arrangement products found in the chlorination of *t*-butyl bromide by *t*-butyl hypochlorite.[24] Similarly, a precedent exists in the chlorination of 1-bromobutane, in which 1,2-dichlorobutane is suggested as arising through an elimination–addition process.[22]

The elimination–addition mechanism could be subject to further modification. As pointed out by a referee the conversion of the alkyl bromide to olefin could be catalyzed by hydrogen bromide by a process involving simultaneous hydrogen abstraction by Br· and loss of Br· which is complexed to HBr.

Finally, in the brominations carried out by means of NBS, it might be expected that if elimination to the olefin (eq 8) occurs, then the allylic substitution product should be formed, as usually happens in NBS brominations. However, our reactions with the deactivated substrate 1-bromobutane were characterized by abnormally long reaction times compared with reactions of unsubstituted hydrocarbons. During the reaction molecular bromine attained a sufficiently large concentration to be visible, and since allylic bromination is dependent upon the concentration of molecular bromine being very small,[20] addition of bromine to the olefin is the predominant reaction.

Experimental Section

Materials. All chemicals were commercially available. Purification of 1-bromobutane was accomplished by washing with concentrated sulfuric acid followed by fractional distillation. Acetonitrile was distilled from phosphorus pentoxide and stored over activated molecular sieve No. 3A. Bromine and N-bromosuccinimide were used without further purification.

Bromination of 1-Bromobutane with Molecular Bromine. The reaction mixture consisted of a 1:6 mole ratio of bromine to the neat alkyl halide. The solutions were degassed by the freeze–thaw method and irradiated in sealed Pyrex ampoules with a 100-W incandescent lamp at 30°. The ampoules were removed after various lengths of time, 1,4-dichlorobutane was added as an external standard, and the reactions were analyzed on a 10 ft × 0.25 in. SE-30 glpc column. Molar amounts of the brominated products were calculated from calibration plots of area ratios *vs.* the authentic samples. Three of the brominated products were identified by comparison of their retention times on three different glpc columns with those of commercially available compounds. 1,1-Dibromobutane was identified by its nmr and ir spectra. The results of these brominations are shown in Table II.

Bromination of 1-Bromobutane with N-Bromosuccinimide. The reaction mixtures consisted of a 1:6 mole ratio of N-bromosuccinimide to the neat alkyl halide. The reaction mixtures were degassed by the freeze–thaw method and irradiated in sealed Pyrex ampoules with two 200-W incandescent lamps at 30°. After 4 hr, the ampoules were analyzed as above and the isomer distribution was found to be 1.00:6.19 (1,3:1,2-dibromobutane).

In a alternative method, reaction mixtures consisted of 1:4 mole ratio of N-bromosuccinimide to the alkyl halide in acetonitrile. The reaction mixtures were degassed by the freeze–thaw method and irradiated in sealed Pyrex ampoules with two 200-W incandescent lamps at 30°. The tubes were removed after varying lengths of times and analyzed as above. The results are shown in Table IV.

Bromination of 1-Bromobutane with Molecular Bromine in Acetonitrile. The reaction mixtures consisted of 1:4 mole ratios of molecular bromine to the alkyl halide in acetonitrile. The reaction mixtures were degassed by the freeze–thaw method and irradiated in sealed Pyrex ampoules with two 200-watt incandescent lamps at 30°. The ampoules were removed after varying lengths of time and analyzed as above.

Bromination of 1-Bromobutane with Added Hydrogen Bromide. The reaction mixtures consisted of a 1:6 mole ratio of molecular bromine to the neat alkyl halide had been saturated with hydrogen bromide (0.34 *M*). The reaction mixtures were degassed by the freeze–thaw method and irradiated at 30°, along with identical reaction mixtures without added hydrogen bromide. The ampoules were removed after varying lengths of time and analyzed as above. The results are shown in Table III.

Acknowledgment. The authors wish to thank the National Research Council of Canada and the University of Alberta for their generous support of this work.

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Activation Parameters for the Electron Transfer between Cyclooctatetraene Dianion and Anion Radical[1]

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Abstract: Rate constants and activation parameters have been determined for electron transfer between cyclooctatetraene (COT) dianion and the anion radical for various COT–solvent–M (where M = Li, Na, K) systems. As determined by electron spin and nuclear magnetic resonance, the rate constant for electron transfer (eq 1) is very dependent upon the solvent and the counterion. Even in ammonia, a relatively protic and ionizing solvent, the rate of electron transfer is dependent upon the counterion. Possible line-broadening mechanisms in this solvent are discussed.

Electron spin resonance (esr) spectral parameters for COT–solvent–M systems are temperature, solvent, and counterion dependent.[2] Of particular interest is the reported rate difference of 10^4 for the electron transfer (eq 1) (where π = COT, and $\pi\cdot^{-}\mathrm{M}^{+}$ and $\pi^{2-}\mathrm{M}_2^{+}$ represent all forms of the ions from tight ion pairs and/or higher agglomerates[3] to dissociated ions) for the

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(1) Anion Radicals in Liquid Ammonia. III. Part II: F. J. Smentowski and G.R. Stevenson, *J. Phys. Chem.*, 73, 340 (1969).

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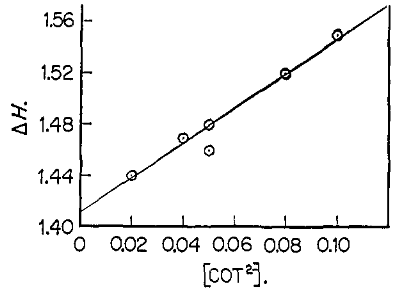


Figure 1. Plot of line width (in Gauss) of the $M_i = 0$ line *vs.* the dianion concentration (in moles per liter) at 0° for the COT–DME–K system.

systems COT–THF–Li and COT–THF–K (where THF = tetrahydrofuran).[2a] Rate differences of less than

$$\pi\cdot^{-}M^{+} + \pi^{2-}M_2^{+} = \pi^{2-}M_2^{+} + \pi\cdot^{-}M^{+} \qquad (1)$$

two orders of magnitude have been reported for the related electron transfer (eq 2) between an anion radical

$$\pi\cdot^{-}M^{+} + \pi = \pi + \pi\cdot^{-}M^{+} \qquad (2)$$

and a neutral molecule, where π = naphthalene,[4] stilbene,[5] 1-naphthyl-1-phenylethane,[6] or an analogous electron transfer between tris-*p*-nitrophenylmethyl radical and its carbanion (eq 3), where π = tris-*p*-nitrophenylmethyl.[7]

$$\pi\cdot + \pi^{-}M^{+} = \pi^{-}M^{+} + \pi\cdot \qquad (3)$$

It is not known whether the rate difference for the electron transfer (1) for the systems COT–THF–Li and COT–THF–K is a specific one. Conductivity measurements on anion radical salts in ethereal solvents[8] indicate a variation of the cation's mobility with its size, while the anion's mobility is relatively insensitive to a change in its size. For the electron transfer (1), where *both* reactants are charged particles, it is of interest to make a detailed study of the solvent and counterion dependence of such a transfer. Recently, techniques have been developed for the preparation of anion radicals in liquid ammonia.[9] Since the effects of ion pairing are not as pronounced in ammonia as they are in ethereal solvents,[9,10] it is of interest to determine if the rate difference found in THF is observed in this solvent. We have measured the rate constants and activation parameters for the electron transfer (1) for the systems COT–DME–K (where DME = 1,2-dimethoxyethane), COT–THF–K, and COT–NH_3–K and have determined the relative rates for the systems COT–NH_3–M (where M = Li, Na, K).

Experimental Section

The COT was purchased from Chemical Procurement Laboratories, Inc., and was degassed and distilled under high vacuum before use. Reduction of COT was effected by liquid ammonia–alkali metal (LAAM), as described previously.[9] Reduction of COT in the ethereal solvents THF and DME has also been described.[2d]

X-Band esr spectra were recorded using a Varian V 4502-15 esr spectrometer with a 12-in. magnet. Line widths are measured between extrema in the first derivative spectrum. Temperature was controlled within ±1° by a Varian V-4557 variable-temperature controller.

Nmr spectra were recorded at room temperature using a Varian A-60 spectrometer. Line widths of the dianion at half-height due to electron transfer (1) were determined from the experimental half-height line width minus the half-height line width when there is no anion radical present. Nmr samples were prepared like the esr samples, except that a heavy wall nmr tube replaced the esr tube on the apparatus.

The COT anion radical and dianion concentrations were obtained by dissolving a known amount of metal in a known concentration of COT in the solvent, using the reported disproportionation equilibrium constant for the particular system.[2b,d,11]

Results

Esr. In the slow exchange region, the rate constant for the electron transfer (1) is given by (4), where ΔH

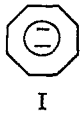
$$k = \frac{\pi(3)^{1/2}(2.83 \times 10^6)(\Delta H - \Delta H^\circ)}{[\mathrm{I}]} \qquad (4)$$

is the line width (measured between the extrema in the first derivative spectrum) of a particular nuclear spin, M_i, ΔH° is the line width in the absence of exchange due to (1), and [I] is the concentration of I in moles per liter. For the fast exchange region, expression 5 is valid,[4a,5,12]

$$k = \frac{(4\pi)(2.83 \times 10^6)\nabla}{(\Delta H - \Delta H^\circ)(3)^{1/2}[\mathrm{I}]} \qquad (5)$$

where ∇ is the second moment (in Gauss^2), ΔH is the line width of the single line, and ΔH° and [I] have been defined. Equation 4 is derived from equations[4c,d,13] for the related electron transfer between an anion radical and its unreduced substrate (eq 2). Equation 4 was used to determine the rate constant of electron transfer (1) for the system COT–DME–K, since slow exchange is observed over the linear range of the log (line width) *vs.* $1/RT$ plot.[2d] Similarly, (5) is appropriate for the system COT–THF–K, where fast exchange is observed over the linear range of the log (line width) *vs.* $1/RT$ plot.[2d] That we are in the region of fast exchange was verified by determining that the esr line was Lorentzian. If a constant concentration of II is maintained, (4) requires that a plot of the hfs line width *vs.* I be linear for the system COT–DME–K (Figure 1). Likewise, for the system COT–THF–K, (5) requires that a plot of the line width *vs.* I^{-1} be linear (Figure 2). The rate constants for the electron transfer (1) are taken from the slopes of these plots.

To determine the rate constant of a particular system, eq 4 and 5 require that the concentration of anion radical II be the same, as the concentration of dianion I is



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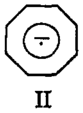

II

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Table I. Equilibrium Dianion I and COT Concentrations Used for the Determination of the Rate Constant for Electron Transfer (1) for the COT–THF–K System at 22°

Sample	I	COT
1	0.40	0.10
2	0.25	0.16
3	0.20	0.20
4	0.13	0.32
5	0.15	0.27
6	0.10	0.40
7	0.05	0.80

varied. From the disproportionation equilibrium (eq 6),[2a,b,d,11] where π = COT, the concentration of the

$$\pi^{2-}M_2^+ + \pi = 2\ \pi\cdot^-M^+ \tag{6}$$

anion radical II is $[\pi\cdot^-M^+] = (K_e[\pi][\pi^{2-}M_2^+])^{1/2}$. The dianion I concentrations were varied by adding different amounts of alkali metal to the solution (*i.e.*, COT–solvent). The product of the equilibrium concentrations of COT and dianion I are held constant, thus the anion radical II concentration is also constant. Table I illustrates the method used to calculate the rate constant. One is able to maintain a constant concentration of II while varying the concentration of I by a factor of 8 for the COT–THF–K system and by a factor of 5 for the COT–DME–K system.

Table II. Activation Parameters at 0° for Electron Transfer (1) for Various COT–Solvent–M Systems

	Systems			
Parameter	COT–DME–K[a]	COT–THF–K[a]	COT–NH$_3$–K[a]	COT–THF–Li[b]
k, l./mole sec	$(2 \pm 1) \times 10^7$	$(3.2 \pm 0.2) \times 10^8$ (*ca.* 10^9)[b]	10^9	$\simeq 10^5$
$\Delta H^\ddagger$, kcal/mole	0	0.7	0	$\simeq 1.4$
$\Delta S^\ddagger$, cal/mole deg	-25 ± 1	-17 ± 1	-17 ± 3	$\simeq -30$
$\Delta G^\ddagger$, kcal/mole	6.8 ± 0.2	5.3 ± 0.2	4.7 ± 1	$\simeq 9.7$
E_a, kcal/mole[c]	0.4	1.2	0.60	$\simeq 1.9$

[a] This work. [b] Reference 2b. [c] Enthalpies of activation are calculated from Arrhenius energies of activation,[2b,d,11] using $\Delta H^\ddagger = E_a - RT$.

Table III. Relative Rates of Electron Transfer (1) for COT–NH$_3$–M Systems in the Slow Exchange Region at 22°

System	$[\mathrm{COT}]_i$[a]	$[M^+]$[a]	$[\pi^{2-}]$[a]	$[\pi]$[a]	$[\pi\cdot^-]$[a]	ΔH	K_e
COT–NH$_3$–K	0.09	0.1	0.05	0.04	0.58×10^{-4}	0.38	1.4×10^{-6}
COT–NH$_3$–Na	1.5×10^{-3}	1×10^{-3}	4.5×10^{-4}	9×10^{-4}	1.1×10^{-4}	0.46	3×10^{-2}
COT–NH$_3$–Li	4.5×10^{-4}	3×10^{-4}	1×10^{-4}	2.4×10^{-4}	1.1×10^{-4}	0.47	0.5

[a] Concentrations in moles per liter.

The rate constant for the COT–THF–K system at 0° was determined from the experimental rate constant at +40° and the known[2d] activation energy. The concentration of II for this system is too low to lend itself to a rate study at 0°. For the system COT–THF–K, a plot of ΔH *vs.* 1/[I] at +40° (Figure 2) gives a straight line of slope 0.70 corresponding to a rate constant of $k = (4.2 \pm 0.3) \times 10^8$ l./mole sec for the fast exchange limit.[14] Table II lists the activation parameters for electron transfer (1) for the COT–THF–K system.

For the system COT–DME–K, a plot of ΔH *vs.* [I] at 0° (Figure 1) gives a rate constant $k = (2 \pm 1) \times 10^7$. From the activation energy of E_a = 0.4 kcal/mole,[2d] and k, the frequency factor is $A = 4.2 \times 10^7$ l./mole sec. The activation parameters for the electron transfer (1) for the system COT–DME–K are listed in Table II.

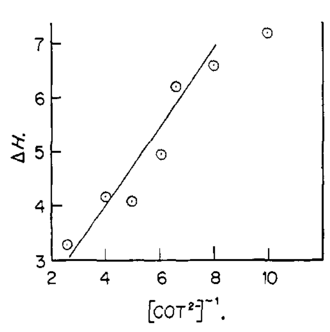

Figure 2. Plot of line width (in Gauss) of the single collapsed line *vs.* the inverse of the dianion concentration (in M^{-1}) at 40° for the COT–THF–K system.

For the system COT–THF–Li at 0°, a plot of ΔH *vs.* [I] over a tenfold variation in dianion I concentration gave a line parallel to the x axis, indicating qualitative agreement with the rate constant of *ca.* 10^5 determined by nmr techniques.[2a]

It was not possible to measure the rates of electron transfer (1) for the systems COT–NH$_3$–M (where M = Li, Na, K) by esr. The accuracy of the measured rate constant is limited by the range of concentrations possible for I. For the COT–NH$_3$–Li and COT–NH$_3$–Na systems, the disproportionation constants[11] indicate the concentration of anion radical II compares with the dianion I. This, coupled with the insolubility of the dianion I does not allow the measurement of the rate constant of electron transfer (1) for these systems. For the COT–NH$_3$–K system, the minimum concentration of anion radical II detectable by esr determines the lower limit of I concentrations (10^{-4} M) through the disproportionation. At intermediate concentrations of I, two anion radicals are observed. The upper limit of I concentrations ($\simeq 10^{2-}$ M) is controlled by its solubility in the solvent. However, estimates of the relative rates of electron transfer (1) for the three systems are made by comparing the line width and dianion I concentration data for similar concentrations of anion radical II (Table III). In spite of the much higher concentration of di-

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(14) C. S. Johnson, Jr., and J. B. Holz, *J. Chem. Phys.*, 50, 4420 (1969). We are indebted to Professor Johnson for a preprint of this manuscript, which enabled us to determine the limit of error for this measurement.

anion I for the COT–NH_3–K system, electron transfer (1) is more rapid for the COT–NH_3–Li system; *i.e.*, the relative rates are $Li^+ > Na^+ > K^+$.

Nmr. In NH_3 both COT and the dianion I (free of any anion radical II) show relatively sharp singlets at 5.9 ppm relative to TMS as a standard. Dissolution of 2 g-atoms of potassium to 1 mole of COT in liquid ammonia led to dianion I samples free of anion radical II. The line widths for COT and the dianion I are 0.6 and 1.3 Hz, respectively. The dianion line width is not changed by the solvated electron.

The rate constant for electron transfer (1) for the system COT–NH_3–K is given by (7),[2a] where $\delta\omega$ = the esr

$$2\pi\Delta\nu = \frac{k[\mathrm{II}](\delta\omega)^2}{(\delta\omega)^2 + k^2[\mathrm{I}]^2} \qquad (7)$$

hyperfine splitting constant in radians per second, and $\Delta\nu$ = the half-height line width due to electron transfer (1). For the COT–NH_3–K system, the esr proton hyperfine coupling constant is 3.28 G.[11] A rate constant of $k = 10^9$ l./mole sec was determined, with the activation parameters calculated from the known[11] activation energy (Table II). Related studies for the systems COT–NH_3–Li and COT–NH_3–Na were not possible for the same reasons the esr studies were not made.

Except when the solvated electron is present, the ammonia resonance has three lines (J = 43.8 Hz) and two small peaks due to ^{15}N, in agreement with previous studies.[15] The chemical shift of the center line is 0.7 ppm relative to TMS.

Discussion

To our knowledge, this work represents the first report of the solvent and counterion dependence of an electron transfer between an organic dianion and anion radical. Previous studies of an electron transfer between an anion radical and a neutral molecule (eq 2) indicate a difference of approximately two orders of magnitude in the rate constants for systems in which the solvent and/or counterion is varied. The unusually large variation in rate constants of as much as 10^4 for electron transfer (1) for different COT systems is largely due to different activation entropies (Table II). The electron transfer (2) for various naphthalene systems (naphthalene–solvent–M)[4b] have a much smaller variation in the rate constant (and activation entropy) than the COT systems. Even in liquid ammonia, a relatively protic and ionizing solvent (ϵ = 18 at 0°), electron transfer (1) varies with metal ion, and the entropy is large and negative for the COT–NH_3–K system. An esr study[11] of the spectral parameters of the systems COT–NH_3–M (where M = Li, Na, K) indicated the importance of the counterion. The presence of ion pairs was deduced from spin concentration and activation energy (of the electron transfer (1)) measurements. Under certain conditions, both the COT–NH_3–Na and COT–NH_3–K systems gave two anion radicals, which apparently differ in the degree of solvation. Even more striking, because the ion concentrations are much less than those used in our work, are the nmr kinetic studies[15,16] in ammonia of ammonia–amide and ammonia–ammonium proton exchange which indicate ion pairing at salt concentrations greater than $10^{-5}M$. Large negative activation entropy terms were found for the exchange reactions.

For most of the COT–solvent–M systems for which activation parameters are known, it appears that the rate of "electron" transfer approximates diffusion-controlled conditions (*i.e.*, rates of $\simeq 10^9$ l./mole sec and low activation energies) in which a sizable reorganization of the ions in the activated complex is required. The reorganization of the counterion's position in its relation to the solvent *and* dianion appear to be important factors affecting the entropy term. Further kinetic studies of both electron transfers (1) and (2) might clarify the differences now noted for these reactions.

Finally, the ease with which liquid ammonia forms a solvated electron[17] might lead one to believe that solvated electron broadening (eq 8 and 9) is present for the

$$\pi + NH_3(e) = \pi\cdot^- + NH_3 \qquad (8)$$

$$\pi\cdot^- + NH_3(e) = \pi^{2-} + NH_3 \qquad (9)$$

COT–NH_3–K system. For systems with high concentrations of dianion I, a study of the esr line widths[11] indicated hfs line broadening of anion radical II from (8) was small relative to broadening due to eq 1. Nmr results of this study indicate that throughout the potassium reduction of COT in ammonia, line broadening of dianion I from (9) is small relative to broadening due to eq 1. Likewise, after 2 g-atoms of potassium (per mole of COT) has been added, and solvated electron is present, broadening of the dianion I line by the solvated electron (eq 10) does not occur.

$$\pi^{2-} + NH_3(e) = \pi^{2-} + NH_3(e) \qquad (10)$$

Acknowledgment. The authors are indebted to Professor C. S. Johnson, Jr., for helpful discussion and to Professor D. H. O'Brien for assistance with the nmr measurements. The authors thank D. L. Hjornevik for technical assistance. Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The authors thank the National Aeronautics and Space Agency for Fellowship support to G. R. Stevenson. The esr spectrometer was made available by the National Science Foundation Grant GP-3767. Support from the Research Council of Texas A&M University is gratefully acknowledged. Time for machine calculations was made available by the Data Processing Center of Texas A&M University.

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