent relaxation time, and ΔG^* is the Gibbs reorganization energy. Assuming that τ_L is equal to 5.8 ps in benzonitrile,[6] the value of ΔG^* for the first reduction step in the TEAP solution is 14.3 kJ mol^{-1}. A slightly higher value is obtained in the presence of TBAP (15.1 kJ mol^{-1}). If the reaction is not perfectly adiabatic, then the preexponential factor is smaller and the value of ΔG^* larger. The outer sphere contribution to ΔG^* can be estimated according to Marcus theory.[3] If one assumes a negligible imaging effect,[5a,22] then ΔG_{os}^* is given by

$$\Delta G_{os}^* = \frac{N_0 e^2}{32\pi\epsilon_0 r_A} \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \tag{13}$$

where r_A is the radius of the reactant, ϵ_{op} is the optical dielectric constant of benzonitrile (2.328), and ϵ_s is its static value (25.2). Assuming that r_A for C_{60} is equal to 0.43 nm,[23] the resulting value of ΔG_{os}^* is 15.8 kJ mol^{-1}. If one assumes that there is no internal reorganization energy, this estimate is remarkably close to the value estimated from the experimental data in the TEAP electrolyte for the first reduction reaction if it is perfectly adiabatic.

On the other hand, if the reaction is not perfectly adiabatic, then the estimate of ΔG^* from experiment is higher and some contribution from inner reorganization expected. This would imply that the anion radical is no longer spherical and undergoes some distortion due to the Jahn-Teller effect.[24] The value of ΔG_{os}^* may also be estimated on the basis of the mean spherical approximation (MSA).[25] This gives a slightly smaller value for ΔG_{os}^*, which is closer to the experimental estimate for a perfectly adiabatic process.

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In order to further assess the activation parameters for reduction of C_{60}, the experimental activation enthalpy ΔH^*_{ex} for reaction 1 in the presence of 0.1 M TEAP was measured in the temperature range of 25–60 °C (see Figure 5). The resulting value, 23.9 ± 1.5 kJ mol^{-1}, is higher than those obtained for ferrocene oxidation,[5a,17] but this undoubtedly reflects a large contribution from the dynamic solvent effect. If reaction 1 is perfectly adiabatic, then ΔH^*_{ex} may be divided into contributions from the inner and outer reorganization enthalpies ΔH^* and from the temperature dependence of the preexponential factor. The appropriate relationship is[26]

$$\Delta H^*_{ex} = \Delta H^* + \Delta H_L - RT/2 \qquad (14)$$

where ΔH_L is the enthalpy associated with the temperature dependence of the longitudinal relaxation time. ΔH_L is estimated to be 11.9 kJ mol^{-1} on the basis of available permittivity data.[27] Thus, the minimum value of ΔH^* is 13.2 kJ mol^{-1}. If the reaction is not perfectly adiabatic, then the contribution to ΔH^*_{ex} from the temperature dependence of the preexponential factor decreases and the value of ΔH^* increases. On the basis of the Marcus model, estimation of the outer sphere contribution to the activation enthalpy requires that the temperature coefficients of the dielectric parameters be known. From eq 13, the corresponding expression for ΔH^*_{os} is

$$\Delta H^*_{os} = \frac{N_0 e^2}{32\pi\epsilon_0 r_A} \left[\frac{1}{\epsilon_{op}} + \frac{T}{\epsilon_{op}^2}\frac{\partial\epsilon_{op}}{\partial T} - \frac{1}{\epsilon_s} - \frac{T}{\epsilon_s^2}\frac{\partial\epsilon_s}{\partial T} \right] \qquad (15)$$

Using tabulated values of $\partial\epsilon_s/\partial T$ (−0.091 K^{-1})[28] and $\partial\epsilon_{op}/\partial T$ (−1.47 × 10^{-3} K^{-1}),[29] the estimate of ΔH^*_{os} is 14.2 kJ mol^{-1}. This result is remarkably close to the value of ΔH^* from experiment, assuming that the reaction is adiabatic.

In assessing the above analysis, it should be kept in mind that departure from perfect adiabaticity for simple electron-transfer reactions can be related to an increase in the importance of inner sphere reorganization on theoretical grounds.[30] There clearly is a need to examine the structure of the anions formed from C_{60} to determine whether they are significantly distorted with respect to the well-known spherical structure of the parent molecule. Then the inner sphere contribution to ΔG^* and ΔH^* could be independently estimated. From an electrochemical point of view, the adiabaticity of the process can be examined by studying the kinetics in a variety of solvents. C_{60} can also be electroreduced in dichloromethane, pyridine, o-dichlorobenzene, and tetrahydrofuran, solvents which are weakly polar. Thus, one expects ion pairing to play a more important role in these systems, so that the necessary kinetic information, namely, values of the standard rate constant, could only be obtained if a thorough study of ion pairing is made as well. On this basis, one must conclude that C_{60} is not the ideal system for testing electron-transfer theory that one might expect without knowledge of the role of ion pairing.

In comparing the present data for reduction of C_{60} with those for Fc oxidation, it is clear that the former reaction is only slightly faster than the later, in spite of the fact that the radius of C_{60} is significantly larger than that of Fc. In assessing this result, one must keep in mind the fact that the outer sphere contribution to the Gibbs activation energy for a reaction in which an anion is formed is larger than that in which a cation is formed, all other reaction parameters remaining the same.[22] Thus, if one were able to oxidize C_{60} reversibly to form the cation radical C_{60}^+ in BzN, then the rate of electron transfer should be approximately an order of magnitude higher.

Conclusions

The present experiments demonstrate clearly that ion association occurs between the anions formed from C_{60} and the TAA$^+$ cations used in the electrolyte with two cations associated with the first anion. Ion association is relatively strong and clearly would be much stronger if small cations such as the alkali metal ions were used. The fact that two cations are associated with the anion radical suggests that the anionic species may be significantly distorted from sphericity.

As expected, the rate constants for electron transfer to C_{60} and C_{60}^- are high because of the large size of the reactant. In comparing the present results with those for other fast electron-transfer reactions involving spherical reactants, one should consider reactions in which anions are formed from the parent molecule. Thus, for the reduction of cobaltacene to form the cobaltacene anion, the rate constants are expected to be an order of magnitude smaller in the same solvent because this system is smaller and thus has a larger value of the outer sphere Gibbs activation energy. One should not compare the present data with those for the oxidation of the same molecule to form the cation radical because both theory and experiment[22] demonstrate that the reaction to form the cation is faster than that to form the corresponding anion.

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