ments, see: R. Daudel and C. Sandorfy, "Semi-empirical Wave-Mechanical Calculations on Polyatomic Molecules", Yale University Press, New Haven, Conn., 1971, and references therein. For a review of ab initio calculations, see: H. F. Schaefer III, "The Electronic Structure of Atoms and Molecules", Addison-Wesley, Reading, Mass., 1972.
(3) (a) P. Pulay and W. Meyer, *J. Mol. Spectrosc.*, **40**, 59 (1971); (b) G. Jalsovszky and P. Pulay, *J. Mol. Struct.*, **26**, 277 (1975).
(4) D. F. Eggers, Jr., *J. Chem. Phys.*, **23**, 2211 (1955).
(5) T. P. Lewis and I. W. Levin, *Theor. Chim. Acta*, **19**, 55 (1970).
(6) B. Galabov and W. J. Orville-Thomas, *Trans. Faraday Soc.*, **68**, 1778 (1972).
(7) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, N.Y., 1955, pp 162–166.
(8) R. C. Golike, I. M. Mills, W. B. Person, and B. Crawford, Jr., *J. Chem. Phys.*, **25**, 1266 (1956).
(9) W. B. Person and D. Steele, "Molecular Spectroscopy", Vol. 2, The Chemical Society, Burlington House, London, 1974, pp 357–438.
(10) B. Crawford, Jr., *J. Chem. Phys.*, **20**, 977 (1952).
(11) W. M. Fletcher and W. T. Thompson, *J. Mol. Spectrosc.*, **25**, 240 (1968).
(12) Reference 7, p 58.
(13) K. Machida, *J. Chem. Phys.*, **44**, 4186 (1966).
(14) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(15) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
(16) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind.
(17) K. Kuchitsu, *J. Chem. Phys.*, **44**, 906 (1966).
(18) J. L. Duncan, D. C. McKean, and P. D. Mallinson, *J. Mol. Spectrosc.*, **45**, 221 (1973).
(19) R. H. Schwendenman, *J. Chem. Phys.*, **44**, 2115 (1966).
(20) W. Meyer and P. Pulay, *J. Chem. Phys.*, **56**, 2109 (1972).

Heats of Formation of Disodium and Dipotassium Cyclooctatetraenide

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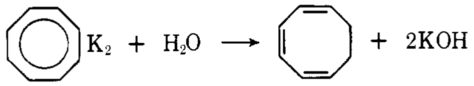
Abstract: Since the solid salts and solutions of the cyclooctatetraene (COT) dianion are known to be more stable and easier to form than those of other hydrocarbons, a determination of the thermodynamic heat of formation of M_2COT (where M is either sodium or potassium) has been carried out. This was done by measuring the enthalpy of the reaction between the dipotassium and disodium salts of COT with water to form cyclooctatriene and KOH_{aq} using calorimetric methods. A thermochemical series was utilized to obtain the heats of formation of these aromatic salts. It was found that the heat of reaction between COT and K^0 is about as exothermic as that between K^0 and water. Both salts (K_2COT and Na_2COT) were found to be more thermodynamically stable relative to the elements in their standard states than is benzene. This stability is attributed in part to the aromatic character of the ten π-electron dianions, but the majority of it is due to the large negative crystal lattice energy. The thermodynamic parameters controlling the stability of the COT dianion and anion radical are discussed for both the solution and solid state.

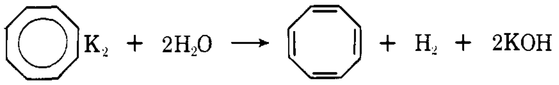
Probably the two most important quantities inherent in any compound are its energy and its structure. The entire concept of aromaticity simply comes from the fact that certain cyclic π-electron systems are of lower energy than would be expected without considering this concept (for example, the heat of formation of benzene is greater than that expected for the hypothetical cyclohexatriene). In the Hückel sense monocyclic π-electron systems with $(4n + 2)$ π electrons are aromatic. However, for the cases of [8]annulene (cyclooctatetraene),[1] [12]annulene,[2] and [16]annulene[3] the neutral molecules will react with alkali metals to form the corresponding aromatic dianions, each containing $(4n + 2)$ π electrons. To date there are no known heats of formation for any of these aromatic salts. Here we wish to report an experimental determination of the heat of formation of the aromatic dipotassium and disodium salts of cyclooctatetraene.

The most common method of obtaining the heat of formation of any compound involves the measurement of the heat of combustion.[4] This method requires very high precision in order to give useful results, and this high precision can only be obtained under very special conditions for organometallic compounds.[5] It would be much more feasible to measure a heat of reaction involving the alkali metal salts of the cyclooctatetraene.

Thielen and Anderson have observed that the addition of water to either the dianion or anion radical of cyclooctatetraene (COT) results in the formation of cyclooctatriene (H_2COT), eq. 1.[6] This reaction would be ideal for the proposed study, since the heat of hydrogenation of neutral COT is known.[7] However, it would first be necessary to eliminate the formation of hydrogen gas as a possible competing reaction (eq 2).



(1)



(2)

Solid crystalline alkali metal salts of COT can be obtained by crystallization from a saturated tetrahydrofuran (THF) solution.[8] In a similar manner yellow crystals of potassium 1,3,5,7-tetramethylcyclooctatetraenide were crystallized from diglyme for x-ray analysis.[9] In that study it was found that the crystal lattice had incorporated two molecules of the solvent (diglyme) for each molecule of tetramethylcyclooctatetraene. Since it is our intention to crystallize the dianion salts from THF, it is necessary that the number of THF molecules incorporated into the crystal lattice be determined prior to the thermodynamic study.

Results and Discussion

NMR analysis of the solution resulting from the addition of 1 ml of D_2O to 2 mmol of solid sodium or potassium salt did not show the presence of THF, indicating that the crystal lattices of neither Na_2COT nor K_2COT incorporate THF.

Allowing the noncondensable gases from the reaction of water with the solid salts of K_2COT and Na_2COT into the vacuum line connected with a Toepler Pump fitted with a gas

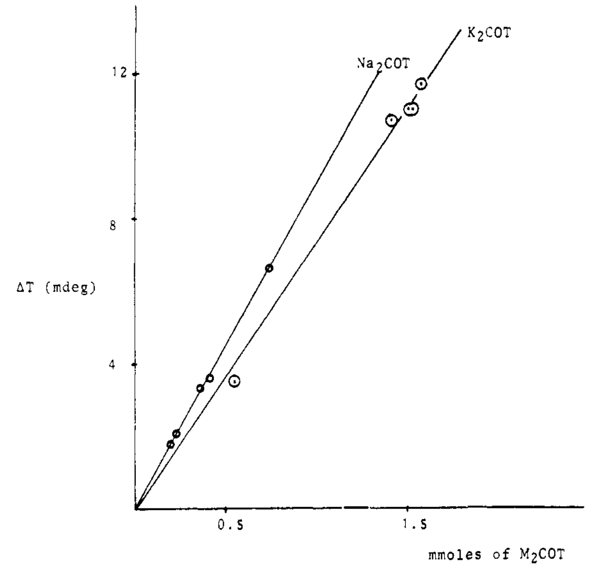


Figure 1. A plot of change in temperature observed in the calorimeter vs. the moles of M_2COT in the evacuated bulb. The slope of this line is 7.47 deg/mol for the potassium system and 8.64 for the sodium system.

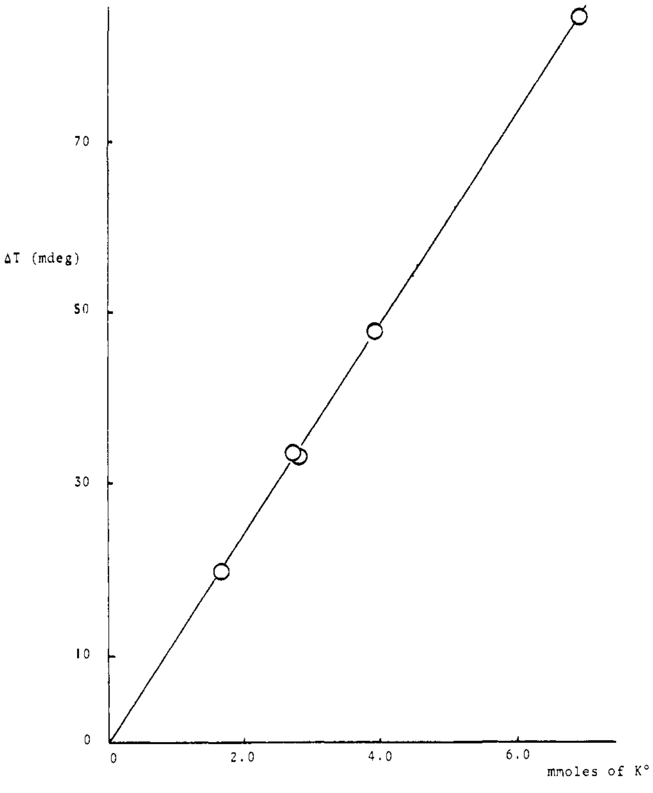


Figure 2. A plot of the change in temperature observed in the calorimeter vs. the moles of potassium metal in the evacuated bulb. The slope of the line is 12.25 deg/mol.

buret resulted in an immeasurable amount of gas pumped into a 1 ml glass bulb. From 0.5 mmol of M_2COT, 0.5 mmol of hydrogen gas would be expected if only reaction 2 were occurring. This amount of H_2 would result in a pressure of about 11 atm in a 1 ml bulb. Since our system could detect a pressure of 0.5 mm, the reaction pathway is described by eq 1 for more than 99.99% of the M_2COT molecules.

The enthalpy of this reaction was measured by breaking glass bulbs containing the dianion salt under 100 ml of water in a modified bomb calorimeter (see Experimental Section) and measuring the heat liberated from the resulting reaction.

Table I. Enthalpies of Reaction with Water

Substance	$\Delta H°$, kcal/mol	$\Delta H°$(lit.), kcal/mol	Ref
K^0	Calibration	-47.2 ± 0.8	10
Na^0	-44.6	-44.3 ± 0.07	10
Cs^0	-45.1	-45.9	11
K_2COT	-28.8 ± 0.7		This work
Na_2COT	-33.3 ± 0.8		This work

A simple plot of ΔT vs. the quantity of salt in the evacuated bulb was found to be linear and have an intercept of (0, 0), Figure 1.

The calorimeter was calibrated by carrying out the same experiment but with bulbs containing distilled potassium metal, Figure 2. Since the quantity of water used to react with either the salt or potassium metal in the evacuated bulb was very large in comparison with the quantity of KOH generated (less than 7 mmol), the reactions were considered to generate KOH_{aq} at infinite dilution.[10] From the heat of reaction for the potassium metal with water, the heat of reaction for the salts can be obtained by simply comparing the slopes of the lines obtained in Figures 1 and 2. The enthalpies of reaction for K_2COT and Na_2COT with H_2O were found to be −28.8 and −33.3 kcal/mol, respectively, Table I.

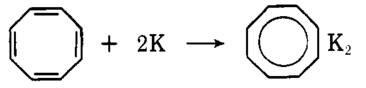
To be certain that the calorimeter was calibrated correctly the heats of reaction for both sodium metal and cesium metal were measured and compared with the values given in the literature, Table I. Excellent agreement was obtained for both of these systems.

From the known heat of hydrogenation of COT[7] the following thermochemical cycle can be constructed to yield the heat of reaction of potassium metal with liquid COT.

	$\Delta H°$, kcal/mol
$H_2COT_{liq} + 2KOH_{aq} \rightarrow K_2COT_{solid} + H_2O_{liq}$	+28.8
$COT_{liq} + H_2 \rightarrow H_2COT$	−25.6
$2K^0 + H_2O_{liq} \rightarrow 2KOH_{aq} + H_2$	−94.4
$COT_{liq} + 2K^0 \rightarrow K_2COT_{solid}$	−91.2

The surprising result is that the reaction between potassium metal and liquid COT to form the aromatic salt is almost as exothermic as the reaction between potassium metal and water. A similar thermochemical cycle constructed for the sodium salt yields an enthalpy of reaction between sodium metal and COT of −86.7 kcal/mol.

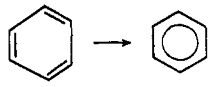
The difference in energy between the planar COT with alternating bond lengths and the tub conformation is about 10 kcal/mol.[12] Therefore, the enthalpy of reaction between planar COT and potassium metal to form the dianion salt (eq 3) is extremely exothermic (−104 kcal/mol).



(3)

$\Delta H° = -104$ kcal/mol

This reaction represents the transformation from the antiaromatic Jahn-Teller distorted system to the aromatic salt. However, it is not analogous to the transformation from the hypothetical cyclohexatriene to benzene (eq 4), since the species in eq 4 are electroneutral.



(4)

$\Delta H° \simeq -30$ kcal/mol[13]

That is, eq 4 truly represents the resonance energy of benzene, but the enthalpy of the reaction represented in eq 3 is a function of many factors including the electron affinity of COT, the ionization potential of potassium, and the crystal lattice energy of the K_2COT.

From the heats of reaction of the M_2COT salts with water and the heat of formation of COT from the elements in their standard states, the heats of formation of K_2COT and Na_2COT are found to be −32.0 and −27.5 kcal/mol, respectively. Subtracting twice the heat of sublimation and adding the ionization potential of potassium metal to −32.0 kcal/mol yields the enthalpy for the reaction shown below.

$$2K^+_g + 2e^-_g + 8C_{gr} + 4H_2 \rightarrow K_2COT \qquad (5)$$

This same process can be carried out for the sodium salt, and the difference in the two resulting enthalpies (36.0 kcal/mol) represents the difference in the crystal lattice energies between K_2COT and Na_2COT. This large difference indicates that the crystal lattice energies are very important in controlling eq 3.

The problem of crystal lattice energies can be circumvented by considering the thermodynamic stabilities of the two salts in solution. The heats of solution of both salts have been determined in hexamethylphosphoramide (HMPA)[8] and are 12.0 and 5.1 kcal/mol for the sodium and potassium salts, respectively. A small correction has been added to the heat of solution for the potassium salt to account for ion association.[14] From these heats of solution to form free solvated ions,[8] the heats of reaction of the alkali metal with COT in HMPA can be calculated.

$$2M^0_{solid} + COT_{soln} \rightarrow 2M^+_{soln} + COT^{2-}_{soln} \qquad (6)$$

Since the single ion heat of solution of the potassium cation in HMPA is −93.6 kcal/mol[15a] (this single ion heat of solution is not absolutely valid as it is based upon the extra thermodynamic assumption, called the TATB assumption),[15b] the heat of reaction of two electrons and COT in the gas phase to form the dianion in solution can be calculated by

	$\Delta H°$, kcal/mol
$2K^0_{solid} + COT_{liq} \rightarrow 2K^+_{soln} + COT^{2-}_{soln}$	−86.1
$2K^+_{soln} \rightarrow 2K^+_g$	+187.2
$2K^+_g + 2e^-_g \rightarrow 2K^0_g$	−200.0
$2K^0_g \rightarrow 2K^0_{solid}$	−15.9
$COT_g \rightarrow COT_{liq}$	−10.3
$COT_g + 2e^-_g \rightarrow COT^{2-}_{soln}$	−125.1

The heat of reaction of potassium metal with COT to form $COT\cdot^-$ can be obtained by introducing the enthalpy of comproportionation,[16] and the enthalpy of solution of COT in HMPA. The enthalpy of solution has not been measured directly. However, the heats of solution for a series of hydrocarbons have been measured by the temperature dependance of the gas solubilities.[17] These enthalpies are always close to zero for hydrocarbons that cannot form hydrogen bonds with the HMPA (i.e., 1,3-butadiene).

	$\Delta H°$, kcal/mol
$COT_{liq} + 2K^0_{solid} \rightarrow COT^{2-}_{soln} + 2K^+_{soln}$	−86.1
$COT^{2-}_{soln} + COT_{soln} \rightarrow 2COT\cdot^-_{soln}$	−5.3
$COT_{liq} \rightarrow COT_{soln}$	$\simeq 0$
$COT_{liq} + K^0_{solid} \rightarrow COT\cdot^-_{soln} + K^+_{soln}$	−45.8

and

$$COT_g + e^-_g \rightarrow COT\cdot^-_{soln} \qquad (7)$$

$$\Delta H° = -70.5 \text{ kcal/mol}$$

It is interesting to note that the enthalpy of reaction between one electron and COT is just a little more than half of that between two electrons and COT to form the dianion. Considering the strong electron-electron repulsion in the dianion, it might be expected that the addition of the second electron would be much more endothermic than the addition of the first. These results are probably explained in part by the aromatic stabilization of the dianion upon obtaining $(4n + 2)$ π electrons. However, it must be remembered that the heats of solution of the COT anion radical and dianion are important factors in determining the enthalpies of the reactions leading to the formation of these two species.

The reaction of the solvated anion radical with a gas phase electron to yield the solvated dianion is given by

$$COT\cdot^-_{soln} + e^-_g \rightarrow COT^{2-}_{soln} \qquad (8)$$

$$\Delta H° = -54.6 \text{ kcal/mol}$$

The enthalpy controlling eq 8 is a function of three factors: the heat of solution of the anion radical, the heat of solution of the dianion, and the electron affinity of the anion radical.

Since the classic work of Brauman and Blair,[18] it is well understood that solvation energies are just as important in the determination of the thermodynamic stability of anionic species in solution as are the intramolecular considerations (i.e., electron affinity, resonance energy, and electron-electron repulsion). For this reason it would be of interest to estimate the relative importance of the three factors controlling eq 8.

The electron affinity of the anion radical of COT in the gas phase can be estimated from MINDO/2 calculations.[19] From these calculations the heat of formation of the COT anion radical (planar and symmetrical) is 47.9 kcal/mol, and that for the dianion is 128.8 kcal/mol.[19] From these numbers the electron affinity of the anion radical is estimated to be 128.8 − 47.9 = 80.9 kcal/mol. This means that the difference in the heat of solution of the dianion and anion radical is about −54.6 − 80.9 = −135.5 kcal/mol. That is, the enthalpy of solution of the dianion is 135.5 kcal/mol more exothermic than that of the anion radical.

The electron affinity of the COT neutral molecule in the gas phase calculated from MINDO/2 is +12 kcal/mol.[19] An experimental determination of this electron affinity yielded a value of +13.3 kcal/mol.[20] Taking the experimental number as the correct one, the heat of solution of the anion radical is found to be −70.5 +13.3 = −57.2 kcal/mol. From eq 8 the heat of solution of the COT dianion plus the electron affinity of the anion radical is then −54.6 − 57.2 = −111.8 kcal/mol. If the electron affinity calculated from MINDO/2 for the anion radical is correct, the heat of solution of the dianion would have to be −192.7 kcal/mol. Further, the crystal lattice energy of K_2COT is given by

	$\Delta H°$, kcal/mol
$2K^+_{soln} + COT^{2-}_{soln} \rightarrow K_2COT_{solid}$	−5.1
$2K^+_g \rightarrow 2K^+_{soln}$	−187.2
$COT^{2-}_g \rightarrow COT^{2-}_{soln}$	−192.7
$2K^+_g + COT^{2-}_g \rightarrow K_2COT_{solid}$	−385

and the resonance energy of the COT dianion would be about 13.3 + 90 − 80.9 = 22.4 kcal/mol. The electron-electron repulsion energy is represented by 90 kcal/mol.[20] The experimentally verified thermodynamic parameters discussed in this report are summarized in Figures 3 and 4.

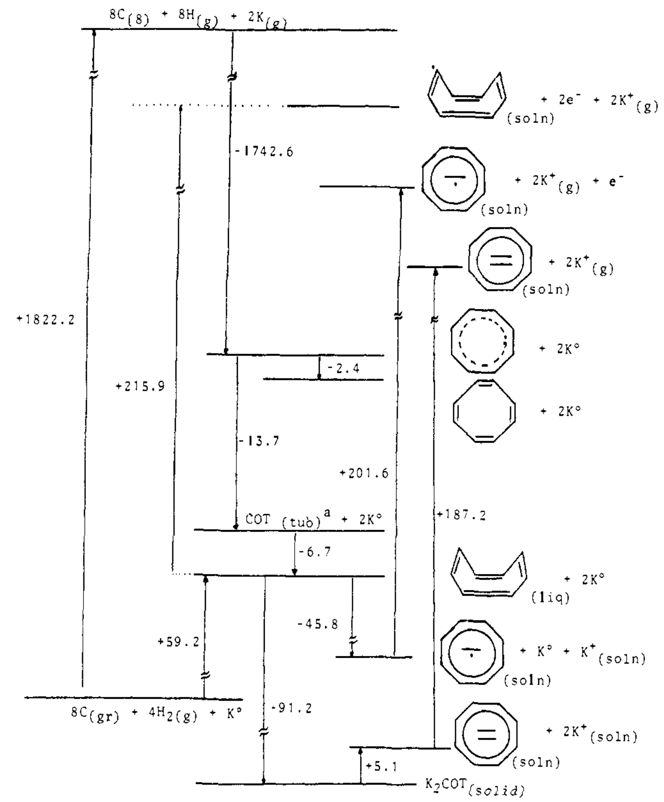


Figure 3. Energy diagram for the COT-K system. All numbers are in kcal/mol. The solvent is HMPA. (a) $COT_{(tub)}$ represents the tub without any resonance stabilization.

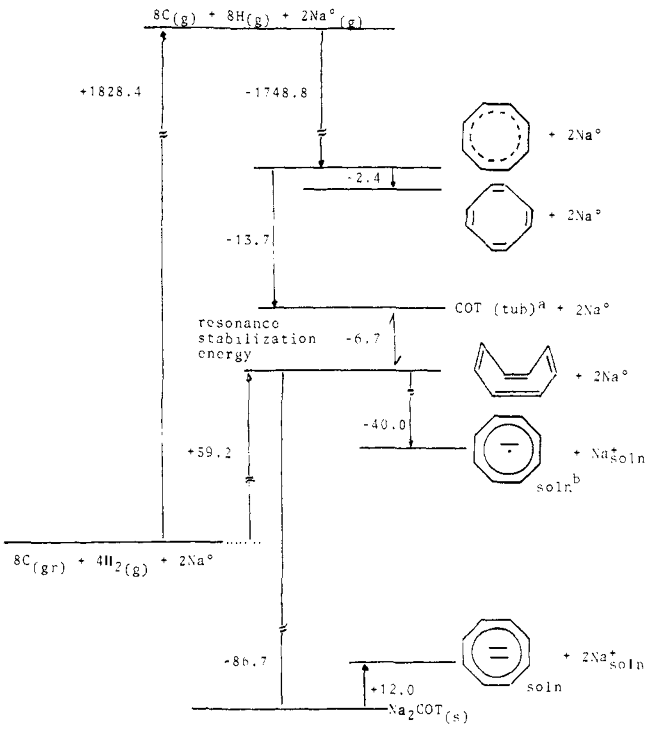


Figure 4. Energy diagram for the COT system. The metal used for reduction is Na^0. All numbers are in kcal/mol. (a) This represents the COT tub without the resonance stabilization energy. (b) The solvent utilized is HMPA.

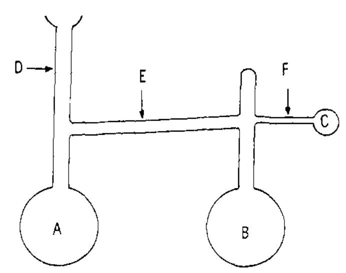


Figure 5. Apparatus used for the preparation of thin glass bulbs of M_2COT.

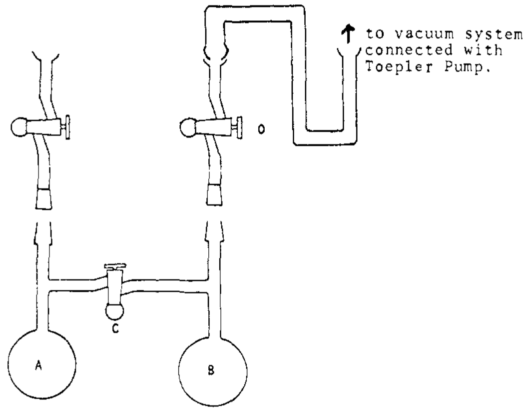


Figure 6. Apparatus which was connected to the Toepler Pump line in order to measure the number of moles of H_2 liberated from the reaction of water and M_2COT.

Experimental Section

The M_2COT salt was prepared in THF in bulb A of the apparatus shown in Figure 5. After charging bulb A with alkali metal, quantities of THF and COT were distilled into bulb A through the vacuum line while maintaining this bulb in liquid nitrogen. The apparatus was then sealed from the vacuum line at point D. After completion of the reaction of the COT with the excess of alkali metal, the THF was separated from the remainder of the alkali metal by passing the THF solution into bulb B. The THF was then distilled back into bulb A, which was immersed into a liquid nitrogen bath, leaving the dry alkali metal cyclooctatetraenide salt in bulb B. The apparatus was then sealed off at point E, and the salt was poured into bulb C and sealed at point F. Alkali metals were distilled directly into the glass bulbs, which we in turn sealed off from the vacuum system.

These glass bulbs containing the COT salt or alkali metal were then placed in the metal bomb. The bulbs were broken with a spring loaded mechanism (modified mouse trap). The trigger was held with a loop of thin cotton thread, and the glass bulb was secured in the bottom of the bomb. The ends of wire (fuse wire for Parr Oxygen Bomb No. 45C10) were fastened to the standard terminals inside the bomb. The water was purged with nitrogen to eliminate dissolved oxygen, and the bomb was flushed with nitrogen to eliminate O_2 from the atmosphere above the water. The bomb was then placed in a modified Parr Adiabatic Calorimeter.

To determine if any hydrogen gas was liberated from the reaction of M_2COT with water, any quantity of hydrogen produced by the reaction was pumped into a gas buret for detection. About 15 ml of THF were distilled into bulb A of the apparatus shown in Figure 6, which contained a weighed portion of alkali metal. About 0.5 equiv of COT were then distilled into bulb A from the vacuum line. This mixture was stirred at room temperature until all of the COT was converted into the dianion. After completion of the reaction, the THF solution was separated from the excess alkali metal by passing this solution into bulb B. The THF was then distilled off. Bulb A was then cleaned, and a quantity of water was added and degassed in a freeze-thaw cycle. The stopcock was then opened and the salt allowed to react with the water. The entire apparatus was connected to the vacuum system, and stopcock D was opened allowing any gases to pass through the U tube, which was placed in a liquid nitrogen bath to trap out any condensables before they could enter the vacuum line. Any noncondensable gases were pumped into a gas buret via a Toepler Pump. No noncondensable gas was detected.

The heat of reaction of the salt or alkali metal with the deoxygenated water in the bomb was measured in the calorimeter. A modified ac-lock-in technique was used to measure the electrical resistance of

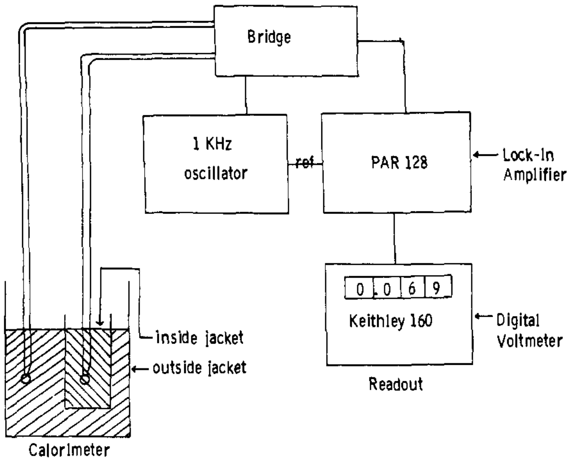


Figure 7. Schematic diagram for the calorimeter used.

the thermistors. A block diagram of the apparatus used can be seen in Figure 7.

A 1 kHz oscillator powers a modified Wheatstone bridge and at the same time provides the reference signal for the null detector. In our case, the null detector is a Princeton Applied Research 128 Lock-in Amplifier. The basic innovation on the ac bridge is the use of operational amplifiers to provide gain and low noise of the unbalanced ac signal. The null detector output (−1.0 to 1.0 V) was connected to a Keithley 160 digital voltmeter, where the unbalanced signal was monitored. When the thermistors were placed inside their respective jackets of the calorimeter, the variable resistors of the ac bridge were changed until the lock-in detector read a null. From this point on, the voltage detected by the lock-in amplifier was interpreted as a temperature difference between the two probes. Calibration showed that the unbalanced signal is a linear function of the temperature difference of the two probes with a slope of $1.80 \pm 0.01\ \mu V/mdeg$, at temperatures where these experiments were carried out. This technique can provide a thermal resolution of 1 μdeg and an accuracy of 0.1% in the millidegree region.

The Toepler Pump connected with the gas buret and NMR systems have been previously described.[17]

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References and Notes

(1) H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 2360 (1963).
(2) J. F. M. Oth and G. Schröder, *J. Chem. Soc. B*, 904 (1971).
(3) J. F. M. Oth, H. Baumann, J. M. Gilles, and G. Schröder, *J. Am. Chem. Soc.*, **94**, 3498 (1972).
(4) E. J. Prosen, "Experimental Thermochemistry", Vol. 1, F. D. Rossini, Ed., Wiley-Interscience, New York, N.Y., 1956, p 129.
(5) (a) W. D. Good, D. W. Scott, and G. Waddington, *J. Phys. Chem.*, **60**, 1080 (1956); (b) C. A. Neugebauer and J. L. Margrave, *ibid.*, **62**, 1043 (1958).
(6) D. R. Thielen and L. B. Anderson, *J. Am. Chem. Soc.*, **94**, 2521 (1972).
(7) R. B. Turner, W. R. Meador, W. von E. Doering, L. H. Knox, J. R. Mayor, and D. W. Wiley, *J. Am. Chem. Soc.*, **79**, 4127 (1957).
(8) G. R. Stevenson and I. Ocasio, *J. Phys. Chem.*, **79**, 1387 (1975).
(9) S. Z. Goldberg, K. N. Raymond, C. A. Harman, and D. H. Templeton, *J. Am. Chem. Soc.*, **96**, 1348 (1974).
(10) E. E. Ketchen and W. E. Wallace, *J. Am. Chem. Soc.*, **73**, 5810 (1951).
(11) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, *Natl. Bur. Stand. (U.S.) Circ.*, 9, 819 (1952).
(12) F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 671 (1962).
(13) G. R. Stevenson, *J. Chem. Educ.*, **49**, 781 (1972).
(14) G. R. Stevenson and I. Ocasio, *J. Am. Chem. Soc.*, **98**, 890 (1976).
(15) (a) G. R. Hedwig, D. A. Owensby, and A. J. Parker, *J. Am. Chem. Soc.*, **97**, 3888 (1975); (b) B. G. Cox and A. J. Parker, *ibid.*, **95**, 402 (1973).
(16) G. R. Stevenson and J. G. Concepcion, *J. Phys. Chem.*, **76**, 2176 (1972).
(17) G. R. Stevenson and L. Echegoyen, *J. Am. Chem. Soc.*, **96**, 3381 (1974).
(18) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **90**, 6561 (1968).
(19) M. J. S. Dewar, A. Harget, and E. Haselbach, *J. Am. Chem. Soc.*, **91**, 7521 (1969).
(20) W. E. Wentworth and W. Ristau, *J. Phys. Chem.*, **73**, 2126 (1969).

The Dioxygen Adduct of *meso*-Tetraphenylporphyrinmanganese(II), a Synthetic Oxygen Carrier

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Abstract: In toluene solutions (−79 °C) dioxygen reversibly binds to Mn(TPP)(py) with replacement of the pyridine to form a five-coordinate complex, rather than by addition to yield a six-coordinate species. The resulting Mn(TPP)(O_2) complex surprisingly exhibits the $S = 3/2$ spin state ($D = -2.48 \pm 0.07\ cm^{-1}$; $\lambda = E/D = 0.3257 \pm 0.0003$; $A_z = -53.1\ (\pm 0.5) \times 10^{-4}\ cm^{-1}$; $A_y = -82.0\ (\pm 0.5) \times 10^{-4}\ cm^{-1}$; $A_{^{17}O} \doteq B_{^{17}O} \doteq 0$). The experimental results, in combination with qualitative bonding considerations, indicate (i) extensive $Mn \rightarrow O_2$ charge transfer and (ii) the appropriateness of an $Mn^{IV}(O_2{}^{2-})$ valency formalism in which the Mn(IV) is in the $^4(t_2{}^3)$ ground state. A linear geometry for the complex can be ruled out. Although further definite conclusions as to structure are not presently possible, we tentatively favor the symmetric, "edge-on" mode of binding.

Studies of dioxygen binding to transition metal complexes are of intrinsic importance, and in addition provide opportunities to attack the fundamental problems of the biological oxygen carriers and oxygenases. The properties of synthetic cobalt(II) and, more recently, iron(II) oxygen carriers have been intensively studied,[2] but manganese(II) was not found to reversibly bind dioxygen.[3]

One way to obtain oxygen adducts of synthetic iron(II) complexes is to use aprotic solvents and low temperatures.[4] Under such conditions the rate of irreversible formation of the stable μ-oxo dimer Fe^{III}-O-Fe^{III} is negligibly slow, and the dioxygen binding is reversible. Since at ambient temperatures a pyridine (py) solution of manganese(II) phthalocyanine (Pc) is oxidized in air to yield (py)(Pc)Mn^{III}-O-Mn^{III}(Pc)(py),[5]