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Formation and Dimerization of Vinylic Radical Anions and Ion Pairs

A Pulse Radiolysis Study

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Absorption spectra of the free-radical anions and their ion pairs with Na^+ and Li^+ of 1,1-diphenylethylene (D), α-methylstyrene (MS) and styrene (S) were recorded by pulse radiolysis of solutions of the hydrocarbon in either neat tetrahydrofuran or tetrahydrofuran containing sodium or lithium tetrahydridoaluminate salts. The spectra indicate that radical anions of 1,1-diphenylethylene and α-methylstyrene associate with Na^+ and Li^+ to give solvent-separated ion pairs; but styrene radical anions form contact ion pairs with Na^+. Rates of reaction of e_s^-, (Na^+C, e_s^-) and (Na^+, e_s^-) with these hydrocarbons and with pyrene and biphenyl were determined and were found to follow the order $e_s^- > (Na^+C, e_s^-) > (Na^+, e_s^-)$ for each solute. Except for 1,1-diphenylethylene, the reactivity of (Na^+, e_s^-) with these and some related hydrocarbons was found to increase slightly with the electron affinity of the hydrocarbon. The rates of dimerization of the radical anions of D, MS and S have been determined and the influence of ion pairing with Na^+ and Li^+ has been studied. The dimerization rates of $(Na^+, MS^{\cdot -})$, $(Li^+, MS^{\cdot -})$ and $(Na^+C, MS^{\cdot -})$ are 6.6×10^8, 1.23×10^9 and 6.42×10^9 dm^3 mol^{-1} s^{-1}, respectively, and the latter value was found to be independent of ionic strength. Absorption spectra of the dimer dianions of D and MS were also recorded.

In a previous paper[1] we described a technique whereby ion pairs of alkali-metal cations with aromatic radical anions formed by pulse radiolysis in tetrahydrofuran (THF) solutions could be prevented from reacting with the counter-ion necessarily formed during the radiolysis. We have now applied these methods to the study of vinylic radical anions and compared our results with those for other aromatic hydrocarbons obtained by pulse radiolysis[2, 3] or flash photolysis[4] in other laboratories.

There have been several reviews on radical anions of unsaturated hydrocarbons[5-10] and their formation is usually accompanied by a shift of the absorption maximum to a longer wavelength. The spectra of radical anions are blue shifted by ion pairing with alkali-metal cations. In etheral solvents these species may exist as solvent-separated or contact ion pairs and the configuration adopted will depend on temperature, the electron affinity of the hydrocarbon, steric effects in the solvent and the metal cation.[6-11] The optical absorption maxima of contact ion pairs move to longer wavelengths as the radius of the cation increases, but those of solvent-separated ion pairs are usually very close to, or the same as, that of the free-radical anion. When the metal cation is complexed by solvating agents, such as crown ethers, then solvent-separated ion pairs only should be formed.

Anionic polymerization of vinylic compounds involves the initial formation of radical anions followed by their dimerization giving two centres for chain growth by monomer addition. The mechanism of dimerization depends upon whether the radical anions are formed by alkali-metal reduction or electron transfer.[12]

The rates of reactions between charged species may be affected by the presence of other ions in the solution. The variable which determines the extent of the effect

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exerted by these ions is known as the ionic strength, which has been treated by the Brønsted–Bjerrum theory combined with the extended Debye–Hückel theory.[13, 14] However, an alternative treatment, based on diffusion theory, has been developed by Logan.[15-17]

EXPERIMENTAL

The experimental techniques and purification of THF and tetrahydridoaluminate salts have already been described.[1] Dicyclohexyl-18-crown-6 (C) (Lancaster-Synthesis, PCR Ltd) was used as supplied. 1,1-Diphenylethylene (D) was distilled from the red-coloured sodium dimer dianion salt.[18] α-Methylstyrene (MS) was purified by washing with 10% aqueous sodium hydroxide, followed by distilled water, dried over calcium hydride and distilled under vacuum. Styrene (S) was treated similarly. Biphenyl (Kodak Ltd) was recrystallised from methanol and dried *in vacuo*. Zone refined pyrene (Koch-Light) was used without further purification.

Solutions containing either sodium or lithium tetrahydridoaluminate were generally saturated with the salt and then filtered *in vacuo*. These solutions are referred to as NAH/THF and LAH/THF, respectively, and specific reference will be made when other than saturated solutions were employed.

RESULTS

SPECTRA OF RADICAL ANIONS AND DIMER DIANIONS

1,1-Diphenylethylene was chosen as the first hydrocarbon for investigation as it resembles chemically typical vinyl monomers such as S and MS. However, the radical anion of this compound is restricted to forming only the dimeric dianion; further head-to-tail addition is prevented by the steric hindrance arising from the phenyl groups.

The spectrum of the radical anion, $D^{\cdot-}$, shown in fig. 1 with absorption maxima at 335, 400 and 1150 nm was recorded by pulse radiolysis of a solution with $[D] = 7.3 \times 10^{-2}$ mol dm^{-3} using 0.2 μs, 40 Gy pulses; the spectrum corresponds to that published elsewhere.[19] The narrow absorption at 330 nm remaining 3 μs after the pulse is probably due to a radical formed by the reaction of $D^{\cdot-}$ with the counter-ion.

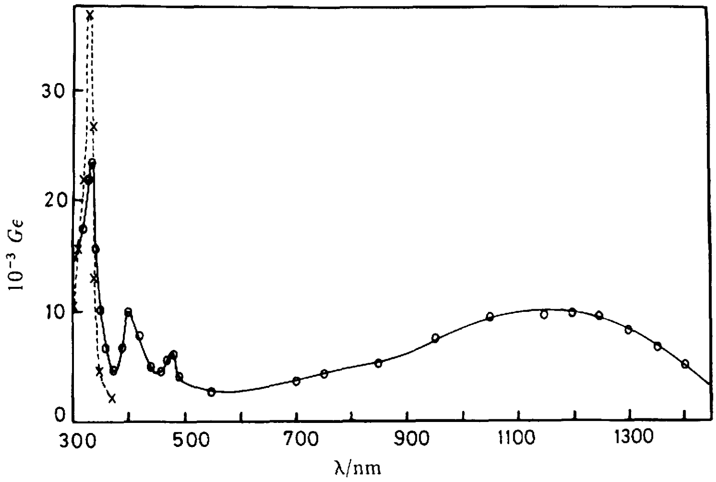

FIG. 1.—Absorption spectra recorded in the pulse radiolysis (0.2 μs, 40 Gy pulse) of 0.073 mol dm^{-3} 1,1-diphenylethylene in THF: ○, end-of-pulse; ×, 3 μs after the pulse.

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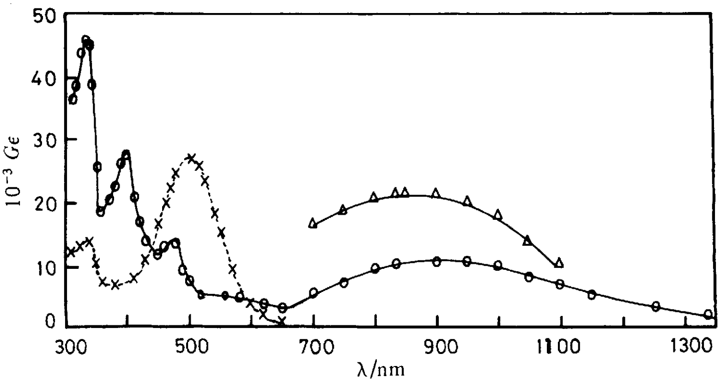

FIG. 2.—Absorption spectra recorded in the pulse radiolysis (0.2 μs, 2 Gy pulse) of 1.5×10^{-3} mol dm^{-3} 1,1-diphenylethylene in NAH/THF: ○, (NA^+, $D^{\cdot -}$); ×, Na^+, $^-DD^-$, Na^+; △, peak of spike (see text).

The spectra of (Na^+, $D^{\cdot -}$) (see fig. 2) and (Li^+, $D^{\cdot -}$) recorded by the pulse radiolysis of D in NAH/THF and LAH/THF, respectively, were found not to exhibit any hypsochromic shift compared with the free ion. The decay of the ion pairs occurred simultaneously with a growth in absorption with $\lambda_{max} = 495$ nm (see fig. 2) which is due to the dimer dianion.[7] The differences in λ_{max} for the long-wavelength absorptions shown in fig. 1 and 2 may be due to the effect of ion-pair formation in the solution containing NAH; however, measurements in this spectral region are subject to some uncertainty. γ-Radiolysis of a solution of D in LAH/THF for 15 min produced the spectrum of the dimer dianion. Pulse radiolysis of solutions in which the tetrahydridoaluminate salts were replaced by sodium tetrahydridoborate resulted only in the formation of (Na^+, $D^{\cdot -}$) and no permanent coloured species were produced.

The absorption spectrum of (Na^+, $MS^{\cdot -}$) is shown in fig. 3 and has maxima at 400 and 575 nm. The spectrum was unchanged when recorded in the presence of crown ether or when Li^+ replaced Na^+. These spectra are similar to those published for $MS^{\cdot -}$ in THF.[20] As in the 1,1-diphenylethylene solutions the absorption spectrum changed with time to yield a spectrum measured at 1600 μs after the pulse which is characteristic of the dimer dianion.[7] Further support for this assignment is provided by the kinetics of formation of this absorption obeying a second-order rate law (see below). The absorption spectra of $S^{\cdot -}$ and (Na^+, $S^{\cdot -}$) are shown in fig. 4, from which it can be seen that ion pairing has caused a hypsochromic shift of 10 nm.

The yields of Na^+, $MS^{\cdot -}$ ion pairs in the NAH/THF solutions were found to be independent of the initial hydrocarbon concentration over the range from 2×10^{-4} to 5×10^{-2} mol dm^{-3}. This is in agreement with the results obtained using *t*-stilbene solutions, for which $G(\text{anion}) = 2.0 \pm 0.1$.[1] Use of this latter value permits evaluation of the molar absorptivities of the ion pairs; the values so obtained are given in table 1.

KINETICS OF FORMATION OF THE RADICAL ANIONS

It has been reported[22] that the reaction

$$(Na^+, e_s^-) + D \rightarrow (Na^+, D^{\cdot -}) \qquad (1)$$

is too slow to be observed by pulse radiolysis and that the value of the rate constant $k_1 \leqslant 10^7$ dm^3 mol^{-1} s^{-1}. However, while recording the spectrum of (Na^+, $D^{\cdot -}$) in the wavelength range 700-1100 nm a sharp spike lasting *ca.* 0.25 μs was observed on the trace at the end of the 0.2 μs pulse. The absorption spectrum at the peak of this spike

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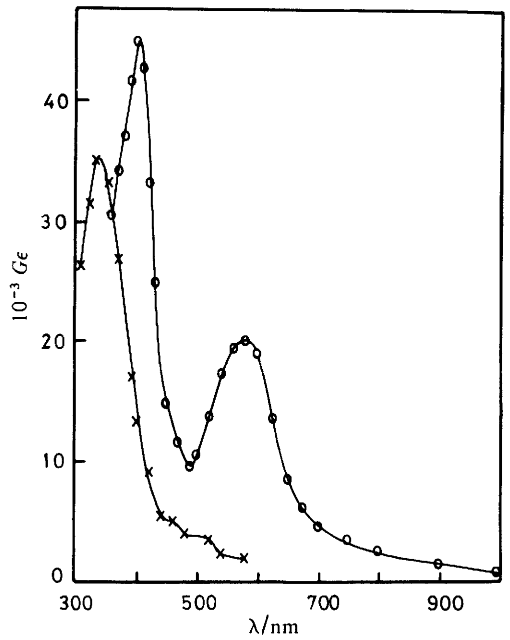

FIG. 3.—Absorption spectra recorded in the pulse radiolysis (0.2 μs, 58 Gy pulse) of 5×10^{-2} mol dm^{-3} α-methylstyrene in NAH/THF: ○, (Na^+, $MS^{\cdot -}$); ×, Na^+, $^-MSMS^-$, Na^+.

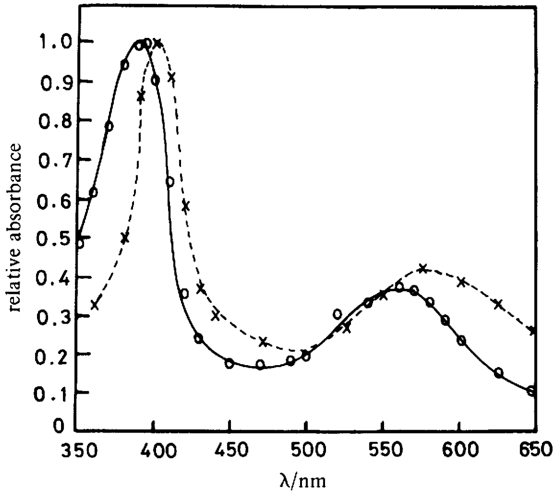

FIG. 4.—Absorption spectra recorded in the pulse radiolysis of 0.01 mol dm^{-3} solutions of styrene in THF, ×, and NAH/THF, ○, normalised to λ_{max}.

was identified as that of the (Na^+, e_s^-) ion pair and is shown in fig. 2. This result indicates that the kinetics of reaction (1) should be observable using pulse radiolysis. Unfortunately, the overlap of the spectral bands of (Na^+, e_s^-) and (Na^+, $D^{\cdot -}$), and the fact that this latter species is also decaying, renders it impossible to accurately monitor reaction (1) by following the decay of the sodium–electron ion pair.

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TABLE 1.—MOLAR ABSORPTIVITIES OF ION PAIRS OF RADICAL ANIONS

ion pair	λ/nm	$\varepsilon/10^4$ dm^3 mol^{-1} cm^{-1} ($\pm 5\%$)
(Na^+, $D^{\cdot -}$)	335	2.3
	400	1.37, 1.05[21]
(Na^+, $MS^{\cdot -}$)	400	2.54
	575	0.88
(Na^+, $S^{\cdot -}$)	400	2.46
	575	0.82

TABLE 2.—RATE CONSTANTS FOR THE FORMATION OF RADICAL ANIONS AND ION PAIRS OF VARIOUS HYDROCARBON SOLUTES IN THF

solute	e.a./eV[b]	reacting species	rate constant /10^{10} dm^3 mol^{-1} s^{-1}	ref.
pyrene	+0.38	e_s^-	12 ± 2	2
			10	4
			11.5 ± 0.3	[a]
		(Na^+, e_s^-)	2.5 ± 0.2	3
			1.4	4
			1.54 ± 0.1	[a]
		(Na^+C, e_s^-)	3.49 ± 0.1	[a]
t-stilbene	+0.35	e_s^-	11.6 ± 0.03	1
		(Na^+, e_s^-)	1.30 ± 0.08	1
		(Na^+C, e_s^-)	3.86 ± 0.07	1
styrene	+0.14	(Na^+, e_s^-)	1.12 ± 0.03	[a]
naphthalene	−0.01	(Na^+, e_s^-)	1.02 ± 0.1	3
α-methylstyrene	−0.05	e_s^-	9.84 ± 0.38	[a]
		(Na^+, e_s^-)	0.84 ± 0.02	[a]
		(Na^+C, e_s^-)	2.78 ± 0.15	[a]
1,1-diphenylethylene	+0.23	(Na^+, e_s^-)	0.74 ± 0.02	[a]
biphenyl	−0.21	e_s^-	11 ± 3	3
		(Na^+, e_s^-)	0.55 ± 0.02	3
		(Na^+C, e_s^-)	2.86 ± 0.1	[a]

[a] This work; [b] obtained by the correlation of Chen and Wentworth[23] from half-wave potentials given in ref. (7).

Therefore, the rate of formation of (Na^+, $D^{\cdot -}$) was followed using the growth in absorption at 400 nm. The growth of absorption obeyed a first-order rate law, the rate constant of which was shown to be proportional to [D] in the range $(4\text{-}20) \times 10^{-4}$ mol dm^{-3} with $k_1 = (7.42 \pm 0.13) \times 10^9$ dm^3 mol^{-1} s^{-1}.

The rates of reaction of e_s^-, (Na^+, e_s^-) and (Na^+C, e_s^-)^1 with MS and (Na^+, e_s^-) with S were monitored by following the decay of the reducing species at either 890 or 990 nm. In each case the reactions followed first-order rate laws at the hydrocarbon concentration used and the observed first-order rate constants varied linearly with the concentration of the hydrocarbons. The rate constants so determined are listed in table 2. In order to provide a direct comparison of work in this laboratory with that

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performed elsewhere,[2-4] the rates of reaction of pyrene with e_s^- and (Na^+, e_s^-) were also measured. In addition, the rates of reaction of (Na^+C, e_s^-) with biphenyl and pyrene were determined. The results obtained in this work and those available from the literature are collected in table 2.

DIMERIZATION OF THE RADICAL ANIONS

The dimerization of the radical anions was studied in both NAH/THF and LAH/THF by following the decay of both absorption maxima in each case. Doses per pulse in excess of 40 Gy were used in order to minimize interference by reactions with radicals[1] and an example of a trace recorded during these experiments is given in fig. 5. Over a wide dose range linear plots were obtained for reciprocal absorbance against time and first-order plots showed marked curvature, thus demonstrating that the dimerization followed second-order kinetics (see fig. 5). The slopes of the second-order plots combined with the molar absorptivities previously determined (table 1) yielded the second-order rate constants listed in table 3.

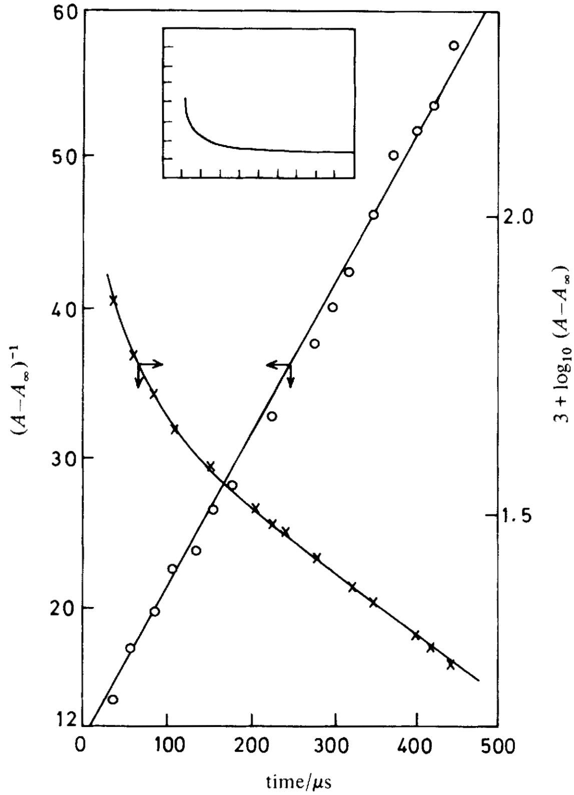

FIG. 5.—Kinetics of the dimerization of (Na^+, $D^{\cdot -}$); $\lambda = 400$ nm, 0.6 μs, 90 Gy pulse. Inset: abscissa, 200 μs div^{-1}; ordinate, 6.92% absorption div^{-1}.

In order to examine the effect of ionic strength on the rate of dimerization of (Na^+, $MS^{\cdot -}$) the solvent system chosen was THF containing various concentrations of NAH and crown ether. It is assumed that in the presence of crown ether the salt is completely

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TABLE 3.—RATE CONSTANTS FOR THE DIMERIZATION OF VINYLIC ION PAIRS

ion pair	rate constant /10^8 dm^3 mol^{-1} s^{-1}	dose range/Gy
(Li^+, $D^{\cdot -}$)	15.5 ± 1.2	45-180
(Na^+, $D^{\cdot -}$)	6.0 ± 0.3	45-180
(Na^+, $D^{\cdot -}$)	5.0^{21}	—
(Li^+, $MS^{\cdot -}$)	12.3 ± 0.3	80-240
(Na^+, $MS^{\cdot -}$)	6.6 ± 0.1	80-240
(Na^+C, $MS^{\cdot -}$)	64.2 ± 0.6	80, 135
(Li^+, $S^{\cdot -}$)	10.9 ± 0.5	60-180
(Na^+, $S^{\cdot -}$)	10.0 ± 0.2	60-180

dissociated and ionic strengths were calculated on this basis. No effect of ionic strength was observed over the range from 2×10^{-4} to 9×10^{-2} mol dm^{-3}.

DISCUSSION

The absorption spectra of radical anions in THF are due to the free ions. The spectra of the ion pairs of $D^{\cdot -}$ and $MS^{\cdot -}$ were indistinguishable from those of their respective free-radical anions and are therefore attributed to solvent-separated ion pairs. These results for ion pairs involving Na^+ contrast with those for *t*-stilbene solutions[1] where a hypsochromic shift was observed. This may be due to the much lower steric crowding experienced by the benzylic carbon atom in the stilbene radical anion compared with its counterparts in $D^{\cdot -}$ and $MS^{\cdot -}$. This supposition is supported by the hypsochromic shift of (Na^+, $S^{\cdot -}$) compared with $S^{\cdot -}$, which also suggests that the electron affinity of the hydrocarbon molecule is not the determining factor in the type of ion pairing in these solutions.

From table 2 it can be seen that the absolute rate constants for the reaction of the solvated electron with the hydrocarbon molecules are *ca.* 10^{11} dm^3 mol^{-1} s^{-1} and those for the analogous reactions of the (Na^+, e_s^-) ion pair are approximately an order of magnitude lower. Consistent with the lower interaction between the Na^+ cation and the electron in the presence of crown ether, the reactivity of the (Na^+C, e_s^-) pair lies between that of the solvated electron and the sodium, electron pair.

The hydrocarbon solutes are also listed in descending order of reactivity towards the (Na^+, e_s^-) ion pair, from which it can be seen that, with the exception of 1,1-diphenylethylene, the differences, although small, do follow the relative electron affinities of the molecules. The slower rate of formation of the (Na^+, $D^{\cdot -}$) ion pair than expected from the position of the parent molecule in the electron affinity scale is probably due to steric hindrance around the benzylic carbon atom.

The formation of a radical anion may be represented by

$$(Na^+, e_s^-) + A \rightleftharpoons (Na^+, A^{\cdot -}) \qquad (2)$$

which, for most aromatic compounds, will lie well over to the right. The production of radical anions may also be regarded as an electron-transfer reaction of a solvated electron, for which a theory has been developed.[24, 25]

Pulse radiolysis of solutions of aromatic hydrocarbons in NAH/THF or LAH/THF has allowed us to record spectra and molar absorptivities (given in table 1) of vinylic radical anions, species which are not sufficiently long-lived to be seen when

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prepared by other methods. The value for the molar absorptivity of (Na^+, $D^{\cdot -}$) found in this work is higher than that reported elsewhere,[21] but in that determination it was assumed that the ion pair did not absorb at the absorption maximum of the dimer dianion Na^+, $^-DD^-$, Na^+ (470 nm). Inspection of fig. 1 and 2 shows this not to be the case. The values for (Na^+, $S^{\cdot -}$) are also a little higher than those obtained for $S^{\cdot -}$ by low-temperature γ-radiolysis in methyltetrahydrofuran glasses.[26]

The narrow absorption at 330 nm recorded 3 μs after the pulses, which is shown in fig. 1, has been ascribed to a radical formed by reaction of $D^{\cdot -}$ with the counter-ion, because absorptions in this wavelength region have been seen in the pulse radiolysis of α-methylstyrene and styrene.[27-30]

The dimer dianions $^-DD^-$ and $^-MSMS^-$ when associated with either the Li^+ or Na^+ cation are considered to be in the form of solvent-separated ion pairs for two reasons. First, dimerization would not be expected to reduce markedly the steric crowding of the benzylic carbon atoms carrying the negative charge. Secondly, the absorption maximum of the dianion of the sodium salt of 1,1,4,4-tetraphenylbutane shifts from 472 nm at 298 K, when it is a contact ion pair, to 501 nm at 203 K, when it is a loose ion pair.[8a] The latter value is close to that recorded in fig. 1 for the dianion.

Comparison of the conditions under which the spectra of the dianions $^-DD^-$ and $^-MSMS^-$ were recorded affords an illustration of the importance of dose on the fate of the ion pair in these pulse-radiolysis studies. The dimer dianion $^-MSMS^-$ was observed following pulses delivering a dose of 58 Gy, which is known to be sufficient to prevent significant decay of the ion pair with other radiolytically produced radicals. At the absorption maximum $G\varepsilon_{340}$ was found to be 36000 and this yields a value of $\varepsilon = 9 \times 10^3$ dm^3 mol^{-1} cm^{-1} per end. Hence this spectrum is in agreement with that characteristic of benzylic anions, *viz.* $\lambda_{max} = 340$ nm and $\varepsilon = 1 \times 10^4$ dm^3 mol^{-1} cm^{-1} per end.[7] In contrast, the much lower dose of 2 Gy used to form the Na^+, $^-DD^-$, Na^+ allowed other reactions to interfere with the dimerization and the yield of dianions was reduced by *ca.* 75%.

TABLE 4.—SIMPLIFIED REACTION SCHEME FOR THE PULSE RADIOLYSIS OF 1,1-DIPHENYLETHYLENE IN NAH/THF

reaction		rate constant /dm^3 mol^{-1} s^{-1}
(3) $e_s^- + D$	$\rightarrow D^{\cdot -}$	10^{11}
(4) $e_s^- + Na^+$	$\rightarrow (Na^+, e_s^-)$	8.0×10^{11}
(1) $(Na^+, e_s^-) + D$	$\rightarrow (Na^+, D^{\cdot -})$	7.42×10^9
(5) $(Na^+, D^{\cdot -}) + (Na^+, D^{\cdot -})$	$\rightarrow Na^+, {}^-DD^-, {}^+Na$	6.0×10^8

The reaction scheme proposed to account for the observations made in the pulse radiolysis of solutions of D in NAH/THF and based on an earlier model[1, 31] is given in table 4. However, for the sake of brevity many of the lesser reactions have been omitted from table 4. The value of the rate constant for reaction (3) has not been measured, but is not expected to differ greatly from those obtained for other aromatic hydrocarbons (see table 2). A similar scheme is applicable to solutions of D in LAH/THF and those where D is replaced by MS or S.

The rate of dimerization of (Na^+, $D^{\cdot -}$) found in this work is similar to that determined by flash photolysis.[21] However, in that determination the ion pair was generated from the dimer dianion by two different routes, where pulse radiolysis affords the radical anion directly.

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The rates of dimerization in table 3 increase along the series $S^{\cdot -} < MS^{\cdot -} < D^{\cdot -}$ when the cation is Li^+ whereas the trend is reversed for the Na^+ cation. These sequences also follow the change in steric crowding of the benzylic carbon atom. The charge distribution in anions has been shown to be influenced by the alkali-metal cation with which they are paired.[32] It might be expected that the effect on the dimerization reaction of ion-pair formation with a cation would be to draw charge to the benzylic carbon, thus reducing repulsive coulombic interaction at the free-radical ends and hence facilitating the reaction. However, the highest rate for the dimerization of $MS^{\cdot -}$ was observed when the Na^+ was complexed by crown ether and the radical anion was, therefore, essentially free. Clearly further experimentation is required to clarify the effect of the nature of the cation on the dimerization rate. The lack of any effect of ionic strength on the rate of dimerization is in keeping with the radical anions being in the form of ion pairs which are overall electrically neutral. Since these studies were carried out with NAH/DCH/THF solutions it can be inferred that Na^+ complexed by crown ether forms ion pairs with the radical anions which spectroscopically closely resemble solvent-separated ion pairs.

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