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THE HEAT OF FORMATION OF POTASSIUM CYCLOOCTATETRAENIDE

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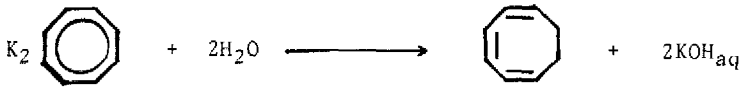
Probably the most important quantities inherent in any compound are its energy and its structure. The entire concept of aromaticity simply comes from the fact that certain cyclic π-electron systems are of lower energy than would be expected without considering this concept (for example the heat of formation of benzene is much greater than that expected for the hypothetical cyclohexatriene). In the Hückel sense monocyclic π-electron systems with 4n π-electrons are antiaromatic. However, for the cases of cyclooctatetraene ([8]annulene),[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 of any of these aromatic salts. Here we wish to report an experimental determination of the heat of formation of the aromatic dipotassium salt of cyclooctatetraene (COT).

Dry dipotassium cyclooctatetraenide[4] does react exothermically with water to form aqueous KOH and cyclooctatriene as shown below.[4,5]



The enthalpy of this reaction was measured by placing glass bulbs containing the dianion salt and sealed under vacuum into a modified bomb calorimeter. Before closing the bomb calorimeter, the bulbs were covered with 100 ml of H_2O. After stabilization of the calorimeter, the bulbs were broken via a spring loaded device, and the heat liberated for the resulting reaction was measured. 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. The amount of potassium metal or potassium salt in the bulbs was not weighed; but after each experiment, the contents of the bomb was titrated for KOH with dilute HCl to obtain the quantity of K° or K_2COT that was in the bulb. Since the quantity of water used to react with either the salt of K° was very large in comparison with the quantity of KOH generated (less than 7 mmoles), the reactions were considered to generate KOH_{aq} at infinite dilution.[7] From the known heat of reaction of potassium metal with water, the heat of reaction for the salt can be obtained by simply comparing the slopes of the lines obtained in Figure 1 with that obtained for the potassium metal. The enthalpy of reaction of K_2COT with H_2O was found to be -28.8 kcal/mole.

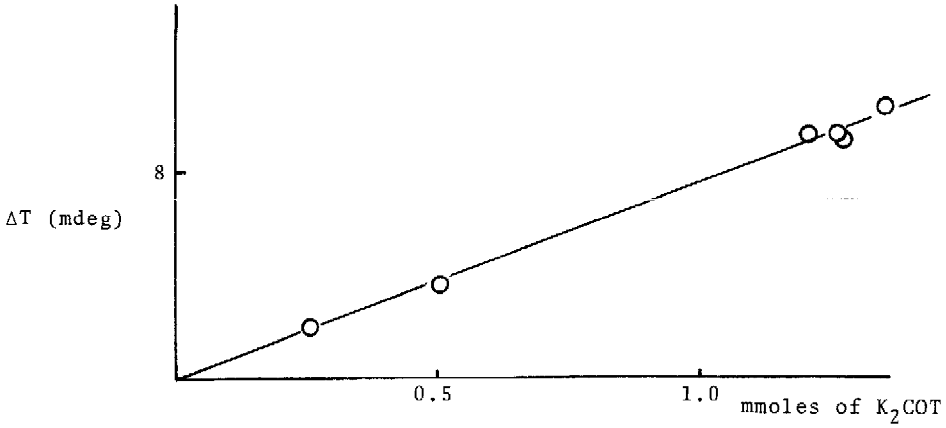


Figure 1. A plot of the change in temperature observed in the calorimeter vs. the moles of potassium metal in the evacuated bulb. The slope of this line is 7.47 deg/mole. The slope of the line obtained for potassium metal is 12.25 deg/mole.

To be certain that the calorimeter was calibrated correctly the heats of reaction of both sodium metal and cesium metal[8] were measured and compared with the values given in the literature, Table 1. Excellent agreement was obtained for both of these systems.

From the known heat of hydrogenation of COT[9] the following thermochemical cycle can be constructed to yield the heat of reaction of potassium metal with liquid COT.

$$H_2COT_{(liq)} + 2KOH_{aq} \rightarrow K_2COT_{(solid)} + H_2O_{(liq)} \quad \Delta H^\circ = +28.8$$
$$COT_{(liq)} + H_2 \rightarrow H_2COT \quad \Delta H^\circ = -25.6$$
$$2K^\circ + H_2O_{(liq)} \rightarrow 2KOH_{aq} + H_2 \quad \Delta H^\circ = -94.4$$
$$COT_{(liq)} + 2K^\circ \rightarrow K_2COT_{(solid)} \quad \Delta H^\circ = -91.2 \text{ kcal/mole}$$

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 and water, see Table 1. All of the enthalpies apply at 25°.

Table 1. Enthalpies of Reaction of the Following Substances with Water

Substance	ΔH°, kcal/mole	ΔH° (lit.)	Reference
K°	calibration	-47.2±0.8	7
Na°	-44.6	-44.3±0.7	7
Cs°	-45.1	-45.9	8
K_2COT	-28.8±0.7		this work

The COT dianion salt is not readily formed from the interaction of neat COT with K°, due to the large negative entropy term and/or the very slow kinetics of formation. However, dilute solutions of COT in tetrahydrofuran (THF) readily dissolve potassium metal to form the COT dianion, which is ion paired with two potassium cations.[10,11] The heat of solution of K_2COT in THF has recently been determined allowing the calculation of the heat of formation from COT and K° of $K^+,COT^=,K^+$ ion aggregate in THF.[12] If ΔH°_{soln} of COT is taken to be close to 0, the enthalpy of formation of the ion aggregate from K° and COT i found to be about -90 kcal/mole. The fact that the reaction between potassium metal and COT is less exothermic in THF than it is with neat COT is due to the large crystal lattice energy of K_2COT.[13]

The difference in energy between the tub and the symmetric planar conformations of COT is about 13 kcal/mole.[14] Therefore, the enthalpy of reaction between symmetric planar COT and potassium metal to form the dianion salt is extremely exothermic (-104 kcal/mole). Since this reaction represents the transformation from the antiaromatic system to the aromatic salt, it is analogous to the transformation from the hypothetical cyclohexatriene to benzene. The enthalpy of this latter transformation is about -30 kcal/mole.[15] In comparing these two numbers, it must be remembered that much of the extra thermodynamic stabilization of the K_2COT is due to the crystal lattice energy.

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4. (a) The solution resulting from the addition of D_2O to the dry K_2COT does not yield an NMR signal for the THF indicating that THF is not incorporated into the crystal lattice structure. (b) The K_2COT was formed in THF by K° reduction of COT. The THF was then removed from the salt under vacuum.

5. (a) D. R. Thielen and L. B. Anderson, J. Am. Chem. Soc., 94, 2521 (1972). (b) Some 1,3,6-cyclooctatriene is also formed, but the heat of hydrogenation of COT to form either isomer is about the same.

6. Two calibrated thermistors were used instead of the mercury thermometers in a Parr adiabatic calorimeter. A modified ac lock-in technique was used to measure the electrical resistance of the thermistors. This technique provides a thermal resolution of 1 μdeg and an accuracy of 0.1% in the region where most of our measurements were taken. The spring loaded device, which crushed the evacuated bulbs, was released electrically. A complete discussion of this calorimeter will appear in a future publication.

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