J. Am. Chem. Soc. **1989**, *111*, 5769–5772

Electron Exchange between Potassium Bis(*tert*-butyl[8]annulene)ytterbate(II) and Potassium Bis(*tert*-butyl[8]annulene)ytterbate(III)

David C. Eisenberg, Steven A. Kinsley, and Andrew Streitwieser*

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720, and Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720. *Received June 20, 1988*

Abstract: Exchange on the ^1H NMR time scale has been observed between potassium bis([8]annulene)ytterbate(II) (**1**) and potassium bis([8]annulene)ytterbate(III) (**2**). The absence of exchange between potassium bis([8]annulene)calcate(II) and **2** demonstrates that the measured exchange is electron exchange rather than ligand exchange. Rates of exchange have been determined between the corresponding *tert*-butyl derivatives, potassium bis(*tert*-butyl[8]annulene)ytterbate(II) (**3**) and potassium bis(*tert*-butyl[8]annulene)ytterbate(III) (**4**), by NMR line broadening techniques; typical second-order rate constants are 5×10^7 M^{-1} s^{-1} at 19.3 °C in tetrahydrofuran (THF) and 1×10^7 M^{-1} s^{-1} in THF containing diglyme. From these results and the activation parameters a mechanism is proposed that involves change in coordination of solvating diglyme.

Unlike the transition metals and actinides, which exist in a variety of oxidation states, the inorganic and organometallic chemistry of the lanthanides is dominated by the trivalent state. Europium, samarium, and ytterbium are also found in the divalent state in which case they are often strong reducing agents, and cerium can be found in the tetravalent state where it is generally a strong oxidizing agent. In a related area, although there have been many studies of the inorganic and organometallic electron-transfer chemistry of the transition metals,[1] there are few studies of the electron-transfer chemistry of the f-elements. The principal such studies are the inorganic redox reactions in aqueous solution of Christensen and Espenson[2] and of Tendler and Faraggi[3] and the inner-sphere electron-transfer properties of cyclopentadienylytterbium compounds, studied by Andersen and coworkers.[4] We recently reported the preparation of potassium bis([8]annulene)ytterbate(II) (**1**) and found it to be closely similar to potassium bis([8]annulene)calcate(II).[5] From this similarity it was concluded that f-orbitals do not play a significant role in the metal–ligand bonding of **1**. The crystal structure of the glyme adduct of **1** shows a sandwich structure typical of bis([8]annulene) f-element compounds. A crystal structure of the diglyme adduct of **2** shows a similar sandwich structure except that **2** has slightly shorter metal-to-ring distances than the Yb(II) compound, as expected for the difference in ionic radii of the two oxidation states of the central metal.[6]

We now report that **1** undergoes exchange on the ^1H NMR time scale with **2**. This exchange is shown to be electron exchange, making this the first organo-f-element system for which the rate of electron exchange has been measured. Activation parameters for the exchange have been determined and a mechanism is proposed.

Experimental Section

General Methods. Air-sensitive compounds were handled under argon either in a Vacuum Atmospheres Model HE 243 dry lab with a HE 93A dry train or with standard Schlenk line techniques. Unless otherwise noted, materials were obtained from commercial suppliers and used without additional purification. ^1H NMR spectra were obtained on UC Berkeley 200 and 250 MHz superconducting FT spectrometers equipped with Cryomagnets Inc. magnets and Nicolet Model 1280 data collection systems. Temperatures were measured with a thermocouple mounted next to the NMR tube. Chemical shifts are reported in ppm with positive shifts reported for peaks downfield of TMS and with peaks referenced to TMS or the upfield residual THF peak taken as 3.58 ppm. For appropriate cases the width at half-height in Hz and the temperature are recorded. Visible spectra were taken on a Cary Model 118 or IBM Model 9430 spectrophotometer. Tetrahydrofuran (THF), toluene, and hexane were distilled from sodium benzophenone or $LiAlH_4$, freeze-thawed three times, and stored with 4A sieves prior to use. Cyclooctatetraene was obtained from BASF, vacuum transferred, and stored over 4A sieves prior to use. *tert*-Butylcyclooctatetraene was prepared as described previously[7] and stirred with 4A sieves prior to use. The reactions in liquid ammonia were carried out as detailed previously.[5]

Potassium Bis(*tert*-butyl[8]annulene)ytterbate(II) (3). Anhydrous *tert*-butylcyclooctatetraene (0.57 g, 3.6 mmol) was added to a blue solution of 0.14 g (3.6 mmol) of potassium and 0.31 g (1.8 mmol) of ytterbium metal in liquid ammonia at −78 °C. Five minutes after removing the dry ice bath, the reaction mixture was green and then underwent rapid color changes to orange and then back to green. After the ammonia was allowed to evaporate, a blue powder was left, which was heated to 200 °C in vacuo to produce 0.93 g (91%) of bright pink product.

A portion of the pink powder (0.73 g) was dissolved in 10 mL of anhydrous, degassed diglyme. The suspension was heated to 140 °C and filtered. The solution was cooled to room temperature, and 50 mL of anhydrous, degassed hexane was carefully added via syringe such that two layers (a lower orange layer and an upper clear layer) formed. As the hexane slowly diffused into diglyme solution, large rectangular crystals formed. Some crystals formed almost immediately, but complete crystallization took 3 days. The solvent was removed by filtration, and the crystals were washed three times with 50 mL of hexane. A second crop of crystals was grown from the filtrate and the hexane wash, affording a total yield of 0.77 g (72%): UV–vis λ_{max} (THF) = 521 nm; ^1H NMR (THF-d_8) 5.26 (m, 7 H), 3.58 (m, 8 H), 3.46 (s, 6 H), 1.52 (s, 9 H). Anal. Calcd for $C_{36}H_{60}O_6K_2Yb$: C, 51.47; H, 7.20. Found: C, 51.60; H, 7.39.

Potassium Bis(*tert*-butyl[8]annulene)ytterbate(III) (4). Freshly cut potassium (0.74 g, 19 mmol) was added to a stirring solution of 1.42 g (8.88 mmol) of freshly distilled and dried *tert*-butylcyclooctatetraene in approximately 50 mL of dry, degassed THF in an argon glovebox. The solution immediately turned from a faint yellow to a medium brown. The solution was stirred for about 2 h and then added dropwise, over the period of about 2 min, to a rapidly stirred suspension of 1.34 g (4.80 mmol) of ytterbium trichloride in 100 mL of dry, degassed THF. After approximately one-third of the dianion solution was added, the trichloride solution turned navy blue. In each of several preparations there was a considerable delay before the solution turned blue, probably because the first step of the reaction is reduction of ytterbium trichloride. The solution was stirred for about 1 h until a pink precipitate could be detected indicating that the ytterbium had been completely oxidized to the tri-

---

[1] For several reviews, see: *Prog. Inorg. Chem.* **1983**, *31*.

[2] Christensen, R. J.; Espenson, J. H. *Chem. Commun.* **1970**, *12*, 756.

[3] Faraggi, M.; Tendler, Y. *J. Chem. Phys.* **1972**, *56*, 3287.

[4] Brennan, J. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 514.

[5] Kinsley, S.; Streitwieser, A., Jr.; Zalkin, A. *Organometallics* **1985**, *4*, 52.

[6] Eisenberg, D. C.; Boussie, T.; Rigsbee, J. T.; Streitwieser, A., Jr.; Zalkin, A., manuscript in preparation.

[7] Miller, M. J.; Lyttle, M. H.; Streitwieser, A., Jr. *J. Org. Chem.* **1981**, *46*, 1977.

0002-7863/89/1511-5769$01.50/0

valent state. (This pink product is apparently an oxidation product of the ytterbate in which either ytterbium trichloride or small quantities of oxygen act as the oxidizing agent.) Then, 100 mL of THF was added, and the solution was filtered. The THF was removed in vacuo, and the blue residue was washed with toluene and pumped dry, yielding 725 mg (31%) of product: Vis λ_{max} (THF) = 602 nm (ϵ = 2000); ^{1}H NMR (THF-d_8) −13.9 (395 Hz, 19.3 °C), −14.7 (456 Hz, 10 °C), −15.5 (502 Hz, 0.0 °C), −16.8 (600 Hz, −10 °C). Satisfactory analysis could not be obtained; however, the spectra are distinctive, and an X-ray structure was determined for the parent compound.[6]

Electron Exchange Studies. Suitable mixtures of **3** and **4** were prepared by oxidation or reduction of the pure compounds to produce a variety of mol fractions of the two compounds (typically between 5 and 20% of the paramagnetic compound to give manageable line widths of 50 to 200 Hz for the exchanging mixtures). NMR tubes were prepared with THF-d_8 containing a known concentration of benzene as a standard; solutions containing 0.005–0.1 M of total ytterbium gave useful spectra with the 200 MHz instrument. Relative mol fractions were determined by comparing the chemical shift of the exchanging peak at a given temperature to the known chemical shifts of the pure compounds. Line widths of the exchange peaks were determined at −10.0, 0.0, 10, and 19.3 °C with the diglyme adduct and at 0.0, 10.0, and 19.3 °C in the absence of diglyme. Line widths of the two pure complexes were also determined at these temperatures.

Rate constants for electron exchange were obtained by inputting the natural line widths of the pure paramagnetic and diamagnetic ytterbium species and the line width of the exchanging species into the equation of Chan, DeRoos, and Wahl[8] for determination of the second-order exchange rate. The results of all runs are summarized in Tables I and II. Activation parameters were obtained by least-squares analysis with the uncertainties given as the standard deviations. These results are also summarized in Tables I and II; rate constants calculated from the activation parameters are also recorded for comparison with the experimental numbers.

Results and Discussion

Distinguishing between Electron Exchange and Ligand Exchange. Dipotassium bis([8]annulene)ytterbate(II) (**1**) is diamagnetic and has a single sharp ^{1}H NMR resonance at 5.47 ppm. The corresponding ytterbate(III) (**2**) salt is paramagnetic and does not have an observable ^{1}H NMR resonance. A mixture of the two compounds dissolved in THF-d_8 does not display the expected resonance of the diamagnetic ytterbium compound. When the solution was cooled to −50 °C, however, a sharp singlet at 5.5 ppm appeared, and as the NMR tube was warmed the signal at 5.5 ppm broadened and disappeared by 0 °C. These results are indicative of some exchange process between the divalent and trivalent ytterbium compounds, either ligand exchange or electron exchange. These two types of exchange were distinguished by using potassium bis([8]annulene)calcate(II).

The similarity between the calcium compound and the divalent ytterbium compound was recently demonstrated.[5] The compounds have essentially the same ^{1}H NMR, IR, X-ray powder pattern, and similar thermal and air stabilities. If the ytterbium(II–III) exchange were ligand exchange, then one would also expect ligand exchange between potassium bis([8]annulene)calcate(II) and **2**. Conversely, if the exchange in the ytterbium system is electron exchange, then exchange between the calcium compound and the ytterbium(III) compound could not occur. A mixture of **2** and the corresponding calcate(II) compound was dissolved in THF-d_8, and proton NMR spectra were recorded at a series of temperatures. The sharp resonance due to the bis([8]annulene)calcate(II) was observable at 5.47 ppm at a variety of temperatures thus supporting the electron exchange mechanism in the ytterbium(II–III) system.

This exchange is thus analogous to the electron exchange between ferrocene and ferricenium ion studied by Wahl and coworkers.[8] They determined the rates of exchange, using NMR line shape analysis, between various ferrocenes while varying the solvent and counterion. We used their treatment (eq 1) to relate the NMR line width of the exchanging species to the natural line widths of the pure paramagnetic and diamagnetic compounds and the rate of exchange. In this equation W_{dp}, W_p, and W_d are the

$$W_{dp} = f_p W_p + f_d W_d + f_p f_d 4\pi(\delta\nu)^2/kc \qquad (1)$$

line widths of the exchanging species, the natural line width of the pure paramagnetic species, and the natural line width of the pure diamagnetic species, respectively, at the appropriate temperature; f_p and f_d are the mol fractions of the paramagnetic and diamagnetic species, $\delta\nu$ is the separation of chemical shifts in Hz between the pure diamagnetic and paramagnetic species at the appropriate temperature; k is the second-order rate constant; and c is the total concentration of ytterbium species. This equation is a simplification of the general line shape equation and is appropriate for two-site exchange with no overall free energy difference in the near fast exchange region.[9]

The *tert*-butyl derivatives were used in the exchange study because the NMR resonance of the *tert*-butyl protons of the paramagnetic ytterbium compound, **4**, is observable whereas the ring protons are not.

Preparation of *tert*-Butyl Analogues of 1 and 2. Potassium bis(*tert*-butyl[8]annulene)ytterbate(III) (**4**) was prepared in high purity by addition of *tert*-butylcyclooctatetraene dianion to a slight excess of ytterbium trichloride in THF. If a slight excess of the dianion is used, a mixture of the divalent and trivalent ytterbium compounds results. The unsubstituted cyclooctatetraene dianion is not a strong enough reducing agent to reduce the unsubstituted ytterbium(III) complex; the reduction potential of the ytterbium(III) complex must therefore be between that of cyclooctatetraene dianion and *tert*-butylcyclooctatetraene dianion.

Use of a large excess of ytterbium trichloride, however, results in formation of significant amounts of a violet, air sensitive, THF-insoluble compound which is also formed on partial exposure of the trivalent compound to oxygen (possibly the triple decker sandwich complex[10]). This compound can be reduced with sodium potassium alloy to potassium bis(*tert*-butyl[8]annulene)ytterbate(II) (**3**). A solution of **3** was prepared in liquid ammonia from a mixture of ytterbium, *tert*-butylcyclooctatetraene, and potassium. The trivalent complex can be reduced conveniently to the divalent complex with potassium, and the divalent complex can be oxidized to the trivalent complex with benzyl bromide, benzyl chloride (the complex is not stable to excess benzyl bromide or benzyl chloride), or ytterbium trichloride; thus, mixtures of different relative concentration of the divalent and trivalent complex could be obtained for NMR line width measurements. The reduction of benzyl halides by Yb(II) is undoubtedly analogous to the known electron-transfer reaction with Sm(II) to form the trivalent lanthanide and benzyl radical.[11] The latter product presumably dimerizes to bibenzyl as with Sm(II) but this was not studied.

Determination of the Rates and Mechanism for Electron Exchange. ^{1}H NMR spectra were taken for mixtures of **3** and **4** at several temperatures. At −78 °C the exchange is frozen out on the NMR time scale as evidenced by the sharp peak at 1.55 ppm due to *tert*-butyl protons of the diamagnetic compound. The group of ring protons centered at 6 ppm for the diamagnetic compound is also relatively sharp, whereas the *tert*-butyl protons of the paramagnetic compound have a resonance which is too broad to observe at this temperature. As the temperature is lowered, the peak at 1.55 ppm broadens and disappears by −40 °C. Between −10 and 20 °C the peak due to exchange involving the *tert*-butyl protons is sufficiently sharp to obtain a reproducible line width measurement and broad enough that effects of shimming on the observed line width are not significant. Rates of exchange were

---

[8] (a) Chan, M. S.; DeRoos, J. B.; Wahl, A. C. *J. Phys. Chem.* **1973**, *77*, 2163. (b) Yang, E. S.; Chan, M. S.; Wahl, A. C. *J. Phys. Chem.* **1980**, *84*, 3094.

[9] Gutowsky, H. S.; McCall, D. W.; Slichter, C. P. *J. Chem. Phys.* **1953**, *21*, 279. McConnell, H. M. *J. Chem. Phys.* **1958**, *28*, 430. Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High Resolution Nuclear Magnetic Resonance*; McGraw-Hill: New York, 1959.

[10] DeKock, C. W.; Ely, S. R.; Hopkins, T. E.; Brault, M. A. *Inorg. Chem.* **1978**, *17*, 625.

[11] Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693. Kagan, H. B.; Namy, J. L.; Girard, P. *Tetrahedron* **1981**, *37* Supplement 1, 175. See the recent review of Kagan et al. (Kagan, H. B.; Namy, J. L. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Eyring, C., Eds.; Elsevier: 1984).

Table I. Second-Order Rate Constants in THF-d_8–Diglyme

[Yb(III)], M	[Yb(II)], M	$10^{-7}k$ (M^{-1} s^{-1}) at temp = 19.3 °C	10.0 °C	0.0 °C	−10.0 °C
0.011	0.114	1.04	0.64	0.32	0.19
0.016	0.067	1.08	0.80	0.32	0.18
0.0048	0.119	0.97	0.72	0.37	0.16
0.034	0.164	0.61	0.77	0.24	0.19
0.024	0.134	0.80	0.77	0.21	0.13
0.011	0.082		0.60	0.26	0.15
0.014	0.082	1.05			
0.0016	0.023	1.50			
0.039	0.080	0.50			
0.021	0.062	1.09			
0.025	0.105	0.96			
	calcd:	0.98	0.58	0.31	0.16
$\Delta H^{\ddagger}$ = 8.8 ± 0.6 kcal mol^{-1}, $\Delta S^{\ddagger}$ = 3 ± 2 eu					

therefore determined in this temperature region.

The results of the NMR line shape analyses are summarized in Table I. The rate constants obtained have some significant quantitative limitations. The importance of maintaining air-free conditions severely limited the experimental techniques available. The paramagnetic Yb(III) compound was present at such low concentration that the only practical approach was in situ preparation by oxidation of the diamagnetic Yb(II) compound present at higher concentration. Benzyl bromide added in a small amount was a convenient oxidizing agent (vide supra). The relative amounts of the two Yb species were determined by NMR integrations. This technique leads to significant probable errors for the paramagnetic compound because the *tert*-butyl peak is relatively broad and far from the benzene peak used as an internal standard. Measurement of the width at half-height of the broad exchanging peak is also subject to some error. Nevertheless, the resulting rate constants have a standard deviation of about 20%. Moreover, the results over a wide concentration range suffice to confirm the second-order kinetics assumed in the derivation of eq 1.[8] Note that the concentrations of the two reactants have been varied by a factor of about eight without a comparable change in the rate constants. These results also indicate that any effect of KBr also present must be relatively small.

The initial NMR studies were performed starting with crystals of the diglyme adduct of the divalent complex in THF-d_8. The results for the rates of exchange as a function of temperature are summarized in Table I and are compared to the rate constants that correspond to the least-squares activation parameters determined by the Eyring equation. The derived $\Delta H^{\ddagger}$ is 9 Kcal mol^{-1}, and $\Delta S^{\ddagger}$ is close to zero.

The rates of exchange (1 × 10^7 M^{-1} s^{-1} at 19.3 °C) are similar to typical rates determined by Wahl et al.[8] in the ferrocene–ferricenium ion case (for example, 4.3 × 10^6 M^{-1} s^{-1} for the unsubstituted system in dichloromethane with PF_6^- as the counterion). The high rate of exchange rules out ligand exchange and confirms the initial conclusion that the exchange is that of electron exchange. Nevertheless, these rates are lower than those expected for diffusion-control, and some activating process is required.

Electron-transfer studies have generally been concerned with systems in which at least one participant is an essentially free ion. Even in the Wahl case (vide supra) the ferricenium ion was considered to be free. In such cases solvent reorganization is important and has been a topic of much study,[12] generally in terms of Marcus theory.[13] In the present case, however, the electron exchange involves neutral ion pairs and triple ions. Potassium salts of cyclooctatetraene dianion compounds are generally contact ion pairs in THF,[14] and contact ion pairs of alkali metal carbanion salts are poorly dissociated in THF.[15] If dissociation to at least one free ion were involved in the ytterbium electron transfer the kinetics would have shown half order dependence on that species. No such dependence is apparent in the results in Table I; despite the large probable errors in the data, the concentrations cover a sufficiently broad range that a half order dependence would be evident.

Scheme I

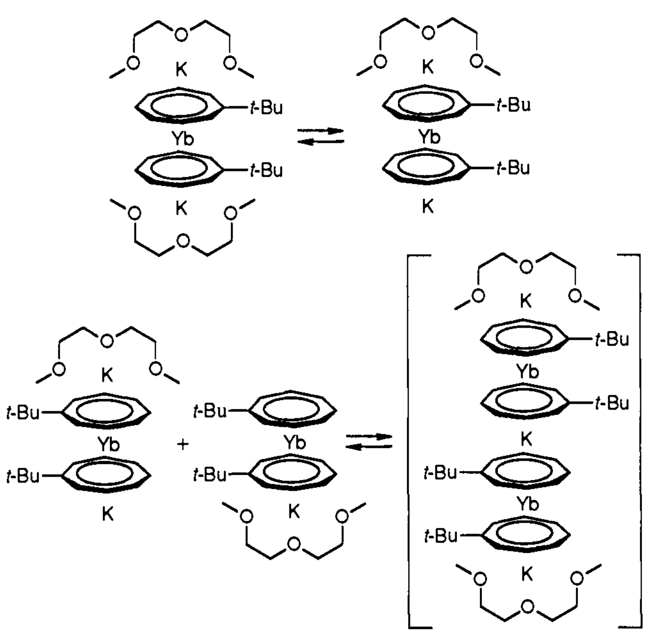


Table II. Second-Order Rate Constants in THF-d_8

[Yb(III)], M	[Yb(II)], M	$10^{-7}k$ (M^{-1} s^{-1}) at temp = 19.3 °C	10.0 °C	0.0 °C
0.044	0.0156	2.9	3.9	1.25
0.0032	0.0088	7.8		
0.0024	0.0216	7.1	2.4	1.28
0.0047	0.0343	5.0	3.6	1.37
0.0048	0.0250	4.5	1.3	0.76
0.017	0.0879	2.6		
0.0081	0.0269	4.3	1.8	0.81
0.040	0.160		4.0	
	calcd:	4.7	2.4	1.11
$\Delta H^{\ddagger}$ = 11.3 ± 1.8 kcal mol^{-1}, $\Delta S^{\ddagger}$ = 15 ± 6 eu				

A reasonable exchange mechanism involves encounter of an ion pair of **4** with the triple ion **3** with transfer of both an electron and *a potassium counterion*. For such an electron transfer that involves concurrent transfer of an ion among neutral species, solvent reorganization may be minimal, and the intrinsic rate of electron transfer may be much greater than that of ion transfer; that is, ion transfer may be the rate-limiting step. It has been pointed out previously that electron exchange among ion-paired species is formally equivalent to atom transfer.[16] In the present case, however, the simplest such mechanism does not appear to be consistent with the small entropy of activation found. Bimolecular associations that involve loss of three degrees of translational freedom are generally associated with entropy changes of the order of 10–20 eu. A reasonable modification of such a mechanism would involve prior dissociation of solvating diglyme from one potassium cation in **3** (Scheme I); with coordination sites at this potassium now available, reaction with **4** would be facilitated, and the entropy gained by loss of the diglyme would

---

(12) For a recent example, see: Hwang, J.-K.; Warshel, A. *J. Am. Chem. Soc.* **1987**, *109*, 715.

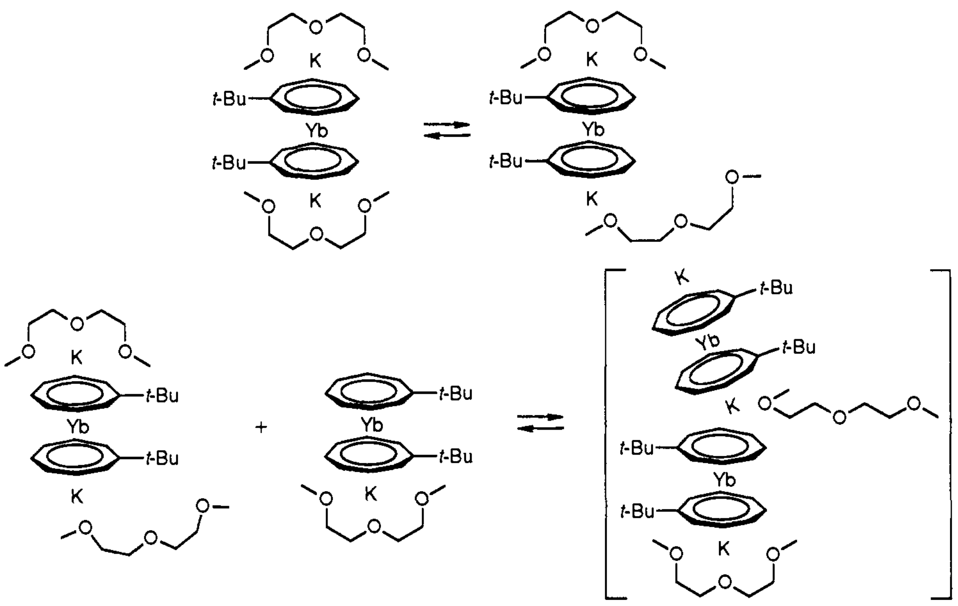
(13) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(14) Cos, R. H.; Harrison, L. W.; Austin, W. K., Jr. *J. Phys. Chem.* **1973**, *77*, 200.

(15) Lundgren, B.; Levin, G.; Claesson, S.; Szwarc, M. *J. Am. Chem. Soc.* **1975**, *97*, 262. Kaufman, M. J.; Gronert, S.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2829–35.

(16) Aten, A. C.; Dieleman, J.; Hoijtink, G. J. *Disc. Faraday Soc.* **1960**, *29*, 182.

Scheme II



compensate for that required in the bimolecular reaction step.

The product association structure in Scheme I is either a short-lived intermediate or a transition state. Evidence that the ytterbium complexes are solvated by diglyme even when only a small amount of diglyme is present in THF solution include the observations that the chemical shift of diglyme changes and the resonance broadens when the paramagnetic ytterbium(III) complex is added to a THF–diglyme solution, whereas the THF resonance is essentially uneffected. To test this revised mechanism a large excess of diglyme was added to the NMR tubes. If loss of diglyme is required for electron exchange, then excess diglyme should lower the rate. However, we found no significant change in the exchange rate. Alternatively, sufficient coordination space around the central potassium may be created if the diglyme loosens from η^3-to-η^1 coordination in a preequilibrium before electron transfer as shown in Scheme II. This mechanism predicts that electron transfer will be faster in THF in the absence of diglyme because THF coordinates potassium cation more weakly than does diglyme. The rates of exchange in THF-d_8 in the absence of diglyme are summarized in Table II. The results again show scatter, but the rates are generally about five times faster than in the presence of diglyme. The activation parameters, although containing a considerable uncertainty, are consistent with this mechanism. Tetrahydrofuran is more basic than diglyme, and its solvation loss involves greater enthalpy but this is more than balanced by the positive entropy of activation associated with loss of a solvating solvent compared to the mere loosening proposed in converting diglyme from η^3-to-η^1 coordination (Scheme II). The fact that exchange is slower in the presence of diglyme also proves that exchange is not occurring by conversion of contact ion pairs to solvent-separated ion pairs which then undergo exchange because diglyme should facilitate the conversion to solvent-separated ion pairs and hence lead to an increase in rate of exchange. A necessity for desolvation has a further corollary: The Marcus equation should apply only to the electron-transfer step itself;[17] the rate constant for this step will necessarily be greater than the experimental rate constant which contains an equilibrium constant for the partial desolvation. Such desolvation may be general for ion pair exchanges (vide infra), and, accordingly, Marcus applications to such systems must be made with due care.[18]

Few rate measurements are available for exchange rates of other cyclooctatetraene ions[19] and are difficult to compare with the present work. In the original work of Katz et al.,[20] the rates are approximate, and it is difficult to discern the role of ion pairs. In the later work of van Willigen[21] on the electron exchange disproportionation of alkali metal ion pairs of cyclooctatetraene radical anion, the fact that the cyclooctatetraene product is nonplanar in its equilibrium state is a complicating factor in interpretation. However, there are several studies involving electron transfer between aromatic hydrocarbon radical anions and the neutral hydrocarbons that are relevant.[22] Even in early studies of such reactions as exchange between sodium naphthalene and naphthalene it was realized that electron transfer is concomitant with cation transfer.[23] The reaction of sodium naphthalene tight or contact ion pairs is two orders of magnitude slower than loose (solvent-separated) ion pairs; the latter are comparable in reactivity to free ions.[24,25] However, the frequency factors for reaction of the tight ion pairs are greater[25] (less negative $\Delta S^\ddagger$) than for loose ion pairs, indicating that desolvation of the cation plays a significant role as suggested in the present study. Typical rate constants for the tight ion pairs are of the order of 10^7 M^{-1} s^{-1}, similar to the results of the present study.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the Department of Energy, under Contract No. DE-AC03-76SF00098.

---

(17) The analogous point has been made for proton-transfer reactions: Murdoch, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 4410.

(18) For a recent review that includes ionic and ion pair systems, see: Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.

(19) For a recent review of redox chemistry of annulenes that includes electron-transfer processes, see: Müllen, K. *Chem. Rev.* **1984**, *84*, 603.

(20) Katz, T. J. *J. Am. Chem. Soc.* **1960**, *82*, 3785. Strauss, H. L.; Katz, T. J.; Fraenkel, G. K. *J. Am. Chem. Soc.* **1963**, *85*, 2360.

(21) van Willigen, H. *J. Am. Chem. Soc.* **1972**, *94*, 7966.

(22) Szwarc, M.; Jagur-Grodzinski, J. In *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley-Interscience: New York, 1974; Vol. 2.

(23) Adam, F. C.; Weissman, S. I. *J. Am. Chem. Soc.* **1958**, *80*, 1518. Zandstra, P. J.; Weissman, S. I. *J. Am. Chem. Soc.* **1962**, *84*, 4408.

(24) Chang, R.; Johnson, C. S., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 2338.

(25) Hirota, N.; Carraway, R.; Schook, W. *J. Am. Chem. Soc.* **1968**, *90*, 3611.