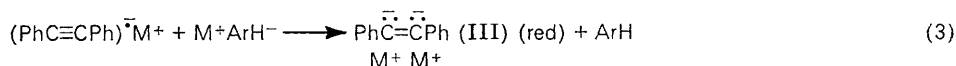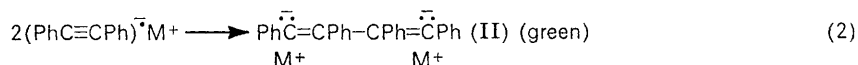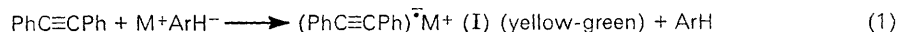# Reactions of Radical Anions. Part VI.[1] The Transfer of an Electron to the Tolan Radical Anion

By **D. A. Dadley** and **Alwyn G. Evans**, Chemistry Department, University College, Cathays Park, Cardiff

When tolan is added to an excess of alkali metal hydrocarbon using tetrahydrofuran as solvent, an electron is added to tolan, at a rate too fast to measure, to form the monomer radical anion (I) which may dimerise to form the dianion (II) or may accept an electron from the excess of alkali metal hydrocarbon to form the monomer dianion (III). When lithium is the gegenion, reaction (3) is much faster than (2), and too fast for us to measure. When potassium is the gegenion, reaction (3) is too slow to observe, and all the monomer radical anion formed in reaction (1) dimerises according to (2). When sodium is the gegenion, reaction (3) is competitive in rate with (2), and the thermodynamic constants obtained for reaction (3) at $0°$ are: sodium phenanthrene, $\Delta G_3^{\ddagger} = 13\cdot5$ kcal. $mole^{-1}$, $\Delta H_3^{\ddagger} = 19\cdot5$ kcal. $mole^{-1}$, and $\Delta S_3^{\ddagger} = 22$ cal. $mole^{-1}$ $deg.^{-1}$; sodium naphthalene, $13\cdot5, 14\cdot5$, and 4, respectively.

$$PhC{\equiv}CPh + M^+ArH^- \longrightarrow (PhC{\equiv}CPh)^{\overset{\cdot}{-}}M^+ \;(I)\;(yellow\text{-}green) + ArH \qquad (1)$$

$$2(PhC{\equiv}CPh)^{\overset{\cdot}{-}}M^+ \longrightarrow \underset{M^+ \qquad M^+}{Ph\overset{\cdot\cdot}{C}{=}CPh{-}CPh{=}\overset{\cdot\cdot}{C}Ph}\;(II)\;(green) \qquad (2)$$

$$(PhC{\equiv}CPh)^{\overset{\cdot}{-}}M^+ + M^+ArH^- \longrightarrow \underset{M^+\;M^+}{Ph\overset{\cdot\cdot}{C}{=}\overset{\cdot\cdot}{C}Ph}\;(III)\;(red) + ArH \qquad (3)$$

When an excess of tolan is mixed with an alkali metal hydrocarbon, reaction (3) does not occur, but there is a slower reaction of the tolan dimer dianion (II) with the excess of tolan to give a blue product ($\lambda_{max.}$ 600 mμ). The results at $0°$ for this reaction are $k_4 = 6\cdot7 \times 10^{-3}$ l. $mole^{-1}$ $sec.^{-1}$, $\Delta G_4^{\ddagger} = 18\cdot6$ kcal. $mole^{-1}$, $\Delta H_4^{\ddagger} = 16\cdot0$ kcal. $mole^{-1}$, and $\Delta S_4^{\ddagger} = -9\cdot5$ cal. $mole^{-1}$ $deg.^{-1}$, when Na^+ is the gegenion.

In a previous paper [2] we studied systems in which tetrahydrofuran solutions of a metal aromatic hydrocarbon and of tolan were mixed under conditions in which there was an excess of tolan. We measured the rates and activation energies for the dimerisation of the tolan radical anions (I) so formed. For systems for which the electron donor is in excess of the tolan, we find that an electron transfer may occur from the excess of donor to the monomer radical anion to give the monomer dianion (III). The kinetics of this electron transfer, and the effect of the nature of the gegenion on its rate, are now described.

In the presence of an excess of tolan the monomer radical anion (I) dimerises to the dimer dianion (II) which then undergoes a much slower reaction with the excess of tolan to give a blue product.

We have studied this reaction using sodium as gegenion.

EXPERIMENTAL AND RESULTS

The experimental technique was the same as that described in Part IV.[2]

With M+ArH− in Excess

(a) *Lithium Phenanthrene as Donor.*—Solutions of lithium phenanthrene of various concentrations were mixed at

$-20°$ in the stop-flow system with a $0\cdot67 \times 10^{-3}$M-solution of tolan, and the change in optical density at 420 mμ was followed,[2] to observe the change in monomer radical anion concentration. In runs 1, 2, and 3 (Table 1), when the

TABLE 1

Effect of $[Li^+Phen^-]$ on the initial rate of reaction between Li^+Phen^- and Li^+Tolan^- at $-20°$

Run	$10^3[Phen^-]$ (M)	Initial rate *	$10^3([Phen^-] - 2[Tolan]\dagger)$ (M)
1	2·0	0·000	0·65
2	1·74	0·000	0·40
3	1·37	0·000	0·02
4	0·60	0·0166	−0·74
5	0·35	0·0055	−0·99

* Units are O.D. $min.^{-1}$ in a 1-mm. cell (λ 420 mμ). † Tolan $0\cdot67 \times 10^{-3}$M.

lithium phenanthrene concentration is greater than twice that of tolan, there is no decrease in absorption at 420 mμ, and hence no dimerisation according to reaction (2) is observed. The monomer radical anion formed according to reaction (1) has been rapidly and completely converted by the excess of lithium phenanthrene into monomer dianion according to reaction (3) between the mixing of the solutions and their arrival in the cell, *i.e.*, in less than 0·2 sec., leaving no monomer radical anion. For runs 4

[1] Part V, A. G. Evans, J. C. Evans, and C. L. James, *J. Chem. Soc. (B)*, 1967, 652.

[2] D. Dadley and A. G. Evans, *J. Chem. Soc. (B)*, 1967, 418.

and 5, the lithium phenanthrene concentration is less than twice that of tolan. Thus, after reaction (1) there is not enough lithium phenanthrene left to convert all the monomer radical anion into dianion according to reaction (3), and the remaining monomer radical anion dimerises according to reaction (2), with a consequent decrease in the optical density at 420 mμ. Runs 4 and 5 give a rate constant of 0·38 l. mole^{-1} sec.$^{-1}$ at $-20°$, which compares well with the value [2] of 0·33 for the dimerisation of sodium tolan.

(b) *Sodium Phenanthrene as Donor.*—When an excess of sodium phenanthrene is added to a given concentration of tolan, the optical density at 420 mμ decreases more rapidly the greater the excess of sodium phenanthrene present. (Neutral phenanthrene cannot be involved here, since it is also present when sodium phenanthrene is not in excess and has no effect; see Part IV.[2]) This is in marked contrast to the case of lithium phenanthrene (above), and shows that, although the donation of an electron to the tolan [reaction (1)] is too fast to measure, the donation of an electron from the excess of sodium phenanthrene to the tolan monomer radical anion [reaction (3)] proceeds at a measurable rate.

At 420 mμ both sodium phenanthrene and sodium tolan absorb strongly so only the combined disappearance of these radical anions can be measured. The tolan monomer radical anion will disappear both by dimerisation [reaction (2)] and by taking up an electron to go to the monomer dianion [reaction (3)]. The excess of sodium phenanthrene will disappear since it acts as donor in reaction (3). We have calculated the component of the initial rate which is due to dimerisation by using the rate constant obtained in Part IV.[2] Subtraction of this from the observed rate gives the rate of reaction between the sodium phenanthrene and the sodium tolan [reaction (3)].

Order in sodium phenanthrene. Solutions were made of various concentrations of sodium phenanthrene and 0·44 × 10^{-3}M tolan at $-19.5°$. The rate of dimerisation of the tolan monomer radical anions [formed by reaction (1)] at·this concentration and temperature is [2] 0·012 O.D. min.$^{-1}$. This value is subtracted from the observed initial rate in Table 2 to give the initial rate for the transfer of the second

TABLE 2
Effect of excess of Na$^+$Phen$^-$ on observed initial rate

10^3[Na$^+$Phen$^-$] (M)	1·48	0·90	0·74
10^3[Tolan] (M)	0·44	0·44	0·44
10^3[Na$^+$Phen$^-$]$_{excess}$ (M)	1·04	0·46	0·30
Observed initial rate *	0·32	0·14	0·09
Calc. initial dimerisation rate *	0·012	0·012	0·012
Calc. initial rate of 2nd electron transfer *...	0·31	0·13	0·08
10^4(Rate of transfer of 2nd electron/ [Na$^+$Phen$^-$]$_{excess}$)	2·98	2·83	2·67

* Rate units are O.D. min.$^{-1}$ in a 1-mm. cell (λ 420 mμ).

electron [reaction (3)]. The plot of log$_{10}$(calculated initial rate of second electron transfer) against log$_{10}$-[NaPhen]$_{excess}$ gives an order of 1·1, *i.e.*, the second electron transfer is first-order in the excess of phenanthrene.

Order in tolan radical anion. The total sodium phenanthrene concentration was kept constant and the tolan concentration varied. This produces a change in [NaPhen]$_{excess}$, but by use of the previous result, that the reaction is first-order in this excess, one may write

$$\text{Rate} = k[\text{NaPhen}]_{excess} \times [\text{NaTolan}]^n$$

and plot (log Rate $-$ log[NaPhen])$_{excess}$ against log[Na-Tolan]. This plot should give a slope equal to the order, n. Table 3 shows the $-18°$ rates in units O.D. min.$^{-1}$ at 420 mμ in a 1-mm. cell. Figure 1 shows that the order in tolan radical anion is 0·95, *i.e.*, first-order.

TABLE 3
Electron transfer from Na$^+$Phen$^-$ to Na$^+$Tolan$^-$; reaction (3)

10^3[Tolan]	10^3[Na$^+$Phen$^-$]	10^3[Na$^+$Phen$^-$]$_{excess}$	R_{obs} *	R_D †	R ‡
4·65	0·765	0·000	0·043	0·043	—
2·36	0·765	0·000	0·045	0·043	—
1·15	0·765	0·000	0·042	0·043	—
0·54	0·765	0·225	0·17	0·021	0·15
0·30	0·765	0·465	0·19	0·006	0·18
0·145	0·765	0·620	0·12	0·001	0·12

* Observed rate. † Calculated dimerisation rate. ‡ $R = (R_{obs} - R_D) =$ initial rate of electron transfer from Na$^+$Phen$^-$ to Na$^+$Tolan$^-$.
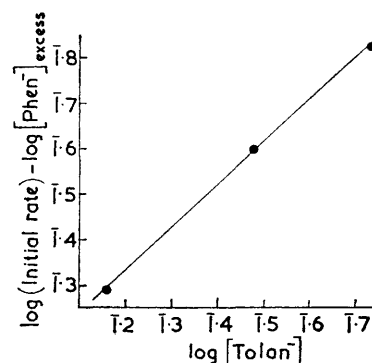

FIGURE 1   Order plot for reaction of Na$^+$Phen$^-$ with Na$^+$Tolan$^-$; reaction (3)

Determination of the activation energy. The solutions used were 0·52 × 10^{-3}M-tolan and 0·97 × 10^{-3}M-sodium phenanthrene, giving an excess sodium phenanthrene concentration of 0·45 × 10^{-3}M. At each temperature, the initial rate, in optical densities per minute at 420 mμ in the 1-mm. cell, was measured, and the rate of dimerisation of 0·52 × 10^{-3}M-tolan radical ions calculated [2] in the same units. This calculated rate was then subtracted from the observed rate to give the rate of electron transfer (Table 4)

TABLE 4
Electron transfer from Na$^+$Phen$^-$ to Na$^+$Tolan$^-$; reaction (3)

Temp.	R_{obs} *	R_D *	R *	Temp.	R_{obs}	R_D	R *
$-4.4°$	1·00	0·14	0·86	$-28.5°$	0·028	0·004	0·024
-8.4	0·83	0·07	0·76	-30.6	0·024	0·003	0·0215
-13.7	0·36	0·03	0·33	-34.1	0·011	0·0015	0·0095
-17.6	0·17	0·02	0·15	-35.6	0·011	0·0011	0·0099
-21.7	0·12	0·01	0·11	-36.7	0·0085	0·0009	0·0076
-25.0	0·069	0·006	0·063				

* See Table 3.

to the monomer radical anion [reaction (3)]. The Arrhenius plot gives an activation energy of 20·0 kcal. mole^{-1} and a rate at $0°$ of 2·5 O.D. min.$^{-1}$. For tolan and an excess of sodium phenanthrene concentrations both equal to 10^{-3}M this would become 10·5 O.D. min.$^{-1}$. This value can now be converted into an absolute rate constant by using the values for the extinction coefficients at 420 mμ of the tolan radical ion (2·0 × 10^4), the monomer dianion (0·89 × 10^4),

and sodium phenanthrene (0.86×10^4). Use of these gives a value at $0°$ for the rate constant of reaction (3): $k_3 = 87$ l. mole^{-1} sec.$^{-1}$.

Thermodynamic constants. The values of $\Delta G_3^{\ddagger}$, $\Delta H_3^{\ddagger}$, and $\Delta S_3^{\ddagger}$, calculated at $0°$ using the values $k_3 = 87$ l. mole^{-1} sec.$^{-1}$ and $E_a = 20$ kcal. mole^{-1} for reaction (3), are 13.5 kcal. mole^{-1}, 19.5 kcal. mole^{-1}, and $+22$ cal. deg.$^{-1}$ mole^{-1}, respectively.

(c) *Sodium Naphthalene as Donor.*—This system behaves similarly to that involving sodium phenanthrene, and it was investigated in the same way.

Activation energy. The results are in Table 5. The

TABLE 5

Electron transfer from Na$^+$Nap$^-$ to Na$^+$Tolan$^-$; reaction (3)

Temp.	R_{obs} *	R_D *	R *	Temp.	R_{obs} *	R_D *	R *
4.8°	4.20	0.57	3.63	−19.5°	0.195	0.018	0.177
0.0	2.24	0.27	1.97	−25.5	0.141	0.0076	0.133
−4.3	1.60	0.16	1.44	−26.9	0.129	0.0063	0.123
−10.0	0.755	0.072	0.68	−31.8	0.054	0.0035	0.0505
−15.0	0.615	0.036	0.580				

* See Table 3.

Arrhenius plot gives $E_a = 15$ kcal. mole^{-1}, and a second-order rate constant at $0°$ for reaction (3) of $k_3 = 94$ l. mole^{-1} sec.$^{-1}$.

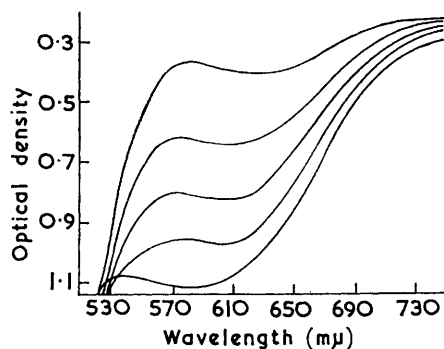FIGURE 2   Absorption spectra drawn at 90-sec. intervals, at $15°$

[Na$^+$Phen$^-$]$_i$ = 7.5×10^{-3}M; [Tolan]$_i$ = 50×10^{-3}M

Thermodynamic constants at $0°$. The results for reaction (3) are: $\Delta H_3^{\ddagger} = 14.5$ kcal. mole^{-1}, $\Delta G_3^{\ddagger} = 13.5$ kcal. mole^{-1}, $\Delta S_3^{\ddagger} = 4$ cal. deg.$^{-1}$ mole^{-1}.

(d) *Potassium Phenanthrene and Potassium Naphthalene as Donors.*—Whilst lithium phenanthrene, sodium phenanthrene, and sodium naphthalene are capable of transferring an electron to the tolan radical anion, this process can not be observed when potassium naphthalene or potassium phenanthrene are donors. (Owing to the high extinction coefficients of the donor ions it was not possible to use a concentration of potassium naphthalene greater than about 6×10^{-3}M or of potassium phenanthrene greater than 3×10^{-3}M.) Over the range $+20°$ to $-30°$, when an excess of potassium phenanthren or of potassium naphthalene was added to tolan, the rate of decrease of optical density at 420 mμ was independent of the excess donor concentration. Furthermore, the activation energy and the rate constant are the same as those found in Part IV [2] for the dimerisation of potassium tolan.

With Tolan in Excess

The spectrum of a solution 7.5×10^{-3}M in sodium phenanthrene and 50×10^{-3}M in tolan was measured at 90-second intervals and $15°$ (Figure 2). Figure 3 shows the
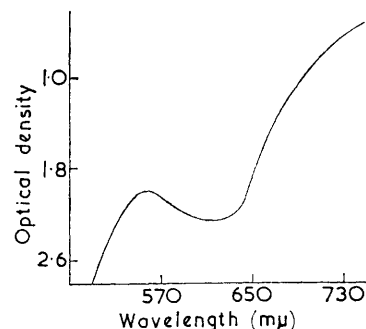

FIGURE 3   Absorption spectrum drawn 3 hr. after mixing, at $15°$

[Na$^+$Phen$^-$]$_i$ = 7.5×10^{-3}M; [Tolan]$_i$ = 30×10^{-3}M

spectrum of a solution 7.5×10^{-3}M in sodium phenanthrene and 30×10^{-3}M in tolan, 3 hr. after mixing, when reaction has ceased; a new peak occurs at 600 mμ, and the dependence of the rate of increase of this peak on the excess tolan concentration and on dimer dianion (II) concentration was measured.

Order in Excess of Tolan.—The results are in Table 6.

TABLE 6

Effect of excess of tolan concentration on rate of optical density increase at 600 mμ at $15°$; [Na$^+$Phen$^-$]$_i$ = 7.5×10^{-3}M

10^3[Tolan]$_{total}$ (M)	10^3[Tolan]$_{excess}$ (M)	Initial rate *
15	7.5	0.033
30	22.5	0.083
50	42.5	0.180

* Rate units are O.D. min.$^{-1}$ in a 1-mm. cell (λ 600 mμ).

The initial rate of increase in optical density at 600 mμ was determined at each tolan concentration. Since the amount of tolan converted into radical anion (I) equals the amount of sodium phenanthrene [see reaction (1)], the [Tolan]$_{excess}$
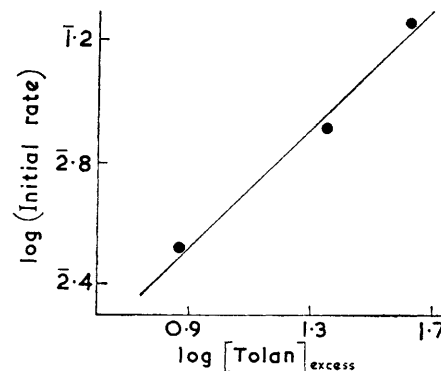

FIGURE 4   Order plot for reaction between Na$^+$PhC̿=CPh–CPh=C̿PhNa$^+$ and tolan

equals [Tolan]$_{total}$ minus [NaPhen]. A plot of log-[Tolan]$_{excess}$ against log(Initial rate) gives the order in excess of tolan as 0.97 (Figure 4). Thus, the reaction producing the 600 mμ peak is first-order in excess of tolan.

Order in Tolan Dimer Dianion.—The effect of the dimer dianion (II) concentration on the initial rate of development of the 600 mμ peak was measured by varying the concentration of sodium phenanthrene added to a constant concentration of tolan (Table 7). The initial dimer dianion

TABLE 7

Order-plot data for the reaction between dimer dianion (II) 2 (Na$^+$) and tolan at 15°; [Tolan]$_{total}$ = 14·5 × 10^{-3}M

10^3[Na$^+$Phen$^-$]	10^3[Dimer dianion]	10^3[Tolan]$_{excess}$	Initial rate *
7·5	3·75	14·5 − 7·5 = 7·0	0·033
5·22	2·61	14·5 − 5·2 = 9·3	0·028
3·26	1·63	14·5 − 3·3 = 11·2	0·021

* Rate units are O.D. min.$^{-1}$ in a 1-mm. cell (λ 600 mμ).

(II) concentration will be half the sodium phenanthrene concentration [see reactions (1) and (2)]. Since the tolan concentration was kept constant, the [Tolan]$_{excess}$ will vary with change in sodium phenanthrene concentration, and
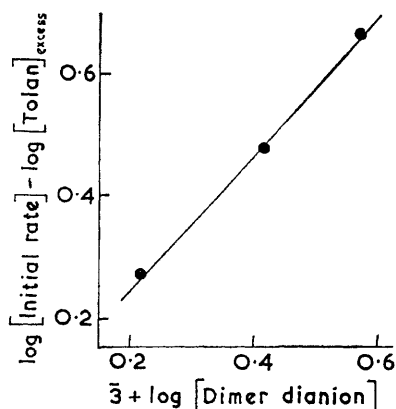

FIGURE 5 Order plot for reaction between Na$^+$PhC̈=CPh–CPh=C̈PhNa$^+$ and tolan

this has to be allowed for, as in Table 7. The order in tolan dimer dianion (II) was determined as follows:

$$\text{Rate} = k[\text{Dimer dianion}]^n \times [\text{Tolan}]_{excess}$$

$$\log \text{Rate} - \log[\text{Tolan}]_{excess} = n \log[\text{Dimer dianion}] + \log k$$

The plot of this equation (Figure 5) gave a value of n of 1·1. Thus, the reaction is first-order with respect to the dimer dianion (II).

Activation Energy.—A solution 7·5 × 10^{-3}M in sodium phenanthrene and 14·5 × 10^{-3}M in tolan was used. The concentration of the dimer dianion (II) was thus 3·75 × 10^{-3}M and the concentration of the excess of tolan was 7·0 × 10^{-3}M. The initial rate of production of the 600 mμ peak was measured at various temperatures (Table 8). The activation energy so found was 16·5 kcal. mole^{-1}.

TABLE 8

Arrhenius plot data for reaction of dimer dianion (II) 2 (Na$^+$) with tolan

Temp.	31·0	24·5	15·0	5·5	−4·3
Initial rate * ...	0·158	0·074	0·033	0·011	0·0045

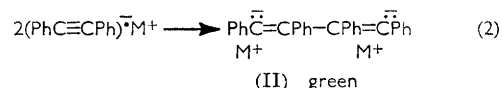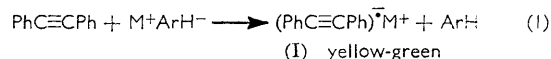* Rate units are O.D. min.$^{-1}$ in a 1-mm. cell (λ 600 mμ).

The Rate Constant.—From Figure 3 the final optical density at 600 mμ of a mixture 30 × 10^{-3}M in tolan and 7·5 × 10^{-3}M in sodium phenanthrene [producing 3·75 × 10^{-3}M dimer dianion (II)] is 2·3. Thus, a rate of increase of optical density at 600 mμ of 2·3 O.D. min.$^{-1}$ corresponds to the disappearance of 3·75 × 10^{-3} mole l.$^{-1}$ of dimer dianion (II) per minute, and 1·0 O.D. min.$^{-1}$ is equivalent to 1·63 × 10^{-3} mole l.$^{-1}$ min.$^{-1}$.

The initial rate at 0° is 0·0065 O.D. min.$^{-1}$ for [Tolan]$_{excess}$ = 7·0 × 10^{-3}M and [Dimer dianion] = 3·75 × 10^{-3}M. Thus, 0·0065 × 1·63 × 10^{-3} mole l.$^{-1}$ min.$^{-1}$ = k_4 × 7·0 × 10^{-3} × 3·75 × 10^{-3} mole^2 l.$^{-2}$, which gives k_4 = 0·0067 l. mole^{-1} sec.$^{-1}$ at 0°.

Thermodynamic Constants.—At 0° the following values are obtained: $\Delta G_4^{\ddagger}$ = 18·6 kcal mole^{-1}, $\Delta H_4^{\ddagger}$ = 16·0 kcal. mole^{-1}, and $\Delta S_4^{\ddagger}$ = −9·5 cal. mole^{-1} deg.$^{-1}$.

DISCUSSION

In Part IV [2] we showed that when sodium naphthalene was added to an excess of tolan in tetrahydrofuran as solvent, there is first an electron transfer (1) to form the tolan monomer radical anion. This reaction, which was too fast to measure, was followed by the dimerisation (2) of the tolan monomer radical anions, and this, although very fast, was measured in a stop-flow apparatus.

PhC≡CPh + M$^+$ArH$^-$ ⟶ (PhC≡CPh)$^{\cdot-}$M$^+$ + ArH (1)

(I) yellow-green

2(PhC≡CPh)$^{\cdot-}$M$^+$ ⟶ PhC̈=CPh–CPh=C̈Ph (2)
 M$^+$ M$^+$

(II) green

We have now shown that when the M$^+$ArH$^-$ is in excess of the tolan, the tolan monomer radical anion formed in reaction (1) may undergo an alternative reaction (3) by accepting an electron from the excess of M$^+$ArH$^-$ to form the dianion of the monomer.

(PhC≡CPh)$^{\cdot-}$M$^+$ + M$^+$ArH$^-$ ⟶ PhC̈=C̈Ph + ArH (3)
 M$^+$ M$^+$

(III) red
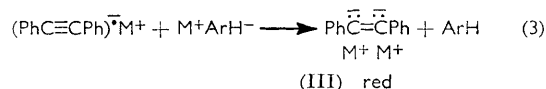
We found in Part IV [2] that the rate of the dimerisation (2) depended on the gegenion, and we again find that the ease of electron transfer (3) to the radical anion depends markedly on the nature of the gegenion. For Li$^+$, reaction (3) is much faster than (2), and too fast for measurement by our present technique. For Na$^+$, reaction (3) is comparable in rate with (2), and we have been able to study it by allowing for the simultaneous occurrence of the dimerisation. For K$^+$, reaction (3) is much slower than (2), and we have not been able to detect its occurrence.

Reaction (3), unlike (2), is sensitive to the nature of ArH$^-$ since this is acting as a donor. We find that the change from sodium naphthalene ($\Delta G_3^{\ddagger}$ = 13·5 kcal. mole^{-1}, $\Delta H_3^{\ddagger}$ = 14·5 kcal. mole^{-1}, and $\Delta S_3^{\ddagger}$ = 4 cal. mole^{-1} deg.$^{-1}$) to sodium phenanthrene (13·5, 19·5, and 22, respectively) has no effect upon $\Delta G_3^{\ddagger}$ but $\Delta H_3^{\ddagger}$ increases by 5 kcal. mole^{-1}. Since the electron affinity of phenanthrene is greater than that of naphthalene

by 0·9 kcal. mole^{-1},[3] we should expect $\Delta H_3^{\ddagger}$ to be greater for sodium phenanthrene than for sodium naphthalene.

The only other electron transfer reactions of this kind which have not been too fast for us to measure are those from sodium chrysene and sodium picene to 1,1,3,3-tetraphenylbut-1-ene.[4] In this case, too, the picene, which has the higher electron affinity by 0·5 kcal. mole^{-1},[3] also has the higher $\Delta H^{\ddagger}$ (by 3·5 kcal. mole^{-1}) for electron transfer. We attribute the fact that we could measure this electron transfer to the olefin to the non-planarity of 1,1,3,3-tetraphenylbut-1-ene requiring the pushing of ArH^{-} and olefin together to bring the phenyl groups of donor and acceptor into contact. In the case of the transfer to sodium tolan, we attribute the fact that we can measure the rate of this electron transfer to the negative charge on the tolan. This will reduce the ease of electron transfer markedly, so it is not surprising that we can follow this reaction but not the electron transfer (1) to neutral tolan.

All these reactions are very rapid. In the presence of an excess of tolan no monomer dianion (III) is formed, but the dimer dianion (II) slowly reacts with the excesss of tolan. This reaction is first-order in tolan dimer dianion (II) and in neutral tolan, and gives a blue product ($\lambda_{max.}$ 600 mμ).

[3] F. A. Matsen, *J. Chem. Phys.*, 1956, **24**, 602.
[4] A. G. Evans and J. C. Evans, *J. Chem. Soc.*, 1963, 6036.