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Carbon Acidity. LII. Equilibrium Acidity of Cyclopentadiene in Water and in Cyclohexylamine[1]

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Abstract: Cyclopentadiene dissolves in water to form a 0.01 M solution. It is 50% ionized in 9 M NaOH, which corresponds to a pK_a of 16.0 (15.6 per hydrogen). The cesium ion pair pK in cyclohexylamine is 16.65 (16.25 per hydrogen) on a scale in which 9-phenylfluorene is assigned a pK of 18.49.

The stability of cyclopentadienyl anion is a cornerstone in modern organic and organometallic chemistry; it plays a key role, for example, in validating the Hückel $4n + 2$ rule. The pK_a value of 15 assigned to cyclopentadiene in Cram's MSAD scale[2] is indeed a rather low value for a hydrocarbon. This value has been quoted frequently, yet rests on an exceedingly tenuous experimental base, especially considering the significance of this number. In 1960, we derived a pK range of 16–20[3] on the basis of qualitative early experiments of Thiele.[4] This range was consistent with a pK of 17 deduced by a simple HMO correlation of hydrocarbon acidities available at that time.[3] In 1962, Dessy, Okuzumi, and Chen[5] found that a methanolic solution of cyclopentadiene can be carbonated in the presence of sodium methoxide but not sodium phenoxide and, accordingly, assigned a pK range of 14–15.

More recently, Bowden et al.[6] have quoted a pK of 15, apparently for aqueous dimethyl sulfoxide solutions. Breslow and Washburn[7] determined the pK_a of cyclopentadiene with lithium dicyclohexylamine and tetramethylenediamine in tetrahydrofuran relative to *tert*-butyl alcohol. They obtained a value of 18.2 in this medium at 35 °C by observing the intensity of the NMR spectrum of cyclopentadienyl anion as a function of *tert*-butyl alcohol. Bordwell et al.[8] have recently communicated a value of 18.1 for the dimethyl sulfoxide standard state.

Schaeffer[9] has reported a value of 15.3 for the pK_a of cyclopentadiene based on a comparison of chemical shift differences between carbon acids and their lithium salts in ether or THF with pK's on the MSAD scale. Finally, Butin et al.[10] have reported that the MSAD scale pK of cyclopentadiene is consistent with polarographic reduction studies of organomercury compounds. Both of the latter determinations have important limitations and cannot be regarded as reliable.

We have recently found that cyclopentadiene is soluble in water to the extent of 0.0103 mol $l.^{-1}$.[11] Spectral changes in the presence of sodium hydroxide permit assignment of a pK value for the aqueous solution. The equilibrium cesium ion pair pK of cyclopentadiene in cyclohexylamine was also determined using our standard hydrocarbon indicators in order to establish a direct comparison of cyclohexylamine and water pK scales.

Experimental Section

Materials. Cyclopentadiene was obtained from its dimer (Aldrich) by distillation onto molecular sieves. Analyses by GC showed only one peak. The cyclopentadiene was used within an hour of its preparation.

9-Phenyl-3,4-benzofluorene (7-phenyl-7*H*-benz[*c*]fluorene) (PBF) and 1,12-(*o*-phenylene)-7,12-dihydropleiadene (PDP) and their cesium ion pair pK's in cyclohexylamine have been described previously.[12] PDP was prepared from material kindly supplied by Professor P. Landsbury.

Equilibrium Acidities. Cyclopentadienylcesium does not absorb in the accessible region in cyclohexylamine solution; hence, measurements in this solvent were made by the single indicator method described previously.[13] The general method involves determination of the absorption of a known mixture of indicator hydrocarbon and its cesium salt in cyclohexylamine on addition of a known amount of cyclopentadiene. The principal change in the recorded procedure was the use of a Vacuum Atmospheres recirculating glovebox, which allowed many of the operations to be carried out readily in an argon atmosphere. Spectroscopic measurements were made with a Cary 118 spectrometer and refer to room temperature. The concentrations of cyclopentadiene added were in the range 0.02–0.16 M, but its cesium salt in equilibrium was 0.1–2.3 $\times 10^{-3}$ M. The results with the two indicators used are summarized in Table I.

Equilibrium measurements in water were made with stock solutions of concentrated carbonate-free sodium hydroxide[14] and aqueous solutions of cyclopentadiene. Freshly distilled cyclopentadiene was shaken with distilled water and centrifuged. The saturated aqueous solution was diluted by a factor of 20 for the stock solution. Various aliquots of this stock solution were added to the NaOH solution cooled in ice. Heat is evolved on mixing, and ice baths were used to minimize evaporation. The stoppered solutions were allowed to warm to room temperature and were pipetted into a 1-cm quartz spectrometer cell. Measurements were made on a Cary 118 spectrophotometer using a corresponding NaOH solution as reference. The absorbance at each wavelength was divided by the cyclopentadiene concentration added to derive an apparent extinction coefficient. The results are summarized in Figure 1.

Results and Discussion

Aqueous solutions of cyclopentadiene (CpH) show a definite $\lambda_{\max}$ 238 nm. As this solution is made more basic, the results in Figure 1 show that this $\lambda_{\max}$ tends to flatten and change to increasing absorption at shorter wavelengths. Unfortunately, the $\lambda_{\max}$ of cyclopentadienyl anion occurs at

Table I. Cesium Ion Pair Acidities in Cyclohexylamine

Indicator	No. of runs	K^c	pK^d
PBF[a]	4	0.118 ± 0.02	16.60 ± 0.07
PDP[b]	5	0.046 ± .008	16.70 ± 0.04
		av pK	16.65 ± 0.05
		pK per hydrogen	16.25 ± 0.05

[a] 9-Phenyl-3,4-benzofluorene; pK = 15.67; λ_{max} in cesium cyclohexylamide (CSCHA) 524, 493 nm (ref 12). [b] 1,12-(*o*-Phenylene)-7,12-dihydropleiadene; pK = 15.36; λ_{max} in CSCHA 392, 446 nm (ref 12). [c] K = [HInd][R$^-$Cs$^+$]/[Ind$^-$Cs$^+$][RH] in which HInd is the indicator hydrocarbon and RH is cyclopentadiene. The concentrations are those at equilibrium at room temperature. Two independent measures of K were made in each run using both λ_{max} of the indicators. [d] pK_a of cyclopentadiene.

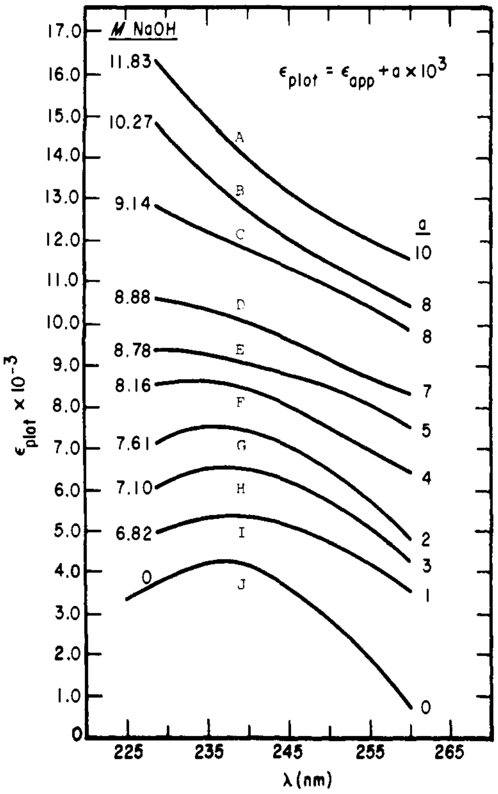

Figure 1. Spectra of cyclopentadiene in aqueous sodium hydroxide solutions. Each spectrum is recorded as $\epsilon_{plot} = \epsilon_{app} + 10^3 a$ in which a is used to offset successive spectra for clarity.

wavelengths too short for direct observation in aqueous sodium hydroxide solutions. Furthermore, because of the readiness of cyclopentadiene to dimerize and the ease of oxidation of its sodium hydroxide solutions despite attempts to exclude air, it was difficult to obtain reproducible apparent extinction coefficients of these alkaline solutions. Nevertheless, by observing the change in the features of the cyclopentadiene spectra with varying sodium hydroxide concentrations, a reliable value of the pK_a of cyclopentadiene in water can be derived.

The spectrum of cyclopentadienylpotassium (CpK) in ether solution has been reported.[15] This spectrum is shown as curve A in Figure 2. The other curves in Figure 2 correspond to mixtures of CpH and Cp$^-$ as calculated from the equation

$$A_{app} = \epsilon_{CpK} f_{Cp^-} + \epsilon_{CpH}(1 - f_{Cp^-})$$

in which ϵ are extinction coefficients and f is the fraction of cyclopentadiene present as the anion. The general shapes of

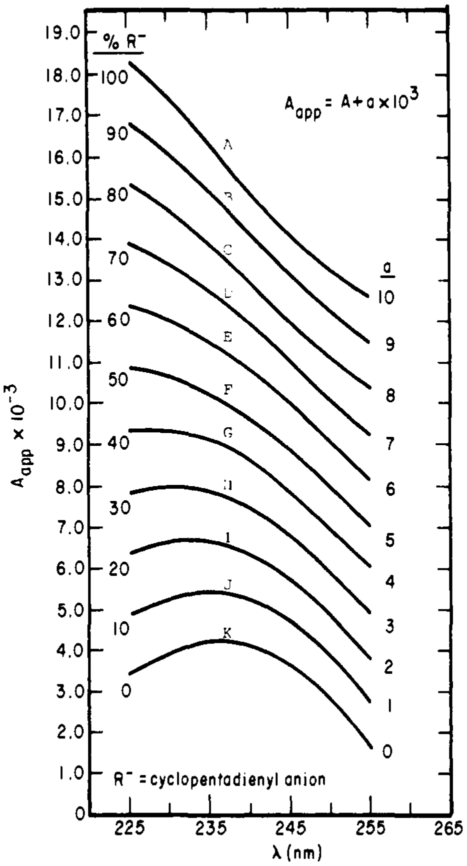

Figure 2. Absorbance curves for various mixtures of cyclopentadiene and cyclopentadienyl anion (R$^-$).

Table II. H_- as a Function of [NaOH] at 25 °C[a]

[NaOH], M	H_-	[NaOH], M	H_-
5.0	15.20	9.0	15.97
6.0	15.40	10.0	16.20
7.0	15.62	11.0	16.42
8.0	15.75	12.0	16.58

[a] Reference 16.

these curves correspond very well to those found in the NaOH solutions. In particular, in curve F in Figure 2, for equal amounts of carbon acid and anion, the maximum associated with CpH has vanished, and the curve is just monotonic. For the aqueous solutions, this behavior is shown for NaOH concentrations close to 9 M. Accordingly, the pK of cyclopentadiene must equal the H_- at this concentration.

Some H_- values for aqueous sodium hydroxide derived from indoles are summarized in Table II[16] and lead to a value of 16.0 for the pK of cyclopentadiene. The table shows that H_- is not a sensitive function of NaOH concentration in this region. Moreover, this represents a relatively small extrapolation from the dilute NaOH region, and this result should not be changed significantly by the use of other H_- indicators. Although extinction coefficients for cyclopentadiene and its anion were necessarily derived from other solvents, even a 25% error in either value would contribute an error of only ±0.1 to the pK. Consequently, an uncertainty of about ±0.2 seems reasonable. This pK_a value for cyclopentadiene is undoubtedly now the most reliable pK for a hydrocarbon in the aqueous standard state. For many purposes, the statistically corrected pK of 15.6 per hydrogen would be more appropriate.

The cesium ion pair pK or pK_{CsCHA} of cyclopentadiene in cyclohexylamine is found to be 16.25 (per hydrogen) (Table I), a value remarkably close to the aqueous pK. The pK_{CsCHA} derives from ion pair equilibria involving various indicator hydrocarbons having delocalized carbanions and refers to an assigned "pK" of 18.49 for 9-phenylfluorene. This assignment is based on several measurements of 9-phenylfluorene in mixed aqueous organic solvents[17] using the H_- method; that is, subject to the usual approximations of the H_- procedure and their dependence on the indicator used, the pK of 18.49 assigned to 9-phenylfluorene is that for the aqueous standard state. If the ion pair equilibria in cyclohexylamine correspond to ionic equilibria in water, the derived pK's for other hydrocarbons are also those for the aqueous standard state. In particular, the true aqueous pK of 9-phenylfluorene cannot differ much from the assigned value of 18.49. For other conjugated hydrocarbons having extensively delocalized carbanions, the approximate independence of relative pK's to solvent[18] suggests that the pK_{CsCHA} values are actually reasonable measures of aqueous ionic pK's. The agreement of the current direct comparison of cyclopentadiene in water and in cyclohexylamine confirms this view. That is, a series of assumptions and approximations comes full circle with satisfactory agreement. This argument applies, of course, only to those carbanions in which the anionic charge is sufficiently delocalized to avoid specific ion pair interaction effects.

Finally, we note that the current experimental determinations are close to previously assigned aqueous pK values. No significant changes in past applications and correlations involving cyclopentadiene are required, but these past applications are now given a sound experimental base.

References and Notes

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Organic Transition States. V. The Diels–Alder Reaction[1]

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Abstract: Ab initio molecular orbital theory has been applied to the study of the Diels–Alder condensation of ethylene and 1,3-butadiene. We find the reaction to proceed preferentially in a concerted manner via a symmetric transition state. Two-step pathways linking reactants and products are found to be higher in energy. Although our calculations suggest that the hex-2-ene-1,6-diyl diradical is locked in a set of conformational niches considerably below the energy of the concerted transition state, they by no means indicate its participation as an intermediate at the top of least activation pathway. Rather its only connection to the reaction is a transition state some 2 kcal/mol higher than the concerted.

Introduction

The Diels–Alder reaction is central to the history of organic chemistry.[7-11] Of major interest has been the deduction from recent experiments of the energy profile of the reaction,[12,13] a full knowledge of which is necessary to perfect our present understanding of the stereochemistry[7b,10,14,15] at both diene and dienophile, the endo-exo ratio,[7b,16,17] the regioselectivity,[8,11e,17d,18,19] the influence of donor- or acceptor-like substituents on the reaction rate,[7c,11d,20,21] the influence of catalysts[22,23] such as Lewis acids, and other effects such as the influence of pressure[24] and the "syn-anti" effect.[25]

Because of the relatively large number of atoms involved, only a few quantum-mechanical attempts have been made to evaluate the energy profile, even on the barest of all Diels–Alder reactions, the addition of ethylene to 1,3-butadiene. Historically, the earliest of such attempts, reviewed by Streitwieser,[26] employed Hückel molecular orbital calculations and were directed at relating the electronic properties of the diene to its reactivity. A second wave of calculations[17,19,21,23] used perturbation theory on a limited number of molecular orbitals, or even only the HOMO and LUMO frontier orbitals, to calculate numerically the relative π-stabilization energies of Diels–Alder transition states.

The first *all-valence electron* calculation is due to Kikuchi.[27] He restricted himself to the perfectly concerted symmetric process in which both new σ bonds are formed at the same rate. Unfortunately, although Kikuchi found an interesting electron transfer from 1,3-butadiene to ethylene in the incipient phase of the reaction, he discovered no energy maxima corresponding to transition states in the total ener-