751. *The Catalytic Action of Anionic Catalysts. Part III.*[1] *Electron-transfer Reactions involving* 1,1,3,3,-*Tetraphenylbut*-1-*ene and Tetraphenylethylene.*

By J. E. Bennett, Alwyn G. Evans, J. C. Evans, E. D. Owen, and B. J. Tabner.

When an electron is transferred from sodium, or from sodium naphthalene, to an excess of 1,1,3,3-tetraphenylbut-1-ene or tetraphenylethylene, a radical ion is formed. Because of steric hindrance this radical ion does not dimerise, but disproportionates to give a di-ion and the olefin. This disproportionation is endothermic; its equilibrium constant and enthalpy have been measured by e.s.r. and visible spectra.

We have made preliminary communications [2, 3] concerning the electron spin resonance (e.s.r.) and the visible spectra shown by tetrahydrofuran solutions of 1,1,3,3-tetraphenylbut-1-ene and tetraphenylethylene after their treatment with sodium or sodium-naphthalene. In this paper we give the results obtained for systems in which the concentration of olefin is greater than or equal to that of sodium or of sodium-hydrocarbon.

Experimental

Materials.—Tetrahydrofuran (B.D.H.) was first purified by storage over " AnalaR " sodium hydroxide pellets and fractional distillation at atmospheric pressure, the fraction of b. p. 64—65° being collected. It was then refluxed over freshly extruded sodium wire and again fractionated. After this process had been repeated several times, the tetrahydrofuran was thoroughly outgassed under a high vacuum and stored over sodium–potassium alloy in ampoules having magnetically operated breakers.

1,1,3,3-Tetraphenylbut-1-ene was prepared as described earlier.[4]

Tetraphenylethylene (Light's) was twice recrystallised from 1,4-dioxan and then sublimed under a high vacuum into the reaction vessel. Generous head and tail fractions were discarded in these distillations, and a sample of the purified solid had m. p. 221° (lit.,[5] 222°).

Sodium-naphthalene was prepared by a high-vacuum adaptation of the method of Scott, Hansley, and Walker; [6] the apparatus is shown in Fig. 1. A known weight of naphthalene, previously sublimed, was placed in side-arm A. Sodium metal (B.D.H.) was refluxed over toluene, washed with light petroleum (b. p. 40—60°), and placed in side-arm B. The rest of the apparatus was thoroughly baked under a high vacuum and sealed at C, H, and I. An excess of sodium was distilled into the vessel V, forming a sodium mirror, and tube B was then sealed off at D. Naphthalene was sublimed from tube A on to the sodium mirror in V, and tube A was sealed at E. Tetrahydrofuran was distilled into vessel V through an alloy trap, this vessel was sealed at F, and the system was left for 30 min. with occasional shaking. The capillary G was then broken and the sodium-naphthalene solution filtered through the sintered-glass filter L (porosity 4) into calibrated bulbs (K for estimation, and M for dilution), which were then sealed.

---

[1] Part II, Evans and George, *J.*, 1962, 141.
[2] Evans, Evans, and Owen, *Proc. Chem. Soc.*, 1961, 339.
[3] Bennett, Evans, Evans, Owen, and Tabner, *Proc. Chem. Soc.*, 1962, 226.
[4] Evans and Price, *J.*, 1959, 2982.
[5] Schlenk and Bergmann, *Annalen*, 1928, **463**, 15.
[6] Scott, Hansley, and Walker, *J. Amer. Chem. Soc.*, 1936, **58**, 2442.

Standardisation of Sodium-naphthalene Solution.—(*a*) *By hydrolysis.* Fragile calibrated bulbs (K; Fig. 1) filled with sodium-naphthalene solution under a high vacuum were broken under distilled water, and the sodium hydroxide formed was titrated with hydrochloric acid to phenolphthalein. (*b*) *Spectrophotometrically.* The sodium naphthalene was diluted with tetrahydrofuran to about 10^{-4} mole l.^{-1}, and its spectrum measured from 333 to 1000 mμ. The extinction coefficient [7] of the 736 and 812 mμ peaks were used for its estimation.

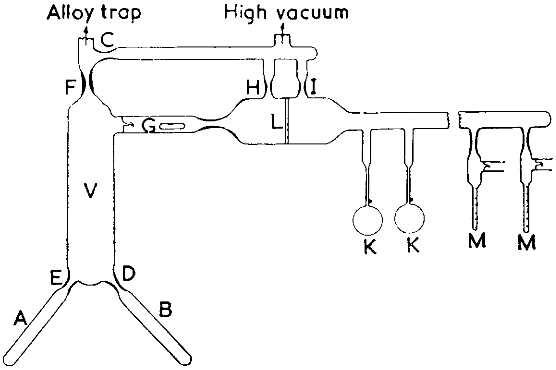


FIG. 1. Apparatus for preparation and estimation of tetrahydrofuran solutions of sodium-naphthalene (for key see text).

Results of the two methods agreed to within 2%. The sodium-naphthalene solution was fairly stable; after 2 weeks its concentrations had fallen by only 5%. It was, however, very sensitive to heat.

Sodium-phenanthrene was prepared and standardised by the same methods.

Measurement of Visible Spectra.—The visible spectra were measured on a Unicam S.P. 500 spectrophotometer provided with a Unicam constant-temperature cell housing; silica cells were used, sealed off from the high-vacuum mixing system. Measurements at low temperatures were carried out by circulating methanol from a Townsend and Mercer " Minus Seventy " bath through the thermostatic device. Dry nitrogen was passed through the cell-carriage compartment to prevent misting of the windows. The temperature was constant to ±2° at −50°, ±0·5° at −20°, and better at higher temperatures. The pipes used for circulating the methanol were as short as possible and heavily lagged.

Measurement of Electron Spin Resonance Spectra. These spectra were measured on a 3·2 cm. wavelength spectrometer, operating at 100 kilocycles magnetic field modulation. The cavity was temperature-controlled, and for low temperatures it was cooled by a nitrogen stream passed through liquid air and heated to the required temperature. The temperature of the cavity, as measured by a thermocouple, remained constant within 0·1° at −30°. To determine the concentration of radicals the spectra were integrated and compared with those of diphenylpicrylhydrazyl solutions of known concentrations. We consider the concentrations to be accurate within ±10%.

RESULTS

Visible Spectra.—A tetrahydrofuran solution of sodium-naphthalene has a characteristic green colour. On its being mixed with a tetrahydrofuran solution of 1,1,3,3-tetraphenylbut-1-ene or tetraphenylethylene at room temperature, the green colour immediately disappears and the solution becomes red (Figs. 2 and 3). The spectra of both these systems show absorptions in the visible region, 479 and 432 mμ for the butene and 466 and 675 mμ for the ethylene. On cooling, there is a decrease in intensity at 479 and 466 mμ and an increase at 432 and 675 mμ (Figs. 2 and 3). These changes in spectra with change in temperature are reversible and indicate two coloured species in equilibrium with each other.

In the case of 1,1,3,3-tetraphenylbut-1-ene, addition of more olefin to the red tetrahydrofuran solution, formed as above, decreases the intensity of the 479 mμ peak and increases that of the 432 mμ peak.

---

[7] (*a*) Paul, Lipkin, and Weismann, *J. Amer. Chem. Soc.*, 1956, **78**, 116; (*b*) Hoijtink, Balk, and Schreus, *Rec. Trav. chim.*, 1957, **76**, 813.

Electron Spin Resonance Spectra.—Electron spin resonance spectra were measured for solutions obtained (*a*) by mixing tetrahydrofuran solutions of sodium-naphthalene and olefin, or (*b*) by allowing the tetrahydrofuran solution of olefin to come into contact with a sodium film and then filtering. In each case it was arranged that [Olefin] $\geqslant$ [Sodium], if necessary by adding neutral olefin to the solutions after filtration. The whole procedure was carried out under a high vacuum and the spectrum measured immediately.

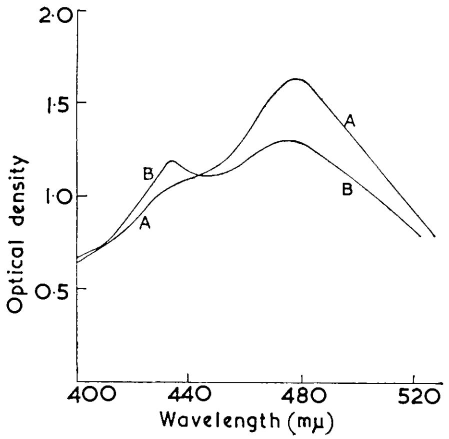


FIG. 2.

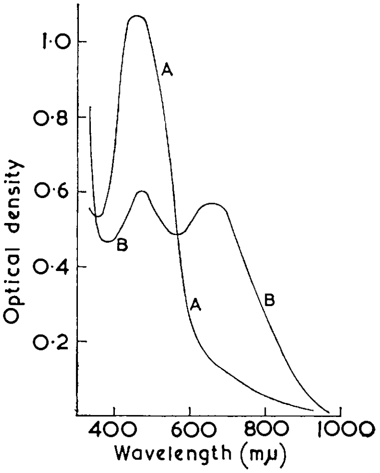


FIG. 3.

FIG. 2. Visible spectra. (A) Solution at 20° obtained by passing 8·8 ml. of a tetrahydrofuran solution of 1,1,3,3-tetraphenylbut-1-ene (1·47 × 10^{-3} mole l.$^{-1}$) over a sodium film and then filtering. Concentration of sodium ions = 1·035 × 10^{-3} g.-atom l.$^{-1}$. (B) Same as (A), cooled to −30°.

FIG. 3. Visible spectrum. (A) Solution at 18° obtained by passing 7·5 ml. of a tetrahydrofuran solution of tetraphenylethylene (9·13 × 10^{-4} mole l.$^{-1}$) over a sodium film and then filtering. To 4·99 ml. of this filtered solution, 5·87 ml. of tetraphenylethylene solution (9·13 × 10^{-4} mole l.$^{-1}$) were added. Concentration of sodium ions (spectroscopically determined) = 8·39 × 10^{-4} mole l.$^{-1}$. (B) Same as (A), cooled to −50°.

Examples of the spectra are given in Fig. 4, which shows that radicals different from the naphthalene radical ion are present in these mixed solutions, and that their concentration increases with decrease in temperature.

Liquid and Solid Products.—(*a*) *From* 1,1,3,3-*tetraphenylbut*-1-*ene.* The solution obtained on mixing of equimolar solutions of sodium-naphthalene and olefin was treated with distilled water. The products obtained by normal methods were: (i) sodium hydroxide, corresponding within 0·5%, to the initial sodium-naphthalene; (ii) 1,1,3,3-tetraphenylbut-1-ene corresponding to 85% of the original olefin; (iii) naphthalene equivalent to that used initially; (iv) 1,1,3,3-tetraphenylbutane corresponding to 10% of the original olefin; and (v) 1,1-diphenylethane corresponding to 5% of the original olefin. (*b*) *From tetraphenylethylene.* The solution obtained on mixing of equimolar solutions of sodium-naphthalene and tetraphenylethylene was treated with distilled water. The products obtained were: (i) sodium hydroxide, corresponding, within 0·5%, to the initial sodium-naphthalene; (ii) tetraphenylethylene, corresponding to 90—95% of the original olefin; (iii) naphthalene equivalent to within 2% to that used initially; and (iv) 1,1,2,2-tetraphenylethane corresponding to 5—10% of the original olefin.

Gaseous Products.—When water was added to the mixed solutions vigorous effervescence occurred. The gas evolved did not condense in a liquid-air trap. A sample was introduced into a mass spectrometer and found to be hydrogen. Quantitative estimation was difficult but the amount evolved was in reasonable agreement with that of the sodium present.

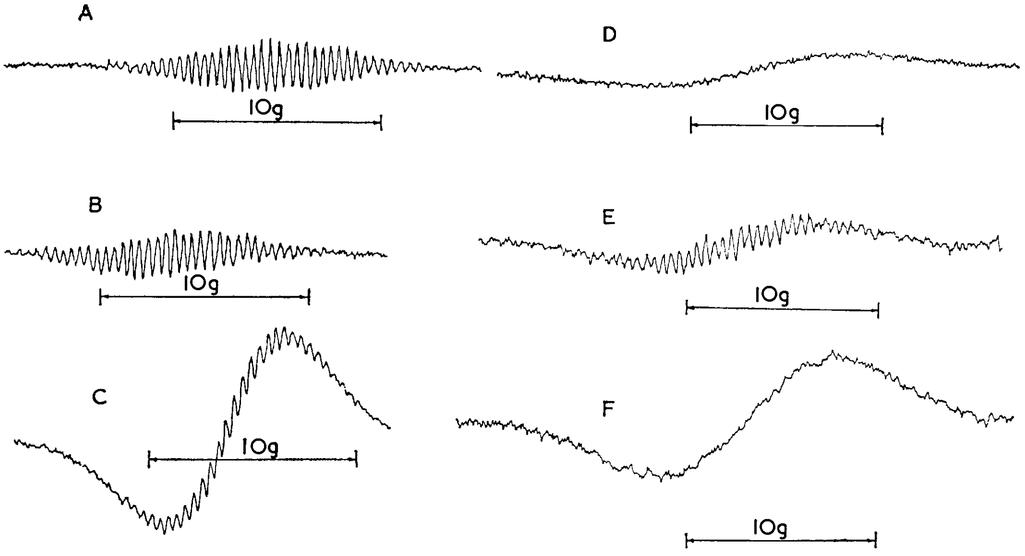


FIG. 4. Electron spin resonance spectra. (A) Solution at room temperature obtained by mixing a tetrahydrofuran solution (1·43 ml.) of $Ph_2C{:}CPh_2$ ($8{\cdot}6 \times 10^{-3}$ mole $l.^{-1}$) with a tetrahydrofuran solution (2·11 ml.) of sodium-naphthalene ($2{\cdot}43 \times 10^{-3}$ mole $l.^{-1}$). Spectrum measured immediately on mixing.

(B) Solution at room temperature obtained by allowing a tetrahydrofuran solution (1·92 ml.) of $Ph_2C{:}CPh_2$ ($2{\cdot}05 \times 10^{-2}$ mole $l.^{-1}$) to come into brief contact with a sodium film, filtering, and then adding a tetrahydrofuran solution (5·92 ml.) of $Ph_2C{:}CPh_2$ ($8{\cdot}6 \times 10^{-3}$ mole $l.^{-1}$).

(C) Same as solution (B), cooled to −40°.

(D) Solution at room temperature obtained by mixing a tetrahydrofuran solution (0·8 ml.) of $CH_3{\cdot}CPh_2{\cdot}CH{:}CPh_2$ (0·902 mole $l.^{-1}$) with a tetrahydrofuran solution (0·83 ml.) of sodium-naphthalene (0·475 mole $l.^{-1}$). Spectrum measured immediately on mixing.

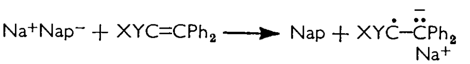
(E) Solution at room temperature obtained by allowing a tetrahydrofuran solution (2·2 ml.) of $CH_3{\cdot}CPh_2{\cdot}CH{:}CPh_2$ (0·902 mole $l.^{-1}$) to come into brief contact with sodium film and then filtering.

(F) Same as solution (E), cooled to −35°.

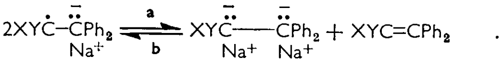
DISCUSSION

Equilibria Involved.—When tetrahydrofuran solutions of sodium-naphthalene and the olefin (1,1,3,3-tetraphenylbut-1-ene or tetraphenylethylene) are mixed, the characteristic green colour disappears. The fact that the visible spectra of the mixture cannot detect the characteristic sodium-naphthalene absorption shows that the concentration of sodium-naphthalene has dropped to less than 10^{-6} mole $l.^{-1}$. The solutions now have a red colour due to the take-up of the electron by the olefin. Electron spin resonance (e.s.r.) measurements show that the naphthalene radical ions have been replaced by another type of radical (Fig. 4). The concentration of these radicals, however, at room temperature is appreciably less than that expected from the original concentration of sodium-naphthalene. Lowering the temperature of the solutions increases the concentration of radicals. This change is reversible and is paralleled by a temperature-dependent equilibrium between two coloured species (Figs. 2 and 3). That a decrease in temperature causes an increase in the concentration of radicals as shown by e.s.r. measurements, and also an increase in absorption at 675 and 432 mμ for the ethylene and the butene systems, respectively, shows that these coloured species must be radical ions. The other coloured species (absorbing at 466 and 479 mμ) can therefore only be di-ions.

We interpret our results according to the following equations:



$$\mathrm{Na^+Nap^-} + \mathrm{XYC{=}CPh_2} \longrightarrow \mathrm{Nap} + \mathrm{XY\dot{C}{-}\underset{Na^+}{\overset{-}{\ddot{C}}}Ph_2} \qquad (1)$$



$$2\mathrm{XY\dot{C}{-}\underset{Na^+}{\overset{-}{\ddot{C}}}Ph_2} \underset{b}{\overset{a}{\rightleftharpoons}} \mathrm{XY\underset{Na^+}{\overset{-}{\ddot{C}}}{-}\underset{Na^+}{\overset{-}{\ddot{C}}}Ph_2} + \mathrm{XYC{=}CPh_2} \qquad (2)$$

where X = Y = Ph for the ethylene, and X = H and Y = $CH_3{\cdot}CPh_2$ for the butene.

In the case of 1,1,3,3-tetraphenylbut-1-ene the radical ion could be written in the alternative way, that is, with the free electron on the tertiary carbon atom, and the negative charge on the secondary carbon atom. More detailed e.s.r. spectra are required to decide this point. Product analysis shows that the radical ions do not combine to form a dimeric di-ion $Ph_2C{\cdot}CXY{\cdot}CXY{\cdot}CPh_2$ because of the great steric hindrance involved in this process; even a n-butyl anion cannot add to these olefins.[8]

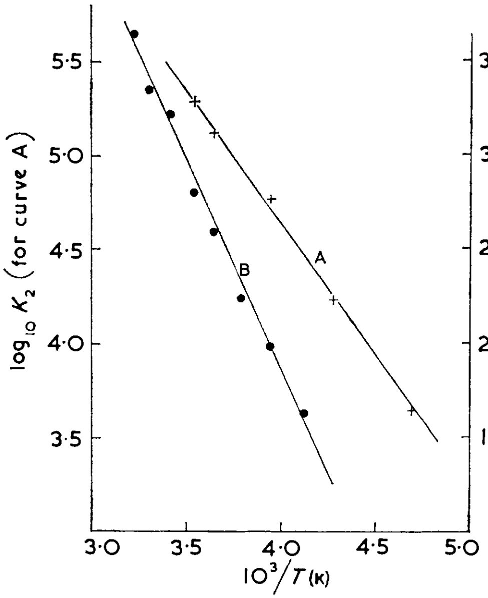


FIG. 5.

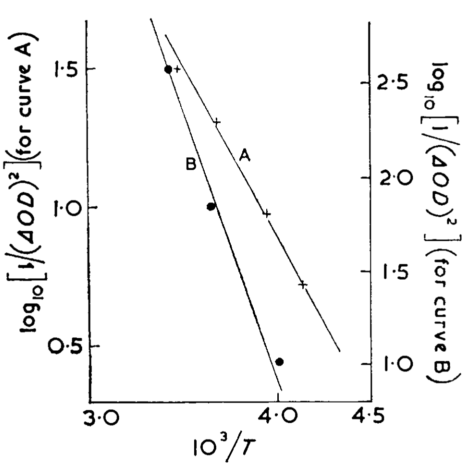


FIG. 6.

FIG. 5. Effect of temperature on the equilibrium constant of reaction (2). (A) A tetrahydrofuran solution (10 c.c.) of 1,1,3,3-tetraphenylbut-1-ene (0·902 mole $l.^{-1}$) passed over sodium film and then filtered. (B) A tetrahydrofuran solution (0·087 ml.) of sodium-naphthalene (0·468 mole $l.^{-1}$) added to a tetrahydrofuran solution (1·90 ml.) of tetraphenylethylene ($2{\cdot}05 \times 10^{-2}$ mole $l.^{-1}$).

FIG. 6. Effect of temperature on the optical density of solutions involved in reaction (2). (A) Same as for Fig. 2. (B) Same as for Fig. 3.

Under the conditions of our experiments, reaction (1) is irreversible, the concentrations of Nap^- being too small to be detected; reaction (2) is reversible, and for both olefins it is endothermic in the 2a direction. Knowing the total olefin concentration, the radical ion concentration (from e.s.r. measurements), and the total sodium concentration (by flame photometer) we have calculated the value of the equilibrium constant K_2 for reaction (2) at different temperatures. In Fig. 5 log K_2 is plotted against $1/T$ over the temperature

---

[8] Evans and George, *J.*, 1961, 4653.

range 20° to —60°, and the slopes of the plots give ΔH_{2a} values of 6 and 11 kcal. mole^{-1} for the butene and the ethylene system, respectively.

The results for sodium-phenanthrene (instead of sodium-naphthalene) give a value from e.s.r. measurements of $\Delta H_{2a} = 11{\cdot}5$ kcal. mole^{-1} for the ethylene.

Using the visible spectra we have smoothed the curve on which the radical-ion absorption appears and taken the difference in optical density between the actual absorption and the smoothed curve, ΔOD, as being proportional to [Radical Ion]. Plotting log $1/(\Delta OD)^2$ against $1/T$ over the temperature range 20° to —60° gives the plots shown in Fig. 6. Since equilibrium (2) lies well to the right at room temperature the initial slopes of these lines will give an approximate value of ΔH_{2a}. The values obtained in this way are 6 and 13 kcal. mole^{-1} for the butene and the ethylene, respectively, in good agreement with those obtained by the e.s.r. method.

Extinction Coefficients.—Since equilibrium (2) lies well to the right we can estimate the extinction coefficient of the di-ion by assuming that equilibrium (2) lies completely to the right. In this way we obtain a minimum extinction coefficient $\varepsilon = 1{\cdot}5 \times 10^4$ and $1{\cdot}8 \times 10^4$ for the di-ions in the butene and the ethylene system, respectively (compare $\varepsilon = 1{\cdot}6 \times 10^4$ for the monoion $\mathrm{Bu{\cdot}CH_2{-}\overset{-}{\ddot{C}}Ph_2}$ absorption peak 428 mμ).[8]

Reaction with Water.—It is interesting that water removes the electron from the radical ion–di-ion system instead of reacting with it. This may be due to steric hindrance: since if a n-butyl anion cannot interact with these olefins one would expect a similar steric difficulty in the approach of a water molecule. The electron must be transferred to the water from the olefin *via* the phenyl groups, and this is not surprising since there is a high degree of conjugation in these ions. The electron transferred in reactions (2a) and (2b) must also be thought of as proceeding through the phenyl groups, since again steric hindrance will prevent the two reagents approaching each other at the olefinic carbon atoms. Hoffman and Zweig[9] have found that water removes the electron from the system (tetraphenylbutatriene)$^-$ to regenerate the original triene. In this case there would be no steric hindrance to the reaction of the water with the ion, and this suggests that this type of electron transfer is determined mainly by the existence of a high degree of conjugation.

Adding 1,1,3,3-tetraphenylbut-1-ene to a solution of the butene–sodium-naphthalene displaces equilibrium (2a) to the left. This is to be expected and explains why in our original communication the spectra shown had a peak at 432 and a shoulder at 479 mμ. This solution was made before we had perfected our technique for stable solutions and was fading rapidly; the concentration of ions was falling, thus causing the relative concentration of the olefin to increase, with the result that equilibrium (2a) was being moved to the left.

Some hydrogenated olefin is found after the mixed solutions are treated with water. We attribute this to some reduction of the olefin by the nascent hydrogen. In the case of the butene ~5% of 1,1-diphenylethane is found. This indicates that a small amount of decomposition of the olefin occurs on reaction of the mixed solutions with water.

Energetics of Electron Transfer.—We give in the Table thermodynamic values for reaction (2a). This reaction involves the transfer of an electron from one radical ion to another, to give a di-ion and an olefin. The results show that in going from the tetraphenylbut-1-ene to the tetraphenylethylene, the increase in stability of the two radical ions is greater than that of the di-ion plus olefin by 5 kcal. mole^{-1}. This may be due to

Thermodynamic values for Reaction (2a).

Olefin	K_{2a} (0°c)	ΔG°_{2a} (0°c) (kcal. mole^{-1})	ΔH_{2a} (kcal. mole^{-1})	ΔS°_{2a} (0°c) (cal. mole^{-1} deg.$^{-1}$)
1,1,3,3-Tetraphenylbut-1-ene ...	$1{\cdot}6 \times 10^5$	$-6{\cdot}5$	6	46
Tetraphenylethylene	$3{\cdot}8 \times 10^2$	$-3{\cdot}2$	11	52

---

[9] Hoffmann and Zweig, *J. Amer. Chem. Soc.*, 1962, **84**, 3278.

some extent to the fact that, in contrast to the position with tetraphenylbut-1-ene, all four phenyl groups of the tetraphenylethylene are involved in conjugation. The equilibrium constants for reaction (2) are such that the radical ions are more favoured in the case of the tetraphenylethylene than for the tetraphenylbut-1-ene.

Although reaction (2a) is endothermic for both olefins, the position of equilibrium at room temperature lies markedly to the right. This is because reaction (2a) is accompanied by a large increase in entropy, perhaps because steric hindrance makes it harder to solvate the two negative charges on the di-ion than to solvate the single charges on the radical ion.

We find in preliminary experiments that the use of lithium instead of sodium gives a marked displacement of the equilibrium of reaction (2) to the left.

In work by Szwarc and his co-workers,[10] an electron was added to 1,1-diphenylethylene. Because of the absence of steric hindrance, the radical ion of 1,1-diphenylethylene, $Ph_2\overset{\overline{\cdot\cdot}}{C}-\dot{C}H_2$, can dimerise to the tail-to-tail di-ion, $Ph_2\overset{\overline{\cdot\cdot}}{C}-CH_2-CH_2-\overset{\overline{\cdot\cdot}}{C}Ph_2$, and equilibria involving this tail-to-tail species were investigated.

Our work is concerned with a different system, the head-to-tail dimer of 1,1-diphenylethylene, $CH_3\cdot CPh_2\cdot CH=CPh_2$. An electron is accepted by this head-to-tail dimer, but because of the presence of great steric hindrance, the resulting radical ion $CH_3\cdot CPh_2-\dot{C}H-\overset{\overline{\cdot\cdot}}{C}Ph_2$ cannot dimerise but can only disproportionate. The same is true of the radical ion produced when tetraphenylethylene accepts an electron.

We thank D.S.I.R. for a Research Studentship to J. C. E., the University of Wales for a Research Studentship to B. J. T., D.S.I.R. for grants to purchase a Unicam S.P. 100 infrared spectrophotometer, and a Metrovick M.S. 3 mass spectrometer, and "Shell" Research Ltd. for the use of the electron spin resonance spectrometer.

Chemistry Department, University College,
Cathays Park, Cardiff, S. Wales.
(J. E. B.) "Shell" Research Ltd.,
Thornton Research Centre, Chester.

[*Received, December 22nd,* 1962.]

---

[10] Jagur, Levy, Feld, and Szwarc, *Trans. Faraday Soc.*, 1962, **58**, 2168.