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The Role of Solvation and Choice of Anion in Controlling the Thermodynamic Stability of the Cyclooctatetraene and Anthracene Dianions

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Abstract: The enthalpies of reaction for the alkali metal salts of the cyclooctatetraene dianion and sodium salt of the anthracene dianion with water were measured calorimetrically. These enthalpies were used in a thermochemical cycle with the heats of solution of the dianions in tetrahydrofuran (THF) and in hexamethylphosphoramide (HMPA) to evaluate the relative importance of solvation upon the thermodynamic stability of these dianions. It was found that the thermodynamic stability of the cyclooctatetraene dianion neutral ion aggregate (COT^{2-}, $2M^+$) in THF and the solvated ions ($COT^{2-} + 2M^+$) in HMPA relative to the gas-phase ions ($COT^{2-}{}_g + 2M^+{}_g$) follow the order Li > Na > K > Rb > Cs. This is attributed to the ion aggregate and cation enthalpies of solvation, which may vary as much as 110 kcal/mol with the choice of cation. In HMPA the single ion solvation enthalpies have been evaluated for the series of cations. The disodium salt of anthracene reacts more than twice as exothermically as does the COT salt.

In solution hydrocarbon anion radicals may disproportionate to form the dianion and neutral molecule as given by[1]

$$2A^{-}\cdot \rightleftarrows A + A^{2-} \tag{1}$$

This disproportionation is extremely facile for some anion radicals that undergo geometry changes upon reduction, like cyclooctatetraene (COT) and tetraphenylethylene.[2,3] In the gas phase, however, doubly charged negative ions from hydrocarbon substrates are unknown, and only one uncontested report of a gas-phase organic dianion has appeared.[4] The very low thermodynamic stability of A^{2-} in the gas phase is due to the very strong electron–electron repulsion, which amounts to about 90 kcal/mol in the COT dianion.[5] Anion solvation and ion association can readily overcome this repulsion term and actually result in an exothermic disproportionation of $COT^{-}\cdot$ in tetrahydrofuran (THF).[6]

The fact that two electrons can be readily added to [8]-annulene either chemically or electrochemically to form the 10π-electron dianion is well documented.[7-9] It is more difficult to generate dianions from aromatic hydrocarbons. For example, the dianion of [6]annulene, which would be antiaromatic in the Hückel sense with $4n$ π electrons, is still unknown even in solution. However, the dianions of fused benzoid aromatics can be generated.[10] Qualitatively, it is thought that these dianions formed from aromatic neutral compounds are less stable than those from $4n$ π-electron annulenes, but no actual heats of formation are known. Here we wish to report an experimental determination of the heat of formation of the disodium salt of anthracene (Na_2AN) and compare it to that for the disodium salt of [8]annulene (Na_2COT). This will yield information as to the thermodynamic stability of these highly reactive dianions and insight into the thermodynamic difference of adding two extra electrons to a formally aromatic system (anthracene) and a nonaromatic system (COT). It must be remembered, however, that the existence of both of these dianion salts is dependent upon solvation and ion association energies in solution and upon crystal lattice energies in the solid form. Indeed, solvation and ion association appear to be the controlling factors upon the thermodynamic stability and chemistry of organic anions and dianions in solution.[11]

Results and Discussion

Solvation of the COT Dianion and Anion Radical. Evacuated glass bulbs containing the Li, Na, K, Rb, and Cs salts of the COT dianion (M_2COT_{solid}) were crushed under 100 mL of water in a calorimeter under conditions similar to those described previously.[12,13] The heat of reaction ($M_2COT_{solid} + 2H_2O_{liq} \rightarrow 2MOH_{aq} +$ cyclooctatriene$_{liq}$) was obtained directly from the slope of a plot of the millimoles of salt vs. the change in temperature of the calorimeter[14] (Figures 1 and 2).[15] The enthalpy obtained from the calorimetry experiments can be combined with the heat of hydrogenation of COT[16] and the heat of reaction of the metal with water[17] to yield the heat of reaction of the metal (M^0) with COT to form the solid salt (M_2COT) as shown in Table I. The heat of hydrogenation of COT used in this calculation was actually measured in acetic acid, but the heat of solution of hydrocarbons in polar and nonpolar solvents is very small, and the difference in the heats of solution of H_2COT and COT is necessarily very small. Thus, −25.6 kcal/mol is a very good estimation of the heat of hydrogenation of liquid COT. NMR analysis of the reaction products of all five dry salts with D_2O has shown that no THF is incorporated into the crystal structure of the M_2COT.

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Table I. Enthalpies of Reaction

reaction	$\Delta H°$, kcal/mol, for M = Li	Na	K	Rb	Cs
$H_2COT_{liq} + 2MOH_{aq} \rightarrow M_2COT_{solid} + 2H_2O_{liq}$	37.3 ± 1.7[a]	33.3 ± 0.8	28.8 ± 0.7	25.1 ± 1.9	30.0 ± 2.5
$COT_{liq} + H_{2_g} \rightarrow H_2COT_{liq}$	−25.6	−25.6	−25.6	−25.6	−25.6
$2M_{solid} + 2H_2O_{liq} \rightarrow 2MOH_{aq} + H_{2_g}$	−106.4	−88.2	−94.0	−93.3	−96.7
$COT_{liq} + 2M_{solid} \rightarrow M_2COT_{solid}$	−94.7[b]	−80.5	−90.8	−93.8	−92.3

[a] These enthalpies in the top row represent the negative of the enthalpies measured in the calorimeter. [b] By propagating the errors, the errors in the numbers in the final row are about ±3 kcal/mol.

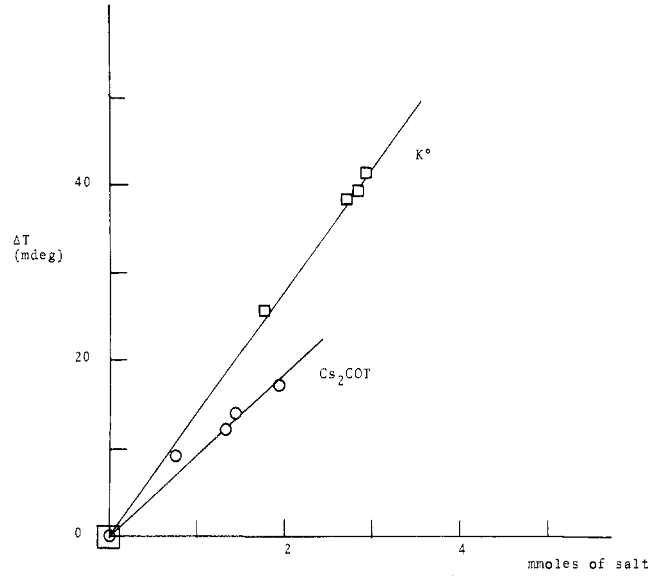


Figure 1. Plots of the change in temperature of the calorimeter vs. the millimoles of solid potassium metal (upper line) and solid Cs_2COT (lower line) in the glass bulbs. The slopes of the lines are proportional to the enthalpies of reaction of the salts with water. The enthalpies are −47.2 and −30.0 kcal/mol, respectively, for K^0 and Cs_2COT.

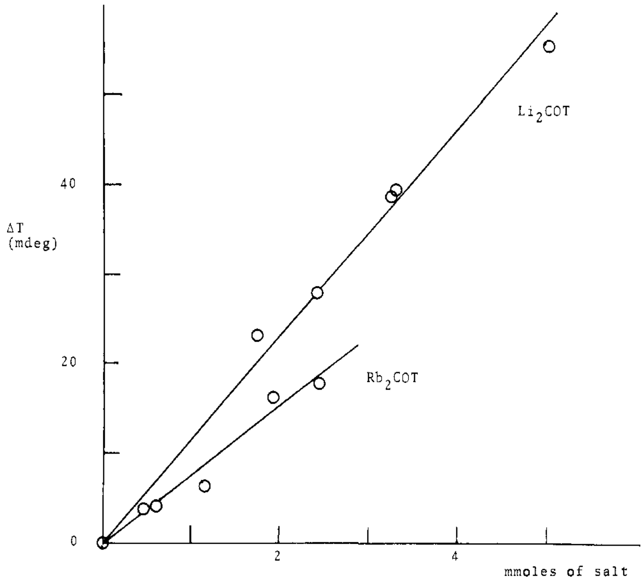


Figure 2. Plots of the change in temperature observed in the calorimeter vs. the millimoles of COT dianion salt in the glass bulbs. The enthalpies of reaction between the salts and water are −37.3 and −25.1 kcal/mol for Li_2COT and Rb_2COT, respectively.

Table II. Solubilities of M_2COT at 25 °C

salt	solubility in THF	solubility in HMPA
Li_2COT	0.96 ± 0.04	0.27 ± 0.01
Na_2COT	0.012 ± 0.002	0.36 ± 0.01
K_2COT	0.56 ± 0.01	0.68 ± 0.01
Rb_2COT	0.64 ± 0.01	0.062 ± 0.007
Cs_2COT	0.096 ± 0.02	0.034 ± 0.006

In THF the alkali metal salts of the COT dianion exist as neutral ion aggregates (both metal ions associated with the dianion) most probably with the lithium cations located above and below the plane of the eight-member ring in a sandwich arrangement;[18] thus $\Delta G°(\text{soln}) = -RT \ln [M^+,COT^{2-},M^+]$. However, in HMPA the ion aggregates are, for the most part, dissociated. The solubilities in both of these solvents are given in Table II.

These solubilities were found to vary only slightly with the temperature, indicating that the enthalpies of solution are small. The solubilities were determined at both 25 °C and 0 °C and the enthalpy of solution was calculated in the usual manner.[19] Both the solubilities and the heats of solution vary considerably for the different alkali metal salts (Tables II and III)

Since all of the dianion salts of COT exist as neutral ion aggregates in THF, the heats of reaction of COT with gas-phase electrons and cations can now be calculated (Table III).

By simply summing the errors for each of the enthalpies given in Table III, the error in the final enthalpies (no. 6 and 8) is estimated to be 5 kcal/mol. From the final enthalpy for the THF system (no. 6) the differences in the heats of solvation of the separated ions in the gas phase for the different ion aggregates can be found. Relative to the separated ions in the gas phase, the $COT^{2-},2Cs^+$ ion aggregate is less stable than the $COT^{2-},2Na^+$ ion aggregate by 374.3 − 318.6 or about 56 kcal/mol and less stable than the $COT^{2-},2Li^+$ ion aggregate by about 110 kcal/mol. *Just the difference between the heats of solvation of the cesium and lithium systems is greater than the entire electron–electron repulsion energy.*

Cox and co-workers[18] found that contact ion pairs are formed with potassium and sodium and that a small fraction of solvent-separated ion pairs is formed with Li^+ in THF. Thus, the heat of solution of the looser Li^+ neutral ion aggregate in THF is much more exothermic than that of the other ion aggregates. Further, this heat of solution is sufficiently more exothermic to more than overcome the weaker ion association in the Li^+ system and render it the most stable. The large thermodynamic stability of the lithium salt relative to the other salts is an indication that the lithium cation is not markedly desolvated upon association with the dianion. This is the same conclusion drawn by Szwarc and co-workers via their disproportionation studies.[23]

In HMPA, unlike in THF, the COT dianion exists mainly as the free solvated dianion, and when Na^+ serves as the cation, no ion association could be detected.[24] However, for the larger cations there exists some ion association between the dianion and one cation. The enthalpy of this ion association is very

Table III. Enthalpies of Reaction

no.	reaction	ΔH°, kcal/mol, for M = Li	Na	K	Rb	Cs	ref
1	$2M_{solid} + COT_{liq} \rightarrow M_2COT_{solid}$	−94.7	−80.5	−90.8	−93.8	−92.3	this work, 13
2	$M_2COT_{solid} \rightarrow COT^{2-},2M^+{}_{THF}$	+2.5	+5.1	+1.1	+0.6	+0.5	this work, 19
3	$2M_g \rightarrow 2M_{solid}$	−77.2	−51.8	−42.8	−41.0	−37.6	20
4	$COT_g \rightarrow COT_{liq}$	−10.3	−10.3	−10.3	−10.3	−10.3	21
5	$2M^+{}_g + 2e^- \rightarrow 2M_g$	−248.6	−236.8	−200.0	−192.3	−178.9	22
6	$COT_g + 2e^-{}_g + 2M^+{}_g \rightarrow COT^{2-},2M^+{}_{THF}$	−428.3	−374.3	−342.8	−336.8	−318.6	
7	$M_2COT_{solid} \rightarrow COT^{2-}{}_{HMPA} + 2M^+{}_{HMPA}$	−2.7	+12.0	+5.1	+7.5	+3.8	this work, 19
8	$COT_g + 2e^-{}_g + 2M^+{}_g \rightarrow COT^{2-}{}_{HMPA} + 2M^+{}_{HMPA}$	−433.5	−367.4	−333.8	−330.0	−315.3	

Table IV. Enthalpies of Reaction and Single Ion Solvation for the Alkali Metal Cations in HMPA

reaction	ΔH°, for M = Li	Na	K	Rb	Cs
$COT_g + 2e^- + 2M^+{}_g \rightarrow COT^{2-}{}_{HMPA} + 2M^+{}_{HMPA}$	−433.5	−367.4	−338.8	−330.0	−315.3
$COT^{2-}{}_{HMPA} \rightarrow COT_g + 2e^-{}_g$	+152	+152	+152	+152	+152
$M^+{}_g \rightarrow M^+{}_{HMPA}$	−141	−108	−93	−89	−82

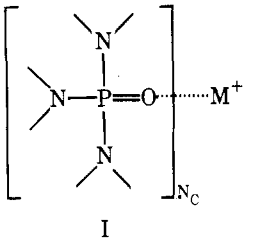
small[25] meaning that the enthalpy difference between $COT^{2-}{}_{HMPA} + 2M^+{}_{HMPA}$ and $COT^{2-},M^+{}_{HMPA} + M^+{}_{HMPA}$ is very small. We can now calculate the enthalpies of formation of the HMPA solvated ions from the gas-phase electrons, COT_g, and $M^+{}_g$, no. 8, Table III. This calculation is identical with that for the THF systems except that the heat of solution of the solid dianion salt in HMPA replaces the heat of solution of the salt in THF. As in THF the heats of solvation of the gas-phase ions grow more exothermic as the size of the cation decreases. Also for the HMPA systems, the difference between the heats of solvation of the cesium and lithium salts (118 kcal/mol) is larger than the electron-electron repulsion energy in the dianion.

Using an extra thermodynamic assumption, the TATB assumption, Parker and co-workers[26] have estimated the single ion heat of solvation of the potassium cation. This value, −93.6 kcal/mol, multiplied by two and added to the enthalpy for $COT_g + 2e^-{}_g + 2K^+{}_g \rightarrow COT^{2-}{}_{HMPA} + 2K^+{}_{HMPA}$ yields the heat of reaction of two gas-phase electrons with COT_g to form the solvated COT dianion:[27]

$$COT_g + 2e^-{}_g \rightarrow COT^{2-}{}_{HMPA} \qquad \Delta H^\circ = -152\ \text{kcal/mol} \tag{2}$$

The enthalpy for the reaction depicted in eq 2 can now be utilized to obtain the single ion heats of solvation for the remaining cations as shown in Table IV.

From Table IV it is clear that the single ion solvation energy becomes more exothermic as the size of the cation decreases. Even for the smaller cations it is very unlikely that a second solvation layer around the cation exists in HMPA, because the very large HMPA molecules prevent the potential second layer from coming close enough to interact electrostatically with the charged center.[27] From the coordination numbers (N_c) the actual bond energies for the solvent-cation bonds, structure I, can be estimated. The coordination numbers for Cs^+, K^+, and Li^+ in HMPA have been found to be 5, 4, and 3, respectively.

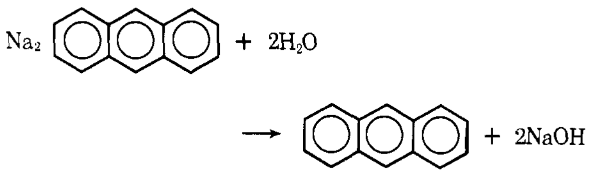


I

These bond energies for the HMPA-Cs^+, HMPA-K^+, and HMPA-Na^+ bonds are $-82/5 = -16$, −23, and −36 kcal/mol, respectively. Further, the three "tight" bonds of 37 kcal/mol result in a more exothermic heat of solvation than do the four or five "looser" solvent-cation bonds.

Heat of Formation of Na_2AN. The anthracene dianion was chosen for comparison to the COT dianion, because it is the simplest dianion from an aromatic hydrocarbon that is stable enough for simple isolation, and it has an electron-electron repulsion energy that is close to that reported for the COT dianion.[28]

In our hands, solid Na_2AN reacted with water to give 9,10-dihydroanthracene exclusively as an organic product (eq 3). This reaction has the same stoichiometry as that observed for the protonation of the dianion in solution.[29]



(3)

Comparing a plot of the change in temperature of the calorimeter vs. the quantity of salt in the evacuated glass bulbs to a similar plot for the Na_2COT salt, *it is found that the anthracene salt reacts with water more than twice as exothermically as does the COT salt* (Figure 3). The enthalpy of the reaction depicted in eq 3 is −79.1 ± 0.9 kcal/mol.

From the heat of hydrogenation of anthracene (−17.0 kcal/mol)[30] the following thermochemical cycle can be constructed to yield the enthalpy of reaction of Na^0 with anthracene and the heat of formation of Na_2AN.

	ΔH°, kcal/mol
$H_2AN_{solid} + 2NaOH_{aq} \rightarrow Na_2AN_{solid} + 2H_2O_{liq}$	+79.1
$AN_{solid} + H_{2g} \rightarrow H_2AN_{solid}$	−17.0
$2Na^0{}_{solid} + 2H_2O_{liq} \rightarrow 2NaOH_{aq} + H_{2g}$	−88.2
$2Na^0{}_{solid} + AN_{solid} \rightarrow Na_2AN_{solid}$	−26.1

The heat of formation of anthracene (AN) is +25.5 kcal/

Table V. Enthalpies of Reaction

	$\Delta H°$, kcal/mol, for π = AN	$\Delta H°$, kcal/mol, for π = COT	ref
$H_2\pi_{solid} + 2NaOH_{aq} \rightarrow Na_2\pi_{solid} + 2H_2O_{liq}$	+79.1	+33.3	this work
$\pi_{solid} + H_{2_g} \rightarrow H_2\pi_{solid,liq}$	−17.0	−25.6[a]	16, 30
$2Na^0_{solid} + 2H_2O_{liq} \rightarrow 2NaOH_{aq} + H_{2_g}$	−88.2	−88.2	17
$2Na^0_g \rightarrow 2Na^0_{solid}$	−51.8	−51.8	20
$\pi_g \rightarrow \pi_{solid,liq}$	−23.4	−10.3	21, 32
$2Na^+_g + 2e^-_g \rightarrow 2Na^0_g$	−236.8	−236.8	22
$\pi_g + 2e^-_g + 2Na^+_g \rightarrow Na_2\pi_{solid}$	−338.1	−379.4	

[a] Solid is for π = AN, and liq is for π = COT.

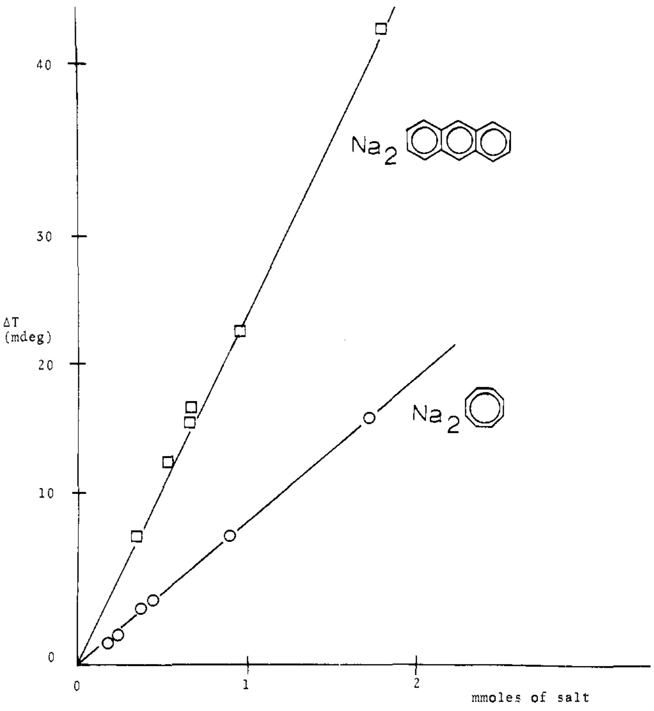


Figure 3. Plots of the change in temperature observed in the calorimeter vs. millimoles of dianion salt in the glass bulbs. The upper line is for the reaction of Na_2AN with water, and the lower line is for the reaction of Na_2COT with water. The enthalpies of reaction are −79.1 and −33.3 kcal/mol for Na_2AN and Na_2COT, respectively. The slopes of the lines are proportional to the enthalpies of reaction.

mol.[31] Thus, the heat of formation of Na_2AN is about −0.6 kcal/mol.

Using the heats of sublimation of sodium[20] and of anthracene,[32] the heat of reaction between the metal and anthracene in the gas phase is found to be −101.3 kcal/mol:

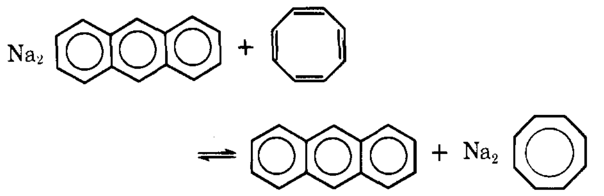
$$2Na_g + AN_g \rightarrow Na_2AN_{solid} \qquad \Delta H° = -101.3 \text{ kcal/mol} \qquad (4)$$

This is 41 kcal/mol less exothermic than the analogous reaction for the formation of Na_2COT;[19a]

$$2Na_g + COT_g \rightarrow Na_2\,COT_{solid} \qquad \Delta H° = -142.6 \text{ kcal/mol} \qquad (5)$$

Conclusions

The factors that control the thermodynamic stability of organic dianions can be divided into two groups: intermolecular effects and intramolecular effects. In the solid salts the only intermolecular effect is the crystal lattice energy. These effects account for the fact that it is more difficult by more than 40 kcal/mol to add two extra electrons to anthracene than it is to cyclooctatetraene (eq 6).



(6)

Although many factors must be considered, we believe that the fact that COT goes from a $4n$ to a $4n + 2$ π-electron system and anthracene diverges from aromatic character upon the addition of the two extra electrons plays a role in the exothermicity of the reaction depicted in eq 6.

Relative to the separated ions in the gas phase, the COT^{2-},$2Cs^+$, COT^{2-},$2Rb^+$, COT^{2-},$2K^+$, and COT^{2-},$2Na^+$ in THF are less stable than COT^{2-},$2Li^+$ by 110, 92, 86, and 54 kcal/mol, respectively. These differences are due to solvation energies. Even larger differences are found in HMPA where they can be shown to be due to cation solvation only. The magnitudes of the cation solvation energies are such that it is clear that solvation is much more important in controlling the thermodynamic stability of these dianion salts than are the intramolecular effects. In both THF and HMPA the solvation energies follow the order Li > Na > K > Rb > Cs in exothermicity for the alkali metal salts of COT^{2-}.

The calculation of the heat of reaction of gas-phase electrons and the sodium cation with AN_g and a comparison with the analogous reaction for COT are given in Table V.

Finally, it was pointed out by a reviewer that the solid dianion that remains in equilibrium with the saturated dianion solution in the solubility experiments may be different from the solid COT dianion salts used in the calorimetry experiments. That is, the solid in equilibrium with dianion solution may be complexed with solvent molecules. There are two experimental facts that indicate that this is not the case. (1) The THF is completely removed from the solid salts under vacuum without heating. This indicates that the THF is not chemically bound to the salts. Thus, only a small correction, if any, would have to be made for the presence of $M_2COT{\cdot}n$THF. (2) HMPA solutions of $Na^+ + AN^{-\cdot}$ and $K^+ + AN^{-\cdot}$ were reacted with water in the calorimeter.[35] After accounting for the heat due to the interaction between the HMPA and the water, the same difference in the single ion heats of solution for K^+ and Na^+ in HMPA was found. It would be even better to fire the alkali metal solutions themselves in HMPA, where only $M^+ + e^-$ are present. However, stability problems with these solutions[36] make the proposed experiments impractical.

Much of the data presented here we cannot adequately explain, such as why the sodium salt of COT behaves differently from the other salts and why this salt is so insoluble in THF.

Experimental Section

The M_2COT and Na_2AN salts were prepared by exhaustive reduction on a freshly distilled alkali metal mirror in THF. The final disappearance of an ESR signal for the anion radical indicated complete formation of the dianion. NMR analysis of the reaction products of the dianion and water supports complete formation of the dianions. After dianion formation the THF solutions were passed through a frit and separated from excess alkali metal. The THF was then stripped off under high vacuum. The solid salts were kept under high vacuum for several hours to ensure complete removal of the THF, after which they were transferred into glass bulbs and sealed off from the apparatus. This procedure has been described previously.[13]

Samples of all salts prepared in this manner were added to water in a vacuum system fitted with a gas buret and Toepel pump so that any liberated hydrogen gas could be measured. For the systems studied here no evolution of hydrogen was observed. Thus, the dianion salts reacted with water to yield the dihydrohydrocarbon. Addition of H_2O to Na_2AN yields 100% 9,10-dihydroanthracene and is a convenient method of preparing this compound.

To ensure that no THF was left incorporated into the crystal lattice of the dry salts, D_2O was added and the mixture submitted to NMR analysis. No THF was observed in the D_2O.

The sealed, evacuated glass bulbs containing the dianion salts were placed into the calorimeter. The bulbs were broken with a spring-loaded mechanism under 100 mL of H_2O and the heat liberated from the reaction was measured. The calorimeter and its calibration have been described previously.[13]

The solubility studies were carried out by generating a saturated solution of the COT dianion salt in THF. The saturated solution was left standing in contact with the solid crystals of salt for 24 h at 25 °C and at 0 °C to ensure equilibrium. The solution was then passed through a glass frit into glass bulbs, which were broken under water. The quantity of COT dianion in the THF was determined by titration of the reaction mixture with HCl. The same procedure was carried out in HMPA except that the dianions were first formed in THF, and the HMPA was added after the THF had been distilled off. The rubidium and cesium salts were found to be only slightly soluble in HMPA. A detailed description of the solubility measurements has already appeared.[19] The heats of solution of the salts were calculated from the two different solubilities at 25 and 0 °C. In THF the dissolution process was assumed to be given by eq 7 and in HMPA by eq 8.

$$M_2COT_{solid} \rightarrow M^+,COT^{2-},M^+{}_{THF} \tag{7}$$

$$M_2COT_{solid} \rightarrow 2M^+{}_{HMPA} + COT^{2-}{}_{HMPA} \tag{8}$$

These enthalpies of solution were carried out several times for each system, and the errors are close to 1 kcal/mol in each case. This error seems large, since the enthalpies (rows 2 and 7, Table III) are of the same magnitude. However, the 1 kcal/mol error is quite small when incorporated into the enthalpy of reaction between COT, gas-phase electrons, and gas-phase alkali metal cations to form the solvated salts. It is this latter enthalpy that is of interest.

Samples of the anthracene dianion were reacted with D_2O, and the NMR analysis of the products showed that 9,10-dideuterioanthracene is the only product. The NMR integrations are only accurate to about 4%; thus some dianion may have been protonated by the THF. This would result in only a small error.

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(14) The actual organic product of the reaction is H_2COT_{liq}, as it is insoluble in water. H_2COT can be seen floating on the water after the reaction.
(15) This enthalpy was calculated from the ratio of the slopes taken from this reaction and that between potassium metal and water. The error in the enthalpy represents a propagation of the standard deviations of the slopes of the lines.
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