and 5 drops of Me_4Si were added. The resulting solution was nearly 0.3 M. The small quantity of C_6D_6 was enough to provide the deuterium lock for the Varian CFT-20 but not enough to interfere with the ^{13}C resonances of the compounds.

Acknowledgments. This work was supported by the National Science Foundation (Grant No. CHE 79-05542) and by a research grant from the North Atlantic Treaty Organization (Grant No. 1101). We are very grateful to Mr. Richard Press of Northwestern University for carrying out a pK_a measurement in pure Me_2SO, to Professor Frederick G. Bordwell for valuable discussions, and to Professor Calvin D. Ritchie for useful comments on the manuscript.

Supplementary Material Available: Table IX, absorptivity of the 4-nitrodiphenylamine anion, Table X, absorptivity, of the 4-nitroaniline anion in Me_2SO-H_2O, Table XI, plots of H_- vs. log c_b for 4-NO_2-DPA indicator, and Table XII, comparison of H_- values from Table I with those predicted by Dolman and Stewart (4 pages). Ordering information is given on any current masthead page.

Homolytic Addition to Benzene. Rate Constants for the Formation and Decay of Some Substituted Cyclohexadienyl Radicals[1a]

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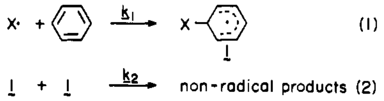
Received March 16, 1981

Abstract: Addition to benzene of $Et_3Si\cdot$, $(EtO)_2\dot{P}O$, and $C_6H_5\cdot$ led to cyclohexadienyl radicals which were detected by EPR and optical modulation spectroscopy. The rate constants for addition of $Et_3Si\cdot$ and $(EtO)_2\dot{P}O$ were found to be $\geq 10^5$ and 2.9×10^3 M^{-1} s^{-1}, respectively, while the rate constants for self-reactions of the resulting cyclohexadienyl radicals were found to be 8.9×10^8 and 6.8×10^8 M^{-1} s^{-1}. EPR parameters and UV-visible spectra of the cyclohexadienyl radicals were reported.

Homolytic aromatic substitution has been the subject of extensive investigation since 1937, when Hey and Waters reviewed the mechanism for the phenylation of aromatic substrates.[2] In its simplest form, the mechanism involves addition of a radical X· to benzene (reaction 1) to form a substituted cyclohexadienyl radical, **1**. Self-reactions of **1** lead to nonradical products, (reaction 2), amongst which are cyclohexadienes and the X-substituted benzene. It is the rate of generation of X·, the concentration of benzene, and the magnitudes of k_1, k_{-1}, and k_2 which determine the reaction products. However, essentially all of the research in this area has been based upon product studies alone[3,4] and rate constants for the elementary reactions of the substituted cyclohexadienyls have rarely been measured or estimated.[3]



a, X = Et_3Si;
b, X = Me_3Si;
c, X = $(EtO)_2PO$;
d, X = Ph

In this work, we have used both electron paramagnetic resonance (EPR) and optical modulation spectroscopy to characterize the spectra of the substituted cyclohexadienyl radicals, **1a–d**, and to measure some of the rate constants for their formation and decay.

Experimental Section

Materials. All materials were commercially available and, with the following exceptions, were used as received. Benzene (Aldrich, Gold Label) was treated with concentrated sulfuric acid, neutralized with aqueous sodium carbonate, and washed with distilled water. It was then dried over magnesium sulfate before being distilled from calcium hydride. Di-*tert*-butyl peroxide (K & K) was washed with aqueous silver nitrate and water, to remove olefinic impurities. It was dried over magnesium sulfate and was finally passed through alumina to remove hydroperoxide impurities. Diethyl phosphite was purified by distillation.

Apparatus. EPR spectra were recorded by using a Varian E104 spectrometer. Radicals were generated by direct photolysis of samples placed in the EPR cavity. The photolysis source was a 500-W mercury arc lamp, and the output of the lamp was filtered through an aqueous solution of cobalt and nickel sulfates which removed much of the visible and most of the infrared radiation. Radical concentrations were measured by double intergration of appropriate lines in the EPR spectra and were calibrated against the signal obtained from a standard, benzene solution of diphenylpicrylhydrazyl. The EPR signal produced by a ruby disk placed inside the cavity was used to correct for differences in sensitivity of the spectrometer to the different solutions. The techniques of kinetic EPR spectroscopy have been described in detail elsewhere.[7]

The optical modulation spectrometer used in this work follows closely upon the design developed by Huggenberger and Fischer[8,9] and has been described elsewhere.[10] Briefly, radicals were generated by photolysis of a solution which was flowed slowly through a standard fluorescence cell. The photolysing light (1000-W Hg/Xe) was modulated as a sin wave by

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(1) (a) Issued as NRCC publication No. 19817. (b) NRCC. (c) University of Strathclyde. (d) Chelsea College.

(2) Hey D. H.; Waters, W. A. *Chem. Rev.* **1937**, *21*, 169-208.

(3) For a review, see: Perkins, M. J. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, pp 231-271.

(4) Some substituted cyclohexadienyls have been detected in solution, e.g., in ·OH addition to benzene[5] and in additions to highly substituted benzenes which gave rise to persistent radicals.[6]

(5) Dixon, W. T.; Norman, R. O. C. *Proc. Chem. Soc., London* **1963**, 97-98. Jefcoate, C. R. E.; Norman, R. O. C. *J. Chem. Soc. B* **1968**, 48-53. Dorfman, L. M.; Bühler, R. E.; Taub, I. A. *J. Chem. Phys.* **1962**, *36*, 549-551. See also: Raghavan, N. V.; Steenken, S. *J. Am. Chem. Soc.* **1980**, *102*, 3495-3499.

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(7) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 193-200.

(8) Huggenberger, C.; Lipscher, J.; Fischer, H. *J. Phys. Chem.* **1980**, *84*, 3467-3474.

(9) Huggenberger, C.; Fishcer, H. *Helv. Chim. Acta* **1981**, *64*, 338-353.

(10) Marriott, P. R.; Castelhano, A. L.; Griller, D. *Can J. Chem.* submitted for publication.

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Table I. EPR Parameters for Substituted Cyclohexadienyl Radicals Measured at 25 °C

radical	g	a^{H_1}, G	$a^{H_{2,6}}$, G	$a^{H_{3,5}}$, G	a^{H_4}, G	a^P, G
	2.002 69[a]	48.0	9.00	2.69	13.14	
1a	2.002 77	40.0	8.13	2.43	12.43	
1b	2.002 80	38.0	8.25	2.43	12.25	
1c	2.002 97	44.7	9.05	2.76	12.96	111.5
1d	2.002 70	45.2	8.92	2.75	13.18	

[a] Eiben, K.; Schuler, R. H. *J. Chem. Phys.* 1975, *62*, 3093-3108.

using a mechanical chopper fitted with sin-shaped irises. The sample was monitored by using an optical detection system consisting of a xenon lamp, monochromator, and photomultiplier tube which were arranged at right angles to the photolyzing beam. The signal from the photomultiplier tube was fed into a ratiometer and then into a lock-in amplifier, (PAR 124A). The reference channel of the lock-in amplifier was driven at the modulation frequency by the signal from a photocell placed in part of the photolyzing light beam. The signals detected in this way were due to transient intermediates, starting materials, and products, all of which could be spearated because of their different phase relationships with the reference signal.[9]

Kinetic experiments using the modulation spectrometer were carried out at a fixed wavelength. The photolyzing beam was filtered by using an aqueous cobalt/nickel sulfate solution which effectively provides a photolysis window between 310 and 340 nm. It was further filtered with glass cutoff filters so that the transmission of light through the sample cell was >90%, ensuring that a uniform radical distribution was obtained throughout the sample. Glass cutoff filters were used in the monitoring beam so that this beam did not cause significant sample photolysis. Analyses for *tert*-butyl alcohol were carried out by using a Varian 3600 vapor-phase chromatograph (VPC) equipped with a 20 ft × $^1/_8$ in. 20% Carbowax 20M column.

Results and Discussion

In EPR studies, X· were generated by UV irradiation of isooctane solutions containing benzene (10% v/v) and the reagents shown in eq 3–5.[11a] For reactions 6 and 7[11] benzene was used

$$t\text{-BuO—OBu-}t \xrightarrow{h\nu} 2t\text{-BuO}\cdot \tag{3}$$

$$t\text{-BuO}\cdot + \text{XH} \rightarrow t\text{-BuOH} + \underset{\textbf{a–c}}{\text{X}\cdot} \tag{4}$$

$$t\text{-BuO}\cdot + (\text{EtO})_2\text{POP(OEt)}_2 \rightarrow t\text{-BuOP(OEt)}_2 + \underset{\textbf{c}}{(\text{EtO})_2\dot{\text{P}}\text{O}} \tag{5}$$

$$t\text{-BuO}\cdot + \text{Ph}_3\text{As} \rightarrow t\text{-BuOAs(Ph)}_2 + \underset{\textbf{d}}{\text{Ph}\cdot} \tag{6}$$

$$\text{PhC(=O)OOC(=O)Ph} \xrightarrow{h\nu} 2\text{CO}_2 + 2\underset{\textbf{d}}{\text{Ph}\cdot} \tag{7}$$

as solvent. The concentrations of liquids were typically 5–10% (v/v), while those of solids were ca. 0.5 M. These systems gave rise to the EPR spectra of the substituted cyclohexadienyl radicals **1a–d**.[12]

The EPR parameters of radicals **1a–d** listed in Table I. are similar to those for cyclohexadienyls obtained by other methods.[13] In particular they show large hyperfine splittings (ca. 40 G) due to the hydrogen atoms geminal to the X substituents. Attempts were made to add other radicals to benzene, e.g. X· ≡ *t*-Bu·, *t*-BuO·, $CF_3O\cdot$, *n*-BuS·, *t*-BuS·, and *n*-$Bu_3Sn\cdot$, all of which were generated by standard methods.[11a] However, no cyclohexadienyls were detected by EPR over the range of temperatures, +25 to −60 °C. This does not necessarily imply that addition is much slower in these cases but may be due to the fact that the reverse reaction is much more efficient; i.e., $k_1 << k_{-1}$. So far as we are aware, products of addition have not been detected in those cases which failed to give spectra of cyclohexadienyls.[11b]

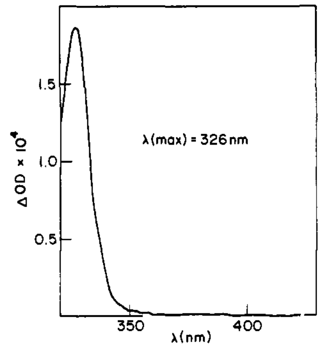

Figure 1. Absorption spectrum of radical **1a**.

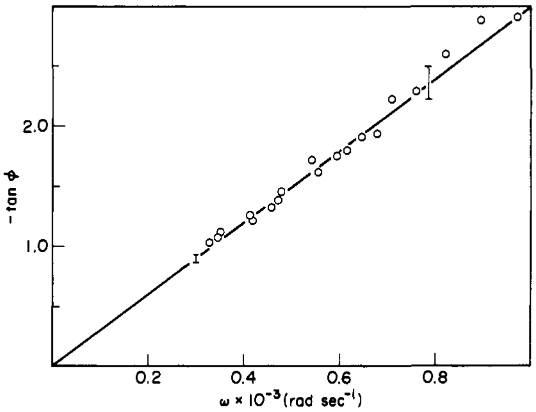

Figure 2. Frequency dependence of ϕ for **1a**.

The EPR technique is particularly advantageous in that the hyperfine splitting patterns generally allow an unequivocal assignment of the radical being formed. However, its major disadvantage is that the spectral signal to noise levels are often poor (<8:1 for **1a–d**) which makes kinetic analysis experimentally difficult. By contrast, the optical absorption spectra of radicals rarely contain fine structure, but current experimental techniques produce signal to noise levels which are more suitable for accurate kinetic analysis. Clearly a combination of techniques can lead to accuracy in both assignments and kinetic data. We therefore applied the optical technique of modulation spectroscopy to complement our EPR results.

Modulation spectroscopy has been used in a variety of applications such as the measurement of fluorescence lifetimes and the study of transients in the gas phase.[14] Recently Fischer and Huggenberger[9] have developed a modulation spectrometer for the study of radicals in the liquid phase, and we have used such as instrument in this work.

Radicals, X·, were generated by using the reactions employed for the EPR experiments, the only difference being that the solutions were flowed through the sample chamber so as to avoid sample depletion and product accumulation. In the absence of benzene, only weak transient absorptions were detected. However, addition of benzene led to strong signals in the region 310–350 nm;[15] see Figure 1. These absorptions were assigned to radicals

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(11) (a) Griller, D. *Magn. Reson. Rev.* **1979**, *1*, 1–23. (b) We thank Professor C. Walling for pointing this out.

(12) For related product studies, see: Eaborn, C.; Jackson, R. A.; Pearce, R. *J. Chem. Soc., Chem. Commun.* **1967**, 920. De Tar, D. F.; Long, R. A. J.; Rendleman, J.; Bradley, J.; Duncan, P. *J. Am. Chem. Soc.* **1967**, *80*, 4051–4057. Sakurai, H.; Hosomi, A. *Ibid.* **1971**, *93*, 1709–1714.

(13) Berndt, A. "Landolt-Börnstein, New Series", Group II, Part b; Fischer, H., Hellwege, K.-H., Eds.; Springer-Verlag: New York, 1977; Vol. 9.

(14) See, for example: Hunziker, H. E. *IBM J. Res. Dev.* **1971**, *15*, 10–26. Atkinson, R.; Cvetanovic, R. J. *J. Chem. Phys.* **1971**, *55*, 659–663. Günthard, H. H. *Ber. Bunsen ges. Phys. Chem.* **1974**, *78*, 1110–1115. Paukert, T. T.; Johnston, H. S. *J. Chem. Phys.* **1972**, *56*, 2824–2838. Parkes, D. A.; Paul, D. M.; Quinn, C. P.; Robson, R. C. *Chem. Phys. Lett.* **1973**, *23*, 425–429. Parkes, D. A.; Paul D. M.; Quinn, C. P. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1935–1951.

(15) The lower limit for detection is a consequence of strong absorption by starting materials.

Table II. Rate Constants for the Formation and Decay of Substituted Cyclohexadienyl Radicals Measured at 25 °C[a]

	radicals	
	1a	**1c**
I_0, M s^{-1}	1.1×10^{-4}	6.7×10^{-5}
τ, s^{-1}	2.3×10^{-3}	3.3×10^{-3}
k_1, M^{-1} s^{-1}	$\geqslant 10^5$	2.9×10^3
$2k_2$, M^{-1} s^{-1}	8.7×10^8	6.8×10^8
λ, nm	320 (sh)	326 (max)
ϵ_λ, M^{-1} cm^{-1}	1.1×10^3	2.5×10^3

[a] Errors ±30% and arise mainly in measurements of I_0 or radical concentrations.

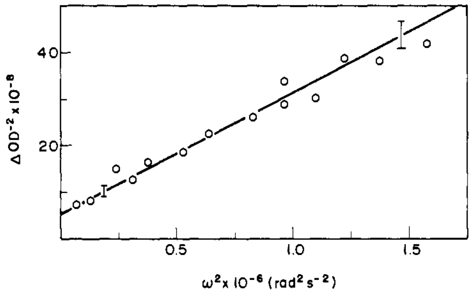

Figure 3. Frequency dependence of ΔOD for **1a**.

1a–d and are similar to those observed for cyclohexadienyl in a matrix isolation experiment.[16]

Rate constants for the self-reactions of **1a** and **1c** were determined by modulation spectroscopy. With use of the lock-in amplifier, signals due to the radicals were resolved into components which were out of phase and in phase with the photolyzing light. The ratio of these components was tan ϕ, where ϕ is the phase angle and their vector sum was proportional to ΔOD[8,9] which was the modulated part of the optical density of the transient.

Plots of $-\tan \phi$ vs. the modulation frequency ω gave the half-lives, τ, for the radicals, eq 8 (Figure 2). Values of τ^{-2} were

$$\omega\tau > 1 \qquad -\tan \phi = \omega\tau \tag{8}$$

proportional to I_0, the maximum rate of radical generation during the modulation cycle, when the latter was varied by the use of neutral density filters. This demonstrated that the radicals were destroyed in bimolecular processes[17] (eq 2 and 9). The half-lives

$$\tau^{-2} = 4k_2 I_0 \tag{9}$$

for radicals **1a** and **1c** are reported in Table II along with values of I_0, which were measured by analyzing the photolyzed mixture by VPC for *tert*-butyl alcohol. Rate constants for self-reaction were calculated from these data (eq 9) and are shown in Table II.

An alternative method of data analysis yielded the extinction coefficients, ϵ, of the radicals. In this approach, plots of ΔOD^{-2} vs. ω^2 gave straight lines of slope a and intercept b which are defined in terms of ϵ, τ, I_0, and l where the latter is the path length of the sample cell in the monitoring direction (eq 10 and 11).

$$a = 4(\epsilon l I_0)^{-2} \tag{10}$$

$$b = 4(\epsilon l I_0 \tau)^{-2} \tag{11}$$

Values of τ were obtained by taking the ratio of $a{:}b$ and were, within experimental error, the same as those obtained in the first graphical procedure (Figure 3). The extinction coefficients obtained by this technique are reported in Table II. The principal source of error in these measurements arises from inaccuracies in the product analysis required to determine I_0. The strong absorption bands at ca. 320 nm observed for these cyclohexadienyl radicals are typical for radicals in which the unpaired electron is extensively delocalized and are quite different to the spectra of alkyl radicals which have strong absorptions below 280 nm.[9,10]

The rate constants for addition to benzene (k_1) can be measured by EPR spectroscopy if conditions can be adjusted so that X· and **1** can be detected at the same time[7] (eq 12). This was a simple

$$\frac{[C_6H_6]}{[\mathbf{1}]} = \frac{2k_2}{k_1}\left\{\frac{[\mathbf{1}]}{[X\cdot]} + 1\right\} \tag{12}$$

matter for **1c** since when isooctane was used as the solvent and $[C_6H_6] = 0.5$ M it was found that $[(EtO)_2\dot{P}O)] = 3.1 \times 10^{-7}$ M and $[\mathbf{1c}] = 6.6 \times 10^{-7}$ M. Combining these results with the value of $2k_2$ (**1c**) obtained by modulation technique gives $k_1(\mathbf{1c}) = 2.9 \times 10^3$ M^{-1} s^{-1}. This rate constant is at least 100 times less than the rate of addition of $(EtO)_3\dot{P}O$ radicals to 1-hexene, since in an experiment where benzene was replaced by 1-hexene (0.01 M), the olefin scavanged all $(EtO)_3\dot{P}O$ radicals. Similar experiments were carried out with $X{\equiv}Et_3Si$ and $[C_6H_6] = 0.01$ M using a flow system. Despite this low benzene concentration, only the spectrum of **1a** could be detected, indicating that $k_1(\mathbf{1a}) \geq 10^5$ M^{-1} s^{-1}.

Summary

Substituted cyclohexadienyl radicals formed by radical addition to benzene can be detected by EPR and optical modulation spectroscopy. With use of these techniques, rate constants for some of the elementary reactions in homolytic aromatic substitution have been measured. The reactions and their kinetics are easily rationalized if benzene is regarded as a somewhat unreactive olefin.[18]

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(16) Jordan, J. E.; Pratt, D. W.; Wood, D. F. *J. Am. Chem. Soc.* **1974**, *96*, 5588–5590. The weak absorptions at ~560 nm found for cyclohexadienyls formed by H abstraction in solution were not detected in these experiments; see: Effio, A.; Griller, D.; Ingold, K. U.; Scaiano, J. C.; Sheng, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 6063–6068.

(17) The EPR results show that the signal of X· can be effectively quenched at the benzene concentrations specified, and the modulation data show that decay kinetics for the cyclohexadienyls are second order. This implies that contributions form k_{-1} to the observed kinetics are negligible at the relatively high radical concentrations attained in this work.

(18) Jackson, R. A. *J. Chem. Soc., Chem. Commun.* **1974**, 573–574.