Relationship between Ion-Pair Dissociation Constants of Some Substituted Cyclooctatetraene Dianions and Electronic Structure

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Abstract: The observed comproportionation equilibrium constant [$K_{\text{obsd}} = (\pi\cdot^-)^2/(\pi^{2-})_{\text{total}}(\pi)$] for several substituted cyclooctatetraene systems has been algebraically related to the charged ion-pair ($\cdot^{2-}$,M$^+$) dissociation constant [$K_d = (\pi^{2-})(\text{K}^+)/(\pi^{2-},\text{K}^+)$]. In hexamethylphosphoramide the sodium salts of all the dianions studied were found to be free of ion pairing. However, for the potassium salts, the K_d's for the charged ion pairs follow the order biscyclooctatetraenyl > naphthocyclooctatetraene > biphenylcyclooctatetraene > cyclooctatetraene > *tert*-butoxycyclooctatetraene. Since ion-pair dissociation constants increase with decreasing charge density (increasing charge delocalization), this order also represents the order of charge delocalization in these dianions. This work represents an application of ESR spectroscopy to the determination of ion-pair dissociation constants of diamagnetic dianions.

In recent years a considerable amount of data concerning the thermodynamic parameters controlling the dissociation of ion pairs of organic mono anions has been accumulated. Ion-pair dissociation constants (K_d's) have been determined by NMR,[1] conductivity,[2] visible spectroscopy,[3] and ESR for paramagnetic ions.[4] The simple solvated electron varies from fully ion paired in diethyl ether,[5] to fully dissociated from the cation in hexamethylphosphoramide (HMPA).[6] Despite this, there is still very little information as to the ion-pair dissociation constants of organic dianions.

In a recent report, Szwarc and coworkers[7] utilized a combination of visible spectroscopy and conductivities to not only obtain the K_d's for the lithium and sodium salts of tetraphenylethylene dianion in tetrahydrofuran, but to obtain the probable structures of these ion pairs. As evidenced by the enthalpies and entropies of disproportionation and ion-pair dissociation, they observed that for the dilithium salt, one Li$^+$ is tightly bound to the dianion and is poorly solvated while the other is loosely bound and highly solvated. However, the two lithium cations rapidly interchange their roles, and a long-time observation would reveal them as identical. The sodium salt, on the other hand, consists of two tightly bound sodium cations.[7] Thus, the dissociations studied by Szwarc and coworkers in tetrahydrofuran are

$$\text{Li}^+,\pi^{2-}//\text{Li}^+ \rightleftarrows \pi^{2-},\text{Li}^+ + \text{Li}^+ \qquad (1)$$

and

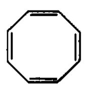
$$\text{Na}^+,\pi^{2-},\text{Na}^+ \rightleftarrows \pi^{2-},\text{Na}^+ + \text{Na}^+ \qquad (2)$$

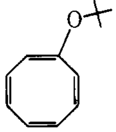
All of this very interesting work was carried out in THF where the dianion exists as either the neutral ion aggregate (dianion ion paired to two cations) or the charged ion pair (dianion ion paired to just one cation).

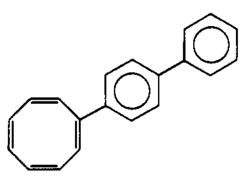
It would be of interest to observe the dissociation constants of ion pairs involving an organic dianion in HMPA, where only the charged ion pair exists in equilibrium with the free dianion ($\pi^{2-},\text{M}^+ \rightleftarrows \pi^{2-} + \text{M}^+$). As evidenced by the work of Szwarc, much information concerning the structure of ion pairs can be obtained from a study of K_d's. Here we wish to report the dissociation constants for a series of substituted potassium and sodium cyclooctatetraenide ion pairs and utilize this information to gain insight as to the degree of charge delocalization in these dianions.

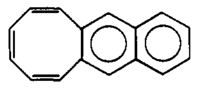
In hydrocarbon anion radicals, the charge density is not normally concentrated in one part of the anion, and thus no ion pairing is observed for these anion radicals in HMPA.[8,9] However, for anion radicals containing polar groups, such as benzoquinone and nitrobenzene anion radicals, ion pairs can be formed in HMPA.[10,11] Thus ion pairing increases as charge becomes localized in the anion.

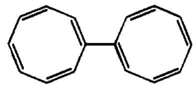
Hydrocarbon dianions sometimes do form ion pairs in HMPA as evidenced by the fact that the disproportionation equilibrium constant for the cyclooctatetraene (COT) anion radical is a function of the alkali metal counterion.[12] Since hydrocarbon anion radicals do not form ion pairs in HMPA, this ion pairing is clearly with the dianion of COT. There is even less coulombic attraction between a solvated cation and a charged ion pair (π^{2-},M$^+$) than there is between a solvated cation and an anion radical. All of this indicates that the formation of the charged ion pair (COT^{2-},M$^+$) is what leads to the cation dependence of the disproportionation equilibrium constant in HMPA. Here we utilize a mathematical relationship between the disproportionation equilibrium constant and the ion-pair dissociation constant (K_d), allowing the determination of K_d for the dianions of the substituted COT systems shown below.


COT

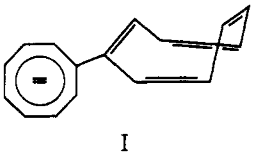

TBCOT


BPCOT


NCOT

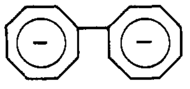

BCOT

Since it is well established that the localization of charge density in anionic species decreases the ion-pair dissociation constant,[10-13] the degree of delocalization of the two extra electrons in the dianion of BCOT (for example) will strongly affect the dissociation constant of the charged ion pair. If the ion-pair dissociation constant (K_d) is the same as that for the COT dianion, the indication will be that the two electrons remain basically in one of the two ring systems as shown in structure I. In this form one of the eight-member ring systems is fully aromatic ($4n + 2$ electrons in the π system), and the other is antiaromatic. If, however, the K_d turns out to be very large in comparison with that for the COT dianion, then the two electrons are delocalized be-



I

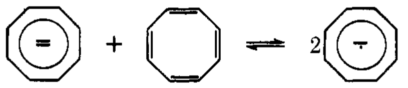
tween the two ring systems, and the dianion should be thought of in terms of two nine π electron ring systems as shown in structure II.



II

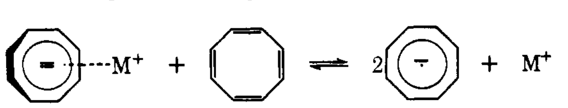
Results and Discussion

If the COT dianion exists free of ion pairing, the comproportionation equilibrium is defined by



(3)

However, if the dianion is ion paired with one alkali metal cation, the equilibrium is given by



(4)

The possibility of the existence of the neutral ion aggregrate or the ion pair of the anion radical is ruled out in HMPA.[14] If the observed equilibrium constant (K_{obsd}) is taken as

$$K_{\mathrm{obsd}} = (\mathrm{COT}\cdot^-)^2/(\mathrm{COT})(\mathrm{COT}^{2-})_{\mathrm{total}} \tag{5}$$

where $(\mathrm{COT}^{2-})_{\mathrm{total}}$ is the sum of $(\mathrm{COT}^{2-},\mathrm{M}^+)$ and (COT^{2-}), the relationship between the triple ion dissociation constant (K_d) and K_{obsd} is then

$$K_{\mathrm{obsd}} = K_f/[1 + (\mathrm{M}^+)K_d^{-1}] \tag{6}$$

where K_f represents the comproportionation equilibrium constant for the system containing only free ions (see eq 3).

From eq 6 it is clear that the addition of alkali metal salts (KI or $\mathrm{NaClO_3}$) to solutions of COT dianion and anion radical in HMPA should lead to a decrease in K_{obsd}. The anion radical concentration is proportional to the amplitude of the overmodulated ESR line, A, and K_{obsd} can be expressed as shown in eq 7, where B is simply a proportionality constant.[14]

$$K_{\mathrm{obsd}} = (BA)^2/(\mathrm{COT})(\mathrm{COT}^{2-})_{\mathrm{total}} \tag{7}$$

No change in K_{obsd} could be detected upon addition of $\mathrm{NaClO_3}$ up to 0.3 M to either the potassium or sodium reduced solutions of COT in HMPA. In order for K_{obsd} to remain constant within experimental error, K_d for the sodium salt $(\mathrm{COT}^{2-},\mathrm{Na}^+)$ must be very large. With the dual cavity technique used here, a change in K_{obsd} of more than 4% resulting in a change in A of 2% would certainly be observed. This means that K_d for $\mathrm{COT}^{2-},\mathrm{Na}^+$ is greater than 0.1 in HMPA. Addition of KI to either the sodium or potassium reduced systems affords a sharp decrease in the observed equilibrium constant.

For the experiments where potassium iodide was added to the sodium reduced system, the sample taken without added salt served as a standard for which K_f is 2.3×10^{-3}.[12] The sample from the same anion radical solution but with added KI was compared to this standard in the dual cavity ESR spectrometer and K_{obsd} obtained from the ratio of the two spectrum amplitudes and the use of eq 7.

Table I. K_d and K_{obsd} for Both Potassium and Sodium Reduced COT–HMPA Solutions

Metal	$[\mathrm{K}^+]_{\mathrm{total}}$, M	$[\mathrm{KI}]_{\mathrm{added}}$, M	$[\mathrm{Na}^+]$, M	$K_d \times 10^3$
K	0.25	0	0	1.6
K	0.32	0	0	1.2
K	0.14	0	0	1.7
K	0.31	0	0	1.3
K	0.36	0.17	0	1.4
Na	0.21	0.21	0.13	0.80
Na	0.12	0.12	0.12	0.91
Na	0.081	0.081	Small	1.0

This value obtained for K_{obsd} was then placed into eq 6, which was solved for K_d using the concentration of added KI minus the concentration of COT dianion for the concentration of potassium ion free of ion pairing, $[\mathrm{K}^+]$.[15] The true value for K_d should be calculated from the use of the concentration of KI minus the concentration of charged ion pair for $[\mathrm{K}^+]$ in eq 6. However, K_d is very small, and the concentration of total dianion is essentially equal to that of the charged ion pair.

A different formulism had to be used for the systems where K_d was determined for the potassium reduced solutions. The dissociation constant (K_d) is given by

$$K_d = [\mathrm{COT}^{2-}][\mathrm{K}^+]/[\mathrm{COT}^{2-},\mathrm{K}^+] \tag{8}$$

Since $[\mathrm{K}^+]$ is equal to the total potassium ion concentration, $[\mathrm{K}^+]_{\mathrm{total}}$, minus the concentration of $\mathrm{COT}^{2-},\mathrm{K}^+$ and $[\mathrm{K}^+]_{\mathrm{total}} = [\mathrm{KI}]_{\mathrm{added}} + [\mathrm{COT}\cdot^-] + 2[\mathrm{COT}^{2-}] + 2[\mathrm{COT}^{2-},\mathrm{K}^+]$, eq 8 can be solved for $[\mathrm{K}^+]$ in terms of K_d and known quantities, eq 9. $[K^0]$ represents the concentration of potassium metal used to reduce the COT in solution, and the concentration of anion radical, being very small, has been neglected.

For the first iteration, K_d was calculated from eq 6 utilizing $[\mathrm{K}^+]_{\mathrm{total}}$ for $[\mathrm{K}^+]$. This value for K_d was then placed into eq 9 and a new value for $[\mathrm{K}^+]$ obtained. The new value for $[\mathrm{K}^+]$ was put back into eq 6 and the iterative process continued until a constant value for K_d was obtained, Table I. Normally five to six iterations were necessary to obtain a constant value for K_d. From eight determinations, the best value for K_d for the COT triple ion in HMPA is $(1.3 \pm 0.3) \times 10^{-3}$.

For all of the compounds studied, K_{obsd} did not vary with the addition of $\mathrm{NaClO_3}$. Thus the sodium salts of all five cyclooctatetraenides are free of ion pairing within our limits of detection.

Addition of KI to the TBCOT-HMPA-M^+ systems lead to an even more dramatic decrease in K_{obsd} than was found for the COT-HMPA-M^+ systems. The data given in Table II yield a K_d of $(2.3 \pm 0.8) \times 10^{-4}$ for the potassium salt of TBCOT in HMPA, Table III.

The dissociation constants for the dianions of BPCOT and NCOT were determined in an identical manner, and the results are given in Table III.

For the BCOT-HMPA-M^+ systems, no change in K_{obsd}

$$[\mathrm{K}^+] = \frac{[\mathrm{KI}]_{\mathrm{added}}/2 + [\mathrm{K}^0]/2 + K_d + \sqrt{(K_d - [\mathrm{K}^0]/2 - [\mathrm{KI}]_{\mathrm{added}})^2 + 4K_d[\mathrm{K}^0]}}{2} \tag{9}$$

Table II. K_d and K_{obsd} for Potassium and Sodium Reduced TBCOT-HMPA Solutions

$K_{obsd} \times 10^6$	$[K^+]_{total}$, M	$[KI]_{added}$, M	$[Na^+]$, M	$K_d \times 10^4$
5.37	0.16	0.052	0	2.51
5.69	0.20	0.080	0	3.4
19.3	0.08	0	0	3.4
6.92	0.11	0.11	0.13	1.3
1.62	0.28	0.28	0.096	1.7
5.14	0.15	0.15	0.11	2.1
24.9	0.07	0.07	0.11	1.9

Table III. Dissociation Constant for the Dipotassium Salts of the Following Dianions

Dianion	$K_d \times 10^4$	Dianion	$K_d \times 10^4$
$TBCOT^{2-}$	2.0 ± 0.8	$NCOT^{2-}$	118 ± 35
COT^{2-}	13 ± 3	$BCOT^{2-}$	>1000
$BPCOT^{2-}$	37 ± 35		

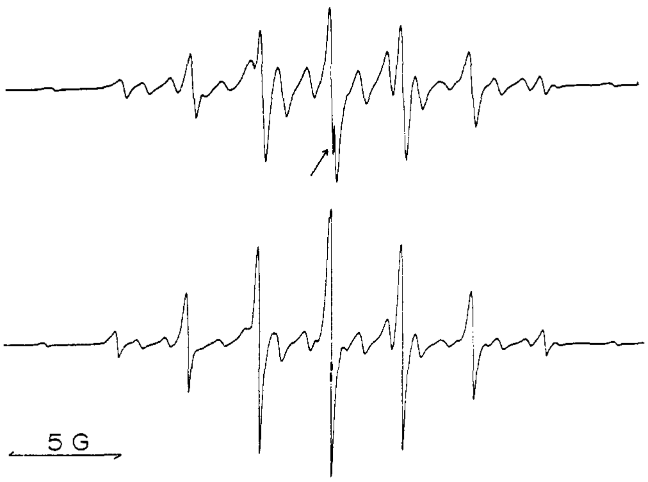


Figure 1. ESR spectra of the anion radicals formed by the reduction of a mixture of TBCOT and COT by sodium in HMPA. The lower was taken from the same anion radical solution but with added potassium iodide (0.1 M). Note that in the lower spectrum the concentration of $COT\cdot^-$ is larger relative to that for $TBCOT\cdot^-$. The spectra were recorded at 25°. The spike indicated by the arrow marks 3391.2 G.

was noted for KI additions up to 0.4 M to either the sodium or potassium reduced solution. Thus the BCOT dianion exists free of ion pairing in HMPA.

From Table III it is clear that ability of the dianions to form ion pairs is $TBCOT^{2-} > COT^{2-} > BPCOT^{2-} > NCOT^{2-} > BCOT^{2-}$. In none of the cases is the error in K_d sufficiently large for this order to be in doubt. Further, experiments carried out with mixtures of dianions confirm this order. When a mixture of COT and TBCOT is reduced in HMPA, both anion radicals can be observed simultaneously. Addition of KI to this solution always results in an increase in the ESR signal due to the COT anion radical relative to that for the anion radical of TBCOT, Figure 1. This, of course, is due to the fact that $TBCOT^{2-}$ has a greater affinity for the potassium cation than does the COT dianion. A similar experiment shows that COT^{2-} has a greater affinity for the potassium cation than does the BPCOT dianion, Figure 2.

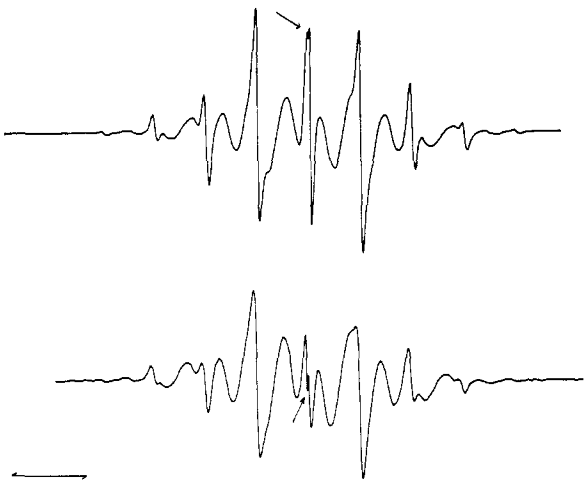
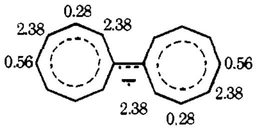


Figure 2. ESR spectra of the anion radicals of BPCOT and COT superimposed, formed by the reduction of a mixture of the two compounds in HMPA by sodium metal. The lower was taken from the same solution but with added potassium iodide (0.1 M). Note that in the lower spectrum the concentration of $COT\cdot^-$ is smaller relative to that for the $BPCOT\cdot^-$. The spectra were recorded at 25°. The spike indicated by the arrow marks 3391.2 G.

The ion pair dissociation constant (eq 8) increases with the delocalization of the two "extra" electrons in the dianions. This is simply a restatement of the fact that ion pairing increases with increasing charge density in HMPA.[10,11] The *tert*-butoxy group acts as an electron donor and tends to concentrate the charge density in the COT moiety and/or provide an attachment point for the cation; thus it has the smallest K_d. In the BPCOT and NCOT systems, the two "extra" electrons are allowed to diffuse into the benzene ring systems, thus diffusing the charge densities in these systems. There is less delocalization in the BPCOT system than in the NCOT system, which is in part due to the relatively large dihedral bond angle between the COT and benzene rings in the BPCOT dianion.[16] However, for both of these systems, the charge density still resides predominantly in the eight-member ring. This is best explained by the fact that the eight-member ring system "needs" the extra electrons to approach aromaticity, while the benzene moieties already contain $4n + 2$ π electrons.

For the BCOT dianion, the charge density is completely delocalized throughout both COT rings, in agreement with structure II. At room temperature the odd electron in the anion radical of BCOT is also fully delocalized throughout the two ring systems.[17] To check if this observation was due to delocalization or rapid intramolecular electron exchange, this anion radical was generated in a 1:1 mixture of tetrahydrofuran and HMPA. The coupling constants shown in structure III were invariant between 25 and −100°. Thus,



III

for both the dianion and anion radical of BCOT, the added electrons are fully delocalized.

It should be noted here that although the line intensities are controlled by the disproportionation equilibrium, the line widths for all of the COT systems studied here are controlled by a rapid electron exchange between the dianion and the anion radical:

$$\pi^{2-} + \pi\cdot^{-} \rightleftarrows \pi\cdot^{-} + \pi^{2-} \tag{10}$$

Ion pairing greatly reduces the rate of electron exchange and thus decreases the ESR line widths, Figure 3. This effect has been observed for a variety of electron exchange reactions involving anion radicals.[18]

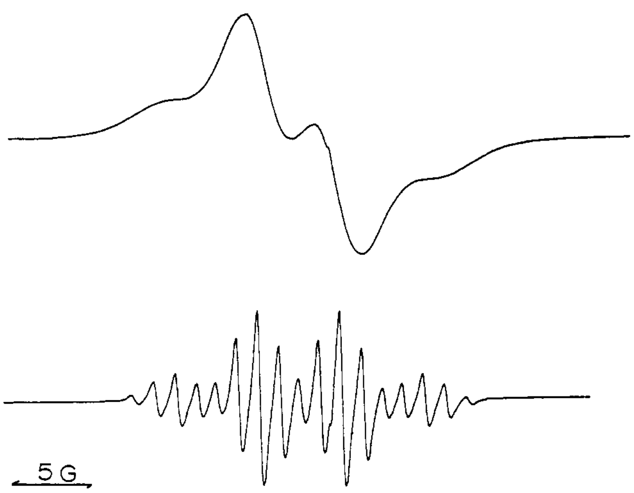


Figure 3. ESR spectrum of the TBCOT-HMPA-Na system. The lower spectrum was taken for the same anion radical solution but with added potassium iodide (0.2 *M*). Note the line narrowing upon addition of the potassium salt.

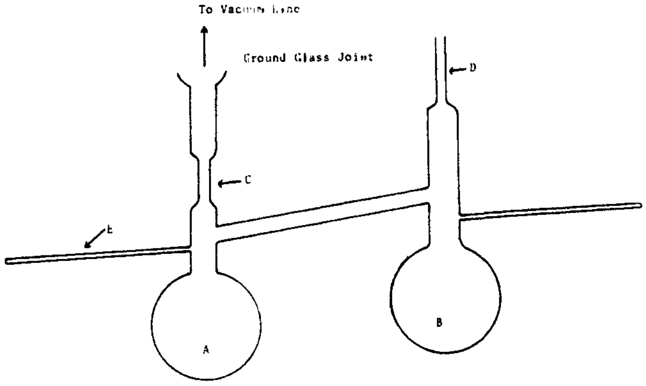


Figure 4. Apparatus used for the addition of salt to the anion radical solutions.

Experimental Section

The observed comproportionation equilibrium constant (K_{obsd}) was measured by the use of an all-glass apparatus shown in Figure 4. A weighed portion of salt (KI or $NaClO_3$) was placed into bulb B, which was subsequently sealed at point D. A known portion of the substituted COT and alkali metal were then placed into bulb A and the entire system was evacuated. The HMPA was then distilled into bulb A, from the solvated electron, and the apparatus was sealed from the vacuum line at point C. After all of the alkali metal was dissolved, a sample was taken in ESR tube E. The remainder of the solution was poured into bulb B. This solution was stirred until all of the salt had dissolved, and the second ESR sample was taken. The two samples were compared for spin concentration using a dual cavity E-9 ESR spectrometer (Varian). All spin concentration comparisons were made from the over-modulated spectra. For the potassium reduced systems, the system Na-HMPA-COT was used as a spin standard.

The HMPA was distilled from calcium hydride before use, and the inorganic salts (Alfa Inorganics) were stored in a vacuum oven at 100° for 48 hr before use.

The substituted cyclooctatetraenes were prepared and purified as previously explained.[14,16,19]

Acknowledgments. We wish to thank the National Institute of Health for support of this work. The NIH support was from Grant No. RR-8102 of the Division of Research Resources.

(1) R. H. Cox, L. Harrison, and W. K. Austin, *J. Phys. Chem.*, **77**, 200 (1973).
(2) For example, see D. G. Oakenfull and D. E. Fenwick, *J. Phys. Chem.*, **78**, 1759 (1974).
(3) M. R. Arick, J. A. M van Broekhoven, F. W. Pijpers, and E. de Boer, *J. Am. Chem. Soc.*, **94**, 7531 (1972).
(4) M. T. Jones in "Radical Ions", E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N.Y., 1968, Chapter 6.
(5) J. L. Dye, M. G. DeBacker, and V. A. Nicely, *J. Am. Chem. Soc.*, **92** 5226 (1970).
(6) N. Gremmo and J. E. B. Randles, *J. Chem. Soc., Faraday Trans. 1*, 1480 (1974).
(7) B. Lundgren, G. Levin, S. Claesson, and M. Szwarc, *J. Am. Chem. Soc.*, **97**, 262 (1975).
(8) J. Chauduri, S. Kume, J. Jagur-Grodzinski, and M. Szwarc, *J. Am. Chem. Soc.*, **90**, 6421 (1968).
(9) A. E. Alegria, R. Concepcion, and G. R. Stevenson, *J. Phys. Chem.*, **79**, 361 (1975).
(10) G. R. Stevenson and L. Echegoyen, *J. Phys. Chem.*, **77**, 2339 (1973).
(11) (a) G. R. Stevenson and A. E. Alegria, *J. Phys. Chem.*, **77**, 3100 (1973); *ibid.*, **78**, 1771 (1974).
(12) G. R. Stevenson and J. G. Concepcion, *J. Phys. Chem.*, **76**, 2176 (1972).
(13) G. R. Stevenson, A. E. Alegria, and A. M. Block, *J. Am. Chem. Soc.*, **97**, 4859 (1975).
(14) (a) G. R. Stevenson and I. Ocasio, *J. Phys. Chem.*, **79**, 1387 (1975); (b) G. R. Stevenson, I. Ocasio, M. Colon, J. G. Concepcion, and A. M. Block, *J. Phys. Chem.*, **79**, 1685 (1975).
(15) (a) It has been previously observed that KI is almost fully dissociated in HMPA. That is, the association constant has been found to be too small to be measured by conductivity.[15b] We have recently found the ion association constant for KI by an indirect method to be about 4 in HMPA.[15c] Thus, for the experiments described here, we can be reasonably certain that the K^+ and not the K^+,I^- becomes associated with the COT^{2-}, due to the fact that the concentration of K^+ is much higher than that for K^+,I^- and that the affinity the COT^{2-} has for the K^+ is much larger than that for the potassium iodide ion pair. (b) P. Bruno, M. D. Monica, and E. Righetti, *J. Phys. Chem.*, **77**, 1258 (1973). (c) G. R. Stevenson and A. E. Alegria, *J. Am. Chem. Soc.*, **97**, 3869 (1975). (d) Sodium chlorate is also almost fully dissociated in HMPA and the same arguments hold for this salt as for KI (see ref 15a).
(16) G. R. Stevenson and L. Echegoyen, *J. Phys. Chem.*, **79**, 929 (1975).
(17) G. R. Stevenson and J. G. Concepcion, *J. Am. Chem. Soc.*, **95**, 5692 (1973).
(18) (a) R. Chang and C. S. Johnson, Jr., *J. Am. Chem. Soc.*, **88**, 2338 (1966); (b) G. R. Stevenson and R. Concepcion, *ibid.*, **96**, 4696 (1974).
(19) G. R. Stevenson and L. Echegoyen, *J. Phys. Chem.*, **79**, 929 (1975).