kcal mol⁻¹ higher than the value of 31.44 ± 0.54 kcal mol⁻¹ obtained in this study. The error in our determination of k_2/k_{-2} needed to rationalize a 3-4 kcal mol⁻¹ increase in $\Delta H_{f,0}$ (CH₃S) is a factor of several hundred in the direction where k_2 would have to be slower or k_{-2} would have to be faster; errors of this magnitude seem unlikely.

Summary

Time-resolved resonance fluorescence detection of $Br(^{2}P_{3/2})$ disappearance following 266-nm laser flash photolysis of $CF_2Br_2/H_2S/H_2/N_2$, $CF_2Br_2/CH_3SH/H_2/N_2$, $Cl_2CO/H_2S/$ HBr/N₂, and CH₃SSCH₃/HBr/H₂/N₂ mixtures has been employed to study the kinetics of reactions 1, 2, -1, and -2 as a function of temperature. In units of 10^{-12} cm³ molecule⁻¹ s⁻¹, Arrhenius expressions which describe our results are $k_1 = (14.2)$ \pm 3.4) exp[(-2752 \pm 90)/T], $k_{-1} = (4.40 \pm 0.92) \exp[(-971 \pm$ 73)/T], $k_2 = (9.24 \pm 1.15) \exp[(-386 \pm 41)/T]$, and $\hat{k}_{-2} = (1.46)$ \pm 0.21) exp[(-399 \pm 41)/T]. By examining Br(²P_{3/2}) equilibration kinetics following 355-nm laser flash photolysis of Br₂/ $CH_3SH/H_2/N_2$ mixtures, a 298 K rate coefficient of (1.7 ± 0.5) $\times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ has been obtained for the CH₃S + Br₂ reaction. To our knowledge, these are the first kinetic data reported for each of the reactions studied. Comparison of A factors and activation energies for reactions 1, -1, 2, and -2 with known kinetic parameters for other radical + H₂S, CH₃SH, HBr hydrogen-transfer reactions suggests that both thermochemistry and electronic properties (i.e., IP - EA) exert important influences on observed reaction rates.

Second and third law analyses of the equilibrium data, i.e., k_1/k_{-1} and k_2/k_{-2} , have been employed to obtain the enthalpy changes associated with reactions 1 and 2. At 298 K, reaction 1 is endothermic by 3.64 kcal mol⁻¹ while reaction 2 is exothermic by 0.14 kcal mol⁻¹. Combining the experimentally determined enthalpies of reaction with the well-known heats of formation of Br, HBr, H₂S, and CH₃SH gives the following heats of formation for RS radicals in units of kcal mol⁻¹: $\Delta H_{f_0}^{\circ}(SH) = 34.07 \pm 0.72$, $\Delta H_{\rm f}^{\circ}{}_{298}(\rm SH) = 34.18 \pm 0.68, \ \Delta H_{\rm f}^{\circ}{}_{0}(\rm CH_{3}S) = 31.44 \pm 0.54;$ $\Delta H_{\rm f}^{\circ}_{298}(\rm CH_3S) = 29.78 \pm 0.44$; errors are 2σ and represent estimates of absolute accuracy. The SH heat of formation determined from our data agrees well with literature values but has reduced error limits compared to other available values. The CH₃S heat of formation determined from our data is near the low end of the range of previous estimates and is 3-4 kcal mol⁻¹ lower than values derived from recent molecular beam photofragmentation studies. 58,64,65

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Comparison of Heterogeneous and Homogeneous Electron-Transfer Rates for Some Nitroalkanes and Diketones

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Redox catalysis has been used to investigate the homogeneous electron-transfer reactions between the substrates (nitroalkane or diketone) and the reduced form of the catalyst, which was terephthalonitrile. The substrates were RNO₂ (R = Me, Et, *i*-Pr, and *t*-Bu) and RC(O)C(O)R (R = Me, Et, and *t*-Bu). The experiments were conducted in acetonitrile solvent at 298 K with three different electrolytes, R_4NClO_4 (R = Et, *n*-Bu, and *n*- C_7H_{15}). The effect of added water and alcohols (methanol, ethanol, and *s*-butanol) was investigated. Formal potentials and standard heterogeneous electron-transfer rate constants, k_s , were also determined. It was found that increasing the size of the cation of the electrolyte resulted in a decrease in k_s but did not affect the rate of the homogeneous electron-transfer reactions. The result is interpreted as a decrease in influence the homogeneous reaction. Addition of the hydroxylic solutes, S, caused diminution of both k_s and the rate constant for homogeneous electron transfer from the anion radical of the substrate to the catalyst. This result is discussed in terms of two models, viz., complexation or adduct formation between the anion radical and S or increasing solvation energy of the anion radical.

Introduction

Factors governing the rates of heterogeneous and homogeneous electron-transfer reactions continue to be of fundamental interest. It has recently been demonstrated¹ that the technique of homogeneous redox catalysis² can be used to determine rate constants for solution electron-transfer reactions between a catalyst redox couple and a substrate couple even when there are no irreversible chemical steps to drive the catalysis reaction. In this way, the rate constant for electron transfer from the radical anion of terephthalonitrile to 2-methyl-2-nitropropane was measured under a variety of conditions. From the known self-exchange rate constant for terephthalonitrile and its radical anion, the self-exchange rate constant for 2-methyl-2-nitropropane and its radical anion was estimated for the first time.

In this technique, mixtures of the catalyst (P) and the substrate (A) are investigated by cyclic voltammetry. The catalyst couple is chosen so that its formal potential, E° _{PO}, is close to that of the

$$\mathbf{A} + \mathbf{e} = \mathbf{B} \qquad E^{\mathbf{e}'}{}_{\mathbf{A}\mathbf{B}} \tag{1}$$

$$P + e = Q \qquad E^{\circ'}{}_{PQ} \tag{2}$$

$$A + Q \stackrel{\kappa_{f_{A}}}{\underset{k_{b}}{\leftarrow}} B + P \qquad \ln K_{3} = (F/RT)(E^{\circ'}{}_{AB} - E^{\circ'}{}_{PQ}) \qquad (3)$$

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substrate, $E^{\circ'}{}_{AB}$, so that reaction 3 has an opportunity to occur to a certain extent. When it does, P is regenerated near the electrode giving enhanced currents at the potential needed to reduce P, and this enhancement is governed by the rate of the solution electron-transfer reaction, eq 3. Analysis of the data affords the rate constants, k_f and k_b . The success of the method depends upon the substrate couple, A/B, having sufficiently sluggish heterogeneous electron-transfer kinetics so that direct reduction of A at the electrode does not interfere.

An interesting feature of the technique is that the response is sensitive to the heterogeneous electron-transfer kinetics of both the substrate (A/B) and catalyst (P/Q) couples as well as the homogeneous solution electron-transfer kinetics as discussed above. Thus, both types of electron-transfer reactions can be characterized under exactly the same experimental conditions. This is relevant because environmental factors are known to affect the rates of both kinds of reaction. For example, the identity of the solvent, the nature and concentrations of hydroxylic solutes are all known to affect the rates of electron-transfer reactions. A major objective of the present work was to determine the nature and extent of these environmental effects.

The technique just described has been used to measure the rates of the solution electron-transfer reactions between terephthalonitrile catalyst and four nitroalkanes (RNO₂; R = Me, Et, *i*-Pr, and *t*-Bu) and three diketones (RC(O)C(O)R; R = Me, Et, and *t*-Bu). The effect of supporting electrolyte and the addition of water or an alcohol has been studied for several of the systems.

Experimental Section

The apparatus and procedures for cyclic voltammetry have been described previously.¹ The numerical procedures for parameter estimation were also the same as those developed earlier.¹ All data were obtained at 25.0 °C in acetonitrile solvent with a hanging mercury drop working electrode (2.56 \times 10⁻² cm²). Potentials are reported with respect to a silver reference electrode (AgRE), a silver wire in contact with 0.010 M silver nitrate and 0.10 M tetra-*n*-butylammonium perchlorate in acetonitrile. Its potential was found to be +0.293 V vs aqueous SCE at 25 °C.

Acetonitrile (UV grade) was from Burdick and Jackson, tetraethylammonium perchlorate (TEAP) was prepared in a previous study,³ tetra-*n*-propylammonium perchlorate (TPrAP) was from Eastman Kodak (Rochester, NY), tetra-*n*-butylammonium perchlorate (TBAP) was from Southwestern Analytical Chemicals (Austin, TX) and tetra-*n*-heptylammonium perchlorate (THpAP) was prepared from tetra-*n*-heptylammonium iodide and silver perchlorate by a previously described method.³ All electrolytes were subjected to three recrystallizations from ethyl acetate and vacuum drying (60 °C) overnight.

Solid catalysts and substrates were recrystallized 2-3 times (usually from ethyl acetate). They were vacuum dried (60 °C) overnight except for terephthalonitrile (1,4-dicyanobenzene), which was dried at atmospheric pressure. Liquid compounds were used as received after purity was verified by ¹H NMR. 3,4-Hexanedione was obtained from Lancaster Synthesis (Windham, NH), and all others were obtained from Aldrich (Milwaukee, WI). Dipivaloyl (2,2,5,5-tetramethyl-3,4-hexanedione) was prepared according to the method of Newman and Arkell.⁴

Results

Example of an Experimental Voltammogram. Backgroundcorrected data and a fit of digital simulation to the experiment are shown in Figure 1. The catalyst (P) was terephthalonitrile (0.26 mM) and the substrate (A) was 2-methyl-2-nitropropane (0.87 mM) with 0.10 M THpAP. The first peak seen on the negative-going sweep is for reduction of the catalyst (P) while the second is due to direct reduction of 2-methyl-2-nitropropane (A). On the return sweep, the single peak seen is for oxidation of the



Figure 1. Cyclic voltammogram of 0.87 mM 2-methyl-2-nitropropane and 0.26 mM terephthalonitrile in acetonitrile with 0.10 M THpAP: scan rate, 100 V/s; circles, simulation including eq 3; parameters, $k_f =$ 6.4×10^5 L mol⁻¹ s⁻¹, $K_3 = 0.048$, $E^{\circ}{}_{AB} = -2.01$ V, $E^{\circ}{}_{PQ} = -1.93$ V; $k_s = 4 \times 10^{-4}$ and 0.15 cm/s for 2-methyl-2-nitropropane and terephthalonitrile, respectively; dashed curve, simulation without eq 3 ($k_f =$ 0).

radical anion of terephthalonitrile (Q). The symbols are the result of a numerical fit (digital simulation¹) to the experimental data.

The dashed curve is calculated with the rate of the homogeneous electron-transfer reaction set to zero, i.e., no catalysis. This curve corresponds to the voltammogram one would obtain for a mixture of two noninteracting species, P and A. It is noteworthy that for this electrolyte and scan rate (100 V/s), the reduction of 2methyl-2-nitropropane is highly irreversible, displaying a peak separation of 950 mV! The difference between the dashed curve and the data reflects the effect of the homogeneous catalysis, eq 3. On the negative-going scan, the current is enhanced at the first peak due to forward reaction 3, which regenerates P to be reduced at the electrode. On the reverse, the single large peak that is seen is due to oxidation of Q. The catalytic effect is even more prominent than on the first half cycle because, in this instance, $K_3 < 1$ so the backward rate of eq 3 is larger than the forward so that B (formed at the second reduction peak) can react quickly with P (which continues to diffuse to the electrode), producing O and A.

All of the kinetic and equilibrium parameters reported in this paper were obtained by analysis of voltammograms like that of Figure 1 or voltammograms of each component alone for the evaluation of formal potentials and heterogeneous electron-transfer rate constants.

Heterogeneous Electron-Transfer Results for Various Electrolytes. Summarized in Table I are the reversible formal potentials,⁵ standard heterogeneous electron-transfer rate constants (k_s) , electron-transfer coefficients (α) , and a variation of α with potential $(d\alpha/dE, V^{-1})$ which has been found to improve the fits to the data for a number of reactions of neutral organic molecules producing anion radicals.^{3,6}

Data for several of the compounds have been acquired in earlier work^{3,6d} under ostensibly identical conditions. The agreement with the present results is generally good. Some of the discrepancies in the magnitude of k_s may be related to slight differences in the level of hydroxylic (presumably water) impurities in view of the marked sensitivity of k_s to such substances (vide infra).

No double layer corrections have been applied. As pointed out earlier,³ there is evidence that tetraalkylammonium cations, particularly the larger ions, are specifically adsorbed at the very

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^{(5) (}a) The quantity actually measured in cyclic voltammetry is the half-wave potential, $E_{1/2}$, which differs from the reversible formal potential, $E^{\circ\prime}$, by a term involving the diffusion coefficients of the oxidized and reduced forms of the couple. Specifically, for the A/B couple, $E_{1/2} = E^{\circ\prime}$, B + $(RT/2F) \ln (D_B/D_A)$.^{5b} In most instances, the diffusion coefficients will be sufficiently similar that the difference between $E_{1/2}$ and $E^{\circ\prime}$ will be less than about 6 mV. See ref 5c for an example. In this paper $E^{\circ\prime}$ will be assumed to equal the measured $E_{1/2}$. (b) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods. Fundamentals and Applications*; Wiley: New York, 1980, p 160. (c) Svanholm, U.; Parker, V. D. J. Chem. Soc., Perkin Trans. 2 1975, 755. (6) (a) Savéant, J. M.; Tessier, J. J. Phys. Chem.

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TABLE I: Results for Heterogeneous Electron-Transfer Reactions^a

compound	electrolyte	<i>E°′</i> , V	k _s , cm/s	α	$d\alpha/dE, V^{-1}$	ref
CH ₃ NO ₂	TEAP	-1.926	0.35	0.55		3
	TBAP	-1.913	3.0×10^{-2}	0.48	0.40	this work
	THpAP	-1.910	5.0×10^{-3}	0.50	0.35	this work
	THPAP	-1.908	3.4×10^{-3}	0.49	0.30	3
CH ₃ CH ₂ NO ₂	TEÂP	-1.956	0.26	0.50		3
· ·	TBAP	-1.945	2.2×10^{-2}	0.49	0.35	this work
	THpAP	-1.940	2.8×10^{-3}	0.50	0.40	this work
	THPAP	-1.936	1.8×10^{-3}	0.48	0.20	3
(CH ₁) ₂ CHNO ₂	TEÂP	-2.000	0.10	0.43		3
	TBAP	-1.984	1.0×10^{-2}	0.45	0.30	this work
	THpAP	-1.965	1.2×10^{-3}	0.47	0.28	this work
	THPAP	-1.973	9.5×10^{-4}	0.47	0.23	3
$(CH_3)_3CNO_2$	TEÂP	-2.00	3.7×10^{-2}	0.45	0.50	6d
	TPrAP	-2.040	$1.0_5 \times 10^{-2}$	0.44	0.20	this work
	TBAP	-2.037	4.1×10^{-3}	0.45	0.25	this work
	TBAP		4.1×10^{-3}	0.43	0.37	6d
	TPeABr		1.8×10^{-3}	0.44	0.37	6d
	THpAP	-2.033	6.5×10^{-4}	0.48	0.35	this work
	THPAP		6.5×10^{-4}	0.43	0.36	6d
biacetyl	TEÂP	-1.718	0.59	0.50		3
•	TBAP	-1.710	0.14	0.42	0.32	this work
	THpAP	-1.700	1.7×10^{-2}	0.45	0.40	this work
	THpAP	-1.708	1.9×10^{-2}	0.43	0.37	3
3,4-hexanedione	TBÀP	-1.730	5.0×10^{-2}	0.42	0.32	this work
	THpAP	-1.755	2.3×10^{-2}	0.42	0.35	this work
dipivaloyl	TEÀP	-1.965	2.7×10^{-2}	0.42	0.40	this work
	TBAP	-1.965	5.5×10^{-3}	0.42	0.40	this work
	THpAP	-1.970	1.9×10^{-3}	0.43	0.40	this work

^a Data obtained at 25.0 °C, with a mercury working electrode, 0.10 M electrolyte, and acetonitrile as solvent. Potentials are referred to the silver reference electrode.

TABLE II: Results for Homogeneous Electron-Transfer Reactions^a

		$k_{\rm f}, L$		k_{11}, L
compound	electrolyte	mol ⁻¹ s ⁻¹	K_3	$mol^{-1} s^{-1}$
CH ₃ NO ₂	THpAP	1.0×10^{7}	1.2	8.2×10^{4}
CH ₃ CH ₂ NO ₂	THPAP	4.2×10^{6}	0.46	1.9 × 10⁴
$(CH_1)_2 CHNO_2$	THpAP	1.6×10^{6}	0.28	4.7×10^{3}
$(CH_3)_3CNO_2$	TPrAP	6.5×10^{5}	0.12	1.9×10^{3}
	TBAP	4.8×10^{5}	0.027	5.8×10^{3}
	THpAP	6.4×10^{5}	0.049	4.7×10^{3}
biacetyl	THpAP ^b	3.0×10^{7}	0.32	1.4×10^{6}
3,4-hexanedione	THpAP ^b	8.0×10^{6}	0.040	8.0×10^{5}
dipivaloyl	TBĂP	3.1×10^{6}	0.31	1.6×10^{4}

^aData obtained at 25.0 °C, with 0.10 M electrolyte, acetonitrile as solvent, and terephthalonitrile as catalyst. Substrate concentrations are 0.6-1.5 mM; catalyst concentrations are 0.06-0.8 mM. ^bN,N-Dimethyl-4-nitroaniline catalyst.

negative potentials required for these reductions. This casts uncertainty on the use of corrections based on the Gouy-Chapman-Stern model of the double layer. As also mentioned earlier,³ the standard correction (based on data for the Hg/0.10 M TEAP, CH_3CN interface⁷), if applied, would yield corrected values of $k_{\rm s}$ about 10 times the apparent values.

Homogeneous Electron-Transfer Rates. The Effect of Electrolyte. Table II summarizes results for the reactions studied. The values of K_3 are computed from the formal potentials for A/B and P/Q that best fit the data. Similarly, the reported $k_{\rm f}$ values are averages of those that best fit a series of voltammograms obtained at various scan rates and catalyst-to-substrate concentration ratios.

For reaction 3, the "cross-relation"⁸ (eqs 4 and 5) provides a

$$k_f^2 = k_{11} k_{22} K_3 f \tag{4}$$

$$\log f = (\log K_3)^2 / [4 \log (k_{11} k_{22} / Z^2)]$$
 (5)

means of computing the self-exchange rate constant, k_{11} , for the substrate couples (Table II). Here k_{22} is the self-exchange rate constant for the catalyst couple $(2.0 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1})^{1.9,10}$ and

Z is the collision number (ca. 3×10^{11} L mol⁻¹ s⁻¹ for molecules of this size⁹).

It is difficult to evaluate the error in the rate measurements. Reproducibility of k_f and K_3 obtained from a series of voltammograms was quite good, typically $\pm 10\%$ for each parameter. Day to day precision was not as good. This is attributed to some variability in residual water content in the solutions studied. As will be seen, both the formal potentials (hence K_3) and rate constants are quite sensitive to the concentration of water. In the studies of heterogeneous electron transfer (Table I), alumina adsorbent was placed in the cell to remove traces of water.¹ For the homogeneous electron-transfer rate measurements, in situ treatment was not possible due to adsorption of substrate, whose concentration must be known.

Electron-Transfer Rates in the Presence of Hydroxylic Solutes. The addition of water or other hydroxylic solutes, ROH, to a dipolar aprotic solvent such as acetonitrile usually brings about a positive shift in the formal potential of a neutral/anion couple.¹¹⁻¹³ The interpretation of these observations is that the anion is stabilized through hydrogen bonding to ROH thus causing the shift in potential. It has also been noted¹² that water suppresses the heterogeneous electron-transfer rate constant for reduction of 2-methyl-2-nitropropane. In view of these results, it was of interest to determine the effect of such solutes on the homogeneous electron-transfer reactions under investigation. To carry out this study, it was necessary to determine first the effect on the formal potentials and the heterogeneous electron-transfer rate constants.

Table III summarizes the results. In all cases, the addition of water or an alcohol causes a positive shift in potential and a

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TABLE III: Results for Heterogeneous Electron-Transfer Reactions in the Presence of Added Hydroxylic Solutes, S^a

compound	electrolyte	[S], M	$\Delta E^{\circ\prime}, \mathrm{mV}$	$k_{\rm s},{\rm cm/s}$
(CH ₃) ₃ CNO ₂	TBAP	0.0 H ₂ O	0	4.1×10^{-3}
		0.056	29	2.7×10^{-3}
		0.14	67	1.8×10^{-3}
		0.20	72	1.4×10^{-3}
		0.33	102	1.1×10^{-3}
		0.61	147	6.0×10^{-4}
		1.17	187	4.0×10^{-4}
	TEAP ^b	0.0 H ₂ O	0	$3.2_5 \times 10^{-2}$
		0.039	23	2.3×10^{-2}
		0.072	40	1.7×10^{-2}
		0.11	53	$1.3_5 \times 10^{-2}$
		0.15	63	1.15×10^{-2}
		0.18	74	1.0×10^{-2}
		0.37	94	5.7×10^{-3}
		0.56	130	4.3×10^{-3}
	TBAP	0.0 CH ₃ OH	0	4.1×10^{-3}
		0.062	10	3.4×10^{-3}
	TBAP	0.0 s-BuOH	0	4.1×10^{-3}
		0.028	4	3.6×10^{-3}
dipivaloyl	TBAP	0.0 H ₂ O	0	5.5×10^{-3}
		0.083	12	4.9 × 10 ⁻³
		0.14	15	4.5×10^{-3}
		0.28	25	4.0×10^{-3}
		0.56	43	3.3×10^{-3}
		1.11	65	2.5×10^{-3}
		2.78	110	1.7×10^{-3}
	TBAP	0.0 EtOH	0	5.5×10^{-3}
		0.043	13	5.0×10^{-3}
		0.17	25	4.0×10^{-3}
		0.86	70	2.3×10^{-3}

^aData obtained at 25.0 °C, with a mercury working electrode, 0.10 M electrolyte, and acetonitrile as solvent. $\Delta E^{\circ\prime}$ is the shift in the formal potential upon addition of the solute, S. ^bRate constants from ref 11. Potentials from unpublished results of D. A. Corrigan.

TABLE IV: Results for Homogeneous Electron-Transfer Reactions in the Presence of Hydroxylic Solutes, S^a

compound	(S), M	$k_{\rm f},$ L mol ⁻¹ s ⁻¹	$k_{\rm b},$ L mol ⁻¹ s ⁻¹	$k_{\rm b}/\beta_0,$ L mol ⁻¹ s ⁻¹
		1.0. 1.1.05	1.0. 24. 1.07	1.0.1.107
$(CH_3)_3CNO_2$	$0.0 H_2O$	4.8×10^{-5}	1.8×10^{7}	$1.8 \times 10^{\prime}$
	0.083	$8.7 \times 10^{\circ}$	9.8 × 10°	4.6×10^{7}
	0.14	8.9 × 10 ⁵	7.6×10^{6}	7.6×10^{7}
	0.28	1.4×10^{6}	4.6×10^{6}	1.8×10^{8}
	0.56	9.2×10^{5}	2.9×10^{5}	6.5×10^{7}
$(CH_3)_3CNO_2$	0.0 s-BuOH	4.8×10^{5}	1.8×10^{7}	1.8×10^{7}
	0.028	4.0×10^{5}	6.5×10^{6}	7.6×10^{6}
dipivaloyl	0.0 H ₂ O	3.1×10^{6}	1.0×10^{7}	1.0×10^{7}
	0.083	4.5×10^{6}	6.2×10^{6}	9.9 × 106
	0.17	4.9×10^{6}	4.0×10^{6}	7.8×10^{6}
	0.22	5.0×10^{6}	3.2×10^{6}	7.2×10^{6}
	0.36	6.1×10^{6}	1.8×10^{6}	5.8×10^{6}
	0.64	6.5×10^{6}	6.4×10^{5}	4.2×10^{6}
	1.19	7.4×10^{6}	1.6×10^{5}	2.3×10^{6}
dipivaloyl	0.0 EtOH	3.1×10^{6}	1.0×10^{7}	1.0×10^{7}
	0.043	3.8×10^{6}	5.9 × 10 ⁶	9.8 × 106
	0.86	3.4×10^{6}	7.0×10^{3}	1.0×10^{5}

^aData obtained at 25.0 °C, with 0.10 M TBAP, acetonitrile as solvent, and terephthalonitrile as catalyst. Substrate concentrations are 0.6-1.5 mM; catalyst concentrations are 0.06-0.8 mM.

reduction in the magnitude of the standard electron-transfer rate constant.

Several homogeneous electron-transfer reactions were investigated in the presence of hydroxylic solutes, and the results are summarized in Table IV.

Discussion

The data obtained in this work provide an opportunity to assess the effects of electrolyte, hydroxylic solutes, and reactant structure on the rates of both heterogeneous and homogeneous electrontransfer reactions. It has long been known that, for reductions of many organic compounds to form the respective anion radicals,



Figure 2. Standard heterogeneous electron-transfer rate constants for nitroalkanes as functions of the hydrodynamic radius of the tetraalkyl-ammonium ions of the supporting electrolyte.

observed values of k_s become smaller as the size of the cation of the supporting electrolyte is increased.^{3,11} (For a review, see ref 3.)

Studies of the temperature dependence of the reduction of nitroethane in TEAP and THpAP yielded a preexponential factor for TEAP that was reasonable for a normal adiabatic electron-transfer reaction. The value for THpAP, however, was about 2% that of TEAP, suggesting that the electron transmission coefficient is much less than unity (nonadiabatic reaction) with the electrolyte having the larger tetraalkylammonium cation.³ The suggestion was made that the electron-transfer reaction was inhibited by a liquidlike film containing tetra-*n*-heptylammonium ions that are known¹⁴ to be specifically adsorbed at the negative potentials required for reduction of nitroalkanes. If this is true, the position of the reactant where electron transfer is most probable will be pushed farther away from the electrode as the size of the electrolyte cation is increased.

With this in mind, the dependence of the observed values of k_s on the size of the cation of the electrolyte was examined. In Figure 2 are plotted values of log k_s for the nitro compounds (Table I) vs the hydrodynamic radii of the tetraalkylammonium ions.¹⁵ Remarkably linear relationships are found with an average slope of $-0.93 \pm 0.06 \text{ Å}^{-1}$. This behavior is reminiscent of the distance dependence of electron tunneling currents,¹⁶ eq 6, where *i* is the

$$i = i_0 \exp[-\beta(d - d_0)] \tag{6}$$

current at distance d, i_0 is its value at d_0 and β is the inverse tunneling decay length, which for molecular electron tunneling has been found to be 0.9 ± 0.1 Å⁻¹. If the electrolyte cations serve as spacers preventing access to the electrode surface, the increasing distance will be the increasing *diameter* of the cations. For the results shown in Figure 2, the slopes should be multiplied by 2.303/2 to give β , resulting in $\beta = 1.1$ Å⁻¹. The data for biacetyl give $\beta = 0.8$ and for dipivaloyl $\beta = 0.7$ Å⁻¹.

Admittedly, other factors must be considered in a complete analysis of the effect of electrolyte cation on the reaction rate. Nevertheless, the results support the idea that adsorbed cations

⁽¹⁴⁾ Gambert, R.; Baumgärtel, H. J. Electroanal. Chem. Interfacial Electrochem. 1985, 183, 315.

^{(15) (}a) The hydrodynamic radii in acetonitrile solvent were estimated by consideration of radii in other solvents^{15b} and correlation with limiting ionic conductivities.^{15c} The values used were as follows (Å): Et_4N^+ , 2.93; Pr_4N^+ , 3.54; Bu_4N^+ , 4.00; *n*-Amyl₄N⁺, 4.44; *n*-Hexyl₄N⁺, 4.7; *n*-Heptyl₄N⁺, 5.0. (b) Matsuura, N.; Umemoto, K.; Takeda, Y. Bull. Chem. Soc. Jpn. 1975, 48, 2253. (c) Kratochvil, B.; Yeager, H. L. Fortschr. Chem. Forsch. 1972, 27, 1.

^{(16) (}a) This general form pertains to electron tunneling between tip and substrate in STM^{16bc} for nonadiabatic intermolecular^{16e} and intramolecular^{16e} electron transfer, and electron transfer from metal electrodes to reagents held at fixed distances.^{16f}
(b) Chang, S.-C.; Yau, S.-L.; Schardt, B. C.; Weaver, M. J. J. Phys. Chem. 1991, 95, 4787. (c) Hansma, P. K.; Tersoff, J. J. Appl. Phys. 1987, 61, R1. (d) Logan, J.; Newton, M. D. J. Chem. Phys. 1983, 78, 4086. (e) Therien, M. J.; Chang, J.; Raphael, A. L.; Bowler, B. E.; Gray, H. B. Struct. Bonding (Berlin) 1991, 75, 109. (f) Li, T. T. T.; Weaver, M. J. J. M. Chem. Soc. 1984, 106, 6107.

form a layer that blocks access of the reactant to the surface, forcing electron tunneling to occur over distances that increase with cation size.

It is also apparent in the data of Table I that the observed values of k_s are affected by the structure of the reactant with increasing size of the alkyl groups causing a decrease in k_s in both series of compounds for all electrolytes examined. Part of this trend may also be due to the effect of distance on tunneling rate. The electroactive moiety (-NO₂ or -C(O)C(O)-) in the freely rotating reactant will, on the average, be farther away from the electrode surface for large alkyl groups than for small.

We turn next to the rates of homogeneous electron-transfer reactions as measured by homogeneous redox catalysis (Table II). Of particular interest in this study was to determine the effect, if any, of cation size on the rate of these reactions. For purposes of comparison, we have chosen to calculate the self-exchange rate constant for the nitroalkane and its radical anion using the cross-relation, eqs 4 and 5. Three electrolytes were used in the investigation of 2-methyl-2-nitropropane, and the total range of the derived self-exchange rate constants is about a factor of 2.5, which is probably barely outside the error limits. The effect of electrolyte is certainly small, much less than the 10-fold change in the heterogeneous rates on going from TPrAP to THpAP.

These results strengthen the interpretation that the effect of cation size on k_s is predominantly a double-layer effect and is not an intrinsic characteristic of the electron-transfer reactions of nitroalkanes in general.

There is clearly a significant structural component to the derived rate constants for self-exchange. In the nitroalkane series, there is about a 10-fold reduction on going from nitromethane to 2methyl-2-nitropropane, somewhat larger than the effect on the heterogeneous rate constants. An even more pronounced diminution in the self-exchange rate constant is seen for the diketones, almost 2 orders of magnitude. Again, this is larger than that observed in the heterogeneous process.

It is worth noting that the self-exchange rate constants for both the nitroalkanes and the diketones are orders of magnitude smaller than those seen for aromatic systems.⁹ This is attributed to localization of charge in the anion radicals of nitroalkanes and diketones, leading to stronger solvation than in delocalized aromatic anions and, hence, a larger outer reorganization energy that contributes to the free energy of activation for electron transfer.

Anions are poorly solvated in dipolar aprotic solvents such as acetonitrile so it is not surprising that substantial stabilization of anion radicals occurs as small amounts of water or alcohols are added to the solution. This stabilization exists only for anions that are not sufficiently basic to remove the hydroxylic proton, a reaction that usually leads irreversibly to hydrogenated products. With the present compounds, the stabilization is sensed by a positive shift in the reversible formal potential as the hydroxylic solute is added.

There are at least two ways of interpreting this effect. In the first, it is considered that discrete adducts (complexes) form between the anion radical and the added solute, e.g., $\{RNO_2^{\bullet-1}\}$ $\{H_2O\}$, $\{RNO_2^{\bullet-1}\}$ $\{H_2O\}_2$, etc. In fact, a number of systems have been treated in this way¹³ (which is analogous to the approach used to evaluate ion pair interactions¹⁷) and stepwise formation constants have been obtained. Second, one can think of the interaction as nonspecific, with the added solute contributing to the free energy of solvation of A and B in the mixed solvent system.

In the case of the formation of discrete complexes, the shift in potential will be given by¹⁸ eq 7 in which $E^{\circ'}{}_{ABS}$ is the reversible

$$\Delta E^{\circ\prime} = E^{\circ\prime}{}_{AB,S} - E^{\circ\prime}{}_{AB} = -(RT/F) \text{ in } \beta_0 \tag{7}$$

potential in the presence of solute, S, $E^{\circ'}_{AB}$ is the potential in dry solvent, and β_0 is the fraction of the anion radical that exists in the "free" (uncomplexed) form at any given concentration of S. When the potential is measured by a dynamic technique such as cyclic voltammetry, eq 7 is valid and independent of the reaction mechanism so long as all of the complexation reactions are fast enough to remain close to equilibrium.

How will complexation affect the apparent value of k_s ? If one supposes that only the "free" form of the anion radical is able to react at the electrode (or, at least, that the complexed forms react much more slowly) and if the complexation reactions are fast on the time scale of the kinetic measurement, then the apparent rate constant in the presence of S, $k_{s,S}$ will be given by eq 8 (see the

$$k_{\rm s,S}/k_{\rm s} = (\beta_0)^{\alpha} \tag{8}$$

Appendix). Here, k_s is the rate constant determined in dry solvent. Equations 7 and 8 may be combined with elimination of β_0 to give

$$\log \left(k_{\rm s,S} / k_{\rm s} \right) = -(\alpha F / 2.303 RT) \Delta E^{\circ}$$
⁽⁹⁾

which shows that plots of log $(k_{s,s}/k_s)$ vs ΔE° must be linear with a slope of $-\alpha F/2.303RT$ if the complexation model is valid.

In the second model, the added solute serves to stabilize B, presumably by hydrogen bonding. As discussed elsewhere,¹⁹ observed formal potentials can be used to evaluate $\Delta\Delta G^{\circ}_{sol}$, the difference between the free energy of solvation of the anion and the neutral partners in a half-reaction. (The solvation energy of neutral A will be much less than that of B, but it will be retained because solvation of A also affects the potentials.) Calculating absolute values of $\Delta\Delta G^{\circ}_{sol}$ requires an absolute value of the reference electrode potential, but this can be avoided if one is interested only in changes in $\Delta\Delta G^{\circ}_{sol}$, because these are simply the changes in the formal potentials. Thus, the observed shifts in formal potential are equal to the change in the difference in free energies of solvation, $\Delta(\Delta\Delta G^{\circ}_{sol})$ (eq 10). Equation 10 will

$$\Delta E^{\circ\prime} = -\Delta (\Delta \Delta G^{\circ}_{sol}) / F \tag{10}$$

be valid if there are no changes in the liquid junction potential, an assumption that is supported by measurements of the ferricinium/ferrocene potential which remains constant within 5 mV on going from 0 to 1 M water in acetonitrile.²⁰

In the model which invokes general stabilization of B through interaction with the hydroxylic solute, the decrease in the observed rate constant upon addition of solute is interpreted as arising from increases in the outer reorganization energy,⁸ λ_0 . It is reasonable to assume that increases in the free energy of solvation, mainly of B (reflected in positive potential shifts), should result in increases in λ_0 . The outer reorganization energy is the energy required to rearrange solvent molecules around B to the configuration they adopt around A but without removal of the electron. If a proportional relationship exists, such that $\Delta\lambda_0 = -k_x \Delta(\Delta \Delta G^{\circ}_{sol})$, the relationship between the rate constants and ΔE° , will be eq 11.

$$\log (k_{s,s}/k_s) = -(k_x F/4(2.303RT))\Delta E^{\circ}$$
(11)

Here it has been assumed that the solute, S, causes no changes in the preexponential factor or the inner reorganization energy. Equation 11 has been formulated to provide a direct comparison with the predictions of the complexation model, eq 9. It should be noted that this model requires some association of S with the neutral substrate, A. If the effect is due to an increase in λ_0 , molecules of S may only reorganize around B as it is transformed to A. They may not dissociate, i.e., be replaced by acetonitrile

⁽¹⁷⁾ Chauhan, B. G.; Fawcett, W. R.; Lasia, A. J. Phys. Chem. 1977, 81, 1476.

^{(18) (}a) The derivation of eq 7 is analogous to that used to compute formal potentials affected by metal-ligand complexation.^{18b} For example, with three discrete complexes, $\beta_0 = (1 + K_1[S] + K_1K_2[S]^2 + K_1K_2K_3[S]^3)^{-1}$ where, in the present case, K_j are the stepwise formation constants of the anion-solute adducts. (b) Galus, Z. Fundamentals of Electrochemical Analysis; Ellis Horwood: Chichester, U.K., 1976; Chapter 14.

^{(19) (}a) For a review, see ref 19b. The free energy of solvation is the change in free energy associated with moving the species from the gas phase into solution. (b) Shalev, H.; Evans, D. H. J. Am. Chem. Soc. 1989, 111, 2667.

⁽²⁰⁾ Lanning, J. A.; Chambers, J. Q. Anal. Chem. 1973, 45, 1010.



Figure 3. Logarithm of the normalized heterogeneous electron-transfer rate constants $(k_{s,S}/k_s)$ in the presence of water vs the shift in formal potential, ΔE° : *, 2-methyl-2-nitropropane, TEAP; ×, 2-methyl-2-nitropropane, TBAP; +, dipivaloyl, TBAP.

molecules, if the process is to be considered as a one-step electron-transfer reaction.

Data from Table III are plotted in Figure 3. Within the scatter in each data set, a generally linear relationship is observed as predicted by both eqs 9 and 11. The slopes for 2-methyl-2nitropropane in TEAP and TBAP correspond to $\alpha = 0.41$ and 0.34, respectively, compared to the measured values (Table I) of 0.45 and 0.43. The slope for TEAP is clearly within experimental error of the value predicted by eq 9 while that for TBAP is probably significantly different from the predicted. For dipivaloyl in TBAP, $\alpha = 0.28$ from the slope, compared to the measured value of 0.42, which is a significant discrepancy.

When interpreted by the model of generalized solvation by S (eq 11), the values of k_x obtained are 1.6 and 1.4 for 2-methyl-2-nitropropane in TEAP and TBAP and 1.1 for dipivaloyl. The results support the assumption of a proportional relationship between changes in the outer reorganization energy and changes in the solvation energy with different proportionality constants for each reactant molecule.

It appears that the effect of added water on the formal potentials and heterogeneous electron-transfer rate constants is better accounted for by the idea of generalized solvation as opposed to the formation of discrete adducts or complexes. However, the distinction is not firmly established. It is possible that a variant of the complexation model, with nonzero rate constants for the complexes, is needed. Also, it may be that both factors are at work, with generalized solvation having its largest effect at higher concentrations of water, where the system becomes a mixed solvent, rather than acetonitrile with a low level of added solute.

The results have been interpreted without discussion of possible effects of water on the structure of the double layer. Unlike the effect of tetraalkylammonium ions which must involve changes in the double layer, the effects of water have been explained entirely as effects on the form, energy, and reactivity of the

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reactant and product. If this is so, it is necessary that similar effects of water be observed in the homogeneous electron-transfer reactions of the nitroalkanes and diketones. The results in Table IV reveal a strong effect of not only water but added alcohols as well. Qualitatively, the forward rate constant is little affected by added hydroxylic solute but the reverse rate constant is strongly attenuated. This is as expected if B is the only participant in electron-transfer reaction 3 that interacts significantly with water. Such interactions will inhibit the reverse reaction in which B gives up an electron to P.

A qualitative interpretation of the results can be offered in terms of the complexation model of the interaction. In that model, only the uncomplexed B is able to react with P. Because the complexation reactions are assumed to be rapid, the interaction with water will affect the rate of the reaction as a prior equilibrium; i.e., the apparent rate constant will be only a fraction of the true rate constant, that fraction being β_0 , the ratio of the concentration of free B to the sum of the concentrations of all forms of B. In this regard, the final column of Table IV contains entries for $k_{\rm b}/\beta_0$ where β_0 was computed from ΔE° (Table III) via eq 7. These entries should be the true reverse rate constants if the complexation model is adequate. The fact that they are roughly constant suggests that the complexation model accounts for most of the effect. The decrease seen at water concentrations above about 0.4 M may be real and could signify the intrusion of general solvation as the mole fraction of water in the system becomes significant.

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Appendix

The Butler-Volmer expression for the rate of the reaction in dry solvent is eq A1, in which A' is the electrode area and $C_{A(x=0)}$

$$\frac{i/FA' = k_{s} [C_{A(x=0)} \exp[-(\alpha F/RT) \times (E - E^{\circ'}_{AB})] - C_{B(x=0)} \exp[(1 - \alpha)(F/RT)(E - E^{\circ'}_{AB})]}{(A1)}$$

and $C_{B(x=0)}$ are the surface concentrations of A and B. Upon substituting $E^{o'}{}_{AB}$ from eq 7 into eq A1, followed by rearrangement, one obtains eq A2. In this modified rate expression,

$$i/FA' = k_{s}\beta_{0}^{\alpha} \{ C_{A(x=0)} \exp[-(\alpha F/RT)(E - E^{\circ}{}_{AB,S})] - [C_{B(x=0)}/\beta_{0}] \exp[(1 - \alpha)(F/RT)(E - E^{\circ}{}_{AB,S})] \}$$
(A2)

 $C_{B(x=0)}/\beta_0$, is recognized as the total surface concentration of all forms of the anion radical, B. The apparent rate constant is $k_{s,S} = k_s \beta_0^{\alpha}$ (eq 8). Thus, when the total concentration of B is used in the analysis of data and the potentials are referenced to the apparent reversible potential in the presence of S, the observed rate constant will be given by eq 8. These conditions are met when cyclic voltammetry is used to determine the kinetic parameters for heterogeneous electron transfer.