Electron Spin Resonance Studies of the Cyclooctatetraenyl Anions[1]

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The e.s.r. spectrum of the cyclooctatetraenyl radical-anion, prepared from the hydrocarbon by reduction with lithium, sodium, and potassium, has been studied in dimethoxyethane and tetrahydrofuran. In addition to the spectrum of the cyclooctatetraenyl radical-anion itself, spectra were obtained which exhibited varying degrees of alkali metal hyperfine splitting, indicating the presence of ion-pair complexes between the radical and the alkali metal cations. The parameters which characterize the spectrum of the uncomplexed radical are: proton splitting, 3.209 ± 0.007 gauss; carbon-13 splitting, 1.28 ± 0.05 gauss; g-factor, $g = 2.0025 \pm 0.0001$; upper limit to the line width, 0.17 gauss; and approximately equal transverse and spin-lattice relaxation times, $T_1 \approx T_2$. The constant for disproportionation of the radical-anion at room temperature is about 5×10^8. The rate of exchange between the radical-anion and the dianion was found to be much faster than the rate of exchange between the radical-anion and the neutral molecule. The compression energy of cyclooctatetraene was estimated to be 21 kcal./mole, and the compression energy of the anions was estimated to be small.

I. Introduction

Cyclooctatetraene, C_8H_8, known to have a tub-shaped conformation, lacks the high degree of conjugative stabilization characteristic of planar aromatic molecules, but its reduction products, the cyclooctatetraenyl anions, have been suggested to be aromatic.[4-6] The π-electron energy levels of the hypothetical flat cyclooctatetraene system are, according to the simple Hückel LCAO molecular-orbital theory

$$E_k = \alpha + 2\beta \cos \frac{2k\pi}{8} \qquad (k = 0,1,\ldots,7) \quad (1)$$

These energy levels, in order of decreasing stability, are $\alpha + 2\beta$; $\alpha + \sqrt{2}\beta$; $\alpha + \sqrt{2}\beta$; α; α; $\alpha - \sqrt{2}\beta$; $\alpha - \sqrt{2}\beta$; and $\alpha - 2\beta$. The π-electron energy of flat cyclooctatetraene in its ground electronic state is therefore $8\alpha + 4(\sqrt{2} + 1)\beta$, while that of the anion-radical is $9\alpha + 4(\sqrt{2} + 1)\beta$ and that of the dianion is $10\alpha + 4(\sqrt{2} + 1)\beta$. The π-electron energy for the non-conjugated cyclooctatetraene with four non-conjugated double bonds having π-electron energy levels at $\alpha + \beta$ and $\alpha - \beta$ is $8\alpha + 8\beta$, while for the non-conjugated anion-radical and dianion it is $9\alpha + 7\beta$ and $10\alpha + 6\beta$, respectively. The approximate theoretical estimates of the delocalization energies of the neutral molecule, the anion-radical, and the dianion, are, therefore, -1.7β, -2.7β, and -3.7β, respectively. Within the framework of the Hückel theory, cyclooctatetraene contrasts with benzene in that the delocalization energy in the former system increases by $|\beta|$ upon the addition of one electron and $2|\beta|$ upon the addition of two electrons, while in the benzene system the delocalization energies of the anions and of the neutral molecule are the same. Consequently, on proceeding from the neutral molecule to the dianion in the cyclooctatetraene system, if the compressional energy of the σ-bonds remains unchanged, there should be an increasing tendency toward the formation of the aromatic structure.[7]

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(2) National Science Foundation Predoctoral Fellow.

(3) Alfred P. Sloan Fellow.

(4) T. J. Katz and H. L. Strauss, J. Chem. Phys., 32, 1873 (1960).

(5) T. J. Katz, J. Am. Chem. Soc., 82, 3784, 3785 (1960).

(6) T. J. Katz, W. H. Reinmuth, and D. E. Smith, ibid., 84, 802 (1962).

(7) (a) Although the hypothetical flat neutral molecule and the anion-radical are in degenerate ground states, Jahn–Teller distortions [cf. H. A. Jahn and E. Teller, Proc. Roy. Soc. (London), A161, 220 (1937)] are probably small. The energy involved is probably less than 2 kcal./mole [L. C. Snyder, J. Phys. Chem., 66, 2299 (1962)] and is neglected in the present discussion. (b) C. A. Coulson [Tetrahedron, 12, 193 (1961)] has shown that if the cyclooctatetraenyl dianion were planar, its geometry would be that of a regular octagon. (c) Calculations [N. L. Allinger, J. Org. Chem., 27, 443 (1962)] employing the Pariser–Parr method also indicate that the anions, unlike the hydrocarbon, should be aromatic. They also demonstrate that benzene should have unequal carbon–carbon bond lengths.

Many benzenoid aromatic hydrocarbons in ethereal solution have been treated with alkali metals to produce the anion-radical and the dianion. In general the equilibrium

$$R + R^= = 2R^{\cdot-} \qquad (I)$$

lies far to the right,[8] in agreement with systematically approximated self-consistent molecular orbital calculations of the energies of the hydrocarbons and of their anions,[9] as well as with the hypothesis that the dianions are destabilized by Coulomb repulsions between the two added electrons. Furthermore, for a number of aromatic hydrocarbons the equilibrium constant is essentially the same, corresponding to a free-energy change of about -0.40 e.v. (-9.2 kcal./mole).[8] However, in the cyclooctatetraene system, if the anions are flat and the compression of the hydrocarbon is sufficiently great, the equilibrium would lie to the left.[6] The presence of a stable radical in solutions formed by treatment of cyclooctatetraene in ethereal solvents with alkali metals has been demonstrated by preliminary investigations.[4]

The investigation reported below has three principal aspects: (1) the identification of the cyclooctatetraenyl radical-anion and the measurement of data pertaining to the equilibrium determining its concentration; (2) the study of intrinsic properties of the electron spin resonance spectra of the cyclooctatetraenyl anion-radical, an investigation particularly significant because this radical is one of the few for which the π-electron spin densities are known from symmetry considerations alone; (3) the study of the role of the cations, with relation to their effects on both the spectra and the chemical properties of the anions.

II. Experimental

Sample Preparation.—The cyclooctatetraene, obtained from the Aldrich Chemical Co., was purified by distillation. The solvents [tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME)] were distilled from $LiAlH_4$ immediately before use. The samples were prepared by adding a piece of alkali metal of known weight to a measured volume of cyclooctatetraene solution in a 5-mm. o.d., 4-mm. i.d. Pyrex tube, degassing immediately on a vacuum line, and allowing the metal to react with the solution. Those samples used for the measurement of the radical concentrations, when not in the spectrometer, were stored at liquid nitrogen temperature.

Electron Spin Resonance Measurements.—The electron spin resonance spectrometer and the special techniques developed to obtain reproducible measurements of spectra with small satellite lines have been described elsewhere.[10-12] The spectrometer sensitivity was calibrated by using THF solutions of α,α'-diphenylpicrylhydrazyl (DPPH) of known concentration. The DPPH and cyclooctatetraene samples were prepared in glass tubes of the

(8) G. J. Hoijtink, E. de Boer, P. H. van der Meij, and W. P. Weijland, Rec. trav. chim., 75, 487 (1956).

(9) N. S. Hush and J. Blackledge, J. Chem. Phys., 23, 514 (1955).

(10) H. L. Strauss, Dissertation, Columbia University, 1960.

(11) H. L. Strauss and G. K. Fraenkel, J. Chem. Phys., 32, 1873 (1960).

(12) J. W. H. Schreurs and G. K. Fraenkel, ibid., 34, 756 (1961).

same size and were degassed in the same way. Since solid DPPH tends to contain solvent of crystallization, the concentrations of its solutions were determined from optical absorption spectra. Lyons and Watson[13] found the absorbency of DPPH to be 29.3 l./g.-cm. in ether, and this value was used in the present work for solutions in THF. The maximum absorption in ether occurs at 5175 Å., while in THF the maximum is at 5166 ± 3 Å. The cyclooctatetraene samples contained ions (in concentrations of approximately 0.5 M) which could have affected both the Q of the spectrometer cavity and the configuration of the r.f. fields, but since only small adjustments had to be made in the balance of the magic-tee bridge of the spectrometer when the DPPH and cyclooctatetraene samples were interchanged, it was concluded the ions had a negligible effect on the measurement of absolute radical concentration.

For the measurements of the temperature dependence of the radical concentration, the sample cavity was placed in a trichloroethylene-filled dewar flask containing a heat exchanger. The e.s.r. spectra of both the cyclooctatetraene and the DPPH were obtained at each temperature in the form of the first derivative and its integral. The areas under the curves for the integral (*i.e.*, the absorption curves), proportional to the e.s.r. absorption intensity, were measured with a planimeter. Checks were made that no decomposition of the DPPH solutions had occurred upon heating and that the sensitivity of the e.s.r. spectrometer had remained essentially constant over the temperature range employed. After concluding the experiments, it was found that the sample cavity contained sufficient magnetic impurities to distort the shape of some of the narrowest lines but not to affect significantly the peak areas.

III. Results

Samples were usually prepared from an approximately equal number of moles of alkali metal and cyclooctatetraene and therefore contained approximately equal amounts of cyclooctatetraene and cyclooctatetraenyl dianion after reaction. Table I summarizes some of the qualitative observations made on a number of samples. The colors varied with concentration, and color changes were observed after storage for many days.

TABLE I

CYCLOOCTATETRAENE SAMPLES[a]—QUALITATIVE RESULTS

Solvent	Metal	Rate of solution of metal	Pre-cipitate	Color[b]	Re-solved spec-trum
THF	Li	Slow	No	Green	Yes
	Na	Slow	Yes	Green	Yes
	K	Fast	No	Red	No
DME	Li	Slow	Yes, blue	Blue-green	Yes
	Na	Slow	Yes	Green	Yes
	K	Very fast	No	Yellow	Yes

[a] These samples had a stoichiometric composition of 0.05 to 0.5 mole per liter of alkali metal and 0.1 to 1 M cyclooctatetraene. [b] The color varies somewhat with the concentration and age of the samples.

Lithium Samples.—Lithium samples of cyclooctatetraene in THF and DME exhibited spectra of nine lines. The lines were equally spaced and had relative intensities approximately in agreement with the intensities expected for a spectrum resulting from hyperfine interaction with eight equivalent protons. Careful measurements on a Li–THF sample with a line width of about 0.4 gauss[14] gave the value a^H = 3.209 ± 0.007 gauss for the proton hyperfine interaction and g = 2.0025 ± 0.0001 for the spectroscopic splitting factor (g-value). The splittings in the spectra of all other samples investigated (see below) were determined with an error of a few per cent from strip-chart recordings, and all were found to be 3.2 gauss.

The DME samples showed one satellite on each side of the five most intense lines of the spectrum. The splitting and intensities of these satellites were meas-

(13) J. A. Lyons and W. F. Watson, *J. Polymer Sci.*, **28**, 141 (1955).

(14) The widths given are 0.866 times the distance between derivative extrema. When the line is Lorentzian, this quantity is the half half-width; when it is not Lorentzian (as, for example, when one apparent line is composed of several overlapping lines), this quantity is only a parameter indicative of the width.

ured by the method used for semiquinone ions.[10,11] The satellites are interpreted as arising from hyperfine interactions from carbon-13 isotopes present in natural abundance. The predicted intensity of the satellites on the basis of this hypothesis is 4.48% of the main line,[11] and a curve computed[15] for a main line and satellites, assuming a Lorentzian line shape, was in excellent agreement with the observed spectrum. The splitting was 1.28 gauss.

In THF the widths of the lines in the spectra of the samples first prepared were too wide to allow the C^{13} satellites to be observed, and attempts were therefore made to obtain line widths of less than 0.4 gauss. The expected satellites were then indeed observed. In addition, however, structure in the form of satellites of much greater intensity and considerably smaller splitting than those of the presumed C^{13} satellites appeared. Although no attempt was made to measure precisely the intensities of the outer satellites because of their overlap with the inner ones, the former had positions corresponding to a splitting of 1.34 gauss, in agreement with the presumed carbon-13 splitting of the Li–DME satellites. The relative intensities of the outer satellites were also as expected.

The appearance of the Li–THF spectrum changed as the lithium dissolved, and thus the extra structure probably arises from an ion-pair complex between the Li^+ ions and the cyclooctatetraenyl radical-anion. The nuclear spin of Li^7 (as well as Na^{23} and K^{39}) is $^3/_2$, and hyperfine interaction between the unpaired electron and the Li^7 nucleus would give rise to four equally spaced hyperfine lines, two on each side of each main line. Thus, if the alkali metal splitting is a, and the position of a hydrogen line is b, the alkali metal satellites would be expected to appear at $b ± (^1/_2)a$ and $b ± (^3/_2)a$. To check that the presumed C^{13} satellites of the Li–THF spectra were not the two outer lines of the lithium satellites, the observed spectrum was compared with curves computed for a main line plus four lithium lines of the intensity and splitting required by such a hypothesis. The inner lithium lines were not resolvable on these computed curves, and therefore the inside and the outside structure cannot both arise from the splitting of one lithium atom.

The spectrum of a sample of stoichiometric composition 0.016 mole of lithium metal per liter of THF and 0.13 M in cyclooctatetraene was examined when only one-quarter to one-half of the lithium had dissolved. The spectrum showed a shoulder on both sides of each line, far inside the expected position of the C^{13} satellite. The C^{13} satellite was not seen in this particular spectrum because of the overlap with the extra lines in the shoulder. A computed spectrum based on Lorentzian line shapes, with a lithium splitting constant of 0.19 gauss, a line width of 0.19 gauss, and with each lithium line assigned an intensity 20% of the main line, fitted the experimental spectrum well. The concentration ratio of the complexed species causing the four lines and of the uncomplexed radical was thus 0.8.

When all the lithium had dissolved, the spectrum shown in Fig. 1 was observed with an extra peak on each side of the main line instead of a shoulder. A curve, for which the line widths and the lithium splitting are taken to be 0.24 gauss, and for which the concentration of the presumed lithium ion-pair is taken to be 71% of the total radical concentration, fits this spectrum, while a curve computed with the same width and splitting parameters, but with 67% of the radicals taken to be ion-pairs, does not. The lithium splittings, 0.19 and

(15) The correction used to adjust for the overlap of lines and the relationship of the width of the lines to the detectability of the satellites are discussed in ref. 11.
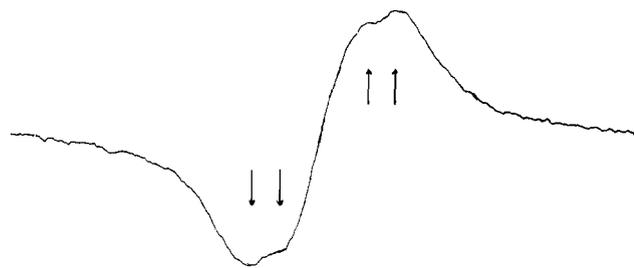
Fig. 1.—Derivative of the e.s.r. spectrum of one-proton hyperfine line of the cyclooctatetraenyl radical-anion prepared with lithium in tetrahydrofuran. The two peaks on each side of the line, indicated by the outside arrows, are about 0.69 gauss apart. This structure is due to a lithium complex with the cyclooctatetraenyl radical-anion.
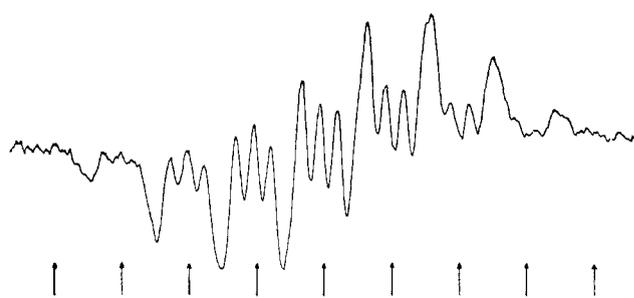

Fig. 2.—Derivative of the e.s.r. spectrum of the cyclooctatetraenyl radical-anion prepared with sodium in tetrahydrofuran. Only the lines of the sodium complex can be seen in this spectrum. The vertical arrows, spaced about 3.21 gauss apart, indicate the position at which the noncomplexed radical would appear if it had the same g-value as the complexed radical. Some of the finer details of the spectrum do not appear on this recording because of over modulation.

0.24 gauss, used to fit the two spectra above are probably not significantly different.

Order-of-magnitude measurements were made of the relaxation times of this sample when it had only partially reacted. The relaxation times T_1 and T_2, determined by the methods of reference 12 to be 2×10^{-7} and 3×10^{-7} sec., are indistinguishable.

Sodium Samples.—The Na–DME samples showed considerable structure beyond that expected for the uncomplexed cyclooctatetraenyl radical-anion. An overlapped peak appeared on each side of the lines of the uncomplexed radical. This extra peak was so broad that adjacent sets of lines (*i.e.*, the main proton lines together with their respective satellites) overlapped, and thus it was impossible to observe the C^{13} satellites.

The Na–DME spectrum, although not analyzed in detail, seemed to consist of four sets of lines superimposed on the proton spectrum with about the same splitting as that found in the Na–THF spectrum, discussed below. The complexed species comprised approximately 60% of the total radical species present in the sample.

Upon first examination, the Na–THF spectrum, shown in Fig. 2, did not appear consistent with any pattern of satellites spaced 3.209 gauss apart with an intensity distribution appropriate to 8 protons, namely nine lines in the ratio 1:8:28:56:70:56:28:8:1. Closer examination, however, revealed that the spectrum could be approximated by overlapping sets of four equally spaced lines of width 0.8 gauss and of splitting 0.9 gauss. The different sets of four lines were spaced 3.2 gauss apart and had appropriate intensity ratios, although no attempt was made to fit all the lines in the spectrum exactly. For example, the center set was approximately 70/56 times as intense as either of the two adjacent sets. There was no evidence of any uncomplexed cyclooctatetraenyl radical-anion.

Potassium Samples.—The K–DME spectra were resolved into lines about 1.3 gauss wide, separated by 3.2 gauss, and with approximately the intensity ratios expected for hyperfine interactions with eight protons. These very wide lines showed no satellites. The spectra of K–THF samples of stoichiometric composition about 0.5 mole per liter of potassium metal and 0.5 M cyclooctatetraene consisted of one line about 6 gauss in width. Samples of the same cyclooctatetraene concentration, but with much less potassium, showed resolved spectra similar to those of the K–DME samples.

Radical Concentration and its Temperature Dependence.—The radical concentration and its temperature dependence from 0 to 43° were measured for samples of cyclooctatetraene treated in THF with both lithium and potassium. The Li–THF sample had a stoichiometric composition of 0.53 mole of lithium metal per liter and 0.39 M cyclooctatetraene which cor-

responds, after complete reaction, to a mixture 0.53 M in Li$^+$, 0.12 M in cyclooctatetraene, and 0.27 M in cyclooctatetraenyl dianion. At 22.5° the radical concentration was 1.7×10^{-5} M, and if this concentration is determined by the equilibrium I, then the equilibrium constant is $K_1 = 9 \times 10^{-9}$. The enthalpy change for this reaction, as determined from the slope of a least squares line fitted to fifteen points of the logarithm of the concentration and the reciprocal of the absolute temperature, is $\Delta H_1 = -(1.03 \pm 0.52)$ kcal./mole.

The measured radical concentration in a K–THF sample 0.34 M in K$^+$, 0.22 M in cyclooctatetraene, and 0.17 M in cyclooctatetraenyl dianion was 1.1×10^{-5} M at 22.5°, implying an equilibrium constant $K_1 = 3.4 \times 10^{-9}$. The enthalpy change, determined from a plot of twelve points, was $\Delta H_1 = (5.64 \pm 0.46)$ kcal./mole.

The line width of the Li–THF spectrum also changed with temperature, from about 0.36 gauss at 0° to 0.55 gauss at 43°. The narrower lines were, however, asymmetric due to a magnetic impurity in the cavity (see above). A straight line of slope -4.2×10^3 per degree fitted an Arrhenius plot of the width well, although the plot appeared to have a slightly less negative slope at low values of $1/T$. The activation energy for the rate process determining the line width is, therefore, about 19 kcal./mole.

IV. Discussion

The e.s.r. spectra obtained by treating solutions of cyclooctatetraene in THF and DME with alkali metals are consistent with the spectrum expected for the cyclooctatetraenyl radical-anion: hyperfine interactions are observed from eight equivalent protons, from carbon-13 in natural abundance distributed in eight equivalent sites, and, in some instances, from nuclei of the alkali metal cations associated with the anion as ion-pair complexes. The very different line widths of the lithium and potassium samples are consistent with n.m.r. studies[5] and are interpreted as resulting from a large difference in the rate of electron exchange between the anion-radical and the dianion in the presence of the two alkali metal cations.

In this section we shall discuss the parameters of the electron spin resonance spectrum, the effect of the cations, and finally the thermodynamics of the radical formation in solution.

Parameters of the E.s.r. Spectrum.—The isotropic proton hyperfine interactions observed in the e.s.r. spectra of free radicals have been interpreted in terms of a π–σ interaction,[16–18] and, we assume, following Mc-

(16) H. M. McConnell, *J. Chem. Phys.*, **24**, 632, 764 (1956); H. M. McConnell and H. H. Dearman, *ibid.*, **28**, 51 (1958); H. M. McConnell and D. B. Chesnut, *ibid.*, **28**, 107 (1958).

Connell,[16] that the proton splitting constant a^H is proportional to the π-electron spin density ρ^π on the carbon atom to which the proton is bonded

$$a^H = Q_{CH}^H \rho^\pi \qquad (2)$$

The proportionality factor Q_{CH}^H is usually taken to be constant for all CH bonds, with a value of about -23 gauss. Detailed examination of the theory of the $\pi-\sigma$ interaction[19,20] indicates, however, that the value of Q_{CH}^H should depend on the hybridization of the carbon atom. While this theory gives $Q_{CH}^H = -23.4$ gauss for a CH fragment with three equivalent sp^2-bonds[19] (120°), it also predicts that for the 135° bonds in a regular octagon, Q_{CH}^H should be only -10.0 gauss.[20]

The nine-line e.s.r. spectrum of the cyclooctatetraenyl radical-anion implies that the unpaired electron is equally distributed between the eight carbon atoms, i.e., $\rho^\pi = 1/8$. From this and the experimental splitting constant it follows that $|Q_{CH}|^H| = 8a^H| = 25.67 \pm 0.07$ gauss. This is slightly larger than the usually accepted value of about 23 gauss for equivalent, 120°, bond angles and is very different from the value of 10 gauss predicted by the $\sigma-\pi$ interaction theory for bonds with 135° angles of hybridization. There are thus three possible conclusions: (1) the cyclooctatetraenyl radical-anion is a planar regular octagon, and the $\sigma-\pi$ interaction theory is incorrect; (2) the radical-anion is a planar regular octagon but the bonds are bent,[21] the angle of hybridization remaining 120°; (3) the radical-anion is in some geometrical arrangement which allows the bond angles to be close to 120°. It seems unlikely that the $\sigma-\pi$ interaction theory would be only fortuitously correct for 120° hybrids. Since other data, discussed below, favor a planar conformation for the radical-anion, these considerations suggest that the σ-bonds are bent, although it would be surprising if the angle of hybridization were not somewhat greater than 120°, and a discrepancy would still remain between the calculated value of $Q_{CH}^H| \gtrsim 23$ and the experimental result $|Q_{CH}^H| = 25.67$. Similar conclusions would apply to the recently observed[22] cycloheptatrienyl radical for which $|Q_{CH}^H$ was found to be between 25.6 gauss[22b] and 27.6 gauss.[22a]

The uncomplexed cyclooctatetraenyl radical-anion has a g-value of 2.0025, a maximum line width of 0.17 gauss,[23] and comparable transverse (T_2) and spin-lattice (T_1) relaxation times. In the regular octagonal conformation the radical would be subject to Jahn–Teller distortions,[7,24,25] and it was suggested[25] that these would lead to three experimental observations: (1) an increase in g from the free-electron value of 2.0023; (2) a large line width; and (3) a decrease in the spin-lattice relaxation time. A re-examination of the Jahn–Teller problem[26] has since led to the suggestion that the cyclooctatetraenyl radical-anion should differ from radical-anions such as that derived from benzene, which has a threefold axis of symmetry, in that planar distortions should have only a small influence on the e.s.r. spectrum. Our experimental observations indicate the absence of

any large effects which can be attributed to the Jahn–Teller theorem.

Effects of the Cations.—Since THF has a dielectric constant of[27] 7.93 at 25°, and the dielectric constant of DME is estimated to be about the same,[28] extensive ion pairing might be expected in these solvents. Indeed, evidence for the presence of such complexes in solutions of anions prepared in these solvents from aromatic hydrocarbons by treatment with alkali metals has previously been obtained.[8,28,29] Hoijtink[8] has shown from conductivity measurements that aromatic anions are complexed with alkali metal cations, and that the amount of complexing varies with the cation and the solvent.

The observation of lithium and sodium hyperfine structure in the e.s.r. spectra of the cyclooctatetraenyl radical-anion is thus consistent with the expected ion-pair formation. Potassium hyperfine structure was not observed, but the great width of the lines in the potassium cyclooctatetraenide spectra and the relatively small magnetic moment of K^{39} might render the observation of such structure impossible. The lithium hyperfine splitting was found to be 0.2 gauss. If the wave function for the lithium in the complex is composed of contributions from a singlet wave function for the lithium ion and a doublet function representing the ground state of the lithium atom, the observed splitting measures the relative contributions of the two. The ratio of the lithium splitting in the complex to the splitting[30] in atomic Li^7 is $0.2/143 = 0.0014$. Similarly, the contribution of the doublet wave function in the sodium (Na^{23}) complex is approximately[30] $0.9/316 = 0.0028$. The extent of complexing of the cations in the different solvents appears to increase in the order Li–DME < Li–THF $\approx$ Na–DME < Na–THF. This series is in agreement with conductivity measurements of solutions of other anions.[31]

Electron exchange reactions, which limit the lifetime of the cyclooctatetraenyl radical-anion, determined the line width of most of the observed spectra. The increase in the line widths, as increasing amounts of potassium were allowed to react with a sample of cyclooctatetraene in THF, confirmed the related n.m.r. observations[5] which suggested that electron exchange was occurring between the radical-anion and the dianion, not between the radical-anion and the neutral molecule. The relative rates of the electron exchange between the radical-anion and the dianion may be estimated from the line widths. These rates depend on the cations in the order: Li < Na < K. A previous estimate from n.m.r. measurements on THF solutions showed that this rate was faster when K^+ was the cation than when Li^+ was by a factor of 10^4. A dependence of the rate upon solvent is indicated by the somewhat narrower lines in DME than in THF.

The rapidity of the exchange reaction between the cyclooctatetraenyl radical-anion and the dianion, and the slowness of the reaction between the radical-anion and the neutral molecule, are different from the usual behavior of aromatic hydrocarbons such as naphthalene. The electron exchange between the naphthalene radical-anion and the neutral molecule is extremely fast. The related radical-anion–dianion reaction[31,32] is slow, and in the perylene system the rate is so slow that it is dif-

(17) A. D. McLachlan, H. H. Dearman, and R. Lefebvre, *J. Chem. Phys.*, **33**, 65 (1960), and references cited therein.

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(19) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

(20) I. Bernal, P. H. Rieger, and G. K. Fraenkel, *ibid.*, **37**, 1489 (1962).

(21) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

(22) (a) D. E. Wood and H. M. McConnell, *J. Chem. Phys.*, **37**, 1150 (1962); (b) J. dos Santos-Veiga, *Mol. Phys.*, **5**, 639 (1962).

(23) Either chemical exchange reactions or small degrees of complexing may contribute to the line width. The value given is thus an upper limit for the line width of the uncomplexed radical.

(24) W. D. Hobey and A. D. McLachlan, *J. Chem. Phys.*, **33**, 1694 (1960).

(25) H. M. McConnell and A. D. McLachlan, *ibid.*, **34**, 1 (1961); H. M. McConnell, *ibid.*, **34**, 13 (1961).

(26) L. C. Snyder and A. D. McLachlan, *ibid.*, **36**, 1159 (1962).

(27) F. E. Critchfield, J. A. Gisson, Jr., and J. L. Hall, *J. Am. Chem. Soc.*, **75**, 6044 (1953).

(28) D. H. Geske and A. H. Maki, *ibid.*, **82**, 2671 (1960).

(29) S. I. Weissman, *Ann. Rev. Phys. Chem.*, **12**, 151 (1961), and references cited therein.

(30) N. F. Ramsey, "Molecular Beams," Oxford University Press, London, 1956, p. 255.
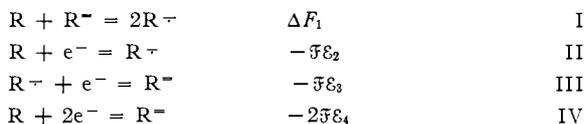
(31) A. C. Aten, J. Dielman, and G. J. Hoijtink, *Discussions Faraday Soc.*, **29**, 182 (1960).

(32) R. L. Ward and S. I. Weissman, *J. Am. Chem. Soc.*, **79**, 2086 (1957); S. I. Weissman, private communication.

ficult to measure. The ease of the exchange between the cyclooctatetraenyl radical-anion and the dianion and the difficulty of the reaction between the radical-anion and the neutral molecule suggest that the nuclear frameworks of the radical-anio· and the dianion are similar, but unlike that of the neutral molecule.

Most hydrocarbon ions show only small shifts in their electronic spectra on change of the cation,[33] but, while crystals of the potassium salt of the cyclooctatetraenyl dianion are nearly colorless,[5,34] solutions of cyclooctatetraene treated with alkali metals are colored, and the color varies with the metal.

Thermodynamics of the Radical Formation.—Consider the following reactions and corresponding free energy changes

$$R + R^= = 2R\cdot^- \qquad \Delta F_1 \qquad\qquad I$$
$$R + e^- = R\cdot^- \qquad -\mathfrak{F}\mathcal{E}_2 \qquad\qquad II$$
$$R\cdot^- + e^- = R^= \qquad -\mathfrak{F}\mathcal{E}_3 \qquad\qquad III$$
$$R + 2e^- = R^= \qquad -2\mathfrak{F}\mathcal{E}_4 \qquad\qquad IV$$

The reduction potentials are related to each other in that

$$2\mathcal{E}_4 = \mathcal{E}_2 + \mathcal{E}_3 \qquad (3)$$

and the free-energy change of reaction I is related to the two one-electron reduction potentials in that

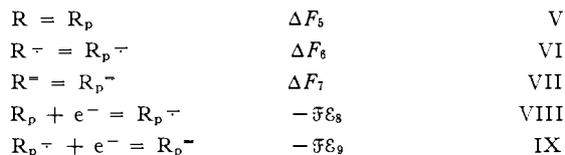$$\Delta F_1 = -\mathfrak{F}(\mathcal{E}_2 - \mathcal{E}_3) \qquad (4)$$

Since only a single two-electron polarographic wave is observed on reduction of the hydrocarbon in 96% dioxane–water,[6] $\mathcal{E}_4 > \mathcal{E}_2$, and, therefore, applying eq. 3 and 4

$$\Delta F_1 = 2\mathfrak{F}(\mathcal{E}_4 - \mathcal{E}_2) > 0 \qquad (5)$$

Thus, the polarographic data imply that the equilibrium I lies to the left, in agreement with e.s.r. data for the equilibrium radical concentration, and conversely.

Consider the following reactions by which the three species R, R·⁻, and R= are converted to the planar forms R_p, $R_p\cdot^-$, and $R_p^=$, and consider the reduction potentials of the latter

$$R = R_p \qquad \Delta F_5 \qquad\qquad V$$
$$R\cdot^- = R_p\cdot^- \qquad \Delta F_6 \qquad\qquad VI$$
$$R^= = R_p^= \qquad \Delta F_7 \qquad\qquad VII$$
$$R_p + e^- = R_p\cdot^- \qquad -\mathfrak{F}\mathcal{E}_8 \qquad\qquad VIII$$
$$R_p\cdot^- + e^- = R_p^= \qquad -\mathfrak{F}\mathcal{E}_9 \qquad\qquad IX$$

The various free-energy changes are related in that

$$\Delta F_1 = \Delta F_5 - 2\Delta F_6 + \Delta F_7 - \mathfrak{F}(\mathcal{E}_8 - \mathcal{E}_9) \qquad (6)$$
$$\Delta F_5 = \Delta F_7 - \mathfrak{F}(2\mathcal{E}_4 - \mathcal{E}_8 - \mathcal{E}_9) \qquad (7)$$
$$\Delta F_6 = (^1/_2)[\Delta F_5 + \Delta F_7 - \Delta F_1 - \mathfrak{F}(\mathcal{E}_8 - \mathcal{E}_9)]$$
$$= \Delta F_7 - (^1/_2)\Delta F_1 - \mathfrak{F}(\mathcal{E}_4 - \mathcal{E}_9) \qquad (8)$$

The experimentally estimated value of the equilibrium constant for reaction I at 25° is $K_1 = 3.7 \times 10^{-9}$ and 9×10^{-9}, respectively, for the K–THF and Li–THF samples. The average value of ΔF_1 is thus

$$\Delta F_1 = 11.2 \text{ kcal./mole } (0.485 \text{ e.v.}) \qquad (9)$$

The potential $\mathcal{E}_4$ has been measured directly, and the potentials $\mathcal{E}_8$ and $\mathcal{E}_9$ have been estimated by empirical

correlations to be (in volts)[6]

$$\mathcal{E}_4 = -1.12, \ \mathcal{E}_8 = -0.46, \ \mathcal{E}_9 = -0.86 \qquad (10)$$

Using these values in eq. 7 and 8

$$\Delta F_5 = \Delta F_7 + 21.2 \text{ kcal./mole} \qquad (11)$$
$$\Delta F_6 = \Delta F_7 + 0.5 \text{ kcal./mole} \qquad (12)$$

Equation 11 shows that the difference in the compression energy of cyclooctatetraene and of its dianion is about 21 kcal./mole, while eq. 12 indicates that, within experimental error, there is a negligible difference in the compression energy of the two anions. If the dianion is planar, then $\Delta F_7 = 0$, and from eq. 11 the compression energy of cyclooctatetraene, ΔF_5, is 21 kcal./mole. The assumption that both the dianion and the radical-anion are planar (i.e., $\Delta F_6 = \Delta F_7 = 0$) is consistent with eq. 12 within experimental error. It is also consistent with the observed rapidity with which electron exchange occurs between the dianion and the anion-radical and the observed position of the disproportionation equilibrium I. It is not consistent with the large proton hyperfine interaction observed for the radical. The possibility that the radical possesses a conformation with nearly 120° bond angles which is more stable than the planar conformation by only a small amount would account for the large hyperfine interaction and would not be inconsistent with the rapidity of the electron exchange reaction in the K–THF system.

The energy required to compress cyclooctatetraene to the planar conformation has also been experimentally studied in two other ways. From the rate of interconversion of single and double bonds in cyclooctatetraene, estimated from the change with temperature of the n.m.r.-splitting pattern of a proton attached to a C^{13} atom in the hydrocarbon, the free energy of activation for the reaction was concluded[35] to be about 13.7 kcal./mole at $-10°$. This was equated with the enthalpy of activation on the assumption, not necessarily valid,[36] that the entropy of activation was negligible. From the rate of racemization of 3,8-dicarboxy-1,2-benz-5,6-(3-bromobenz)-cyclooctatetraene, the activation energy of racemization of this compound was estimated to be 27 kcal./mole, and the suggestion was made that this should be an upper limit for the potential barrier to the inversion of cyclooctatetraene.[37] These interpretations are based on the implicit assumption that the transition states for the interconversions are in fact planar.

In the above discussion the role of the cations has, of necessity, been neglected. The large influence of the cations is apparent in the enthalpies and entropies measured for reaction I in Li–THF and K–THF solutions. In the former case $\Delta H_1 = +5.6$ kcal./mole and $\Delta S_1 = -20$ e.u., while in the latter $\Delta H_1 = -1$ kcal./mole and $\Delta S_1 = -40$ e.u. In the absence of further knowledge of the interactions between the oppositely charged ions, interpretation of these values is not possible.

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