polarizability of the halogens. We have tested this correlation on many series of reactions by plotting activation energy against the reciprocal polarizability of the stable molecular reactant. Near linear plots were obtained for 12 homologous reaction series, including more than 60 atom transfer reactions for which data were available.[31]

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# Kinetics of Electron Transfer between the Dimeric Dianions of 1,1-Diphenylethylene and Perylene or Tetracene

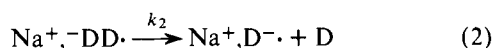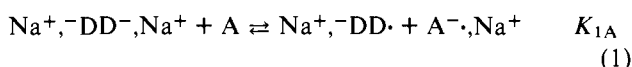**S. Lillie, S. Slomkowski, G. Levin, and M. Szwarc***

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Abstract: Kinetics of the electron transfer initiated reaction taking place in THF between the disodium salt of the dimeric dianion of 1,1-diphenylethylene, $Na^+,\bar{C}(Ph)_2CH_2CH_2\bar{C}(Ph)_2,Na^+ = Na^+,^-DD^-,Na^+$, and perylene, Pe, or tetracene, Te, was investigated at ambient temperature by stop-flow technique. It was shown that the studied process involves three steps, namely, $Na^+,^-DD^-,Na^+ + Pe$ (or Te) $(k_{-1}) \rightleftarrows Na^+,^-DD\cdot + Pe^-\cdot,Na^+$ (or $Te^-\cdot,Na^+$) (k_1) [$K_{Pe} = k_1/k_{-1}$ and $K_{Te} = k_1'/k_{-1}'$], $Na^+,^-DD\cdot \rightarrow D + D^-\cdot,Na^+$ (k_2) (D = $CH_2{:}CPh_2$), and $D^-\cdot,Na^+ + Pe$ (or Te) $\rightarrow D + Pe^-\cdot,Na^+$ (or $Te^-\cdot,Na^+$). The reaction $Na^+,^-DD\cdot + Pe$ (or Te) $\rightarrow 2D + Pe^-\cdot,Na^+$ (or $Te^-\cdot,Na^+$) appears to be insignificant and does not contribute to the overall kinetics. The observed kinetics is accounted for by the stationary state approximation ([$Na^+,^-DD\cdot] \ll [Pe^-\cdot,Na^+]$) with the second step being rate determining. The results led to $k_2K_{Pe} = 0.9 \pm 0.1$ s^{-1}, $k_2K_{Te} = 27 \pm 6$, $k_2/k_{-1} \approx k_2/k_{-1}' \approx 10^{-5}$ M, $k_1 = (2 \pm 1) \times 10^4$ M^{-1} s^{-1}, and $k_1' = (16 \pm 8) \times 10^5$ M^{-1} s^{-1}.

Reduction of 1,1-diphenylethylene, D, by alkali metals yields dimeric dianions, $Ph_2\bar{C}CH_2CH_2\bar{C}Ph_2 = {}^-DD^-$, which may be back-converted into D on reaction with anthracene,[1] A, or pyrene, π, e.g.,

$$Na^+,Ph_2\bar{C}CH_2CH_2\bar{C}Ph_2,Na^+ + 2A$$
$$\rightleftarrows 2CH_2{:}CPh_2 + 2A^-\cdot,Na^+$$
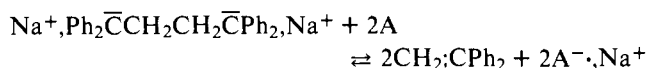
Kinetic results demonstrated that the conversion proceeds in two steps, e.g.,

$$Na^+,^-DD^-,Na^+ + A \rightleftarrows Na^+,^-DD\cdot + A^-\cdot,Na^+ \qquad K_{1A}$$
$$(1)$$

$$Na^+,^-DD\cdot \xrightarrow{k_2} Na^+,D^-\cdot + D \qquad (2)$$

(2) being followed by a rapid electron transfer

$$Na^+,D^-\cdot + A \rightarrow D + A^-\cdot,Na^+$$
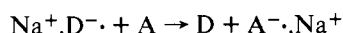
Reaction 3

$$Na^+,^-DD\cdot + A \rightarrow 2D + A^-\cdot,Na^+ \qquad (3)$$
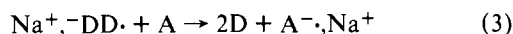
which might be expected to contribute to the overall process is not observed. As will be shown later, the spontaneous decomposition of $Na^+,^-DD\cdot$ is fast and the hypothetical reaction

Figure 1. Typical plots of $(x_\infty/[Pe]) \ln \{(x_\infty - x_0)/(x_\infty - x)\} - (x - x_0)/[Pe]$ vs. time. The zero ordinate of the a and b lines is shifted by 1 and 2 units, respectively. The slopes give the values of k_2K_1. (a) $[Pe]_0 = 8.9 \times 10^{-3}$ M, $[Pe^-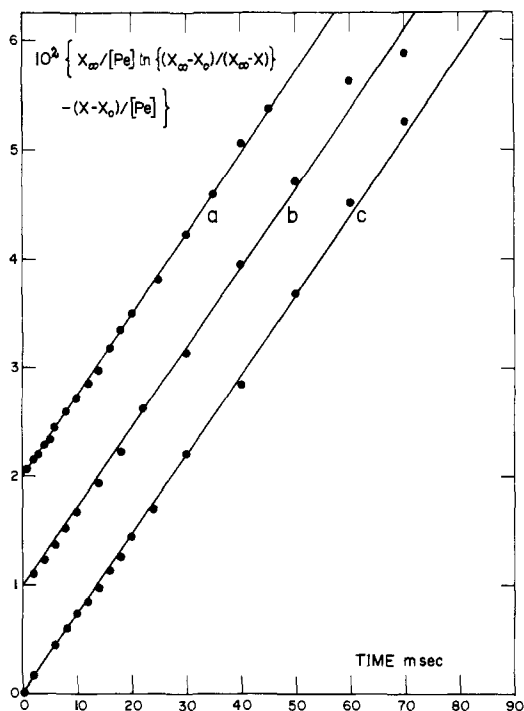\cdot,Na^+]_\infty = x_\infty = 1.5 \times 10^{-3}$ M; (b) $[Pe]_0 = 4.25 \times 10^{-3}$ M, $[Pe^-\cdot,Na^+]_\infty = x_\infty = 1.9 \times 10^{-4}$ M; (c) $[Pe]_0 = 2.5 \times 10^{-3}$ M, $[Pe^-\cdot,Na^+]_\infty = x_\infty = 2.4 \times 10^{-4}$ M.

3, which probably is slower than (1), cannot effectively compete with reaction 2.

More powerful electron acceptors might accelerate (3) and make its rate comparable to that of (2). With this in mind we investigated the decomposition of $Na^+,^-DD^-,Na^+$ induced by perylene, Pe, and tetracene, Te. Electron affinities of these hydrocarbons exceed by ~ 0.3 V that of anthracene,[3] and indeed their addition to a solution of $Na^+,^-DD^-,Na^+$ leads to a reaction completed in a fraction of a second. Nonetheless, even in these systems we found reaction 2 to be much faster than reactions $Na^+,^-DD\cdot + Pe$ (or Te) $\rightarrow 2D + Pe^-\cdot,Na^+$ (or $Te^-\cdot,Na^+$).

Experimental Section

Commercially acquired perylene and tetracene (Aldrich Chemicals) were vacuum sublimed before being used. Diphenylethylene (D) was prepared from benzophenone by reacting it with MeMgI and dehydrating the resulting alcohol, the preparation and the subsequent purification being described elsewhere.[1] The purified 1,1-diphenylethylene was kept in evacuated ampules and never exposed to the air. Its conversion into $Na^+,^-DD^-,Na^+$ was accomplished in THF with distilled metallic sodium as the reducing agent, its concentration being determined spectrophotometrically ($\lambda_{max} = 470$ nm, $\epsilon = 5.4 \times 10^4$). THF solutions of perylene or tetracene prepared on a high-vacuum line were stored in evacuated ampules equipped with break-seals. Concentration of the hydrocarbons was determined spectrophotometrically (for Pe $\lambda_{max} = 387$ nm, $\epsilon = 1.21 \times 10^4$, $\lambda_{max} = 408$ nm, $\epsilon = 2.65 \times 10^4$, $\lambda_{max} = 436$ nm, $\epsilon = 3.5 \times 10^4$; for Te $\lambda_{max} = 473$ nm, $\epsilon = 0.8 \times 10^4$).

The decomposition of $Na^+,^-DD^-,Na^+$ was studied by stop-flow technique using a Durrum stop-flow spectrophotometer and the procedure described elsewhere.[4] The reaction with Pe was monitored at 578 nm (λ_{max} of $Pe^-\cdot,Na^+$, $\epsilon = 5.9 \times 10^4$) or at 678 nm (another λ_{max} of $Pe^-\cdot,Na^+$, $\epsilon = 0.66 \times 10^4$). The absorbance at 470 nm (λ_{max} of $Na^+,^-DD^-,Na^+$, $\epsilon = 5.4 \times 10^4$) was followed in two runs, and the results were compatible with those obtained at λ_{max} of $Pe^-\cdot,Na^+$. The 1:2 stoichiometry of the reaction was established by adding Pe to a solution of $Na^+,^-DD^-,Na^+$ in an all-glass apparatus using the pre-

viously described system[5] in which any destruction of Na^+, $^-DD^-,Na^+$ by impurity could be avoided.

The initial concentration of $Na^+,^-DD^-,Na^+$ in the Durrum cell was assumed to be given by $\frac{1}{2}$ of the final concentration of the resulting radical anions determined at 1-2 s after each run. Partial destruction of $Na^+,^-DD^-,Na^+$ in the feeding syringes necessitated this procedure. To purge the flow system the reagents were pushed through the cell three times before the kinetics of the conversion was followed after stopping the flow on the fourth push.

Partial destruction of $Na^+,^-DD^-,Na^+$ in the feeding syringes results from protonation yielding HDD^-,Na^+ or HDDH. Appropriate experiments demonstrated that the reaction of HDD^-,Na^+ with Pe is much too slow to contribute to the studied kinetics. Also the reaction $HDDH + Na^+,^-DD^-,Na^+ \rightarrow 2HDD^-,Na^+$ is too slow to be of significance. Moreover, $Na^+,^-DD^-,Na^+$ does not react with $Pe^-\cdot$ or $Te^-\cdot$. Therefore, only Pe or Te and $Na^+,^-DD^-, Na^+$ are the reagents participating in the investigated process.

To avoid any complications arising from different reactivities of free ions and ion pairs, an excess (ca. tenfold) of Na^+,BPh_4^- was added to the stock solution of $Na^+,^-DD^-,Na^+$. Our results refer therefore to the reactions involving ion pairs.

## Oxidation of $Na^+,^-DD^-,Na^+$ by Perylene

Kinetic results were derived from the oscilloscope tracings following the absorbance monitored at 578 nm (at low initial concentrations of $Na^+,^-DD^-,Na^+$) or at 678 nm (when the initial concentration of the dianions was ten times higher). It was demonstrated that identical results were obtained at intermediate concentrations of $Na^+,^-DD^-,Na^+$ whether the absorbance was monitored at 578 nm or at 678 nm. The following treatments were applied to our data: (a) The equilibrium,

$$Na^+,^-DD^-,Na^+ + Pe \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Na^+,^-DD\cdot + Pe^-\cdot,Na^+ \quad K_{Pe}$$
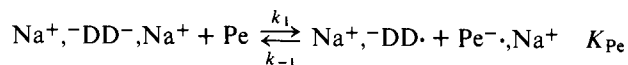
is assumed to be established at the onset of our observations (~ 2 ms after mixing the reagents) and maintained during the course of each run. Reaction 2,

$$Na^+,^-DD\cdot \xrightarrow{k_2} D + D^-\cdot,Na^+$$
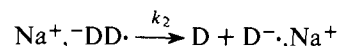
seems to be rate determining and is followed by the rapid electron transfer

$$Pe + D^-\cdot,Na^+ \rightarrow Pe^-\cdot,Na^+ + D$$
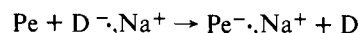
Denoting $[Pe^-\cdot,Na^+]_t$ and $[Pe^-\cdot,Na^+]_\infty$ by x and x_∞, respectively, we deduce the relation

$$dx/dt = k_2K_{Pe}(x_\infty - x)([Pe]_0 - x)/x$$

provided that all the time the concentration of $Na^+,^-DD\cdot$ is very low.

Since $[Pe]_0 \gg [Pe^-\cdot,Na^+]_\infty$ the approximation $[Pe]_t = [\overline{Pe}] = [Pe]_0 - \frac{1}{2}[Pe^-\cdot,Na^+]_\infty$ is justified and then the integration gives

$$(x_\infty/[\overline{Pe}]) \ln \{(x_\infty - x_0)/(x_\infty - x)\} - (x - x_0)/[\overline{Pe}]$$
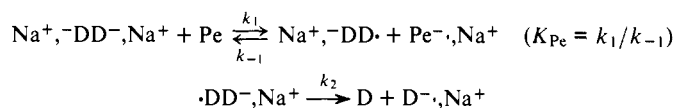$$= k_2K_{Pe}t$$

Straight lines exemplified by Figure 1 result when the left-hand side of this equation is plotted against time. Their slopes yield k_2K_{Pe} listed in the third column of Table I.

(b) In scheme (a) it was tacitly assumed that $K_{-1}[Pe^-\cdot, Na^+]$ is much greater than k_2. Had this not been the case then the concentration of $Na^+,^-DD\cdot$, provided again that it is very low, should be given by the stationary approximation, i.e.,

$$dx/dt = k_2K_{Pe}(x_\infty - x)([Pe]_0 - x)/(x + k_2/k_{-1})$$

Assuming $[Pe]_0 - x \simeq [\overline{Pe}]$ = constant, the integration leads to a linear relation of $(x - x_0)^{-1} \ln \{(x_\infty - x_0)/(x_\infty - x)\}$ on $t/(x - x_0)$. Typical straight lines representing such a relation are shown in Figure 2; their slopes and intercepts yield

Table I

$$Na^+,{}^-DD^-,Na^+ + Pe \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Na^+,{}^-DD\cdot + Pe^{-\cdot},Na^+ \quad (K_{Pe} = k_1/k_{-1})$$

$$\cdot DD^-,Na^+ \xrightarrow{k_2} D + D^{-\cdot},Na^+$$

$10^3[Pe]_0$, M	$10^4[Pe^{-\cdot},Na^+]_\infty$, M	Treatment (a) k_2K_{Pe}, s	Treatment (b)		
			k_2K_{Pe}, s	$10^5\ (k_2/k_{-1})$, M	$10^{-4}k_1$, M s
9.95	11.4	0.77	0.82	0.07	117
8.9	15.1	0.74	0.89	4.4	2.0
8.1	15.1	0.99(?)	1.17(?)	14. (?)	0.9(?)
6.95	14.3	0.77	0.86	0.3	28.7
5.70	12.0	0.86	0.97	2.1	4.6
5.05	10.4	0.90	1.02	3.0	3.4
4.70	12.2	0.85	1.01	4.8	2.1
4.00	10.6	0.84	0.98	0.8	12.3
2.95	15.1	0.63	0.84	Neg	Neg
1.85	12.2	0.67	0.97	Neg	Neg
Av		0.78 ± 0.09	0.95 ± 0.10		
4.24	1.92	0.75	0.89	1.9	4.7
3.74	1.76	0.84	0.95	1.7	5.6
3.24	1.91	0.82	0.96	2.4	4.0
2.72	1.84	0.88	1.03	2.4	4.3
2.45	2.39	0.74	0.85	0.8	10.6
2.01	1.91	0.80	0.94	2.4	3.9
1.71	2.29	0.76	0.86	1.3	6.6
1.22	2.12	0.84	1.00	1.8	5.6
0.72	2.24	0.77	0.86	1.4	6.1
0.44	2.16	0.73	1.00	0.7	14.3
Av		0.79 ± 0.05	0.93 ± 0.07	1.7 ± 0.7	6.4 ± 3.4
9.9	0.65^a	0.67	0.65	Neg	Neg
9.9	0.82^b	1.13	1.16	0.2	5.5
9.9	0.68^a	0.91	1.17	1.8	6.3
9.9	0.81^b	1.12	1.28	1.2	1.1
6.9	0.66	0.79	0.89	0.9	1.0
	0.69	0.77	0.73	Neg	Neg
Av		0.90 ± 0.19	0.98 ± 0.26	1.0 ± 0.7	3.5 ± 2.8

^{a} Monitored at 578 nm. ^{b} Monitored at 678 nm.

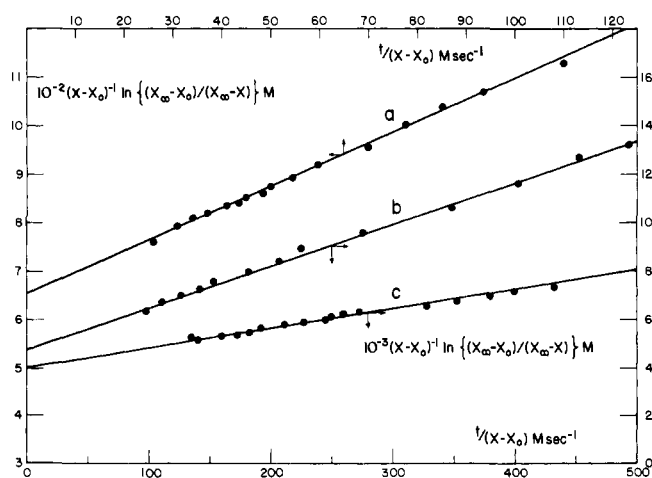**Figure 2.** Typical plots of $(x - x_0)^{-1} \ln\{(x_\infty - x_0)/(x_\infty - x)\}$ vs. $t/(x - x_0)$. The slopes give $k_2K_1[Pe]/(k_2/k_{-1} + x_\infty)$ while the intercepts give $1/(k_2/k_{-1} + x_\infty)$. The conditions of the respective experiments are given in the caption of Figure 1.

Figure 3. Plot of F/R vs. t/R. $F = [Pe]_0 \ln U - x_\infty \ln V$, $R = \ln (U/V)$. $U = ([Pe]_0 - x)/([Pe]_0 - x_0)$, $V = (x_\infty - x)/(x_\infty - x_0)$. Slope gives k_2K_{Pe}, intercept $-k_2/k_{-1}$. (O) $[Pe]_0 = 8.9 \times 10^{-3}$ M; $[Pe^{-\cdot},Na^+]_\infty = 1.5 \times 10^{-3}$ M; (△) $[Pe]_0 = 5.7 \times 10^{-3}$ M; $[Pe^{-\cdot},Na^+]_\infty = 1.2 \times 10^{-3}$ M. F/R in units 10^{-4} M, t/r in ms.

$k_2K_{Pe}[\overline{Pe}]/(x_\infty + k_2/k_{-1})$ and $1/(k_2/k_{-1} + x_\infty)$, respectively.

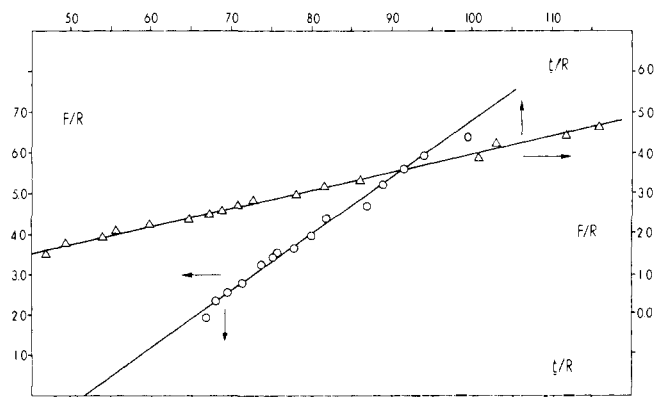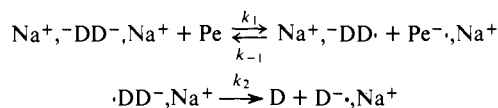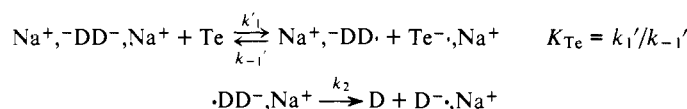The slopes and intercepts are experimentally reliable, allowing us to calculate with fair accuracy the values of k_2K_{Pe} listed in the fourth column of Table I. However, the ratio k_2/k_{-1} is given by a small difference of two large values: $1/$ intercept and x_∞. Therefore it is less reliable and the negative values of k_2/k_{-1} deduced from some of our runs are not surprising. Nevertheless, it is safe to conclude from our data that k_2/k_{-1} is smaller than 10^{-4} M.

Table II[a]

$$Na^+,^-DD^-,Na^+ + Pe \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Na^+,^-DD\cdot + Pe^-\cdot,Na^+$$

$$\cdot DD^-,Na^+ \xrightarrow{k_2} D + D^-\cdot,Na^+$$

$10^3[Pe]_0$, M	$10^3[Pe^-\cdot,Na^+]_\infty$, M	$10^3[Pe^-\cdot,Na^+]_0$, M	k_2K_{Pe}, s	$10^5(k_2/k_{-1})$, M^{-1}	$10^{-4}k_1$, M s
9.95	1.14	0.11	0.84	1.9	4.4
8.90	1.51	0.16	0.95	9.2	1.0
6.95	1.43	0.11	0.87	2.7	3.2
5.70	1.20	0.12	0.99	5.1	1.9
4.71	1.22	0.11	0.98	6.3	1.6
5.05	1.04	0.09	1.21	10.1	1.2
3.98	1.07	0.07	1.07	5.4	2.0
2.93	1.51	0.09	0.87	6.0	1.4
1.85	1.22	0.13	1.10	7.3	1.5
Av			1.0 ± 0.1	$(6 \pm 3) \times 10^{-5}$	$(2 \pm 1) \times 10^4$

[a] Treatment (b), the approximation $[Pe]_t = [\overline{Pe}]$ = constant is not applied.

Table III[a]

$$Na^+,^-DD^-,Na^+ + Te \underset{k_{-1}'}{\overset{k'_1}{\rightleftarrows}} Na^+,^-DD\cdot + Te^-\cdot,Na^+ \qquad K_{Te} = k_1'/k_{-1}'$$

$$\cdot DD^-,Na^+ \xrightarrow{k_2} D + D^-\cdot,Na^+$$

$10^5[Te]_0$, M	$10^5[Te^-\cdot,Na^+]_\infty$, M	$10^5[Te^-\cdot,Na^+]_0$, M	k_2K_{Te}, s	$10^5(k_2/k_{-1}')$, M^{-1}	$10^{-5}k_1'$, M s
48.5	15.0	3.3	33	3.2	10
37.4	14.9	2.9	18	1.6	11
34.0	14.9	2.6	26	2.0	13
29.3	13.7	2.1	31	3.0	10
24.9	13.7	1.8	27	2.1	13
25.4	18.0	2.4	21	0.9	23
21.2	16.7	2.2	22	0.7	31
17.2	13.5	1.8	38	2.1	18
51.5	18.3	3.9	23	0.8	30
30.8	20.5	5.3	23	2.1	11
23.9	18.7	3.9	31	4.8	6.5
Av			27 ± 6	$(1.6 \pm 1) \times 10^{-5}$	$(16 \pm 8) \times 10^5$

[a] Treatment (b) but the approximation $[Te]_t = [\overline{Te}]$ = constant is eliminated.

The values of k_1 listed in the last column of Table I are obtained by combining k_2K_{Pe} with k_2/k_{-1}. The large uncertainties of the latter permit us to deduce only the lower limit of k_1, namely $k_1 > 10^4$ M^{-1} s^{-1}.

The exact solution of the above differential equation leads to a linear relation of $\{[Pe]_0 \ln U - x_\infty \ln V\}/\ln (U/V)$ on $t/\ln (U/V)$ with the intercept given by $-k_2/k_{-1}$ and the slope equal to $k_2K_{Pe}([Pe]_0 - x_\infty)$. U denotes $([Pe]_0 - x)/([Pe]_0 - x_0)$ and V is $(x_\infty - x)/(x_\infty - x_0)$. Such relations are exemplified by Figure 3. The slopes are again experimentally reliable and hence k_2K_{Pe} is fairly well determined, its average value being (1.0 ± 0.1) M. However, k_2/k_{-1}'s, although given now directly by the intercepts, are uncertain due to their low magnitudes and long extrapolation. The results derived from this treatment are collected in Table II. The k_2K_{Pe} insignificantly differ from those given in Table I, but the k_2/k_{-1}'s appear to be more reliable than those obtained from the approximate treatment. Their average value, calculated from ten experiments, is $(6 \pm 3) \times 10^{-5}$ M.

The conditions for the applicability of steady state approximation require the concentration of $Na^+,^-DD\cdot$ to be substantially lower than those of $Na^+,^-DD^-,Na^+$ and $Pe^-\cdot,Na^+$. This seems to be the case. All attempts to find transient absorbance that could be attributed to $Na^+,^-DD\cdot$ were in vain.

Moreover, the observation of an isosbestic point at 530 nm provides another justification for the inequality $[Na^+,^-DD\cdot] \ll [Pe^-\cdot,Na^+]$. The steady state seems to approach the state of equilibrium 1 implying the inequality $k_{-1}[Pe^-\cdot,Na^+] > k_2$, i.e., k_2/k_{-1} cannot be greater than 5×10^{-5} M.

Oxidation of $Na^+,^-DD^-,Na^+$ by Tetracene

Studies of the system $Na^+,^-DD^-,Na^+ + Pe$ were supplemented by similar investigations involving tetracene, Te, as the oxidizing agent. The low solubility of tetracene in THF forced us to work only with low concentrations of that hydrocarbon, making these studies less extensive than the previous ones. The observed kinetics was consistent with the steady state mechanism (b) and since $[Te]_0$ was never much greater than $[Te^-\cdot]_\infty$, the approximation $[Te]_t = [\overline{Te}]$ = constant could not be used. The results are summarized in Table III. It is gratifying to note similar magnitudes for k_2/k_{-1}' and k_2/k_{-1} given in Table II, namely $k_2/k_{-1}' = (1.6 \pm 1) \times 10^{-5}$ M compared with $(6 \pm 3) \times 10^{-5}$ M deduced for k_2/k_{-1}. A common value of k_2 is demanded for both processes and since k_{-1} as well as k_{-1}' are nearly diffusion controlled both should be about 10^{10} M^{-1} s^{-1} (k_{-1}' could be slightly larger than k_{-1}, see, e.g., ref 6). This justifies the similarity of magnitudes of k_2/k_{-1}' and k_2/k_{-1}.

Table IV[a]

System	$k_2 K_{aromatic}$, s	Kinetically calcd, ϵ in mV based on ϵ(A)	Determined potentiometrically, ϵ in mV based on ϵ = 0 for biphenyl
Pyrene	1.6×10^{-7}	516	505
Anthracene	1.85×10^{-5}	(624)	624
Perylene	0.9	901	917
Tetracene	27	988	1025

[a] $59 \times \log \{k_2 K_{aromatic}/k_2 K_A\} = \epsilon_{aromatic} - \epsilon_A$ in mV; A = anthracene.

Final Conclusions

In both systems, Pe and Te, the intermediate $Na^+,^-DD\cdot$ decomposes spontaneously and not as result of the reactions

$$Na^+,^-DD\cdot + Pe \text{ (or Te)} \rightarrow 2D + Pe^-\cdot,Na^+ \text{ (or } Te^-\cdot,Na^+)$$
(3)

This suggests that k_2 is large. Assuming k_{-1} or k_{-1}' to be $\sim10^{10} M^{-1} s^{-1}$ we find $k_2 \simeq 10^5-10^6 s^{-1}$. The largeness of k_2 is justified by several observations and deductions reported here, and the previously estimated[7] low value is erroneous.

Our present findings lead to $k_1 \approx 10^4$ and $k_1' \approx 10^6 M^{-1} s^{-1}$. The rate constant of the hypothetic reaction 3 cannot be greater, and most probably is smaller, than that of the former reaction. Since [Pe] is always smaller than 10^{-2} M and [Te] smaller than 10^{-3} M, the rate of (3) cannot effectively compete with the spontaneous decompositions of $Na^+,^-DD\cdot$.

The gain in the delocalization of electrons resulting from the

$-CH_2-CH_2-$ bond fission and the formation of double bonds greatly contributes to its weakness. Indeed, combining the finding of Spach et al.[8] with our present data we find the equilibrium constant of $Na^+,^-DD\cdot \rightleftarrows D + D^-\cdot,Na^+$ to be ~10.

Finally, further evidence supporting the proposed mechanism is provided by comparison of our present findings, viz., $k_2 K_{Pe}$ and $k_2 K_{Te}$, with the previous ones, i.e., $k_2 K_A$ (see ref 1) and $k_2 K_\pi$ (see ref 2). As pointed out earlier[2] the ratios

$$k_2 K_\pi : k_2 K_A : k_2 K_{Pe} : k_2 K_{Te}$$

are related to the differences of the redox potentials in THF of the respective hydrocarbons in a process leading to the formation of ion pairs. The latter were obtained by potentiometric titration[3] and Table IV shows a satisfactory agreement between the kinetic and potentiometric results.

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Flash Photolysis of Na^+, $C^-(Ph)_2CH_2CH_2C^-(Ph)_2,Na^+$. Redox Potential of 1,1-Diphenylethylene and Rate Constant of Dimerization of Its Radical Anion

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Abstract: Flash photolysis of THF solutions of $Na^+,C^-(Ph)_2CH_2CH_2C^-(Ph)_2,Na^+ = Na^+,^-DD^-,Na^+$ demonstrated that absorption of visible light leads to electron photoejection, $Na^+,^-DD^-,Na^+ \rightarrow Na^+,^-DD\cdot + e^-,Na^+(h\nu)$, and not to photodissociation, $Na^+,^-DD^-,Na^+ \rightarrow 2D^-\cdot,Na^+(h\nu)$. In the presence of an excess of 1,1-diphenylethylene, D, the ejected electron is captured by this hydrocarbon. The thermal or photolytic decomposition of $Na^+,^-DD\cdot$ into $D + D^-\cdot,Na^+$ is virtually completed within 100 μs, and thereafter the radical anions of 1,1-diphenylethylene, $D^-\cdot,Na^+$, are the only transients present in the system. Their absorption spectrum was recorded and the rate constant of their dimerization, regenerating $Na^+,^-DD^-,Na^+$, was found to be $0.5 \times 10^9 M^{-1} s^{-1}$. In the presence of mixtures of triphenylene (Trph) or biphenyl (B) and D, the following equilibria are established: $D^-\cdot,Na^+ + Trph \rightleftarrows D + Trph^-\cdot,Na^+$ (K_{Trph}) or $D^-\cdot,Na^+ + B \rightleftarrows D + B^-\cdot,Na^+$ (K_B). The return of the system to its initial state ($Na^+,^-DD^-,Na^+$) is retarded then by the decrease of $D^-\cdot,Na^+$ concentration. The kinetic data obtained in the presence of D and those derived from studies of mixtures $Na^+,^-DD^-,Na^+ + D + Trph$ or B allowed us to calculate K_{Trph} and K_B and hence to determine the redox potential of D.

We found that flash photolysis of the disodium salt of 1,1,4,4-tetraphenylbutane dianions (dimers of 1,1-diphenylethylene radical anions, $D^-\cdot,Na^+$),

$$Na^+,C^-(Ph)_2CH_2CH_2C^-(Ph)_2,Na^+ = Na^+,^-DD^-,Na^+$$
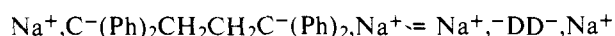
leads to extensive bleaching of its absorption ($\lambda_{max} = 470$ nm, $\epsilon = 5.2 \times 10^4$). This photolysis is induced by absorption of

visible light and was investigated in $\sim2 \times 10^{-6}$ M THF solution of the dimer. Shortly after a flash the original spectrum of $Na^+,^-DD^-,Na^+$ reappears, its original intensity being retained even after numerous flashes, although each initially bleached the solution to about 80%.

Two primary processes could be induced by flash: (1) photodissociation