

1145. The Catalytic Action of Anionic Catalysts. Part VI.¹ The Interaction of Sodium Aromatic Hydrocarbons with 1,1,3,3-Tetraphenylbut-1-ene.

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In the reaction of 1,1,3,3-tetraphenylbut-1-ene with sodium aromatic hydrocarbons, the ease of electron transfer increases with decrease in the electron affinity of the hydrocarbon. In most cases the reaction is either extremely rapid or does not occur at all, but, for sodium chrysene and sodium picene, the rate could be measured spectrophotometrically and was found to be of the first order in each reagent, the activation enthalpies being 13.4 and 16.9 kcal. mole⁻¹, respectively. No reverse reaction was found when the forward reaction was extremely rapid, but when there was no transfer in the forward direction a very rapid reverse reaction was obtained.

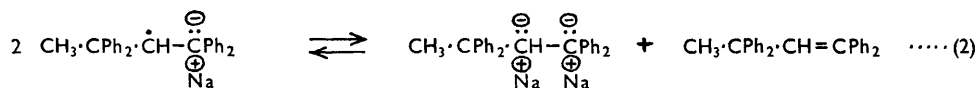
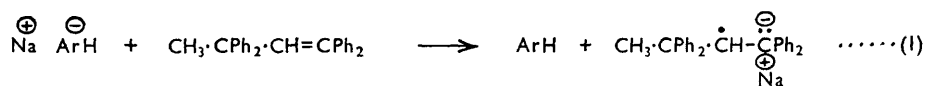
A PRELIMINARY communication² concerned the rate of electron transfer from sodium aromatic hydrocarbons to 1,1,3,3-tetraphenylbut-1-ene. In this Paper we give the details.

EXPERIMENTAL

The apparatus, purification of materials, and techniques are the same as used previously.^{1,3}

Spectra.—The visible spectra of the olefin mono-negative and di-negative ions³ are different from those of the aromatic hydrocarbon mononegative ions (sodium chrysene has absorption peaks at 399, 495, and 650 mμ and sodium picene at 404, 505, and 690 mμ). Thus, the electron transfer can be followed by the change in visible spectrum. The optical density of tetrahydrofuran solutions of sodium chrysene of known strength (estimated as described earlier for sodium naphthalene³) gave values of $\epsilon_{399} = 2.37 \times 10^4$, $\epsilon_{495} = 1.26 \times 10^4$, and $\epsilon_{650} = 0.8 \times 10^4$. In the same way values of $\epsilon_{404} = 1.7 \times 10^4$, $\epsilon_{505} = 2.19 \times 10^4$, and $\epsilon_{690} = 0.456 \times 10^4$ were obtained for sodium picene.

The reactions involved are:³



The positions of the electrons shown on the butene ions are formal and do not indicate their actual location.

¹ Part V, Evans and Tabner, *J.*, 1963, 5560.

² Evans, Evans, and Tabner, *Proc. Chem. Soc.*, 1962, 338.

³ Evans, Evans, Owen, and Tabner, *Proc. Chem. Soc.*, 1962, 226; Bennett, Evans, Evans, Owen, and Tabner, *J.*, 1963, 3954.

RESULTS

Rapid Electron Transfer.—The results of electron transfer from $(\text{ArH})^-$ to the olefin are given in Table 1, and those from $(\text{Olefin})^-$ to the aromatic hydrocarbon in Table 2. At the concentrations shown, electron transfer was complete where it occurred; this was shown by the change in both the visible spectrum and the electron spin resonance (e.s.r.) spectrum.

Slow Electron Transfer.—The transfer of an electron from sodium chrysene and sodium picene to the olefin is slow enough to be measured spectrophotometrically. When tetrahydrofuran solutions of sodium chrysene, or sodium picene, and 1,1,3,3-tetraphenylbut-1-ene were mixed, the green colour of the mononegative ion of the sodium chrysene or sodium picene was slowly replaced by an orange-red colour. The optical density of the sodium chrysene or sodium picene colour decreased with time until it could not be measured, while that of the olefin mono- and di-negative ion system increased to a value which remained constant. Cells containing solutions of sodium chrysene or of sodium picene were kept at the same temperature as controls, and for these the optical densities remained constant.

TABLE 1.

Aromatic hydrocarbon (ArH)	Electron affinity * (ev)	$[\text{Na}^+(\text{ArH})^-]$ (10^{-3} mole l. ⁻¹)	$[\text{Olefin}]$ (10^{-3} mole l. ⁻¹)	Rate of electron transfer
Naphthalene	2.59	0.38	1.07	Rapid
Phenanthrene	2.63	34.3	42.7	Rapid
Chrysene	2.76	0.414	5.62	Slow
Picene	2.78	1.52	8.23	Slow
Pyrene	2.96	0.755	9.05	No transfer
Anthracene	3.11	2.15	7.7	No transfer
Perylene	3.32	2.88	7.6	No transfer

* See Matsen, *J. Chem. Phys.*, 1956, **24**, 602.

TABLE 2.

Aromatic hydrocarbon (ArH)	$[\text{ArH}]$ (10^{-3} mole l. ⁻¹)	$[(\text{Olefin})^-]$ * (10^{-3} mole l. ⁻¹)	Rate of electron transfer
Chrysene	0.95	0.90	No transfer
Pyrene	1.01	0.91	Rapid
Perylene	1.15	0.98	Rapid
Naphthacene	0.88	0.78	Rapid

* $[(\text{Olefin})^-]$ would be the concentration of mononegative ions if equilibrium (2) lay completely to the left.

Electron Transfer from Sodium Chrysene.—The electron transfer was followed by the decrease with time of the sodium chrysene peaks at 399 and 650 $m\mu$. The optical density at 650 $m\mu$ needs no correction for overlap with absorption by the reaction products until near the end of the reaction, and then only very slightly. The optical density at 399 $m\mu$ needs an initial correction, owing to slight overlap by the olefin absorption, and, towards the end of the reaction, a correction for overlap by the olefin mono- and di-negative ion system. The results obtained are the same whichever of these peaks is used to follow the reaction.

Order of Reaction.—The order in olefin was found to be unity from the dependence of initial rate on $[\text{Olefin}]$ (see Table 3). In two experiments with $[\text{Olefin}] \gg [\text{Sodium chrysene}]$, the

TABLE 3.

Dependence of initial rate of reaction at 30° on initial $[\text{Sodium chrysene}]$ and $[\text{Sodium picene}]$.

$[\text{CPh}_2\text{Me}\cdot\text{CH}\cdot\text{CPh}_2]_i$ (mole l. ⁻¹)	$[\text{Sodium}^+$ chrysene ⁻] _i (mole l. ⁻¹)	$[\text{Sodium}^+$ picene ⁻] _i (mole l. ⁻¹)	Initial rate (mole l. ⁻¹ sec. ⁻¹)	Initial rate $\frac{[\text{Na}^+\text{ArH}^-][\text{Olefin}]}{(\text{l. mole}^{-1} \text{ sec.}^{-1})}$
5.62×10^{-3}	4.14×10^{-4}		1.57×10^{-8}	6.7×10^{-3}
1.86×10^{-3}	4.14×10^{-4}		0.503×10^{-8}	6.59×10^{-3}
5.7×10^{-4}	4.14×10^{-4}		1.59×10^{-9}	6.73×10^{-3}
5.55×10^{-3}	9.1×10^{-4}		3.39×10^{-8}	6.7×10^{-3}
5.52×10^{-3}		4.57×10^{-4}	1.29×10^{-10}	5.0×10^{-6}
2.6×10^{-1}		4.57×10^{-4}	6.05×10^{-9}	5.02×10^{-6}
5.5×10^{-3}		1.05×10^{-3}	2.85×10^{-10}	4.9×10^{-6}

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reaction order in the latter obtained from an analysis of the optical density-time curves was unity (see Table 4). The order of reaction in sodium chrysene, determined from the dependence of initial rate on [Sodium chrysene], was also unity (see Table 3).

Thus, the rate of electron transfer = $k[\text{Sodium chrysene}][\text{Olefin}]$; the values of k so obtained are given in Table 5.

TABLE 4.

First-order dependence of reaction rate on [Sodium chrysene] at 30° when 1,1,3,3-tetraphenylbut-1-ene is in excess.

	$[\text{CPh}_2\text{Me}\cdot\text{CH}\cdot\text{CPh}_2]_i = 5.63 \times 10^{-3}$ mole l. ⁻¹ .				$[\text{Sodium chrysene}]_i = 4.14 \times 10^{-4}$ mole l. ⁻¹ .		
Time (hr.)	0	1	2	3	4	5	15
Optical density *	0.328	0.289	0.248	0.215	0.185	0.158	0.038
Rate constant †	—	0.13	0.14	0.14	0.14	0.15	0.14

* 1 mm. cell, 650 mμ. † First-order (hr.⁻¹).

Temperature-dependence.—The effect of temperature is shown in Table 5. The activation-enthalpy is 13.4 ± 0.5 kcal. mole⁻¹.

Irreversibility of Reaction.—The fact that when [Butene] \gg [Sodium chrysene] first-order kinetics hold up to, at least, 88% reaction (Table 4) shows that, so far as we can determine, the reaction is irreversible under these conditions.

TABLE 5.

Thermodynamic values for electron transfer from Na⁺ArH⁻ to 1,1,3,3-tetraphenylbut-1-ene.

ArH	k (l. mole ⁻¹ sec. ⁻¹) at					ΔH^\ddagger	ΔG_{30}^\ddagger	ΔS_{30}^\ddagger
	30°	35°	40°	50°	60°			
Chrysene *	6.61	9.58	13.18	26.73	48.4	13.4	20.8	-24.4
Picene †	5.0	—	9.98	27.2	59.1	16.9	25.2	-27.4

* All k values in 10⁻³ l. mole⁻¹ sec.⁻¹. † All k values in 10⁻⁶ l. mole⁻¹ sec.⁻¹. ΔH^\ddagger and ΔG^\ddagger in kcal. mole⁻¹. ΔS^\ddagger in cal. mole⁻¹ deg.⁻¹.

Extinction Coefficient.—Equilibrium (2) lies well on the di-ion side at room temperature,² and this enables us to calculate a minimum extinction coefficient for the olefin di-ion of $\epsilon = 1.55 \times 10^4$, compared with our values $\epsilon = 1.51 \times 10^4$ for sodium naphthalene and $\epsilon = 1.6 \times 10^4$ for sodium film.³

Electron Transfer from Sodium Picene.—The rate of decrease with time of the sodium picene peaks at 404 and 690 mμ were measured to obtain the initial rate. The technique was as for sodium chrysene. The results are given in Tables 3 and 5. Again we find that the rate of electron transfer = $k[\text{Sodium picene}][\text{Olefin}]$, and in the conditions of our experiments the electron transfer goes to completion. The minimum extinction coefficient of the olefin di-ion is $\epsilon = 1.4 \times 10^4$.

DISCUSSION

The results found for electron transfer involving 1,1,3,3-tetraphenylbut-1-ene are similar to those for tetraphenylethylene,¹ except that there is slow transfer to 1,1,3,3-tetraphenylbut-1-ene in the case of sodium chrysene and sodium picene, whereas the corresponding reactions for tetraphenylethylene are extremely rapid.

The difference in the activation enthalpies of electron transfer from sodium chrysene and sodium picene to the tetraphenylbutene is 3.5 kcal. mole⁻¹ (Table 5). The difference in the calculated electron affinities⁴ of chrysene and picene is 0.5 kcal. mole⁻¹. It would be surprising if the overall change in the heat of reaction were so much smaller than the change in activation enthalpy, and this apparent anomaly probably arises because the calculated electron affinities refer to single ions in the gas phase, whereas our experimental values involve ion pairs in solution, and thus the dissociation energy and heat of solution of the ion pairs Na⁺ArH⁻ are also involved.

⁴ Matsen, *J. Chem. Phys.*, 1956, **24**, 602.

In its ability to take up an electron in tetrahydrofuran with sodium as the gegenion, 1,1,3,3-tetraphenylbut-1-ene lies between picene and pyrene. In this it is similar to tetraphenylethylene;¹ but, since the electron transfer from sodium chrysene and sodium picene to 1,1,3,3-tetraphenylbut-1-ene occurs only with difficulty (a large excess of the olefin was used in our experiments), whereas the transfer to tetraphenylethylene is too rapid for measurement even at equivalent olefin and Na^+ArH^- concentrations, the ability of tetraphenylethylene to take up an electron is the greater.

The temperature-independent factor is 9×10^7 l. mole⁻¹ sec.⁻¹ for the sodium chrysene reaction and 2×10^7 l. mole⁻¹ sec.⁻¹ for sodium picene. It is not surprising that these factors are low since the molecules involved in these electron transfers are so large, thus reducing the probability of a sterically favourable collision. Since butyl-lithium is prevented by steric hindrance from reacting with 1,1,3,3-tetraphenylbut-1-ene⁵ to give the ion pair, $\text{CPh}_2\text{Me}\cdot\text{CHBu}\cdot\text{CPh}_2^-\text{Li}^+$, it is clear that the Na^+ArH^- will also be unable to approach this sterically hindered position in order to effect the electron transfer. We believe that this transfer occurs between the aromatic rings of the donor and the acceptor molecule; the position of the free electron, shown formally in our reaction schemes, is of course not fixed on the secondary carbon atom but also moves in the field of the terminal phenyl groups. Electron transfer between phenyl groups will also occur in the disproportionations of the type shown in equation (2), and in analogous reactions involving tetraphenylethylene.

We thank D.S.I.R. for a Research Studentship (to J. C. E.), and for a grant towards the purchase of the e.s.r. spectrometer, also Imperial Chemical Industries Limited for the loan of thermostat equipment.

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[Received, May 28th, 1963.]

⁵ Evans and George, *J.*, 1961, 4653.
