neopentane the rate of positive ion migration is apparently quite slow. The effects in CCl_4 are explainable in terms of a series of fast, conservative, vertical transitions. The apparently different behavior of $(CH_3)_4C$ and CCl_4 may be due to the electron vacancies being well shielded in the C–C bonds, requiring large electron-hopping distances and, hence, a slow rate. The half-occupied lone pair of Cl_3–Cl^+ would overlap much more strongly with a neighboring chlorine, leading to very rapid charge migration.

Temperature-Dependent Electron Spin Resonance Studies. I. Cyclooctatetraene Anion Radical

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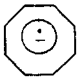
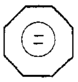
Abstract: Ion pairing affects the esr spectra of cyclooctatetraene (COT) anion radical (I), influencing the line widths of the individual hyperfine splitting, the activation energy of the line-broadening process, and the spin concentration. For this reason, the electron transfer (eq 5) and the disproportionation (eq 2) are replaced by their ion-pair counterparts, eq 6 and 7. When the concentration of dianion II is greater than 0.03 *M* for the system COT–DME–Na from −30 to +10°, the major source of line broadening is that due to electron transfer from dianion II to anion radical I. Other contributions to line broadening, such as that from the disproportionation and ion-pairing phenomena, are minor.

The importance of ion pairing in solution chemistry has long been recognized.[1] More recently, the study of ion pairing has received added impetus from esr,[2,3] conductance,[4] and optical[5] measurements. The various stages of solvation of the ion can be exemplified by



I



II

$$\underset{\text{III}}{RM = R\cdot^-M^+} = \underset{\text{IV}}{R\cdot^-\|M^+} = \underset{\text{V}}{R\cdot^- + M^+} \qquad (1)$$

where III, IV, and V are contact, solvent-separated, and dissociated ion pairs.

Weissman and co-workers[2] were the first to recognize the importance of applying electron spin resonance (esr) to the study of ion pairing. Most of the esr work on ion-pairing phenomena has recently been reviewed.[6] Because of the unfavorable disproportionation equilibrium (eq 2) for the cyclooctatetraene (COT) anion radical (I),[7] the concentration of ions in solution is

$$\text{pi} + \text{pi}^{2-} \rightleftharpoons 2\text{pi}^- \qquad (2)$$
$$\text{pi} = \text{COT}$$

quite high (near 1 *M*) and ion pairing is expected to play a role. This study is concerned with the influence of ion pairing on the COT anion radical (I).

Experimental Section

The COT was purchased from Chemical Procurement Laboratories Inc. and was degassed and distilled under high vacuum before use.

The anion radicals were prepared by reduction of the COT with potassium or sodium metal mirrors or lithium metal in either dimethoxyethane (DME) or tetrahydrofuran (THF) using standard techniques.

Activation energies are determined from the slope of ln (line width) *vs.* $1/RT$ plots.[8] Line widths are measured between the extrema in the first-derivative spectrum. In the linear region of the ln (line width) *vs.* $1/RT$ plot, all hyperfine components of the same system give the same line width. Spectra of each system were run at several different metal and COT concentrations to verify that the energy of activation for the line broadening is independent of the concentration of the dianion. The concentration of the dianion was low enough that a visible amount of the dianion salt did not precipitate out of solution.

For the system COT–DME–Na kinetics for the line-broadening process was determined over the temperature range −30 to +10°. The dianion II concentration was maintained at 0.034 *M* for each run. Three different concentrations were prepared, with the concentration of COT equal to 1.30, 0.64, and 0.32 *M*, respectively. Details are given in Table I. The results are the average of three kinetic runs.

The spectra were recorded using the X band of a Varian V-4502-15 esr spectrometer with a 12-in. magnet. Temperature was controlled within ±1° by a Varian V-4557 variable-temperature controller.

Coupling constants and line widths were taken directly from the calibrated chart paper.

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[1] (a) E. Grunwald, *Anal. Chem.*, **26**, 1696 (1954); (b) S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *J. Am. Chem. Soc.*, **76**, 2597 (1954); (c) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958).

[2] (a) N. M. Atherton and S. I. Weissman, *ibid.*, **83**, 1330 (1961); (b) P. J. Zandstra and S. I. Weissman, *ibid.*, **84**, 4408 (1962); (c) F. C. Adam and S. I. Weissman, *ibid.*, **80**, 1518 (1958).

[3] (a) A. H. Reddoch, *J. Chem. Phys.*, 43, 225 (1965); (b) N. Hirota and R. Kreilick, *J. Am. Chem. Soc.*, **88**, 614 (1966); (c) R. Chang and C. S. Johnson, *ibid.*, **88**, 2238 (1966).

[4] (a) P. Chang, R. V. Slates, and M. Szwarc, *J. Phys. Chem.*, **70**, 3180 (1966); (b) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *ibid.*, **69**, 612 (1965); (c) C. Carvajal, K. J. Tolle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **87**, 5548 (1965).

[5] (a) T. E. Hogen-Esch and J. Smid, *ibid.*, **88**, 307, 318 (1966); (b) *ibid.*, **87**, 669 (1965); (c) J. Smid, *ibid.*, **87**, 655 (1965).

[6] (a) N. Hirota, *J. Phys. Chem.*, **71**, 127 (1967); (b) M. C. R. Simons, *ibid.*, 71, 172 (1967).

[7] (a) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784, 3785 (1960); (b) H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *ibid.*, **85**, 2360 (1963).

[8] (a) R. L. Ward and S. I. Weissman, *ibid.*, **79**, 2086 (1957); (b) M. T. Jones and S. I. Weissman, *ibid.*, **84**, 4269 (1962); (c) W. L. Reynolds, *J. Phys. Chem.*, **67**, 2866 (1963); (d) E. deBoer and C. MacLean, *J. Chem. Phys.*, 44, 1334 (1966).

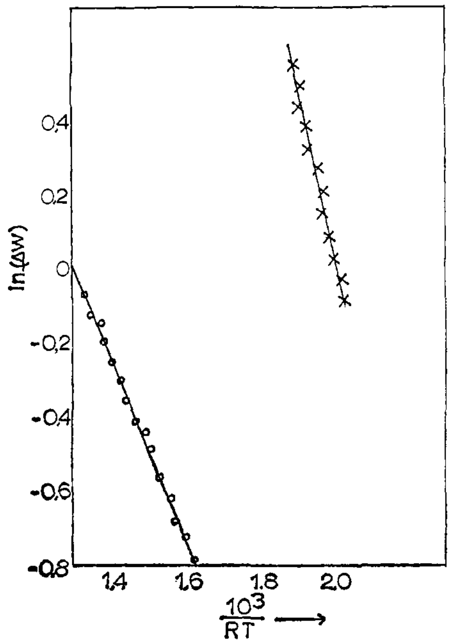

Figure 1. Plot of ln (line width) *vs.* $10^3/RT$ for DME systems: ×, Na reduction; ○, Li reduction.

Results

Six systems (COT–solvent–metal) are studied, where the solvent is 1,2-dimethoxyethane (DME) or tetrahydrofuran (THF), and the metal is lithium, sodium, or potassium. Ion pairing affects the esr spectra of COT anion radical I influencing the line widths of the individual hyperfine splitting (hfs), the activation energy of the line-broadening process, and the spin concentration. For all systems (COT–solvent–metal) studied, successive additions of metal to 0.5 *M* COT leads to a wider line. Over the linear range of the ln (line width) *vs.* $1/RT$ plot (Figures 1 and 2) the same activation energy is obtained for different amounts of metal added. For five of the six systems it was found that the activation energy of the line-broadening process over the linear range of the ln (line width) *vs.* $1/RT$ plot was independent of the dianion II concentration. The activation energy for the system COT–THF–Na could not be measured.

Figures 3 and 4 are plots of the relative spin concentration *vs.* *T*, varying the solvent and the counterion.

Details are now given for the various systems (COT–solvent–metal) studied.

COT–DME–Li and COT–THF–Li. The activation energies for those factors affecting the line width in the systems COT–DME–Li are 2.4 and 1.7 kcal/mole, respectively. The spin concentration of the lithium systems increases quite dramatically upon lowering of the temperature. Comparing the line widths of the lithium systems with the other metal systems, the line from the lithium salt is much narrower than the line of the sodium or potassium systems.

COT–DME–Na and COT–THF–Na. The activation energy for those factors affecting the line width in the system COT–DME–Na is 4.1 kcal/mole, highest of any of the systems studied. The activation energy for the system COT–THF–Na could not be measured. High (0.5 *M*) or low (0.03 *M*) concentrations of COT gave metal splitting, even at the lowest temperatures.

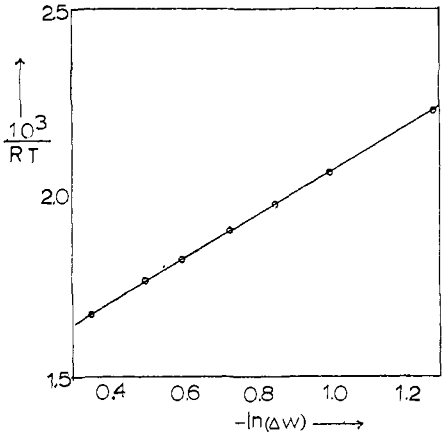

Figure 2. Plot of −ln (line width) *vs.* $10^3/RT$ for the system COT–THF–Li.

The spin concentration is not detectable below −20 to −40°, depending upon the concentration of COT; the lower temperatures are reached by systems of higher concentrations of COT. The COT–THF–Na system is the only one of the six which exhibits metal splitting. Near 70°, however, we observe the appearance of only the nine-proton splittings, apparently due to broadening of the metal splittings. Near 110° the nine lines merge to one due to fast exchange conditions. The anion radical I is thermally stable (greater than 30 min) to 115°; above this temperature the anion radical decomposes and cannot be reversibly recovered. The thermal stability of I is much greater than monohomocyclooctatetraene anion radical,[9] which undergoes rapid decomposition above 0°.[9a] The COT–DME–Na system is quite different from the COT–THF–Na system. Nine lines are observed in the temperature range from −90 to +90°. Likewise, unlike the COT–DME–Na system, for the COT–THF–Na system the spin concentration increases as the temperature is raised.

Kinetics of the line-broadening process for the system COT–DME–Na were studied. From a line-width study of this system for three different concentrations of COT, it was determined that the line-broadening process from −30 to +10° is one-half order in COT concentration. Details are given in the Experimental Section and Table I.

Table I. Line Width for Various Concentrations of Neutral COT in the System COT–DME–Na at −20°[a]

Sample	(COT), *M*	Line width, gauss	Line width/ $(\mathrm{COT})^{1/2}$
1	0.32	0.416	0.74
2	0.64	0.605	0.76
3	1.30	0.845	0.74

[a] The COT dianion concentration in this system is 0.034 *M* for each sample.

COT–DME–K and COT–THF–K. The activation energies for those factors affecting the line width in the systems COT–DME–K and COT–THF–K are 0.4 and 1.2

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[9] (a) F. J. Smentowski, R. M. Owens, and B. D. Faubion, submitted for publication; (b) R. Reike, M. Ogliaruso, R. McClung, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 4729 (1966); (c) T. J. Katz and C. Talcott, *ibid.*, **88**, 4732 (1966).

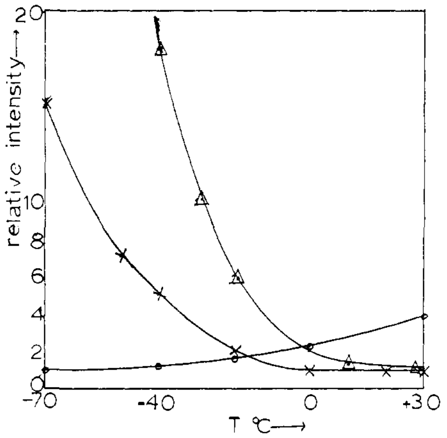

Figure 3. Plot of temperature against the relative intensity of the esr signal for DME systems: ○, K reduction; ×, Na reduction; △, Li reduction.

kcal/mole, respectively. The potassium systems characteristically give smaller changes in line width and relative spin concentration as a function of temperature than the other systems. The COT–DME–K system gives nine lines between −70 and +50°. The COT–THF–K system gives one line over the entire temperature range from −40 to +90°. For the system COT–THF–K the spin concentration is not detectable below −20 to −40°, depending upon the concentration of COT; the lower temperatures are reached by higher COT concentrations. In both potassium systems, the spin concentration increases with temperature.

Discussion

COT Anion Radical (I) and Ion Pairing. Recently, the effects of ion pairing on esr spectra have been noted by Weissman and Zandstra.[2b] They have found from line-width studies of sodium naphthalenide in THF that eq 3 and 4, instead of (3) alone, are needed to describe the difference in the rate of the electron transfer from the naphthalenide to naphthalene with different counterions.

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

$$\mathrm{pi}\cdot^-\mathrm{M}^+ + \mathrm{pi} = \mathrm{pi} + \mathrm{pi}\cdot^-\mathrm{M}^+ \qquad (4)$$

Similarly, we have found that anion radical I, which undergoes disproportionation (eq 2) and electron transfer (eq 5)[7] (where pi = COT), is influenced by the effects of ion pairing as studied by the activation energy of the line-broadening process, the line width of the proton splittings, and the spin concentration of I. Because of ion pairing, (2) and (5) are replaced by (6) and (7), where $\mathrm{pi}^{2-}\mathrm{M}_2{}^+$ and $\mathrm{pi}\cdot^-\mathrm{M}^+$ represent all forms of the ions from tight ion pairs to dissociated ions.

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

$$\mathrm{pi}\cdot^- + \mathrm{pi}^{2-} = \mathrm{pi}^{2-} + \mathrm{pi}\cdot^- \qquad (5)$$

$$\mathrm{pi} + \mathrm{pi}^{2-}\mathrm{M}_2{}^+ = 2\mathrm{pi}\cdot^-\mathrm{M}^+ \qquad (6)$$

$$\mathrm{pi}\cdot^-\mathrm{M}^+ + \mathrm{pi}^{2-}\mathrm{M}_2{}^+ = \mathrm{pi}^{2-}\mathrm{M}_2{}^+ + \mathrm{pi}\cdot^-\mathrm{M}^+ \qquad (7)$$

First, let us consider the effects of ion pairing on the activation energy of the line-broadening process and the line widths of anion radical I. If the concentration of dianion II is varied, the same activation energy is derived for a particular system (COT–solvent–metal). However, a different activation energy is obtained for a different system. Similarly, Jones and Weissman[8b] have observed the independence of the activation energy on the concentration of pi^- for the electron transfer in eq 8, where pi = tris-*p*-nitrophenylmethyl. (We can consider eq 8 as derived from eq 5 by removal of a negative charge from each reactant.) Addition of tris-*p*-nitrophenylmethide to tris-*p*-nitrophenyl methyl radical did not change the activation energy of line broadening due to eq 8. However, the activation energy did change with solvent or counterion. Likewise, addition of the methide does give faster electron transfer and broadens the hyperfine line. All of the above-mentioned properties characteristic for tris-*p*-nitrophenyl methyl systems have been observed by us for COT systems. An implied assumption in a comparison of the two different radicals is that the major source of line broadening is due to eq 8 and 7, respectively. Information is available on this point for one of the COT systems (*vide infra*).

$$\mathrm{pi}^-\mathrm{M}^+ + \mathrm{pi}\cdot = \mathrm{pi}\cdot + \mathrm{pi}^-\mathrm{M}^+ \qquad (8)$$

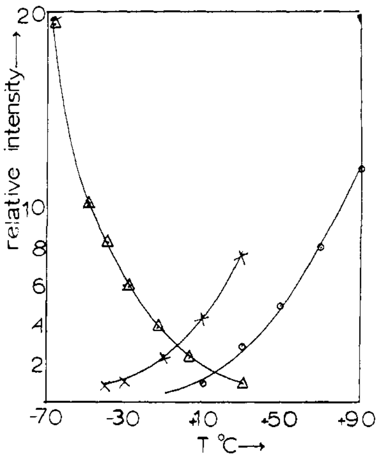

Figure 4. Plot of temperature against the relative intensity of the esr signal for THF systems: ⊙, K reduction; ×, Na reduction; △, Li reduction.

Next, let us consider the variation in the spin concentration for anion radical I as a function of temperature, solvent, and counterion. This dependence of the spin concentration on these variables reflects the different requirements of solvation of anion radical I and dianion II, thus affecting the disproportionation (6). For the systems giving higher spin concentrations at lower temperatures, it is conceivable that the dianion II might almost entirely be converted to the anion radical I at even lower temperatures.

Line-Width Studies. Either the rate of disproportionation (6) or the rate of electron transfer (7) is first order in concentration of dianion II (eq 9 and 10). Because of their independence of dianion II, other types of line broadening such as ion-pair broadening,[2a,3,10] intramolecular types of broadening,[11] spin–spin exchange,[12] etc., are minor sources of line broadening for systems containing high concentrations of

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(10) A. H. Reddoch, *J. Chem. Phys.*, 41, 444 (1964).

(11) (a) G. K. Fraenkel, *ibid.*, 42, 4275 (1965); (b) J. H. Freed and G. K. Fraenkel, *ibid.*, 41, 3623 (1964); (c) B. L. Barton and G. K. Fraenkel, *ibid.*, 41, 695 (1964); (d) D. Kivelson, *ibid.*, 33, 1094 (1960).

(12) G. E. Pake and T. R. Tuttle, Jr., *Phys. Rev. Letters*, 3, 423 (1959).

dianion II. Next the question must be asked whether we can determine if the line broadening for systems containing high concentration of the dianion II is due to the disproportionation (6) and/or the electron transfer (7). If we consider that at a particular temperature equilibrium conditions prevail for the disproportionation (6) and the electron transfer (7), then for the disproportionation (6), relation 9 holds, where pi = COT. Like-

$$\text{rate} = k(\text{pi}\cdot^{-})^2 = k'(\text{pi}^{2-}) \qquad (9)$$

wise, if we consider that at a particular temperature equilibrium conditions prevail for the disproportionation (6) and the electron transfer (7), then for the electron transfer (7), relation 10 holds. where pi = COT.

$$\text{rate} = k''(\text{pi}\cdot^{-})(\text{pi}^{2-}) \qquad (10)$$

Because the disproportionation equilibrium is so heavily in favor of the dianion II and the neutral molecule[7] ($Ke \simeq 10^{-9}$), the concentration of dianion II is approximately constant if a given amount of metal is added to varying amounts of COT. Utilizing this fact and replacing the anion-radical concentration with the expression derived from the disproportionation equilibrium, (9) and (10) become (11) and (12), where pi = COT.

$$\text{rate} = k^{\text{III}}(\text{pi}) \qquad (11)$$

$$\text{rate} = k^{\text{IV}}(\text{pi})^{1/2} \qquad (12)$$

Therefore, line broadening due to disproportionation can be distinguished from that due to electron transfer by observing the effect of COT on the line width. If the line width is first order in COT, then line broadening is due to the disproportionation. If the line width is one-half order in COT then the line broadening is due to electron transfer from dianion II to anion radical I. The line width may be neither first order nor one-half order in COT, in which case line broadening would be due to both disproportionation and electron transfer. For the system COT–DME–Na, over the linear range of the ln (line width) *vs.* $1/RT$ plot, the line width is one-half order in COT (Table I). Thus the major source of line broadening for this system when the dianion concentration is greater than 0.03 M is due to electron transfer for the temperature range -30 to $+10°$.

Comparing the three salts of anion radical I in the same solvent and with identical concentration of dianion II, it is found that the line widths follow the order $K^+ > Na^+ > Li^+$. Electron transfer is so rapid with the potassium salt that in THF only fast exchange conditions prevail.

Summary and Conclusions

The influence of ion pairing appears to be a major factor in the variation of the physical properties of anion radical I. The activation energy of the electron transfer between dianion II and anion radical I is very dependent upon the solvent and the counterion, but independent of the concentration of dianion II. The line widths of the individual hfs are a logarithmic function of the temperature (Figures 1 and 2) and are dependent upon the solvent and the counterion. Likewise, for the system COT–DME–Na, the major source of line broadening is due to electron transfer from dianion II to anion radical I when the dianion concentration is greater than 0.03 M (Table I). The variation of spin concentration with temperature, solvent, and counterion is indicative of the influence of ion pairing on the disproportionation (6). It indicates that the requirements of solvation differ for anion radical I and dianion II. The resonance energy of dianion II and anion radical I are identical, 1.66 β. Stoichiometrically, if only the resonance energy determined the thermodynamic stability of the disproportionation (6), then anion radical I would be favored, since COT itself has little resonance energy.[13] Either preferential solvation of anion radical I over the dianion II explains the direction of the disproportionation (6), and/or other factors such as the total resonance energy of the system becomes important.

Acknowledgment. The authors are indebted to Professors E. A. Meyers and B. J. Zwolinski for helpful discussion. 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.

(13) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.