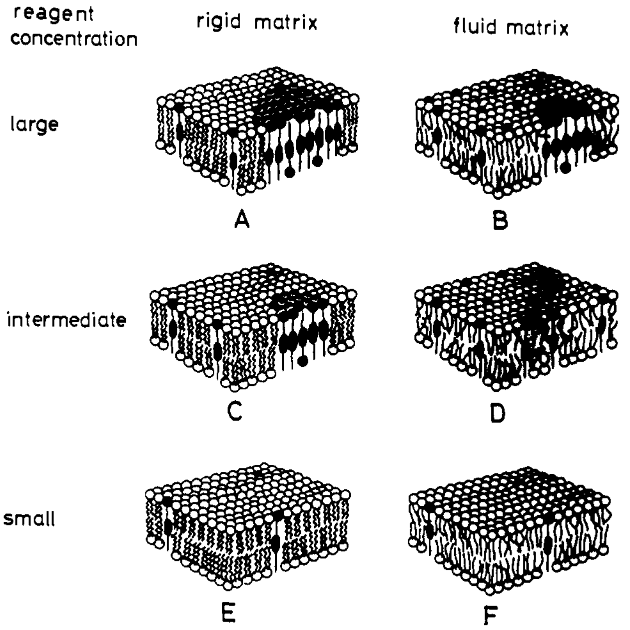

Figure 11. Schematic illustrations of the mode of reagent distribution in the crystalline and liquid-crystalline bilayer matrix.

coincides with Cu^{2+}-assisted phase separation. It is reported that the chelate formation can accelerate the hyrolysis.[29,30] However, this does not hold true in the present case, and Cu^{2+} only lowers the catalytic rate via the change of the membrane physical state.

Concluding Remarks

The membrane physical state is directly related to functions of the synthetic bilayer systems. It has been reported from these laboratories that inflection regions are noted in the Arrhenius plots of acyl transfer,[31] proton abstraction,[32] decarboxylation,[33] and nucleophilic cleavage of phosphate esters[34] that proceed in the dialkylammonium membrane matrix. These inflections are usually present at or near the phase transition temperature of the matrix membrane, and the apparent activation energies are greater at temperatures below T_c than above T_c. These results certainly point to the importance of the fluidity of the membrane matrix in controlling reaction rates; however, it was not clear in the past studies why the membrane fluidity should affect the reaction rate. The present investigation provides at least a partial answer to this question. It is now established that the distribution of membrane-forming reagents (substrate and catalyst) in the bilayer matrix is highly dependent of the membrane physical state (crystalline or liquid crystalline). This factor should have been influencial in reactions that involve hydrophobic reagents such as mentioned above, although we did not have means to determine the reagent distribution in those cases. The azobenzene amphiphile is a superior reagent in this respect, since its mode of aggregation (eg., cluster formation) in the membrane can be readily inferred by absorption spectroscopy. The cluster formation depends mainly on the molar ratio (two-dimensional concentration) of a reagent in the bilayer matrix and on the physical state of the matrix membrane. The nature of the head group is an additional factor. These situations are illustrated in Figure 11. When the reagent concentration is large, large clusters are formed in the rigid bilayer matrix (A). As the matrix becomes fluid, the cluster size (and number) decreases and the monomeric species increases (B). In the intermediate reagent concentration, the cluster is formed in the rigid matrix (C) but not in the fluid matrix (D). At small concentrations, the cluster is not formed in the rigid matrix (E) or in the fluid matrix (F). We examined the reactivity change due to formation of the bilayer cluster of a phenyl ester substrate and the activity change of the histidine catalyst due to formation of bilayer clusters. We have now at hand means to control the reactivities of both catalyst and substrate via the physical-state change. The principle of reaction control obtained in these systems should be applicable to other reactions.

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(29) Buckingham, D. A.; Marzilli, L. G.; Sargeson, A. *J. Am. Chem. Soc.* **1967**, *89*, 2772-2773, 4539-4540.

(30) Ohkubo, K.; Arima, H.; Yoshinaga, K. *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 287-290.

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(32) Okahata, Y.; Tanamachi, T.; Kunitake, T. *Nippon Kagaku Kaishi* **1980**, 442-449.

(33) Kunitake, T.; Okahata, Y.; Ando, R.; Shinkai, S.; Hirakawa, S. *J. Am. Chem. Soc.* **1980**, *102*, 7877-7881.

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An Azocine Anion Radical and Heats of Formation of Azocine Dianions

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Abstract: 3,8-Dimethyl-2-methoxyazocine was reduced to its anion radical in hexamethylphosphoramide (HMPA). The ESR spectrum of the DMMA anion radical resembles one recorded from a monosubstituted cyclooctatetraene anion radical where the substituent is an electron-withdrawing group. Calorimeteric techniques were utilized to study the thermodynamic stability of the DMMA dianion. This dianion is more stable relative to the metal and neutral molecule than is either the cyclooctatetraene (COT) or *tert*-butoxycyclooctatetraene dianion. The unexpected stability of $DMMA^{2-}$ is attributed to strong interactions between the cation (Na^+) with the oxygen and/or nitrogen atoms. This same interaction shifts the disproportionation of $DMMA^{-\cdot}$ to the right in solvents where ion association is prevalent.

Like COT, the azocines undergo a two-electron reduction to give planar dianions that are aromatic in nature.[1] Using CV studies, 3,8-dimethyl-2-methoxyazocene (DMMA) undergoes a two-electron addition at about 2.5 V (it varies a little with the choice of solvent). The behavior is consistent with the reduction of DMMA directly to the aromatic dianion (reaction 1).[1] A surprising result in this study (Paquette and co-workers[1]) is the fact that at the polarographic half-wave potential, the DMMA radical anion is easier to reduce than is the parent molecule, and the anion radical has never been observed. In fact, Paquette and co-workers have mentioned that the anion radical, if it does exist

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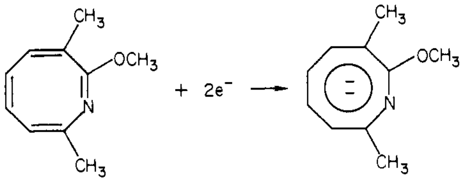
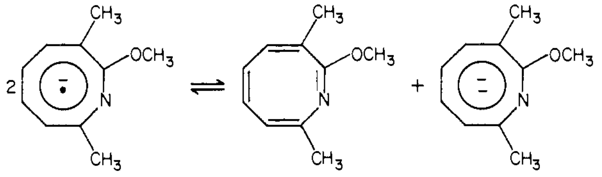
(1) Anderson, L. B.; Hansen, J. F.; Kakihana, T.; Paquette, L. A. *J. Am. Chem. Soc.*, **1971**, *93*, 161.



(1)

at all, is immediately reduced to the dianion by the addition of a second electron.

Here we wish to report the existence of the DMMA anion radical along with its electron distribution and thermodynamic stability. This anion radical exists in equilibrium with the dianion and neutral molecule (reaction 2) in hexamethylphosphoramide (HMPA) where both the anion and dianion are free from ion association.



(2)

The alkoxyazocines, which first became available through the efforts of Paquette and his research group,[2] exist in a tub conformation without conjugative stabilization. This is very similar to the situation for cyclooctatetraene (COT). Since the alkoxyazocines can be reduced, either electrochemically or by chemical means[1,2] to yield the planar aromatic dianions, we were interested in measuring the thermodynamic stability of this new dianion and seeing the effect of the substitution of a single nitrogen for a single carbon moiety in the eight member system upon the transfer of electrons to DMMA.

Results and Discussion

DMMA$^{-}\cdot$, ESR. Reduction of DMMA in hexamethylphosphoramide (HMPA) with Na metal, using the same technique as previously described,[3] leads to the formation of an anion radical solution yielding a strong ESR signal. This strong ESR signal is poorly resolved, but the main features are clearly due to five nearly equivalent proton splittings (Figure 1). The ESR spectrum is best simulated by including a splitting due to three protons with a coupling constant of 6.35 G, two of 6.05 G, two of 1.33 G, three of 1.10 G, three of 0.35 G, and a nitrogen with a splitting of 0.56 G (the smaller splittings have no effect other than to broaden the lines and were obtained from a better resolved spectrum). Under conditions of higher resolution, lower DMMA concentrations, many more hyperfine lines can be obtained (Figure 2). However, it is difficult to obtain this spectrum using the necessary slow scan conditions, since the anion radical is unstable and endures for only a short time. By recording a magnified view of the first few lines of this spectrum, it is possible to obtain values for the smaller coupling constants (Figure 3). Thus, even though the ESR spectrum of DMMA$^{-}\cdot$ is very complex and fleeting, the coupling constants can be obtained through a combination of the poorly and well resolved spectra (Table I). The assignments were made by making use of INDO calculations (Table I). Considering the complexity of the system the agreement between the INDO calculated coupling constants and the experimental is very good. It is interesting that the vast majority of the spin density is on positions 2, 4, 6, and 8 of the ring system. This closely resembles the ESR spectrum taken of an anion radical of a COT system with a group extending the conjugation attached.[4] For example, phenyl cyclooctatetraene anion radical yields a pentet due to four equivalent protons and a quartet due to three equivalent protons with a smaller coupling constant.[4] This is exactly the case for the DMMA system. The introduction of the nitrogen in the ring system of COT appears to have the same effect upon the spin density as putting an electron-withdrawing group on the eight-member ring.

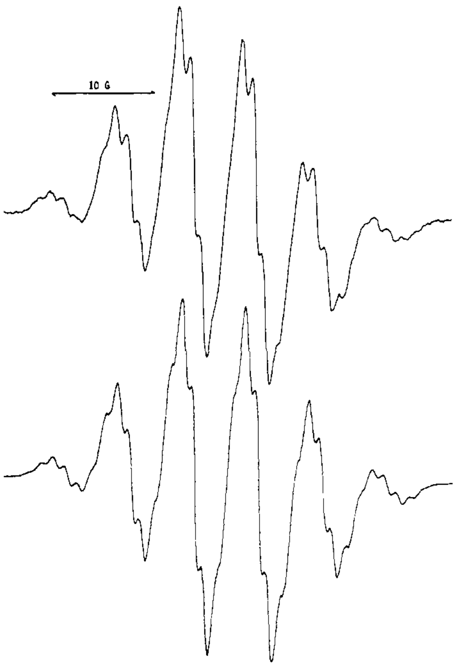


Figure 1. Low-resolution ESR spectrum of DMMA$^{-}\cdot$ at 25 °C. The lower spectrum is a computer simulation generated from the coupling constants shown in Table I and a line width of 0.42 G. The solvent is HMPA.

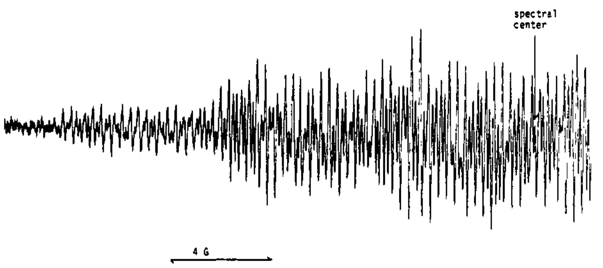
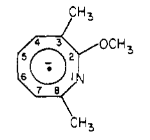


Figure 2. ESR spectrum of DMMA$^{-}\cdot$ at 0 °C. Only half of the spectrum is shown. The solvent is HMPA, and the arrow marks the center of the spectrum. Decomposition of the anion radical results in the high-field line intensities being smaller than predicted.

Table I. ESR Coupling Constants and INDO-Calculated Coupling Constants and p_z Spin Densities for the Anion Radical of DMMA



position	atom	exptl coupling const, G	INDO, ρ_{p_z}	INDO,[a] $^{16}\rho_{p_z}$	INDO coupling const
1	N	0.56	−0.049	0.78	−1.28
2	H(OCH$_3$)	0.35	0.294		1.04
3	H(CH$_3$)	1.10	−0.080	1.29	−3.20
4	H	6.05	0.356	5.70	−8.87
5	H	1.33	−0.159	2.54	4.39
6	H	6.05	0.363	5.81	−8.76
7	H	1.33	−0.134	2.15	3.93
8	H(CH$_3$)	6.35	0.330	5.38	17.1

[a] These represent the coupling constants calculated from the McConnell relationship ($A = Q\rho$) using 16 G for Q. These values give much better agreement with the experimental coupling constants than do the values taken directly from the INDO calculation.

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[2] Paquette, L. A.; Hansen, J. F.; Kakihana, T. *J. Am. Chem. Soc.* **1971**, *93*, 168.

[3] Stevenson, G. R.; Concepcion, J. G. *J. Phys. Chem.* **1972**, *76*, 2176.

[4] (a) Stevenson, G. R.; Concepcion, J. G.; Echegoyen, L. *J. Am. Chem. Soc.* **1974**, *96*, 5452. (b) Stevenson, G. R.; Echegoyen, L. *J. Phys. Chem.* **1975**, *79*, 929.

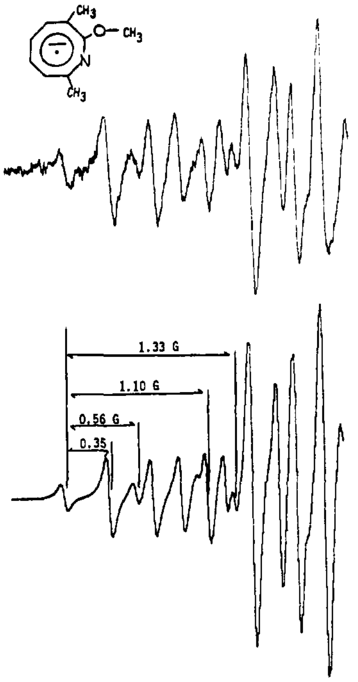
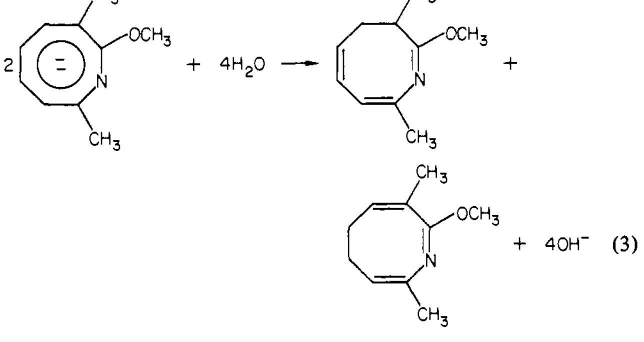


Figure 3. First few lines of the ESR spectrum of DMMA$^{-}\cdot$ in HMPA at 25 °C. The lower spectrum is a computer simulation generated from the coupling constants indicated and a line width of 0.055 G.

The reduction of DMMA in THF results only in a diamagnetic solution that is devoid of an anion radical. In tetrahydrofuran (THF) the anion radical of DMMA disproportionates to form the dianion and neutral molecule (reaction 2). Ion association favors this disproportionation in COT systems.[5] Both the anion radical and the dianion are associated with cations in THF, while there is no ion association with either the COT anion or dianion with the sodium cation in HMPA.[5] The absence of ion association with Na^+ in HMPA makes the observation of DMMA$^{-}\cdot$ possible in this solvent.

Thermodynamic Stability of DMMA^{2-}. The dianion of DMMA was produced by exhaustive reduction of DMMA with both potassium and sodium metals. The solvent was distilled from the dianion salt under high vacuum leaving the blue green $Na^+{}_2DMMA^{2-}$ and rusty brown $K^+{}_2DMMA^{2-}$ crystalline salts, which are solvent free and can be stored for days at room temperature under high vacuum without noticeable decomposition.

Samples of the crystalline dianion salts were sealed into evacuated thin-walled bulbs. The glass bulbs were broken under 100 mL of water in a modified solution calorimeter as previously described.[6] The products of the reaction between the DMMA dianion and water have been previously determined,[2] and the reaction that takes place in the calorimeter is shown below.



$\Delta H°$ = −53.2 ± 2.0 kcal/mol of solid $K^+{}_2DMMA^{2-}$ salt
$\Delta H°$ = −38.4 ± 1.1 kcal/mol of solid $Na^+{}_2DMMA^{2-}$ salt

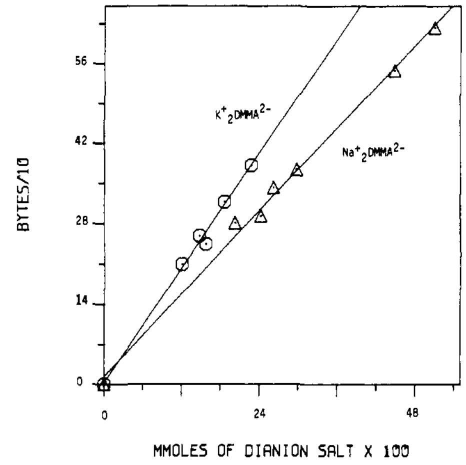


Figure 4. Plots of the change in the temperature of the calorimeter in computer bytes vs. the number of millimoles of DMMA dianion salts in the glass bulbs.

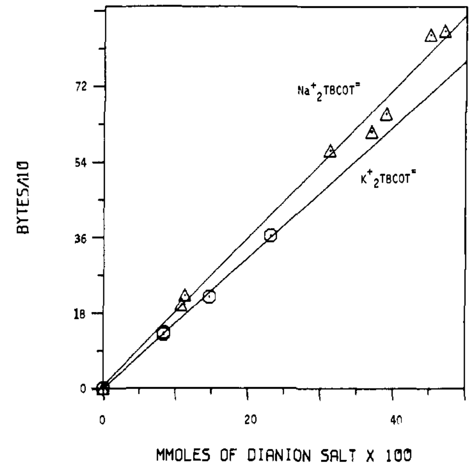
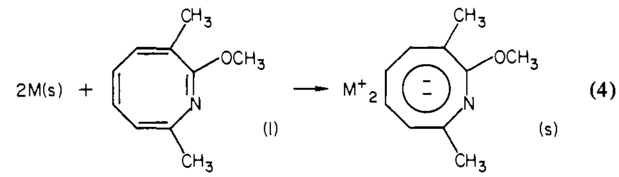


Figure 5. Plots of the change in the temperature of the calorimeter in computer bytes vs. the number of millimoles of TBCOT dianion salts in the glass bulbs.

Plots of the change in the temperature of the calorimeter vs. the millimoles of solid dianion salt in the glass bulbs are linear (Figure 4). Multiplying the slopes of these lines by 0.0319 cal/byte yields the enthalpies of reaction 3 for both the potassium (−53.2 ± 2.0 kcal/mol) and the sodium (−38.4 ± 1.1 kcal/mol) salts. When these numbers are subtracted from twice the heat of reaction of either sodium or potassium with water[7] and added to the heat of hydrogenation of DMMA,[8] the heat of formation of the dianion salts from the metal and neutral DMMA in their standard states are obtained (reaction 4).



$\Delta H°$ = −67 ± 3 kcal/mol of $K^+{}_2DMMA^{2-}$ salt formed
$\Delta H°$ = −76 ± 2 kcal/mol of $Na^+{}_2DMMA^{2-}$ salt formed

It would be best to compare the enthalpies for reaction 4 with similar enthalpies for dimethylmethoxycyclooctatetraene, but this

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[5] Stevenson, G. R.; Ocasio, I. *J. Am. Chem. Soc.* **1976**, *98*, 890.

[6] Stevenson, G. R.; Zigler, S. S.; Reiter, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 6057.

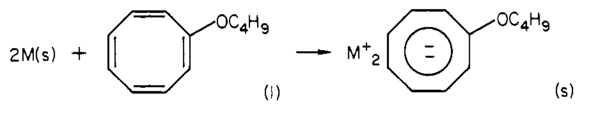
[7] The heats of reaction of sodium and potassium metal with water are −44.1 and −47.0 kcal/mol, respectively, see: Gunn, S. R. *J. Phys. Chem.* **1967**, 71, 1386.

[8] Since neutral DMMA exists in a tub conformation without conjugation, the double bonds do not interact with each other or with the nitrogen. Thus, the heat of hydrogenation must be very similar to that for COT (−26 kcal/mol).

Table II. Thermodynamic Parameters of Disproportionation for Several Eight-Member Ring Systems in HMPA in the Absence of Ion Association

anion radical	$\Delta H^\circ_{\text{disp}}$, kcal/mol	K_{disp} (0 °C)	ref
$COT^{-}\cdot$	+4.6 ± 0.7	7.5×10^2	4a, 3
$TBCOT^{-}\cdot$	+3.2 ± 0.3		4a
$DMMA^{-}\cdot$	+7.0 ± 1.0	1.3×10^5	this work
phenylcyclooctatetraene$^{-}\cdot$	+3.7 ± 0.5		4a

compound is unknown. However, *tert*-butoxycyclooctatetraene (TBCOT) does possess the the same number of methyl groups and has the same empirical formula. Both the dipotassium and disodium dianion salts of TBCOT in the solid state (Figure 5) react exothermically with water to yield the dihydro adducts of TBCOT, and the enthalpies of reaction are −49.8 ± 1.1 and −56.4 ± 2.0 kcal/mol, respectively. When these data are treated in the same manner as described for the DMMA systems, the heats of formation of $K^+{}_2TBCOT^{2-}$ and $Na^+{}_2TBCOT^{2-}$ from the solid metal and liquid hydrocarbon are obtained (reaction 5).

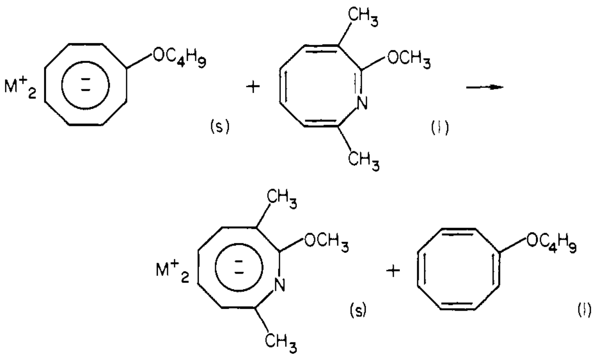


(5)

$\Delta H^\circ = -70 \pm 2$ kcal/mol of $K^+{}_2TBCOT^{2-}$ salt formed

$\Delta H^\circ = -58 \pm 3$ kcal/mol of $Na^+{}_2TBCOT^{2-}$ salt formed

By combining the enthalpies of reactions 4 and 5, we can obtain the heats of electron transfer from $TBCOT^{2-}$ to DMMA (reaction 6). For the potassium system the electron transfer is almost thermally neutral, while that for the sodium system is endothermic by about 18 kcal/mol. The strong cation dependence necessarily means that crystal lattice energies and the specific interactions between the dianions and cations vary from $M^+{}_2TBCOT^{2-}$ to $M^+{}_2DMMA^{2-}$. It is possible that a strong interaction between the oxygen atoms in $TBCOT^{2-}$ and $DMMA^{2-}$ are resulting in an increased stability of these two salts. To see if this is the case, we decided to compare the thermodynamic stability of $TBCOT^{2-}$ to that of COT^{2-}. If the cation has a special interaction with the oxygen in $TBCOT^{2-}$, this dianion (in the solid state) should be as thermodynamically stable as is COT^{2-} despite the fact that the electron-releasing nature of the *tert*-butoxy group should destabilize the TBCOT dianion relative to the COT dianion.

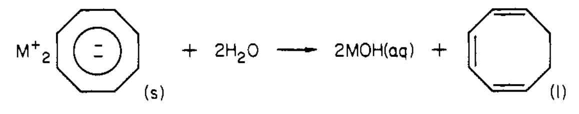


(6)

$\Delta H^\circ = -3 \pm 5$ kcal/mol when M = K

$\Delta H^\circ = +18 \pm 5$ kcal/mol when M = Na

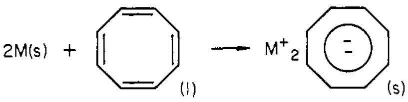
As previously published,[9] the data collected for the reaction of $K^+{}_2COT^{2-}$(s) and $Na^+{}_2COT^{2-}$(s) in the old bomb type calorimeter have inherent error[10] and must be corrected. These calorimetric measurements were repeated using the new computer-interfaced calorimetry equipment (reaction 7). The heats of formation of the COT dianion salts and the enthalpies of electron transfer from $TBCOT^{2-}$ to COT are shown in reactions 8 and 9



(7)

$\Delta H^\circ = -40.5 \pm 1.4$ kcal/mol for M = K

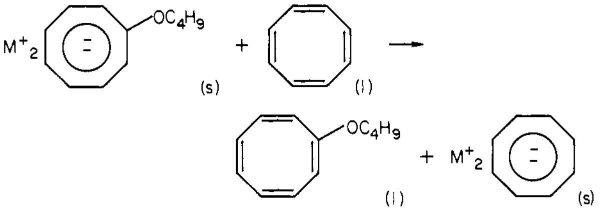
$\Delta H^\circ = -56.1 \pm 0.7$ kcal/mol for M = Na



(8)

$\Delta H^\circ = -79.5 \pm 2.0$ kcal/mol for M = K

$\Delta H^\circ = -57.7 \pm 1.5$ kcal/mol for M = Na



(9)

$\Delta H^\circ = -9.3 \pm 3.0$ kcal/mol for M = K

$\Delta H^\circ = -0.3 \pm 3.0$ kcal/mol for M = Na

Just as we suspected, the thermodynamic stability of $Na^+{}_2TBCOT^{2-}$ is well within experimental error of that for $Na^+{}_2COT^{2-}$ relative to their respective neutral molecules and sodium metal, and the electron-releasing character of the *tert*-butoxy group does not manifest itself in a decreased stability of the TBCOT dianion. Thus, a specific interaction between Na^+ and the TBCOT dianion must enhance the stability of this system. This interaction between the oxygen and the metal cation is not as strong when K^+ serves as the cation.

Disproportionation. The equilibrium constant for the disproportionation of $DMMA^{-}\cdot$ (eq 10) can be obtained from the amplitude of the overmodulated ESR signal (A) as previously described.[4a,11] This is true since the concentration of $DMMA^{-}\cdot$ is proportional to A, and $[DMMA^{-}\cdot] = BA$, where B is a proportionality constant.

$$K_{\text{disp}} = [DMMA^{2-}][DMMA]/[DMMA^{-}\cdot]^2 = [DMMA^{2-}][DMMA]/(BA)^2 \quad (10)$$

Samples were generated by dissolving a small amount of sodium metal in an excess of DMMA in HMPA. This assures that the concentrations of dianion and neutral molecule are large relative to that for the anion radical. Under these conditions, a simple plot of ln A vs. $1/RT$ should be linear and have a slope of $^1/_2\Delta H_{\text{disp}}$. The variable temperature ESR data were sent directly into the computer and were doubly integrated. Plots of the ln of the double integral (ln A) vs. $1/RT$ are linear, and the slopes indicate that the enthalpy of disproportionation (reaction 2) is more endothermic for the DMMA anion radical than it is for the anion radicals of either COT or TBCOT (Table II). However, by comparing the ESR intensities of $COT^{-}\cdot$ and $DMMA^{-}\cdot$ solutions in HMPA it was found that K_{disp} is smaller for $COT^{-}\cdot$ than it is for $DMMA^{-}\cdot$, but $DMMA^{-}\cdot$ can be seen. The disproportionation equilibrium constant is much much greater for the DMMA systems than it is for the COT systems in solvents where ion association is prevalent, as evidenced by the fact that $DMMA^{-}\cdot$ cannot be observed in these solvents. It seems reasonable that $DMMA^{2-}$ is particularly susceptible to ion association, as the cation may become "sandwiched" between the oxygen and nitrogen atoms, as in I. Ion association is known to shift disproportionation equilibria for COT systems to the right.[5] It is possible that there is some ion association between $DMMA^{2-}$ and Na^+ even in

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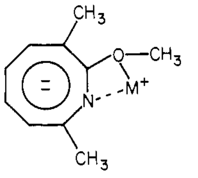
[9] Concepcion, R.; Reiter, R. C.; Stevenson, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 1778.

[10] Stevenson, G. R.; Ocasio, I.; Bonilla, *J. Am. Chem. Soc.* **1976**, *98*, 5469.

[11] Stevenson, G. R.; Valentin, J.; Williams, E.; Caldwell, G.; Alegria, A. E. *J. Am. Chem. Soc.* **1979**, *101*, 515.



I

HMPA. This would explain the larger K_{disp} for DMMA$^{-}\cdot$ than for COT$^{-}\cdot$.

Conclusions

The spin distribution in the DMMA anion radical (free of ion association) is similar to that of a monosubstituted COT anion radical, where the substituent acts as an extension of the π conjugation (i.e., a phenyl group). The dianion of DMMA readily ion pairs with metal cations in solvents other than HMPA, which drives the disproportionation far to the right and accounts for the fact that the DMMA anion radical has not been observed prior to this report. The stabilities of the dianions of DMMA and TBCOT are enhanced by the interaction of the cation with the nitrogen and/or oxygen atoms in the solid state. The crystal lattice energies of these solid dianion salts appear to play a more dominant role in controlling the heats of formation from the neutral molecules and sodium metal than do aromaticity considerations and the effect of the nitrogen upon the aromatic character of the dianion.

Experimental Section

X-band ESR spectra were recorded on a Varian E-4 spectrometer that is interfaced to a 64K MINC II computer system. The temperature was controlled within ±2 °C with a Varian V-4557 variable temperature controller, which was calibrated with an iron–constantan thermocouple.

Solvent-free dianion salts were prepared as previously described,[11] and they were placed into thin-walled evacuated glass bulbs. To ensure that no THF was left in the dianion salts, D_2O was added and the solution submitted to NMR analysis. No THF was found in the D_2O. Other glass bulbs were broken under 100 mL of water in a modified cell of a Parr solution calorimeter.[6] The data collection, analysis of the calorimeter contents, and calorimeter apparatus were exactly as previously described.[6]

The anion radicals were generated via alkali-metal reduction in freshly distilled HMPA under high vacuum as described earlier.[5] After complete dissolution of the metal mirror, an ESR sample was sealed off from the apparatus. Two samples (one from a COT reaction and one from a DMMA reaction) were compared for spin concentration. The ESR data were collected with the maximum modulation amplitude as described by Goldberg[12] to minimize the error in obtaining the relative anion radical concentration from the double integral of the ESR signal. The ESR data were sent directly into the computer for double integration, and the numerical value obtained from the computer was used for A. Since the DMMA anion radical solutions were slowly decomposing, a correction had to be applied to A to account for this loss of anion radical. The half-life of the anion radical in HMPA is 23 min at 0 °C. This short half-life, coupled with the fact that 1-h scan times are necessary to record a well-resolved spectrum containing over 3000 ESR lines, makes it impossible to record a full well-resolved spectrum.

The DMMA was synthesized by the method of Paquette and coworkers.[13] The purity of the final fractionally distilled product was found to be greater than 98% via VPC and NMR analysis.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We are grateful to the National Science Foundation for the purchase of the computer system.

Registry No. DMMA anion radial, 69134-59-4; DMMA dianion, 86709-88-8.

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(12) Goldberg, I. B. *J. Magn. Reson.* **1978**, *32*, 233.

(13) Paquette, L. A.; Kakihana, T.; Hansen, J. F.; Phillips, J. C. *J. Am. Chem. Soc.*, **1971**, *93*, 152.

Azide–Water Competition in Solvolysis Reactions. A Revisit of the Reactivity–Selectivity Relationship[1,2]

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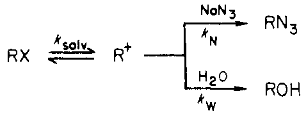
Abstract: The suggested linearity between the logarithms of the solvolysis rate constant (k_{solv}) of RX and the selectivity (k_N/k_W) in capture of the intermediate cation R^+ by water (W) and N_3 (N) in 80% acetone was reinvestigated by using extended literature data. The assumptions involved in deriving the k_N/k_W values, such as first-order dependency on the nucleophile concentration in its reaction with R^+ and the temperature, solvent, nucleofuge, and other extrapolations required for obtaining the parameters, were discussed. The extended log k_{solv} vs. log (k_N/k_W) plot, which is based on the revised set of values, is not linear and composed of five regions: (a) Ritchie's constant selectivity region; (b) a border region where the selectivity increases more than the reactivity and which may be an artifact; (c) an apparent reactivity–selectivity (RS) region with an appreciable scatter of the points, where log (k_N/k_W) decreases on decreasing k_{solv} (the reaction with N_3^- in this region is diffusion controlled and the plot reflects a log k_{solv} vs. log k_W relationship); (d) a low k_{solv} and nearly constant low selectivity region where hindrance to nucleophilic approach to the intermediate may sterically enforce a preassociation ion pair mechanism on the reaction; (e) an inverted RS region, where the selectivity increases on decreasing k_{solv} and where the reaction with N_3^- is mostly S_N2. The various mechanistic regions were discussed in relationship to the existence and the lifetimes of the cationoid intermediates.

According to the reactivity–selectivity principle (RSP), in a series of similar reactions the less reactive reagent shows the highest selectivity. The principle is used extensively in the study of organic reactions mechanisms and was reviewed recently several times.[3,4b,c] However, many examples contradicting the RSP

Scheme I



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(1) Presented in part at the Euchem Conference on Correlation Analysis in Organic Chemistry (CAOC II), July 18–23, Hull, England, Abstract 0/19.

(2) Preliminary communications: (a) Ta-Shma, R.; Rappoport, Z. *Tetrahedron Lett.* **1982**, *23*, 781. (b) Rappoport, Z.; Ta-Shma, R. *J. Org. Chem.* **1982**, *47*, 5207.