Table IV[a]

System	k_2K_{aromatic}s	Kinetically calcd, ϵ in mV based on ϵ(A)	Determined potentiometrically, ϵ in mV based on $\epsilon = 0$ 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] $59 \times \log\{k_2K_{\text{aromatic}}/k_2K_{\text{A}}\} = \epsilon_{\text{aromatic}} - \epsilon_{\text{A}}$ in mV; A = anthracene.

Final Conclusions

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

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

This suggests that k_2 is large. Assuming k_{-1} or k_{-1}' to be $\sim 10^{10}\ \mathrm{M^{-1}\,s^{-1}}$ we find $k_2 \simeq 10^5$–$10^6\ \mathrm{s^{-1}}$. 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 $k_1' \approx 10^6\ \mathrm{M^{-1}\,s^{-1}}$. 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 $\mathrm{Na^+,{}^-DD\cdot}$.

The gain in the delocalization of electrons resulting from the $\mathrm{-CH_2-CH_2-}$ 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 $\mathrm{Na^+,{}^-DD\cdot \rightleftarrows D + D^-\cdot,Na^+}$ to be ~ 10.

Finally, further evidence supporting the proposed mechanism is provided by comparison of our present findings, viz., k_2K_{Pe} and k_2K_{Te}, with the previous ones, i.e., k_2K_{A} (see ref 1) and k_2K_{π} (see ref 2). As pointed out earlier[2] the ratios

$$k_2K_{\pi}:k_2K_{\text{A}}:k_2K_{\text{Pe}}:k_2K_{\text{Te}}$$

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.

In conclusion, we wish to thank the National Science Foundation for supporting this investigation and Dr. A. Rainis for his technical help.

References and Notes

(1) J. Jagur, M. Levy, M. Feld, and M. Szwarc, *Trans. Faraday Soc.*, **58**, 2168 (1962).
(2) D. Gill, J. Jagur-Grodzinski, and M. Szwarc, *Trans. Faraday* Soc., **60**, 1424 (1964).
(3) J. Jagur-Grodzinski, M. Feld, S. L. Yang, and M. Szwarc, *J. Phys. Chem.*, **69**, 628 (1965).
(4) A. Rainis, R. Tung, and M. Szwarc, *J. Am. Chem. Soc.*, **95**, 659 (1973).
(5) (a) K. J. Toelle, T. Shimomura, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **89**, 796 (1967); (b) T. Shimomura, J. Smid, and M. Szwarc, *ibid.*, **89**, 5743 (1967).
(6) R. V. Slates and M. Szwarc, *J. Phys. Chem.*, **69**, 4124 (1965).
(7) J. Jagur-Grodzinski and M. Szwarc, *Proc. R. Soc. London, Ser. A*, **288**, 224 (1965).
(8) G. Spach, H. Monteiro, M. Levy, and M. Szwarc, *Trans. Faraday Soc.*, **58**, 1809 (1962).

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

$$\mathrm{Na^+,C^-(Ph)_2CH_2CH_2C^-(Ph)_2,Na^+ = Na^+,{}^-DD^-,Na^+}$$

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 $\sim 2 \times 10^{-6}$ M THF solution of the dimer. Shortly after a flash the original spectrum of $\mathrm{Na^+,{}^-DD^-,Na^+}$ 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

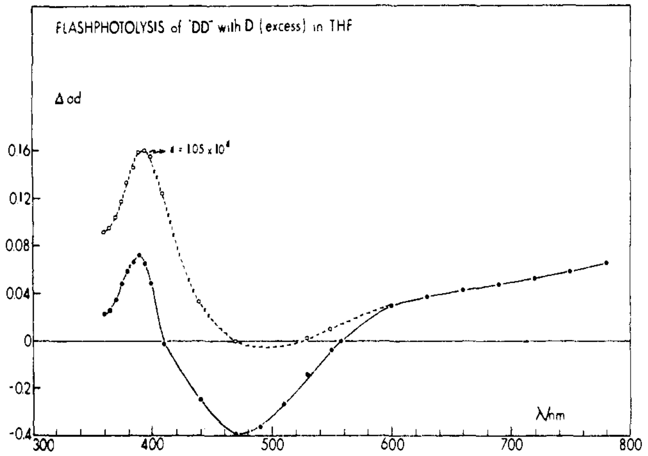

Figure 1. The difference spectrum of flash-photolyzed $\mathrm{Na^+,{}^-DD^-,Na^+}$ ($\sim 2 \times 10^{-6}$ M) in THF in the presence of a large excess of D recorded at 100 μs after flash (solid line). The absorption spectrum of $\mathrm{D^-\cdot,Na^+}$ calculated from the difference spectrum after correction for the bleaching of $\mathrm{Na^+,{}^-DD^-,Na^+}$ (dashed line). It has been assumed that $\mathrm{D^-\cdot,Na^+}$ does not absorb at 470 nm (λ_{max} of the dimer). Note the different scales of the absorbance and bleaching.

$$\mathrm{Na^+,{}^-DD^-,Na^+} \xrightarrow{h\nu} \mathrm{2D^-\cdot,Na^+} \tag{1}$$

(2) electron photoejection

$$\mathrm{Na^+,{}^-DD^-,Na^+} \xrightarrow{h\nu} \mathrm{Na^+,{}^-DD\cdot + e^-,Na^+} \tag{2}$$

$\mathrm{e^-,Na^+}$ denoting an associate of solvated electron with sodium cation.

The products of reaction 1 are expected to dimerize and regenerate the original dimer,

$$\mathrm{2D^-\cdot,Na^+} \xrightarrow{k_3} \mathrm{Na^+,{}^-DD^-,Na^+} \tag{3}$$

In fact, this dimerization is believed to be responsible for the formation of the dimer when a solution of 1,1-diphenylethylene is contacted with alkali metal or mixed with a solution of sodium biphenylide.[1]

The reactions following electron photoejection may be more complex. The $\mathrm{e^-,Na^+}$ formed in the photolysis may recombine with $\mathrm{Na^+,{}^-DD\cdot}$ and regenerate directly or indirectly the dimer, viz.,

$$\mathrm{Na^+,{}^-DD\cdot + e^-,Na^+} \xrightarrow{k_4} \mathrm{Na^+,{}^-DD^-,Na^+} \tag{4}$$

(direct regeneration)

or

$$\mathrm{Na^+,{}^-DD\cdot + e^-,Na^+} \rightarrow \mathrm{X} \rightarrow \mathrm{Na^+,{}^-DD^-,Na^+} \tag{5}$$

(indirect regeneration)

X could be a triplet of $\mathrm{Na^+,{}^-DD^-,Na^+}$ formed by the primary recombination, which eventually decays into the ground state of the dimer. Alternatively, the initially formed $\mathrm{Na^+,{}^-DD\cdot}$ might be spontaneously decomposed or photolyzed into D and $\mathrm{D^-\cdot,Na^+}$, i.e.,

$$\mathrm{Na^+,{}^-DD\cdot} \xrightarrow{\Delta \text{ or } h\nu} \mathrm{D + D^-\cdot,Na^+} \tag{6}$$

or suffer another electron photoejection caused by the flashed light,

$$\mathrm{Na^+,{}^-DD\cdot} \xrightarrow{h\nu} \mathrm{2D + e^-,Na^+} \tag{7}$$

Either of these reactions eventually would yield $\mathrm{D^-\cdot,Na^+}$, and the latter should recombine into the dimer.

Our first task in this study was to establish which of the two primary photolytic reactions, (1) or (2), dominates under our experimental conditions.

Experimental Section

1,1-Diphenylethylene was prepared from benzophenone through Grignard reaction with MeMgI followed by dehydration of the resulting alcohol.[2] This procedure yields a product free of biphenyl. The residual benzophenone is removed from the thus prepared hydrocarbon by contacting it with metallic potassium followed by high-vacuum fractionation that yields the pure 1,1-diphenylethylene (D). The latter was kept in evacuated ampules and never exposed to the air.

The flash-photolytic technique applied in our studies was described elsewhere.[3] The THF stock solution of $\mathrm{Na^+,{}^-DD^-,Na^+}$ ($\sim 10^{-3}$ M) was kept in a storage flask to which was attached a 10-cm long cylindrical cell equipped with optically flat windows. The stock solution was diluted 1000-fold in the cell by a procedure described previously.[4] Such a dilution is attained without introducing any fresh solvent and therefore the solution to be photolyzed is not contaminated by any impurities. The half-lifetime of the flash was about 25 μs and appropriate filters prevented the UV light from reaching the cell.

The progress of the dark reaction was monitored by following the absorbance of the photolyzed solution at the desired wavelength and the results were displayed on an oscilloscope.

Photodissociation or Electron Photoejection?

Let us consider the behavior of the photolyzed system if the photodissociation were the primary photoinduced reaction. The dark reaction arises from the recombination of $\mathrm{D^-\cdot,Na^+}$ and its course should not be affected by the presence of any initially added D. It is known that D does not add to $\mathrm{Na^+,{}^-DD^-,Na^+}$, and, surely, reaction 8 could not compete effectively with recombination 3, even if the concentration of D exceeded the concentration of radical anions by a factor of 10 or 20.

$$\mathrm{D + D^-\cdot,Na^+} \rightarrow \mathrm{\cdot DD^-,Na^+} \tag{8}$$

One expects, therefore, that:

(1) The primary photolytic event should not be affected by the addition of D. The degree of bleaching should be the same whether 1,1-diphenylethylene was or was not added to the photolyzed solution. This, indeed, is the case.

(2) The transient absorbance recorded at 100 μs after flash should be identical in both cases. It should characterize the absorbance of $\mathrm{D^-\cdot,Na^+}$.

(3) The return of the system to its initial state monitored by the transient absorbance or bleaching should be governed by the second-order law, i.e., $1/\Delta(\mathrm{OD})$ should be linear with time at any wavelength chosen for the monitoring.

Although expectation 1 has been fulfilled, expectations 2 and 3 were not. In the presence of a 10–20-fold excess of D a typical difference spectrum recorded 100 μs after flash is shown in Figure 1. It reveals a sharp absorption band at $\lambda_{max} = 390$ nm and an absorbance at longer wavelengths (>550 nm) followed up to 800 nm. The pronounced bleaching of the dimer absorption had its maximum at 470 nm. The optical densities at 390, 470, and 750 nm were in the ratio 1:6:0.8 which remained virtually unchanged as the difference spectrum decayed. In addition, two isosbestic points appeared at 408 and 565 nm.

The difference spectrum became imperceptible in less than 10 ms. Its decay, monitored at either wavelength, obeyed the second-order kinetics, i.e., $1/\Delta(\mathrm{OD})$ is linear with time. Typical second-order plots are shown in Figure 2, their slopes being $(2.0 \pm 0.2) \times 10^3$ at 470 nm, $(9\text{–}10) \times 10^3$ at 390 nm, and $(12\text{–}13) \times 10^3$ at 750 nm, all in units of OD/s.

Different results were obtained in the absence of D, e.g., in $\sim 2 \times 10^{-6}$ M solution of $\mathrm{Na^+,{}^-DD^-,Na^+}$ with $[\mathrm{D}] < 10^{-7}$ M. The difference spectrum, again recorded at 100 μs after a flash, is shown in Figure 3. The absorbance at 390 nm was

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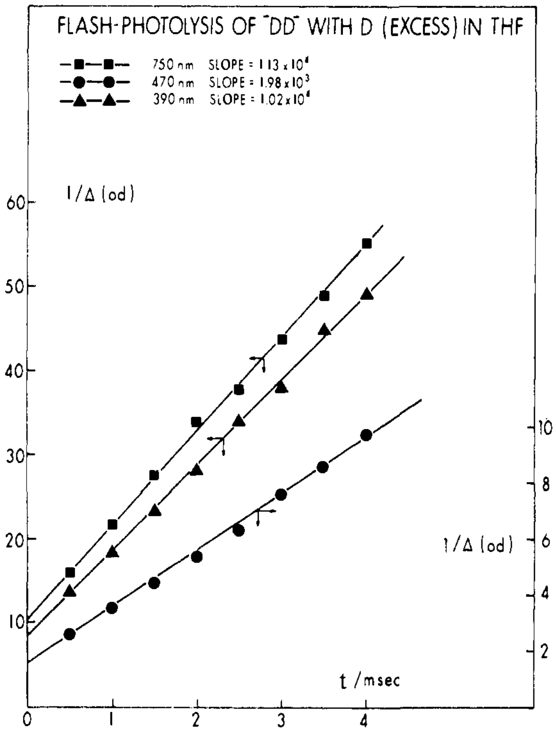

Figure 2. Typical plots of $1/\Delta(\mathrm{OD})$ vs. time obtained by monitoring the dark reaction proceeding in the presence of a large excess of D at 470, 390, and 750 nm.

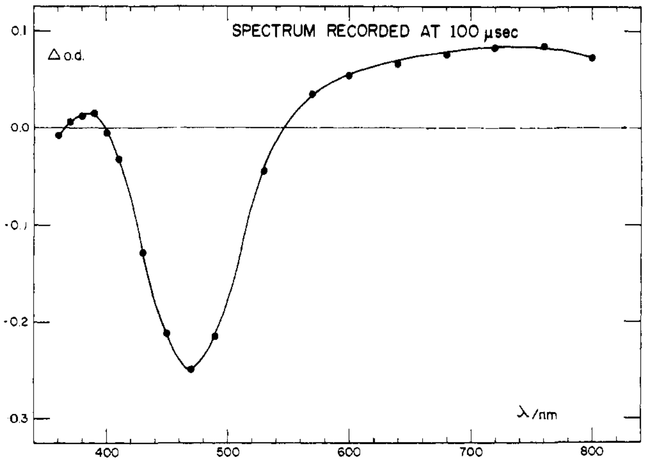

Figure 3. The difference spectrum of flash-photolyzed $\mathrm{Na^+,{}^-DD^-,Na^+}$ in THF in the absence of the unreduced D recorded at 100 μs after flash. Note (OD 390)/(OD 470) = 0.06 while in the presence of excess D the ratio is 0.18.

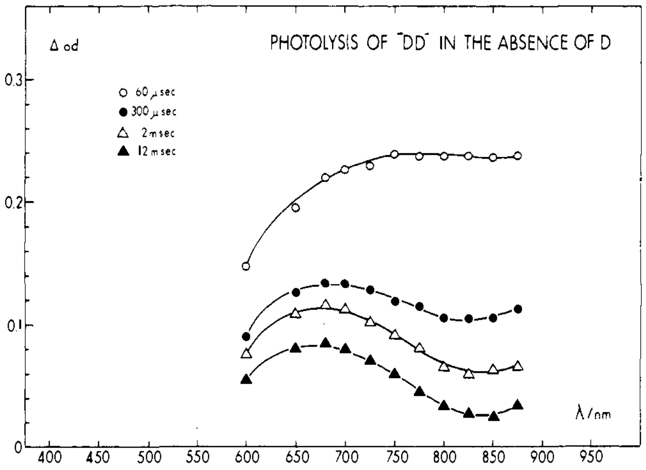

Figure 4. Changes with time of the transient absorption spectrum at longer wavelength after flashing THF solution of $\mathrm{Na^+,{}^-DD^-,Na^+}$ in the absence of D.

much lower than that observed at that time in the presence of D, although the degree of bleaching at 470 nm was comparable in both cases. On the other hand, the absorbance at longer wavelengths was relatively more intense than that recorded in the presence of D, and the shape of the spectrum observed in this region was changing with time. These findings are revealed in Figure 4.

The kinetics of the dark reaction monitored at 470 nm was more complex and lacked the simplicity of the process observed in the presence of D. Strangely enough, in the absence of D the reaction was much slower than in its presence, and a new transient seemed to be formed during the first millisecond, its absorption reaching maximum at about 650–700 μs after a flash. In fact, at later stages of the process, the reaction monitored at 470 or 750 nm appeared to obey first-order kinetics, k_u = 14–17 s^{-1}, and the transient spectrum was still perceptible at 90 ms after a flash, while it vanished in about 10 ms in the presence of an excess of D.

In view of the above observations the photodissociation cannot be the dominant primary process resulting from the irradiation of $\mathrm{Na^+,{}^-DD^-,Na^+}$. We have to conclude that the absorbed light induces electron photoejection and yields $\mathrm{Na^+,{}^-DD\cdot}$ radical ions. The subsequent dark reactions taking place in the presence of an excess of D, or of some other electron acceptor, will be discussed now, whereas consideration of the processes taking place in the absence of D will be postponed to a future communication.

The Fate of $\mathrm{Na^+,{}^-DD\cdot}$ Radical Ions

We expect most of the electrons photoejected from the $\mathrm{Na^+,{}^-DD^-,Na^+}$ dimers to be captured by D whenever a large excess of this hydrocarbon is present in the system. Therefore, under these conditions the initial products of flash photolysis should form an equimolar mixture of $\mathrm{D^-\cdot,Na^+}$ and $\mathrm{Na^+,{}^-DD\cdot}$. The following subsequent reactions could be then visualized: (a) $\mathrm{Na^+,{}^-DD\cdot + D^-\cdot,Na^+ \rightarrow Na^+,{}^-DD^-,Na^+ + D}$ (return to the initial state of the system); (b) $\mathrm{2Na^+,{}^-DD\cdot \rightarrow Na^+,{}^-DD^-,Na^+ + 2D}$; (c) spontaneous or photolytic decomposition of $\mathrm{Na^+,{}^-DD\cdot}$ yielding $\mathrm{D + D^-\cdot,Na^+}$; (d) recombination of $\mathrm{2D^-\cdot,Na^+}$ into $\mathrm{Na^+,{}^-DD^-,Na^+}$; reaction 3.

Recent studies[5] of oxidation of $\mathrm{Na^+,{}^-DD^-,Na^+}$ by perylene or tetracene showed that these oxidants remove one electron from the dimeric dianions yielding $\mathrm{Na^+,{}^-DD\cdot}$ which, in turn, spontaneously decomposes into $\mathrm{D + D^-\cdot,Na^+}$. Oxidation of $\mathrm{Na^+,{}^-DD\cdot}$ by perylene or tetracene is *too slow* and cannot compete with its unimolecular dissociation. A similar conclusion was drawn in the previous studies[1,6] when anthracene, pyrene, and dimethylanthracene were the oxidants. Kinetic data obtained in ref 5 show that the rate constant of spontaneous decomposition of $\mathrm{Na^+,{}^-DD\cdot}$ has to be greater than 10^4 s^{-1} and probably as high as 10^5 s^{-1}. In that case reactions a and b cannot efficiently compete with the spontaneous decomposition augmented by photodecomposition, if any, that lead to the formation of $\mathrm{D^-\cdot,Na^+}$ radical anions. Consequently, at ~100 μs after a flash only the latter radical anions would be left in the system as the transient intermediates.

Absorption Spectrum of $\mathrm{D^-\cdot,Na^+}$

The arguments presented in the preceding section imply that the difference spectrum shown in Figure 1 results from the bleaching of the photolyzed $\mathrm{Na^+,{}^-DD^-,Na^+}$ and from the absorbance of the formed $\mathrm{D^-\cdot,Na^+}$. Correcting the transient absorbance for the bleaching of the dimer, we constructed the dotted curve shown in Figure 1 and interpreted it as the spec-

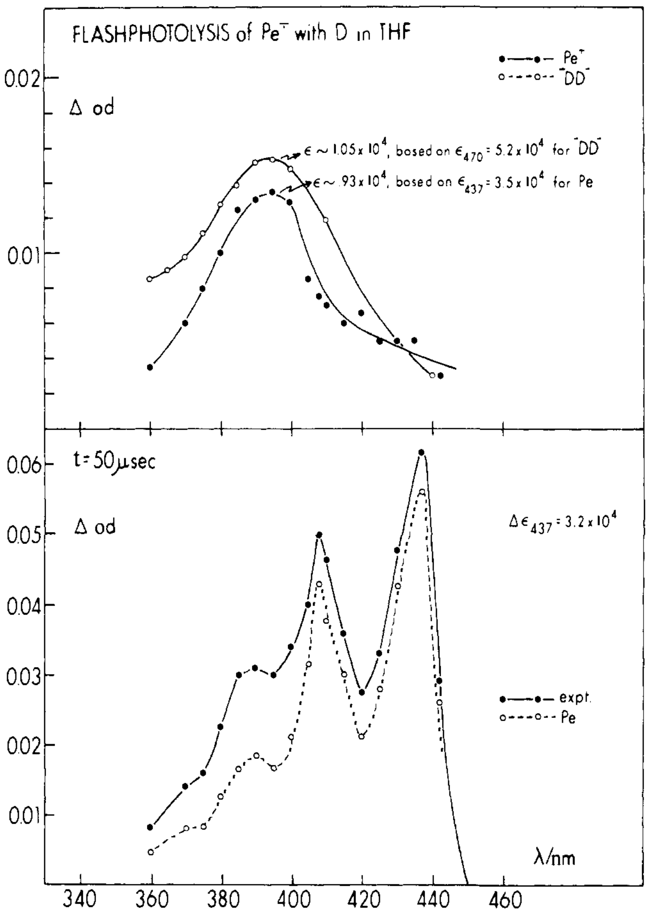

Figure 5. Lower part, solid line: the difference spectrum recorded 100 μs after flashing a THF solution of Pe$^-$·,Na$^+$ containing large excess of D. Dashed line: calculated absorption of Pe formed by the photolysis. Upper part: calculated spectrum of D$^-$·,Na$^+$ (full circles) and that obtained from the photolyses of Na$^+$,$^-$DD$^-$,Na$^+$ + D (open circles).

trum of D$^-$·,Na$^+$. Its extinction coefficient (based on $\epsilon = 5.2 \times 10^4$ for the dimer at 470 nm) was calculated to be 1.05×10^4 at its $\lambda_{\max}$ of 390 nm, provided that D$^-$·,Na$^+$ does not absorb at 470 nm ($\lambda_{\max}$ of Na$^+$,$^-$DD$^-$,Na$^+$).

These findings were confirmed by flash photolyzing sodium perylenide, Pe$^-$·,Na$^+$, in the presence of an excess of D. Photolysis of Pe$^-$·,Na$^+$ leads to electron photoejection[12] and the formation of Pe. In the presence of a large excess of D the formation of D$^-$·,Na$^+$ is expected as a result of capture of the photoejected electrons. The difference spectrum recorded at 50 μs after a flash is shown in Figure 5. The dotted line depicts the absorption of Pe calculated from the extent of Pe$^-$·,Na$^+$ bleaching ($\lambda_{\max} = 578$ nm, $\epsilon = 5.9 \times 10^4$). Subtraction of the dotted line from the continuous one gives the absorption spectrum of D$^-$·,Na$^+$. The latter, shown in the upper part of Figure 5, compares satisfactorily with the more reliable spectrum derived from the results of flash photolysis of Na$^+$,$^-$DD$^-$,Na$^+$ and drawn in the same scale in that figure.

The absorption spectrum of *free* D$^-$· radical anions, obtained at 77 °K by radiolysis of solutions of D in glassy MeTHF, was reported by Hamill.[7] The shape of that spectrum closely resembles the one shown in Figure 1, and from those data the extinction coefficient at the peak's maximum (~400 nm) is calculated to be 0.9×10^4, in good agreement with our findings. However, Hamill's spectrum, when compared with ours, is shifted toward longer wavelength. This may not be surprising; the spectra of tight ion pairs (formed in our system) are shifted to UV when compared with those of the free ions (formed in Hamill's system).

Kinetics of the D$^-$·,Na$^+$ Dimerization

The return of the photolyzed dimer solution to its initial state rigorously obeys the second-order law, provided that D is present in excess. Plots of 1/(OD) vs. time are linear at any wavelength chosen for monitoring the reaction up to 90% conversion. This implies that the regeneration of Na$^+$,$^-$DD$^-$,Na$^+$ arises from dimerization of a single species, or from encounters of two species present in equimolar concentrations.

The latter possibility seems remote. The only feasible scheme requires reaction a,

$$\mathrm{Na^+,{}^-DD\cdot + D^-\cdot,Na^+ \rightarrow Na^+,{}^-DD^-,Na^+ + D} \quad \text{(a)}$$

to be responsible for the observed dark process, and simultaneously it demands slowness of reaction 3, the dimerization of D$^-$·,Na$^+$, and of reaction b, the bimolecular disproportionation of Na$^+$,$^-$DD· radicals. Even if such kinetic relations would be fulfilled, powerful arguments could be raised against this mechanism. The above scheme requires the unimolecular rate constant of Na$^+$,$^-$DD· decomposition to be lower than 10^2 s^{-1}, because the observed bimolecular reaction is not perturbed during 9 ms. Such a slowness of the decomposition is emphatically negated by the results reported in ref 5. Moreover, another observation discussed in the following section of this paper contradicts the assumption of a slow decomposition of Na$^+$,$^-$DD·. In the presence of an excess of triphenylene, flash photolysis of Na$^+$,$^-$DD$^-$,Na$^+$ yields at about 100 μs after flash twice as large an amount of sodium triphenylenide, Trph$^-$·,Na$^+$, as the amount of the photobleached Na$^+$,$^-$DD$^-$,Na$^+$. This could only be possible had triphenylene been capable of oxidizing very rapidly Na$^+$,$^-$DD· through the reaction

$$\mathrm{Na^+,{}^-DD\cdot + Trph \rightarrow 2D + Trph^-\cdot,Na^+}$$

However, the results reported in other studies[1,2,5,6] conclusively demonstrate that more powerful oxidants, namely pyrene, anthracene, tetracene, or perylene, cannot compete with the spontaneous decomposition of Na$^+$,$^-$DD·.

These arguments, as well as the similarity of the transient spectra observed in the presence of an excess of D in flash photolysis of Na$^+$,$^-$DD$^-$,Na$^+$ and of Pe$^-$·,Na$^+$, convince us that only the dimerization of D$^-$·,Na$^+$ contributes to the dark reaction. The slopes of the lines 1/(OD 470) combined with the extinction coefficient of Na$^+$,$^-$DD$^-$,Na$^+$ at 470 nm lead to a value of 5×10^8 M^{-1} s^{-1} for the bimolecular rate constant k_3 of this reaction measured by the number of consumed moles of D$^-$·,Na$^+$.

The rate constant of 470 nm return was found to be unaffected by the degree of bleaching. The intensity of flashed light was reduced by painting the walls of the filter troughs, thus decreasing the degree of bleaching from 80 to 15% without affecting the slopes of the lines.

Photolysis of Na$^+$,$^-$DD$^-$,Na$^+$ in the Presence of Triphenylene or Biphenyl

The difference spectrum recorded at 100 μs after flashing a solution of Na$^+$,$^-$DD$^-$,Na$^+$ mixed with triphenylene, Trph, and D ([Trph]/[D] = 2:1) was fully accounted for by bleaching of the dimer and formation of an equivalent amount of Trph$^-$·Na$^+$. For example, the ratio of the transient absorbance at 400 nm to the bleaching of 470 nm was found to be 0.220. The extinction coefficients of Trph$^-$·,Na$^+$ and ½Na$^+$,$^-$DD$^-$,Na$^+$ are at those wavelengths 1.23 and 0.7×10^4, and 0.27 and 2.6×10^4, respectively. Hence, the calculated ratio based on the 2:1 stoichiometry is 0.227 in full agreement with the observation. This demonstrates that the reaction

$$\mathrm{Na^+,{}^-DD^-,Na^+ + 2Trph \xrightarrow{h\nu} 2D + 2Trph^-\cdot,Na^+}$$

Szwarc et al. / Flash Photolysis of Na$^+$,C$^-$(Ph)$_2$CH$_2$CH$_2$C$^-$(Ph)$_2$,Na$^+$

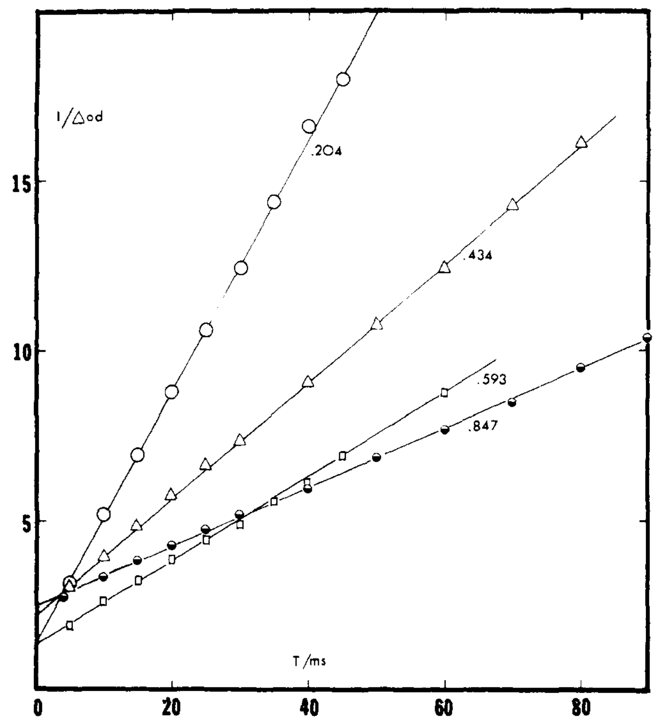

Figure 6. Plots of 1/(OD 470) vs. time for different [Trph]/[D] ratios. The slopes have to be corrected when used for the plot shown in Figure 7, because of the change in the effective extinction coefficient at 470 nm due to the absorbence of Trph^{-}·,Na^{+}.

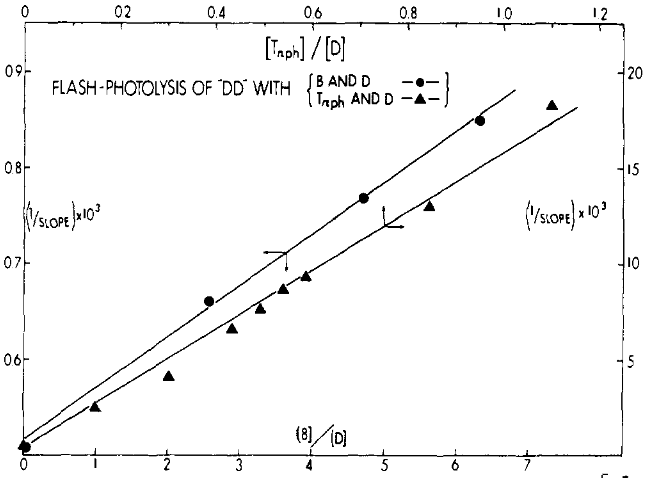

Figure 7. The square root of reciprocals of the corrected slopes of the lines 1/Δ(OD 470) vs. time (see the caption to Figure 6) plotted as functions [Trph]/[D] (triangles) or [B]/[D] (circles).

Table I. Dependence of the Slopes (s) of the Lines 1/Δ(OD 470) vs. Time on the Ratio [Trph]/[D] or [B]/[D]

[Trph] × 10^5	[D] × 10^5	[Trph]/[D]	Slope × 10^{-2}, $(OD)^{-1}$ s^{-1}	Corr^a slope × 10^{-2}, $(OD)^{-l}$ s^{-1}
0	~100		19.8	19.8
2.75	13.5	0.204	3.67	3.29
2.32	7.86	0.302	2.29	2.05
4.79	11.0	0.434	1.70	1.52
2.81	5.68	0.495	1.47	1.32
4.75	8.76	0.542	1.27	1.14
5.93	10.0	0.593	1.21	1.08
4.61	5.44	0.847	0.87	0.78
5.41	4.90	1.04	0.606	0.54
[B] × 10^5	**[D] × 10^5**	**[B]/[D]**		
0	~100		19.8	
25.0	9.70	2.58	15.2	
18.0	3.82	4.71	13.0	
22.1	3.50	6.32	11.8	

[a] Correction arises from the absorption of Trph^{-}·,Na^{+} at 470 nm. Its extinction coefficient being 0.27 reduces the effective extinction coefficient from 5.2 × 10^4 for Na^{+},$^{-}$DD^{-},Na^{+} to 4.66 × 10^4. This leads to a correction factor of 0.90. Correction is not necessary for the reactions retarded by biphenyl (see text).

is over in about 100 μs. The return of the system to its initial state is very slow under these conditions; nevertheless, the original amount of Na^{+},$^{-}$DD^{-},Na^{+} is eventually re-formed. The reaction, monitored by the absorbance at 470 nm, strictly obeys the second-order law, but the slopes of the lines giving 1/Δ(OD) vs. time depend on the ratio [Trph]/[D] as shown by the data given in Table I and illustrated by Figure 6.

It seems that the equilibrium

$$D^{-}\cdot,Na^{+} + Trph \rightleftarrows D + Trph^{-}\cdot,Na^{+} \qquad K_{Trph}$$

is maintained during the dark reaction and the course of the latter is determined by the recombination of D^{-}·,Na^{+} radical anions (reaction 3). Hence,

$$\begin{aligned} 2d\Delta[Na^{+},{}^{-}DD^{-},Na^{+}] &= d\{[D^{-}\cdot,Na^{+}] + [Trph^{-}\cdot,Na^{+}]\} \\ &= \{1 + K_{Trph}[Trph]/[D]\}\, d[D^{-}\cdot,Na^{+}] \end{aligned}$$

and

$$2d\Delta[Na^{+},{}^{-}DD^{-},Na^{+}]/dt = k_3[D^{-}\cdot,Na^{+}]^2$$

Therefore,

$$\begin{aligned} &d\Delta[Na^{+},{}^{-}DD^{-},Na^{+}]/\Delta[Na^{+},{}^{-}DD^{-},Na^{+}]^2 \\ &\qquad = 2k_3dt/\{1 + K_{Trph}[Trph]/[D]\}^2 \end{aligned}$$

In these equations $\Delta[Na^{+},{}^{-}DD^{-},Na^{+}] = [Na^{+},{}^{-}DD^{-},Na^{+}]_0 - [Na^{+},{}^{-}DD^{-},Na^{+}]_t$ represents the concentration of the bleached dimer. The latter is given by the decrease in the absorbance at 470 nm/ϵ_{eff}, and the effective molar absorbance, ϵ_{eff}, is $10\{\epsilon({}^{-}DD^{-})_{470} - 2\epsilon(Trph^{-}\cdot)_{470}\} = 4.66 \times 10^5$. The concentration of D^{-}·,Na^{+} is negligible and its ϵ at 470 low; hence, its presence negligibly contributes to the monitored absorbance.

In agreement with this derivation, the plots of 1/Δ(OD 470) vs. time are strictly linear, their slopes s being a function of [Trph]/[D], viz.,

$$(1/s)^{1/2} = (\epsilon/2k_3)^{1/2} + K_{Trph}(\epsilon/2k_3)^{1/2}[Trph]/[D]$$

This relation is shown graphically in Figure 7.

A similar study has been conducted with biphenyl, B, substituting for triphenylene. Again, the reaction obeyed second-order law; the presence of biphenyl slowed it down when compared with the reaction performed in the presence of D but in the absence of B. The square roots of the reciprocals of the slopes of the lines giving 1/Δ(OD 470) as $f(t)$ plotted vs. [B]/[D] are also shown in Figure 7 and the pertinent data are listed in Table I. Since neither D^{-}·,Na^{+} nor B^{-}·,Na^{+} absorb at 470 nm, the $\epsilon_{eff} = \epsilon(Na^{+},{}^{-}DD^{-},Na^{+})$.

Redox Potential of 1,1-Diphenylethylene

The plots shown in Figure 7 allow us to calculate the equilibrium constants K_{Trph} and K_B

$$D^{-}\cdot,Na^{+} + Trph \rightleftarrows D + Trph^{-}\cdot,Na^{+} \qquad K_{Trph}$$

and

$$D^{-}\cdot,Na^{+} + B \rightleftarrows D + B^{-}\cdot,Na^{+} \qquad K_B$$

Their values were found to be 3.67 and 0.041, respectively, their ratio providing the equilibrium constant of

$$B^{-}\cdot,Na^{+} + Trph \rightleftarrows B + Trph^{-}\cdot,Na^{+}$$

viz., 89. Thus, the difference of the redox potentials of these hydrocarbons (in a process yielding ion pairs in THF) determined from the results of our kinetic study is 115 mV. The potentiometric titration[8] leads to a difference of 113 mV in agreement with the kinetic findings. The redox potential of 1,1-diphenylethylene appears to be higher than that of biphenyl but lower than that of triphenylene. Accepting Bergman's[9] value for the redox potential of triphenylene, namely −2.49 V (vs. SCE), we find the redox potential of D (vs. SCE) to be −2.52 V. Recent unpublished polarographic determination by Bard[10] gives a value of −2.59 V in DMF with 0.1 M TBAP as supporting electrolyte.

An apparent discrepancy noted in the earlier stage of this research is now accounted for by the magnitude of K_{Trph} and K_B. The transient spectrum recorded 100 μs after flashing a $Na^{+},{}^{-}DD^{-},Na^{+}$ solution containing about 20-fold excess of biphenyl showed unmistakably the characteristic features of the $B^{-}\cdot,Na^{+}$ absorption, an intense peak at 400 nm and a weaker, broad band peaking at 630 nm. However, the absorbance at 400 nm was by ~35% weaker than would be calculated from the 470-nm bleaching and the assumed 2:1 stoichiometry, this being in contrast with the results obtained in the presence of triphenylene when the observed and calculated intensities agreed well. The value of K_B shows that for $[B]/[D] \approx 30$ the ratio $[B^{-}\cdot,Na^{+}]/[D^{-}\cdot,Na^{+}]$ should be about 1.2. Since the absorbance of $D^{-}\cdot,Na^{+}$ at 400 nm is about five times lower than that of $B^{-}\cdot Na^{+}$, the above "discrepancy" is now explained.

Comparison of Present Findings with Those Reported by Matsuda et al.[11]

Dimerization of $D^{-}\cdot,Na^{+}$ radical anions was previously investigated in this laboratory by stop-flow technique. A solution of $Trph^{-}\cdot,Na^{+}$, containing a large excess of Trph, was mixed with a small excess of D. This led to a relatively slow dimerization of $D^{-}\cdot,Na^{+}$, since its concentration was kept low. Monitoring the reaction at 470 nm allowed the calculation of an apparent rate constant k' related to k_3 (dimerization constant of $D^{-}\cdot,Na^{+}$) by the relation

$$(1 + K_{Trph}[Trph]/[Trph^{-}\cdot,Na^{+}])^2 k' = k_3$$

The only method available at that time for calculating K_{Trph} was very susceptible to experimental errors and this difficulty, coupled with the technical problems of experimentation, resulted in a greatly erroneous value of $K_{Trph} = 6.2 \times 10^{-2}$ instead of the presently found 3.67. However, using the reported values of k' and of $[Trph]/[Trph^{-}\cdot,Na^{+}]$ together with the presently derived value of K_{Trph}, we find values of k_3 varying from 3 to 6×10^8 M^{-1} s^{-1}, whereas the value of k_3 now directly determined is 5×10^8 M^{-1} s^{-1}. The previously claimed[11] value $k_3 = 1.5 \times 10^6$ M^{-1} s^{-1} should be discarded.

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References and Notes

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

(2) J. Jagur, M. Levy, M. Feld, and M. Szwarc, *Trans. Faraday Soc.*, **58**, 2618 (1962).

(3) G. Rämme, M. Fisher, S. Claesson, and M. Szwarc, *Proc. R. Soc. London, Ser. A*, **327**, 481 (1972).

(4) Reference 2, p 470.

(5) S. Lillie, S. Slomkowski, G. Levin, and M. Szwarc, *J. Am. Chem. Soc.*, preceding paper in this issue.

(6) D. Gill, J. Jagur-Grodzinski, and M. Szwarc, *Trans. Faraday Soc.*, **60**, 1424 (1964).

(7) W. H. Hamill, "Radical Ions", E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N.Y., 1968, p 321.

(8) J. Jagur-Grodzinski, M. Feld, S. L. Yang, and M. Szwarc, *J. Phys. Chem.*, **69**, 628 (1965).

(9) I. Bergman, *Trans. Faraday Soc.*, **50**, 829 (1954).

(10) We wish to thank Dr. Allen Bard for his kindness in providing us with his unpublished result.

(11) m. Matsuda, J. Jagur-Grodzinski, and M. Szwarc, *Proc. R. Soc. London, Ser. A*, **288**, 212 (1965).

(12) E. D. Lillie, D. Van Ootegham, G. Levin, and M. Szwarc, *Chem. Phys. Lett.*, **41**, 216 (1976).

Chemical Bonding and Reactivity in Nickel–Ethene Complexes. An ab Initio MO–SCF Study

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Abstract: A number of nickel–ethene complexes with various additional ligands have been studied using *ab initio* MO-SCF calculations. Nickel(0)-olefin complexes are found to have C–C bond distances much longer than normal double bonds. Special interest has been focused on parameters relevant to the Dewar–Chatt–Duncanson model for the olefin–metal interaction. Attempts have also been made to estimate the reactivity of the ethene molecule in different nickel complexes. Reactions such as nucleophilic addition and cycloaddition are discussed. Cationic nickel(II) complexes are the main candidates for promotors of nucleophilic addition and the cyclic insertion reaction. By contrast, cyclobutane formation and other related, cyclic product forming reactions probably require nickel(0) complexes as promotors.

Organometallic reactions are frequently complex and theoretical models which could serve as a guide for experimental work are highly desirable. We have been particularly interested in the factors that promote cycloaddition and nucleophilic addition to complexed olefins.[2,3] The major factors are likely to be the charge on the complexed olefin relative to the free olefin and the metal, as well as the general weakening of the double bond due to the interaction with the metal. These

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