

Dimerization of the Radical Anions of 1,1-Diphenylethylene

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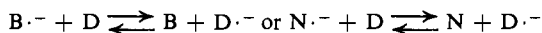
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Abstract: Radical anions of 1,1-diphenylethylene, $D\cdot^-$, were formed in hexamethylphosphoramide (HMPA) through electron transfer from sodium biphenylide or naphthalenide. In this solvent radical anions do not associate with the cations. The kinetics of their dimerization, $2D\cdot^- \rightarrow ^-DD^-$ (k_-), and of their addition to the olefin, $D\cdot^- + D \rightarrow ^-DD\cdot$ (k_p), were investigated. The following values were obtained, $k_- \sim 10^5 M^{-1} \text{sec}^{-1}$ and $k_p \approx 10^4 M^{-1} \text{sec}^{-1}$, showing that the dimerization of the free $D\cdot^-$ ions is slightly slower than that of $D\cdot^-, Na^+$ ion pairs, while their addition to the olefin is much faster than that of ion pairs. The extremely low rate constant of dimerization of $D\cdot^-, K^+$ in cyclohexane ($10^{-2} M^{-1} \text{sec}^{-1}$) observed by Evans is discussed. We were unable to repeat their experiments because rigorously purified 1,1-diphenylethylene dissolved in cyclohexane does not produce any blue solution when contacted with sodium-potassium alloy.

Dimerization of radical anions of 1,1-diphenylethylene, $D\cdot^-, Na^+ = PhC=CH_2\cdot^-, Na^+$, in tetrahydrofuran (THF) was studied by Matsuda, *et al.*¹ The reaction $2D\cdot^-, Na^+ \rightarrow Na^+, ^-DD^-, Na^+$ ($^-DD^- = Ph_2\bar{C}CH_2CH_2\bar{C}Ph_2$) obeyed second-order law, the respective rate constant being $k_{\pm} = 1-2 \times 10^6 M^{-1} \text{sec}^{-1}$. Reactivities of ion pairs often differ from those of free ions, and therefore we were interested in determining the rate of dimerization of free $D\cdot^-$ radical ions and comparing it with that of the relevant ion pairs. We investigated, therefore, the dimerization of diphenylethylene radical ions in hexamethylphosphoramide (HMPA) since it was shown²⁻⁴ that various alkali salts are virtually completely dissociated in this solvent.

Results

The kinetics of dimerization was investigated in a stopped-flow system described elsewhere.⁵ Solutions of the hydrocarbon ($D = CH_2=CPh_2$) in HMPA were mixed with an excess of sodium biphenylide ($B\cdot^-$) or naphthalenide ($N\cdot^-$) dissolved in the same solvent. The exothermic electron-transfer reactions of free radical ions are extremely fast⁶ ($k_{\text{transfer}} > 10^8 M^{-1} \text{sec}^{-1}$) and, hence, the equilibria



are established in a fraction of a millisecond. The progress of the reaction was monitored by the optical density at 495 m μ (λ_{max} of $^-DD^-$). The kinetics of each run obeyed second-order law as illustrated by Figure 1.

In the experiments performed with sodium biphenylide, $[B\cdot^-]_0 \approx 10 \times 10^{-5} M$ and $[D]_0 \approx 5 \times 10^{-5} M$, the conversion of D to $D\cdot^-$ was virtually complete at the onset of the reaction. The dimerization was very fast; the bimolecular rate constant was determined to be about $10^5 M^{-1} \text{sec}^{-1}$.

(1) M. Matsuda, J. Jagur-Grodzinski, and M. Szwarc, *Proc. Roy. Soc. (London)*, **A288**, 212 (1965).

(2) A. Cserhegyi, J. Chaudhuri, E. Franta, J. Jagur-Grodzinski, and M. Szwarc, *J. Am. Chem. Soc.*, **89**, 7129 (1967).

(3) J. Chaudhuri, S. Kume, J. Jagur-Grodzinski, and M. Szwarc, *ibid.*, **90**, 6421 (1968).

(4) A. Cserhegyi, J. Jagur-Grodzinski, and M. Szwarc, *ibid.*, **91**, 1892 (1969).

(5) J. Jagur, M. Levy, M. Feld, and M. Szwarc, *Trans. Faraday Soc.*, **58**, 2168 (1962).

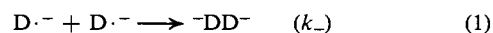
(6) S. Arai, D. A. Grey, and L. Dorfman, *J. Chem. Phys.*, **46**, 2572 (1967).

The conditions maintained in the runs performed with sodium naphthalenide are described in Table I. The large excess of $N\cdot^-$ and of naphthalene assured a constancy of the $[N\cdot^-]/[N]$ ratio in each experiment and, therefore, the ratio $[D\cdot^-]/[D]$ was maintained constant throughout the process. Due to the large excess of

Table I. Kinetics of Dimerization of $D\cdot^-$ Ions

D \cdot^- formed from Na $^+$, B \cdot^- ($K_{\text{transfer}} = 1250$)				
$[D]_0 \times 10^5 M$	$[B\cdot^-]_0 \times 10^5 M$	$[B]_0, M$	$k_{\text{ap}} \approx k_- \times 10^{-4} M^{-1} \text{sec}^{-1}$	
6	13	0.1	10	
6	13	0.1	13	
6	13	0.1	8	
D \cdot^- formed from Na $^+$, N \cdot^- ($K_{\text{transfer}} = 250$)				
$[D]_0 \times 10^5 M$	$[N\cdot^-]_0 \times 10^5 M$	$[N]_0, M$	$[N]/[N\cdot^-]$	$k_{\text{ap}} \times 10^{-4} M^{-1} \text{sec}^{-1}$
3.4	59	0.37	620	1.2
5.0	52	0.38	730	1.2
3.6	52	0.51	980	0.4 (?)
3.2	42	0.64	1540	0.4
5.0	40	0.73	1840	0.35

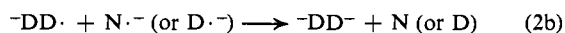
naphthalene the concentration of $D\cdot^-$ was low, and this conveniently slowed down the dimerization. Two independent reactions could contribute to the observed process, *viz.*



and



the latter being followed by a rapid electron-transfer



Denote by K the equilibrium constant of the electron transfer process



Under our experimental conditions $[D]/[D\cdot^-] = [N]_0/[N\cdot^-]_0 K = r = \text{constant}$. Hence

$$2d[-DD^-]/dt = \{(k_- + rk_p)/(1 + r)^2\} \{[D]_0 - 2[-DD^-]\}^2$$

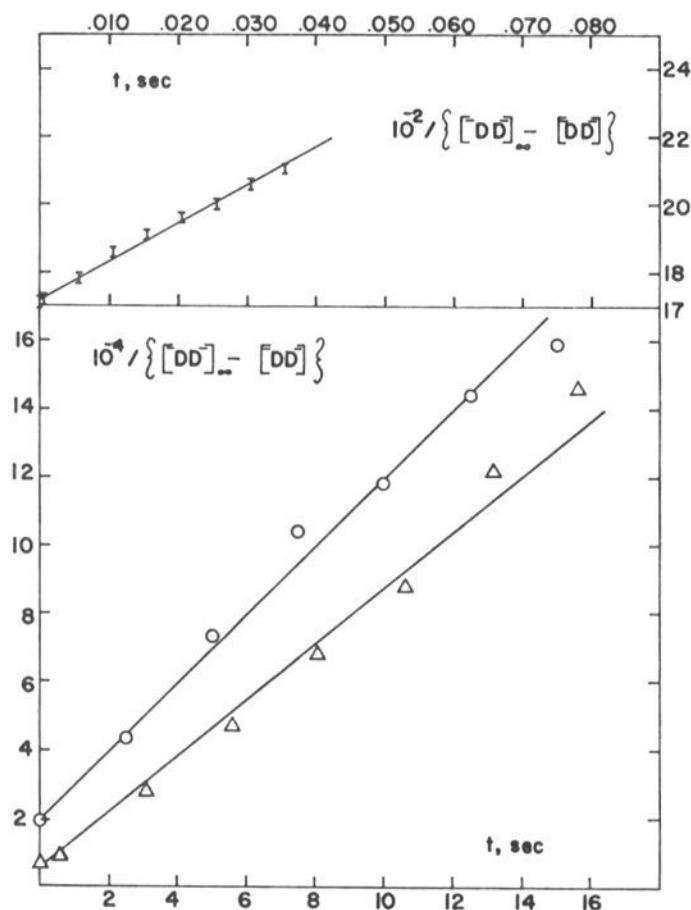


Figure 1. Plot of $1/([DD]_{\infty} - [DD])$ vs. time: stopped-flow experiments at $495\text{ m}\mu$; electron transfer from sodium naphthalene; $[DD]$ in normality.

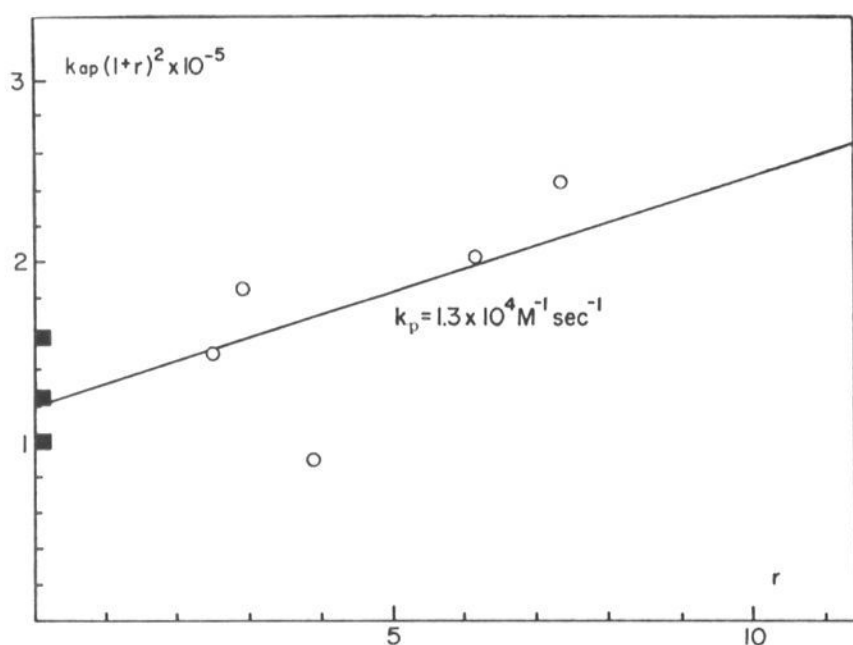


Figure 2. Plot of $k_{ap}[1+r]^2$ vs. r : ■, electron transfer from sodium biphenyl, $K_B = 1250$; ○, electron transfer from sodium naphthalene, $K_N = 250$.

i.e., each run obeyed second-order kinetics with an apparent rate constant

$$k_{ap} = (k_- + rk_p)/(1+r)^2$$

The observed values of k_{ap} are listed in Table I. The following procedure was adopted to calculate k_p and K . For various values of K the parameter r was calculated, and then $k_{ap}(1+r)^2$ was plotted vs. r . Eventually that value of K was chosen for which the experimental points fitted best a straight line. This procedure led to $K \approx 250$; the resulting line, $k_{ap}(1+r)^2$ vs. r , is shown in Figure 2, its slope being $1.3 \times 10^4 M^{-1} \text{ sec}^{-1}$. However, in view of experimental difficulties this value gives only the order of magnitude of k_p .

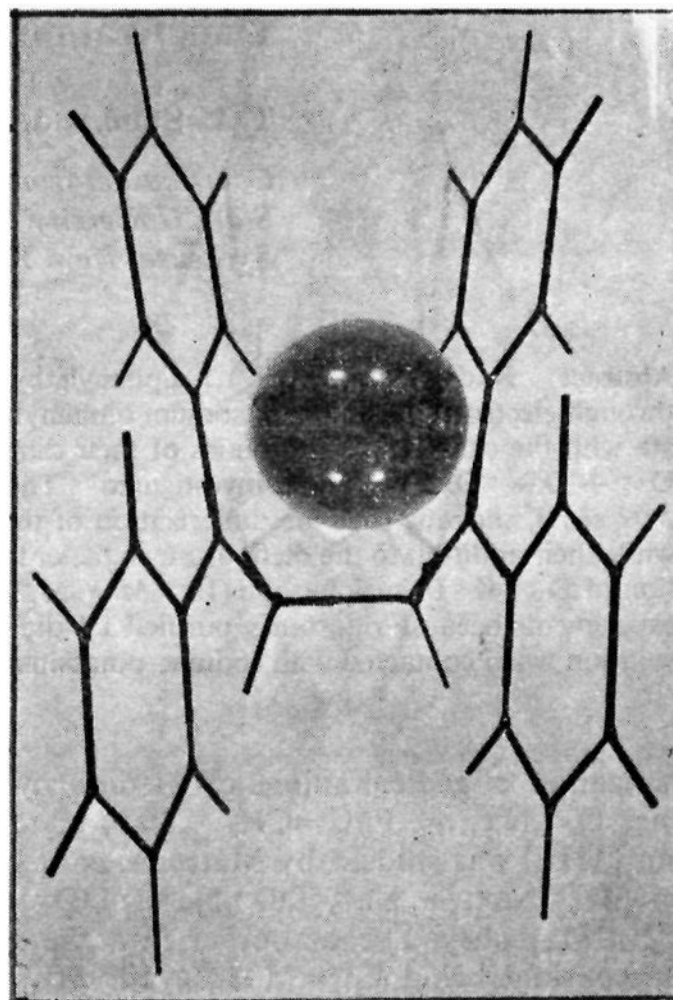
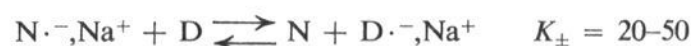


Figure 3. The molecular model of the monosodium salt of the dimeric dianion of 1,1-diphenylethylene in a *cis-cis* conformation.

Discussion

Let us examine the above data in the light of past findings. The equilibrium constant, K_{\pm} , of the electron-transfer reaction involving ion pairs in THF was previously determined,¹ *i.e.*



K_{\pm} is related to the equilibrium constant, K' , by the equation

$$K'/K_{\pm} = K_{\text{diss}, D^{\cdot-}, Na^+} / K_{\text{diss}, N^{\cdot-}, Na^+}$$

Here K' is the equilibrium constant of the reaction $N^{\cdot-} + D \rightleftharpoons N + D^{\cdot-}$ involving the free ions in THF, $K_{\text{diss}, N^{\cdot-}, Na^+}$ and $K_{\text{diss}, D^{\cdot-}, Na^+}$ denote the dissociation constants of the $N^{\cdot-}, Na^+$ and $D^{\cdot-}, Na^+$ ion pairs, respectively, in that solvent. The former was determined directly⁷ to be $1 \times 10^{-7} M$; the latter should be greater than the dissociation constant of sodium polystyrene⁸ and is estimated, therefore, to be $\sim 5 \times 10^{-7}$. Thus, the probable value of K' seems to be within the range 100–200 in fair agreement with the value of 250 derived for K (the latter refers to the same equilibrium established in HMPA).

The dimerization of free $D^{\cdot-}$ ions is *not faster* than that of ion pairs. This is plausible. The repulsion between the two approaching negative ions should slow down the process when compared with the one involving ion pairs. In fact, k_- may be smaller than claimed by us because a fraction of $D^{\cdot-}$ ions could be associated with Na^+ , even in HMPA, and the pairs would then contribute more to the dimerization than the free ions. Un-

(7) P. Chang, R. V. Slates, and M. Szwarc, *J. Phys. Chem.*, **70**, 3180 (1966).

(8) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *ibid.*, **69**, 612 (1965).

fortunately, technical difficulties prevented us from examining this possibility.

Esr investigation of $^{-}DD^{-}$ in HMPA showed that the concentration of radical ions is less than $\sim 10^{-7} M$ even in 0.1 M solution. Hence, the equilibrium constant of the reaction, $^{-}DD^{-} \rightleftharpoons 2D\cdot^{-} - K_D^{-}$, cannot be greater than $\sim 10^{-13} M$ and the unimolecular rate constant of $^{-}DD^{-}$ dissociation must be lower than 10^{-8} sec^{-1} . The high degree of $^{-}DD^{-}$ stability in HMPA is somewhat surprising. However, the lack of dissociation could be accounted for if each $^{-}DD^{-}$ dianion were associated with one Na^{+} ion giving a stable pair depicted in Figure 3.

The high rate of the reaction $D\cdot^{-} + D \rightarrow ^{-}DD\cdot^{-}$, k_p , is plausible. The addition of styrene to free polystyryl anion proceeds with bimolecular rate constant of about $6 \times 10^4 M^{-1}$ in a variety of solvents,⁹ and D is a more reactive monomer than styrene;¹⁰ hence its addition to free polystyryl anion should be even faster. However, the radical anion is expected to be less reactive toward the addition than the carbanion and thus our findings may be rationalized.

Dimerization of $D\cdot^{-}, K^{+}$ ion pairs in cyclohexane was studied by Evans.¹¹ The reported reaction was extremely slow, e.g., for $[D\cdot^{-}, K^{+}]_0 \approx 5 \times 10^{-4} M$ more than 100 hr was needed to consume 90% of the radicals. Strangely enough, at higher concentrations ($> 10^{-3} M$) the process was too fast to allow even the observation of the blue color attributed to $D\cdot^{-}$, and the red dimer was formed instantaneously. This observation indicates that the dimerization is accelerated by at least a factor of 1000 as the concentration of the reagents increases by a factor of 2–3.

These findings are puzzling and the very low rate constant of dimerization claimed by Evans, *et al.*, is unexpected. The authors attributed the slowness of the dimerization to the low dielectric constant of cyclohexane, arguing that this should greatly increase the repulsion between the approaching negative radical ions and raise the activation energy of their combination. However, their reactants were present as ion pairs (dipoles) and not as free ions, and our present studies show that even the free ions dimerize very fast.

(9) M. Szwarc, "Carbanions, Living Polymers, and Electron-Transfer Processes," Interscience Publishers, New York, N. Y., 1968, Chapter VII.

(10) M. Shima, D. N. Bhattacharyya, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **85**, 1306 (1963).

(11) (a) A. G. Evans and J. C. Evans, *Trans. Faraday Soc.*, **61**, 1202 (1965); (b) A. G. Evans, *Proc. Roy. Soc. (London)*, **A302**, 331 (1968).

We examined, therefore, the cyclohexane system. Our findings do not agree with those reported by Evans, *et al.*

1. Evans reported the formation of a blue species ($\lambda_{\text{max}} 630 \text{ m}\mu$ ($\epsilon 1.45 \times 10^4$)) when $\sim 10^{-4} M$ solution of D in cyclohexane is contacted with sodium-potassium alloy (potassium being the reactive metal). The blue species is claimed to be $D\cdot^{-}, K^{+}$ and its identity was established by its esr spectrum. Unfortunately, the reported spectrum is poorly resolved (the lines being about 1 G wide) and the argument based on its structure may be questionable.

Our attempts to repeat these experiments failed. Pure 1,1-diphenylethylene in cyclohexane solution (see ref 12 for the method of purification) does not produce *any* colored solution when in contact with sodium-potassium alloy, although a red precipitate is formed on the surface of the metal.

2. Sodium-potassium alloy reacts with benzophenone dissolved in commercial cyclohexane or in the solvent refluxed over sodium and thereafter distilled under high vacuum. The resulting solution is blue and absorbs at $\lambda_{\text{max}} 630 \text{ m}\mu$; *i.e.*, the spectrum seems to be identical with the blue solution described by Evans. The solubility of the potassium ketyl in cyclohexane is due to the presence of some complexing impurities still left in conventionally purified solvent. Potassium benzophenylene and the dimer of potassium diphenylethylenide are insoluble in cyclohexane if the solvent is purified by being left overnight in contact with the blue solution and then redistilled.

3. The purification procedure of diphenylethylene described by Evans¹³ (refluxing at atmospheric pressure over potassium hydroxide pellets followed by distillation under reduced pressure) is bound to oxidize a fraction of the hydrocarbons to benzophenone. It is probable, therefore, that this ketone was present in his system.

It is not our intention to account for the results reported by Evans.¹¹ We wish, however, to stress that his observations may refer to some other reactions than the dimerization of $D\cdot^{-}, K^{+}$.

Acknowledgment. We acknowledge the financial support of this investigation by the National Science Foundation and by the Petroleum Research Fund administered by the American Chemical Society. We thank also Dr. A. Cserhegyi for technical help.

(12) G. Spach, H. Monteiro, M. Levy, and M. Szwarc, *Trans. Faraday Soc.*, **58**, 1809 (1962).

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