

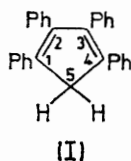
Radical-anion Intermediates. Part VII.¹ Reactions of the 1,2,3,4-Tetra-phenylcyclopenta-1,3-diene Radical Anion

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1,2,3,4-Tetraphenylcyclopenta-1,3-diene in tetrahydrofuran reacts with alkali metals at 203 K to form a radical anion. At higher temperatures the radical anion is unstable and decays to give the corresponding anion. The rate of the decay is sensitive to the nature of the counterion. The e.s.r. spectrum of the radical anion has been obtained and is dominated by a large (1 : 2 : 1) triplet splitting of 2.53 mT.

THE preparation of the fluorenyl anion by reaction of fluorene with an alkali metal in a solvent such as tetrahydrofuran proceeds *via* the fluorene radical anion.² The radical anion is unstable and decays quickly to the anion. It is necessary to study the reaction with alkali metal at low temperatures (*ca.* 200 K) if the radical anion is to be observed.

The fluorenyl anion has been of interest to other workers since it has proved to be a suitable system for the study of equilibria between contact and solvent separated ion pairs.³⁻⁵ Similar equilibria have also been found for the fluorene radical anion² although they have naturally proved more difficult to study quantitatively due to the decay which occurs at higher temperatures. We have studied the radical anions of a number of substituted fluorenes^{6,7} and benzofluorenes⁸ in addition to that of fluorene itself, and have found that the decay can be kinetically either first or second order with respect to the radical anion. The kinetic order found experimentally appears to be determined by a number of factors including temperature, solvent, and the nature of the counterion.



It was hoped that a study of the radical anion of 1,2,3,4-tetraphenylcyclopenta-1,3-diene (I) might prove of interest since it would be expected to behave somewhat similarly to fluorene and steric factors might well be found to be significant in the radical anion decay.

EXPERIMENTAL

All operations were performed using standard high vacuum techniques.

Materials.—Tetrahydrofuran was purified as described.⁹ 1,2,3,4-Tetraphenylcyclopenta-1,3-diene (Emanuel) was recrystallised from absolute alcohol immediately before use. Lithium, sodium, and potassium were washed in light petroleum before use.

Procedure.—Tetrahydrofuran solutions of 1,2,3,4-tetra-phenylcyclopenta-1,3-diene were prepared as described.² The concentration of these solutions was in the range

¹ Part VI, B. J. Tabner and T. Walker, *J.C.S. Perkin II*, 1973, 1201.

² D. Casson and B. J. Tabner, *J. Chem. Soc. (B)*, 1969, 887.

³ T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, 1966, **88**, 307, 318.

⁴ E. de Boer, A. H. Grotens, and J. Smid, *J. Amer. Chem. Soc.*, 1970, **92**, 4742.

1— 5×10^{-3} M and the radical anion was prepared from these solutions as described.⁹

Spectroscopic Measurements.—U.v.—visible absorption spectra were recorded on a Unicam SP 800 spectrophotometer over the temperature range 300—240 K using the constant temperature cell housing described.⁹ E.s.r. spectra were recorded on a Varian E3 spectrometer and the temperature of the samples was controlled by means of a Varian E4557 variable temperature unit. Temperature control was $\pm 0.2^\circ$ over the range required for this study. The rate of decay of the radical anion was followed by monitoring the decrease in intensity of the major line in the e.s.r. spectrum. The radical anion concentration was determined by comparison of the area beneath the spectrum with that of the perylene radical anion of known concentration. The concentrations as determined were considered to be accurate to within 10%. N.m.r. spectra were recorded at room temperature on a Varian spectrometer.

Calculations.—Values of velocity constants, ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger were obtained with the aid of an I.C.L. 1909 computer. Reconstructions of e.s.r. spectra were obtained with the aid of a Digico Micro 16 computer.

RESULTS

Spectra.—1,2,3,4-Tetraphenylcyclopenta-1,3-diene, in tetrahydrofuran solution, reacts with alkali metals at 203 K to give the corresponding radical anion. The resulting blue solutions had characteristic e.s.r. and visible absorption spectra (see Table 1). A typical e.s.r. spectrum of the

TABLE 1

The absorption spectra of the radical anion and anion obtained from 1,2,3,4-tetraphenylcyclopenta-1,3-diene in tetrahydrofuran

Counterion	$\lambda_{\max.}/\text{nm}$	
	Radical anion ^a	Anion ^b
Li ⁺	590, 660	495, 584
Na ⁺	592, 662	500, 587
K ⁺		~500, 582

^a Recorded at 203 K. ^b Recorded at 293 K.

radical anion (with Na⁺ as the counterion) is shown in Figure 1. The spectrum is dominated by a large triplet splitting of 2.53 mT.

A typical visible region absorption spectrum of the radical anion is shown in Figure 2A. When the temperature was raised above 203 K the intensity of this absorption decayed and was accompanied by a simultaneous decay in intensity of the e.s.r. spectrum. The rate of decay was very rapid

⁵ J. Smid, *Angew. Chem. Internat. Edn.*, 1972, **11**, 112.

⁶ D. Casson and B. J. Tabner, *J. Chem. Soc. (B)*, 1970, 1565.

⁷ D. Casson and B. J. Tabner, *J. Chem. Soc. (B)*, 1972, 445.

⁸ D. Casson and B. J. Tabner, *J. Chem. Soc. (B)*, 1970, 1560.

⁹ D. Casson and B. J. Tabner, *J. Chem. Soc. (B)*, 1969, 572.

when potassium was the counterion and for this particular counterion it was not possible to record the u.v.-visible



FIGURE 1 The e.s.r. spectrum of the 1,2,3,4-tetraphenylcyclopenta-1,3-diene radical anion in tetrahydrofuran at 203 K with lithium as the counterion

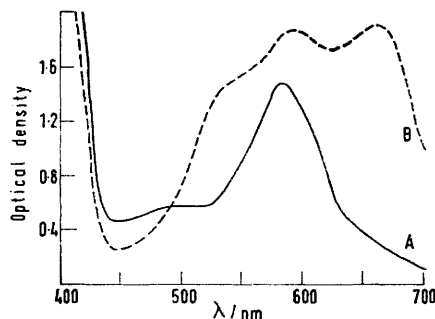
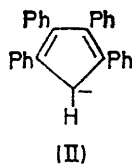


FIGURE 2 A, Absorption spectrum of the 1,2,3,4-tetraphenylcyclopenta-1,3-diene radical anion in tetrahydrofuran at 203 K, with lithium as the counterion; B, absorption spectrum of the 1,2,3,4-tetraphenylcyclopenta-1,3-dienyl anion in tetrahydrofuran at 258 K, with lithium as the counterion

absorption spectrum during the period that the blue colour persisted. After standing at room temperature for some time the e.s.r. absorption completely disappeared irrespective of which alkali metal was the counterion and a different visible region absorption spectrum was obtained (see Figure 2B). The details of the absorption spectrum of the decay product, for each of the counterions studied, are summarised in Table I.

In order to determine the nature of the decay product a tetrahydrofuran solution of the radical anion (with lithium as the counterion) was prepared under identical experimental conditions to those used in recording the various spectra. The radical anion was allowed to decay at room temperature and the vessel opened to the atmosphere when the colour quickly disappeared. Tetrahydrofuran was then removed and an n.m.r. spectrum of the product recorded. This latter spectrum was identical to that of 1,2,3,4-tetraphenylcyclopenta-1,3-diene obtained before reaction, and showed no evidence of any other products. It was therefore deduced that, as with other similar hydrocarbons,^{2,6-8} the major decay product was the corresponding anion (II).



Kinetics.—The kinetics of the radical anion decay were studied by recording either the decrease in the intensity of

the visible region absorption spectrum, or the decrease in the intensity of the e.s.r. absorption. The former technique was used for following the reaction at temperatures > 243 K and the latter technique for following the reaction at temperatures < 243 K. Measurements using both techniques on the same system at the same temperature gave identical values for the velocity constant within experimental error. When potassium was the counterion the decay was very rapid even at 203 K and it was not possible to obtain reliable measurements for this system.

The reaction curves for each system were analysed by plotting the functions $1/(a-x)$ and $\log(a-x)$ against time. When lithium was the counterion the plots were found to be first order with respect to the radical anion concentration in the region 257–273 K and second order with respect to the radical anion concentration in the region 217–240 K (see Figure 3). In the intermediate temperature region the reaction curve responded well to an order analysis based on expression (1) where R represents the

$$d[R]/dt = k_1[R] + k_2[R]^2 \quad (1)$$

radical anion. It appears, therefore, that there is a simple change from second- to first-order kinetics as the temperature is raised. When sodium was the counterion the analysis plots gave first-order kinetics, but showed a slight curvature at temperatures < 217 K indicating the same deviation from simple first-order kinetics was occurring.

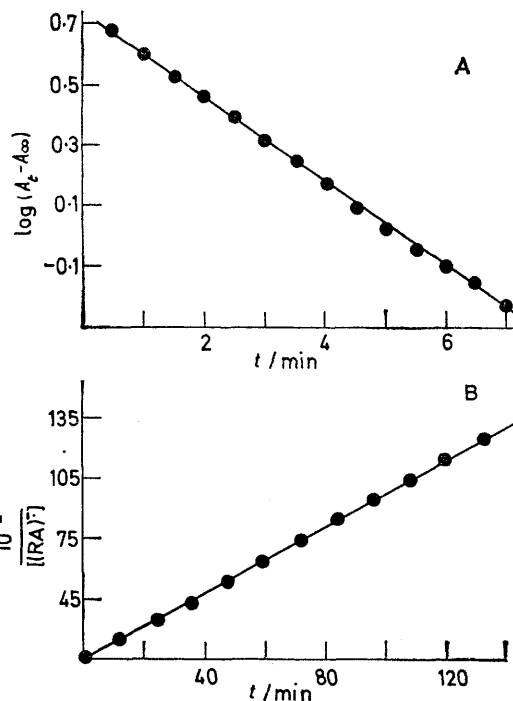


FIGURE 3 A, Plot of $\log_{10}(A_t - A_\infty)$ against t for the decay of the 1,2,3,4-tetraphenylcyclopenta-1,3-diene radical anion, with lithium as the counterion, at 264.5 K; B, plot of $1/[(RA)^-]$ against t for the decay of the radical anion $(RA)^-$, with lithium as the counterion, at 228.5 K

The temperature dependence of the velocity constant for each of the systems studied is given in Table 2. The values of ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger (at 298 K), together with the values of the velocity constant at 298 K are summarised in Table 3.

TABLE 2

Temperature dependence of the velocity constant for the decay of the 1,2,3,4-tetraphenylcyclopenta-1,3-diene radical anion for different counterions in tetrahydrofuran

Counterion	k/s^{-1}	$T/^\circ C$	$E/kJ\ mol^{-1}$
Lithium	1.90×10^{-2}	-1.0	90.3
	1.45×10^{-2}	-3.4	
	7.94×10^{-3}	-6.5	
	5.47×10^{-3}	-8.5	
	2.74×10^{-3}	-13.3	
	2.61×10^{-3}	-13.5	
Lithium *	1.97×10^{-3}	-16.3	
	4.20	-33.5	45.6
	2.61	-39.0	
	1.41	-44.5	
	7.78×10^{-1}	-50.0	
4.38×10^{-1}	-55.4		
Sodium	6.24×10^{-2}	-5.5	79.0
	3.27×10^{-2}	-11.0	
	1.50×10^{-2}	-16.5	
	6.63×10^{-3}	-22.0	
	3.12×10^{-3}	-28.0	
	9.34×10^{-4}	-33.5	

* In $l\ mol^{-1}\ s^{-1}$.

TABLE 3

Summary of the values of ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger at 298 K for the different counterions in tetrahydrofuran

Counterion	Reaction order	$\Delta G^\ddagger/kJ\ mol^{-1}$	$\Delta H^\ddagger/kJ\ mol^{-1}$	$\Delta S^\ddagger/J\ mol^{-1}\ K^{-1}$
Li ⁺	1	74.4	87.8 ± 3.6	46.0
Li ⁺	2	58.1	43.5 ± 0.9	-49.7
Na ⁺	1	70.6	76.1 ± 2.5	18.0

DISCUSSION

E.s.r. Spectrum.—The e.s.r. spectrum obtained of the 1,2,3,4-tetraphenylcyclopenta-1,3-diene radical anion (Figure 1) is dominated by a large triplet splitting with $a_H(2) = 2.53 \pm 0.02$ mT. A closer examination of the spectrum reveals that each line in this triplet is further split with $a_H(6) = 0.18 \pm 0.02$ mT. A computer simulation based on these splitting constants was in good agreement with the experimental spectrum. Unfortunately the line-width in the experimental spectrum was unusually large compared with that typically obtained for similar radical anions and could not be further improved despite many attempts. It was not possible therefore to determine the exact values for the splitting constants associated with the six protons responsible for the smaller splitting.

A simple Hückel molecular orbital calculation on 1,2,3,4-tetraphenylcyclopenta-1,3-diene reveals that, in the radical anion, the *ortho*- and *para*-protons in the rings attached to C-1 and -4 of the cyclopentadiene ring have spin densities of 0.0570 and 0.0688 respectively (see Table 4). Allowing a fairly typical value for Q of $|2.8|$ mT, the predicted splitting constants are 0.16 and 0.19 mT respectively. It seems very reasonable therefore to attribute the splitting constant of 0.18 mT to the interaction of the unpaired electron with these six protons.

Kinetics.—As with the other similar reactions reported in previous Parts the rate of the radical anion decay is

found to be sensitive to the nature of the counterion. The radical anion is most stable when Li⁺ is the counterion and least stable when K⁺ is the counterion. The counterion is therefore important in the rate-determining step of these reactions and is presumably, therefore, involved in the formation of the transition state. It appears reasonable to suggest that the counterion aids the localisation of the negative charge at the methylene carbon.

TABLE 4

Comparison of experimental and calculated splitting constants (in mT) for the 1,2,3,4-tetraphenylcyclopenta-1,3-diene radical anion

	Position						
	C-5	<i>o</i> ^a	<i>m</i> ^a	<i>p</i> ^a	<i>o</i> ^b	<i>m</i> ^b	<i>p</i> ^b
Experimental	2.53	0.18		0.18			
Calculated ^c		0.16	0.01	0.19	0.05	0.00	0.06

^a Values for the phenyl groups attached to C(1) and C(4).

^b Values for the phenyl groups attached to C(2) and C(3).

^c Calculated with $\alpha_1 = \alpha_4 = \alpha_c - 0.25\beta_{cc}$.

Two factors are therefore important in determining the rate of the reaction, (i) the coulombic interaction between the radical anion and the counterion and (ii) the solvation of the counterion. ΔH^\ddagger for the reaction would be expected to increase with an increase in coulombic interaction (*i.e.* to increase from K⁺ to Li⁺) and decrease with increased solvation of the counterion (*i.e.* to increase from Li⁺ to K⁺). The experimental results indicate that of these two factors the solvation of the counterion is the most important. This conclusion is supported by the more positive ΔS^\ddagger for Li⁺ compared to Na⁺. This would be expected if the degree of solvation of the counterion was reduced in the transition state compared to the radical anion.

It was hoped that the study of the 1,2,3,4-tetraphenylcyclopenta-1,3-diene radical anion might reveal some interesting steric factors in these reactions. However, the evidence for an important steric consideration in this decay is not obvious. Perhaps the only evidence comes from a comparison of the values of ΔH^\ddagger and ΔS^\ddagger for the two counterions. The values of ΔH^\ddagger and ΔS^\ddagger vary only slightly as the counterion is changed from Li⁺ to Na⁺ and this could well be a result of increased steric considerations compared to the analogous reaction of the fluorene radical anion where the values of ΔH^\ddagger and ΔS^\ddagger differ more markedly.

Again, as with the fluorene radical anion, there is a change of kinetic order, as the temperature is decreased, when Li⁺ is the counterion. In the case of the fluorene radical anion conductivity measurements indicate *ca.* 10% dissociation in the second-order decay region.² The bimolecular decay is therefore favoured by those conditions in which the counterion is strongly solvated and hence is less able to aid the localisation of the negative charge at the methylene carbon.

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