obliterate the spectrum completely, are not present. Thus, the equilibrium must lie to the left.

The analogous equilibria in derivatives of polynuclear aromatic hydrocarbons have always been found to lie to the right.[18] The reversal of this equilibrium in the cycloöctatetraene system must be attributed to geometrical considerations: On the right of reaction (1) two molecules are flat, while on the left only one is so. That the electron affinity of the monoanion exceeds that of the hydrocarbon implies that the energy required to flatten the molecule when the first electron enters exceeds the extra coulombic energy the second must overcome. This conclusion, which will be discussed in detail in the future, has also been derived from two other independent experimental sources: (1) polarographic data, the reversible one-step two-electron reduction of cycloöctatetraene contrasting with the two-step one-electron reductions of polynuclear aromatic hydrocarbons in aprotic solvents[18,19,20]; and (2) electron spin resonance data, the cycloöctatetraenyl anion-radical[21] being directly observable.

The above and other data[12,21] make clear that the eight-membered ring with ten π electrons unlike the parent hydrocarbon must be highly resonance stabilized and flat, either due to the increased delocalization energy to be gained by aromatization in the new reference frame or to the relief of an unfortunate effect associated in a hypothetically planar symmetric cycloöctatetraene molecule with a formal partial occupancy of a degenerate pair of non-bonding molecular orbitals.[22]

(18) G. J. Hoijtink, E. De Boer, P. H. van der Meij and W. P. Weijland, *Rec. trav. chim.*, **75**, 487 (1956); N. S. Hush and J. Blackledge, *J. Chem. Phys.*, **23**, 514 (1955).

(19) S. Wawzonek, E. W. Blaha, R. Berkey and M. E. Runner, *J. Electrochem. Soc.*, **102**, 235–242 (1955); A. C. Aten, C. Büthker and G. J. Hoijtink, *Trans. Faraday Soc.*, **55**, 324 (1959); P. H. Given, *J. Chem. Soc.*, 2684 (1958).

(20) Preliminary experiments (with Mr. William Bahary) in this laboratory have confirmed the reversibility of the reduction in aqueous media by use of a.c. methods, while polarographic experiments in anhydrous acetonitrile indicate that protonation is not involved.

(21) T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, **32**, 1893 (1960).

(22) H. C. Longuet-Higgins, "Theoretical Organic Chemistry. Papers presented to the Kekule Symposium organized by the Chemical Society, London, 1958," Butterworths Scientific Publications, London, 1959, p. 9 ff.; D. P. Craig, Chapt. I in ref. 2.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK 27, NEW YORK
THOMAS J. KATZ

RECEIVED JUNE 6, 1960

THE CHEMICAL INTERACTION OF THE CYCLOOCTATETRAENYL ANIONS

Sir:

Experiments employing high resolution n.m.r. methods have uncovered a number of significant aspects of the chemistry of the cycloöctatetraenyl anions: the divalent anion[1] and the anion radical.[2]

In tetrahydrofuran solution 0.6 molar in cyclooctatetraene the resonance due to the eight cyclooctatetraene hydrogen nuclei appears as a single sharp peak 125.35 cps. to lower applied field than the lowest of the two solvent bands. As increasingly larger amounts of potassium metal are allowed to dissolve in this solution, the observations summarized in Fig. 1 are made: thus, (1) the sharp resonance line of cycloöctatetraene is seen to decrease in intensity without concomitant broadening; (2) when the peak has decreased to less than about 10% of its initial intensity a very broad band becomes superimposed directly on the initial peak, which itself remains sharp; (3) the initial sharp peak disappears as the broad peak narrows; and (4) finally, this latter peak narrows to a single sharp line of identical intensity to the resonance of the original cycloöctatetraene. In the course of these events, exactly two moles of potassium are observed to dissolve, and if more potassium is initially present, this excess remains at the end.

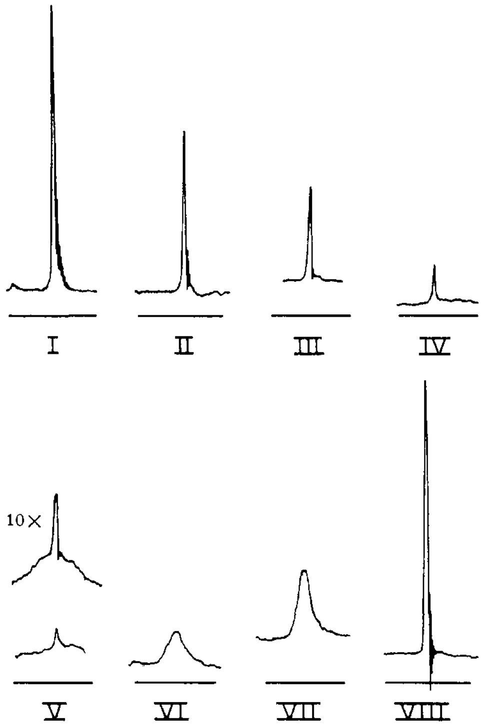


Fig. 1.—Cycloöctatetraene (0.6 formal, in THF) treated with increasing amounts of potassium, from I, no K to VIII, two moles; chemical shifts (from lower solvent band), half-width, and relative areas integrated over a 30-cycle range follow: I, 125.32 cps., <1 cps., 1.0; II, 126.50, <1 cps., 0.7; III, 127.20, <1 cps., 0.5; IV, 127.69; ?, ?; V, 127.94, ~18, 0.6; VI, 124.90, 8, 0.7; VII, 125.06, 4, 1.0; VIII, 125.00, <1, 1.0. Spectra were determined on a Varian 60 mc. high resolution n.m.r. spectrometer equipped with superstabilizer.

The resonance spectrum of the solvent remains throughout unchanged and exceedingly well resolved: The two tetrahydrofuran proton resonances are observed as complex spin-spin multiplets of over a dozen peaks each. Although the concentration of paramagnetic species must, therefore, be small (< 10^{-3} *M*), the presence of the cyclooctatetraenyl anion-radical in low concentrations (2.6×10^{-5} *M* at half-reaction[3]) has been demon-

(1) T. J. Katz, THIS JOURNAL, **82**, 3784 (1960).

(2) T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, **32**, 1893 (1960).

(3) T. J. Katz and H. L. Strauss, unpublished results.

strated.[2] It is electron exchange between the cyclooctatetraenyl dianion and the anion-radical, the proton resonance of which occurs nine megacycles outside the n.m.r. range to either side,[4] which readily accounts for the observed broad resonance line of the dianion just before two moles of potassium have dissolved. These data—the observed half-width of the broad line in spectrum V, the concentration ratio at this stage of dianion to cyclooctatetraene (about 100:3), and the known equilibrium constant for the disproportionation of the anion-radical[3] allow calculation of the second order rate constant for exchange between the dianion and the anion-radical: *ca.* 1×10^9 liters mole^{-1} sec.$^{-1}$.[5]

That the n.m.r. spectrum of cyclooctatetraene itself is throughout sharp implies that electron exchange between the anion-radical and the hydrocarbon is more than one hundred thousand times slower than between the anion-radical and the dianion, the exact opposite of the behavior observed in polynuclear aromatic systems.[6] The superposition of a sharp line due to cyclooctatetraene on the broad dianion peak, with little chemical shift between them implies that exchange between these species also is relatively slow. The lack of exchange reactivity of the hydrocarbon, cyclooctatetraene, by comparison with its dianion finds most ready explanation if *the dianion and the anion-radical are both planar*, the electron exchange being almost unactivated only in the absence of appreciable geometrical change.

The n.m.r. spectra in the lithium cyclooctatetraene system are equally revealing. The decrease in intensity of the continually sharp cyclooctatetraene resonance is accompanied by the rise of a line which narrows to field-determined width and expected intensity when two moles of lithium dissolve. At half reaction the lines are separated by 2 cycles. These observations and those of fully resolved *esr.* spectra of intensity comparable to those in the potassium series imply a considerably slower electron exchange rate (*ca.* ten thousandfold) in the lithium series. Although the cations were, for convenience, neglected above, their role is clearly significant.[7]

Acknowledgment.—The invaluable assistance of Mr. John S. Martin, who skillfully and patiently determined the n.m.r. spectra is gratefully acknowledged.

---

(4) Nine megacycles is in frequency units the previously reported[2] proton hyperfine interaction observed in the esr. spectrum of the anion-radical.

(5) The relationship between the half half-width, $\Delta\nu$, of the proton n.m.r. line due to exchange of the dianion ($R^=$) with the anion radical ($R^{\div}$) is

$$2\pi\Delta\nu = \frac{k(R^{\div})(\delta\omega)^2}{(\delta\omega)^2 + k^2(R^=)^2}$$

where k is the second order rate constant for exchange and $\delta\omega$ is the *esr.* proton hyperfine splitting in angular frequency. If $k(R^=) >> \delta\omega$ the *esr.* spectrum will be broad and in the n.m.r.

$$2\pi\Delta\nu = \frac{(R^{\div})(\delta\omega)^2}{k(R^=)^2}$$

That the width of the broad n.m.r. line is independent of temperature, while the enthalpy of disproportionation of the anion-radical is negative[3] seems in accord only with the choice of the exchange sharpening term. The independent deduction that the hyperfine splitting of the *esr.* spectrum would only be resolvable when small amounts (<10%) of potassium were dissolved is, in fact, confirmed.

(6) R. L. Ward and S. I. Weissman, This Journal, **79**, 2086 (1957); A. Carrington, F. Dravnieks and M. C. R. Symons, *J. Chem. Soc.*, 947 (1959).

(7) The relationship of the cations to the cyclooctatetraenyl anions is now still ill-defined, although strong ion pairing, such as probably occurs in the better known polycyclic aromatic alkali metal adducts, undoubtedly is involved.

(8) P. Balk, G. J. Hoijtink and J. W. H. Schreurs, *Rec. trav. chim.*, **76**, 813 (1957); G. J. Hoijtink, E. de Boer, P. H. van der Meij and W. P. Weijland, *Rec. trav. chim.*, **75**, 487 (1956).

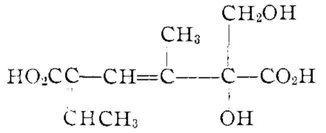
Department of Chemistry
Columbia University
New York 27, New York
Thomas J. Katz

Received June 6, 1960

STEREOCHEMISTRY OF NECIC ACIDS

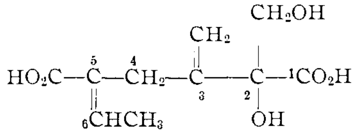
Sir:

In a previous paper[1] from this Laboratory, structure I was proposed for riddellic acid, the alkaline hydrolysis product of riddelliine.



$$\begin{array}{c} CH_3CH_2OH \\ HO_2CC-CH=C-C-CO_2H \\ CHCH_3OH \end{array}$$

I



$$\begin{array}{c} CH_2CH_2OH \\ HO_2C-\overset{5}{C}-\overset{4}{C}H_2-\underset{3}{C}-\underset{2}{C}-{}^1CO_2H \\ {}_6CHCH_3OH \end{array}$$

II

In view of the results recently reported on the structure of isoseneciphyllic acid,[2] the structure of riddellic acid has been reinvestigated[3] and evidence has now been obtained favoring structure II.

The establishment of structure II for riddellic acid and a similar structure for seneciphyllic acid[2] has reduced the unknown stereochemical factors in the structures of the majority of C_{10} necic acids to that of the *cis-trans* isomerism of the 5,6 double bond. The problem of the absolute configuration of the C_2 still has been unstudied.

The usefulness of n.m.r. spectroscopy in establishing the stereochemistry of olefins and olefinic acids has been demonstrated recently in several cases.[4,5,6,7] We have determined the n.m.r. spectra of a number of *cis* and *trans* trisubstituted olefinic acids and their esters and have gathered significant data pertaining to the geometry of these acids. The results are given in the table.

An examination of the table reveals: (1) The relative positions of the resonance lines of the olefinic proton are characteristic of its stereochemistry; (2) The shielding value of the single proton in the *trans* compound is always lower than that of the corresponding *cis* isomer. (3) An insignificant

---

(1) R. Adams and B. L. Van Duuren, This Journal, **75**, 4638 (1953).

(2) T. Masamune, *Chem. and Ind.*, 21 (1959).

(3) The details of these investigations will be presented shortly in a forthcoming publication.

(4) L. M. Jackman and R. H. Wiley, *Proc. Chem. Soc.*, 196 (1958).

(5) R. R. Fraser, *Can. J. Chem.*, **38**, 549 (1960).

(6) J. W. K. Burrell, L. M. Jackman and B. C. L. Weedon, *Proc. Chem. Soc.*, 263 (1959).

(7) S. Fujiwara, H. Shimizu, Y. Araba and S. Akahori, *Bull. Chem. Soc. Japan*, **33**, 428 (1960).