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Electron Photoejection and its Application in Studies of Electron Transfers

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Abstract: The principle of electron photoejection technique is explained. This approach leads to the formation of transient spectra of unstable intermediates, allowing their recording and providing their extinction coefficients. Moreover, it permits determination of their electron affinities and the rates of their reactions, whether spontaneous or with some added substrates. Application of this technique to studies of disproportionation of radical anions have been most profitable. It led to the determination of the forward and backward rate constants of disproportionation of a variety of radical anions, and to discovery and quantification of some subtle features of these reactions. Electron photoejection technique provided the data characterizing the electron transfer initiation of anionic polymerization and clarified some of its features. Other opportunities provided by the electron photoejection in studies on electron transfer processes are suggested.

Electron Photoejection and its Application in Studies of Electron Transfer

In the parlance of a common chemist, an electron transfer is a phenomenon leading to the transmission of an electron from location D (a donor) to location A (an acceptor). Such event may take place by an intra- or inter-molecular process. A more physically minded scientist considers any sudden change in the electron density distribution of an investigated system as an electron transfer, whether associated or not with photon absorption or emission.

In this talk I wish to describe the electron photoejection technique, a valuable tool in kinetic studies of some electron transfer processes. The results obtained using this technique will be reviewed and their significance discussed.

A flash light of λ>300 nm (light of shorter wavelength is harmful in these studies) ejects electrons from various carbanions, radical-anions, or dianions$^{1)}$. In the dark period following the flash the irradiated system rigorously returns to its initial state through a variety of electron transfer processes. Hence, the flashing may be repeated again and again. The results

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observed each time are highly reproducible, indicating the absence of any lasting side reactions.

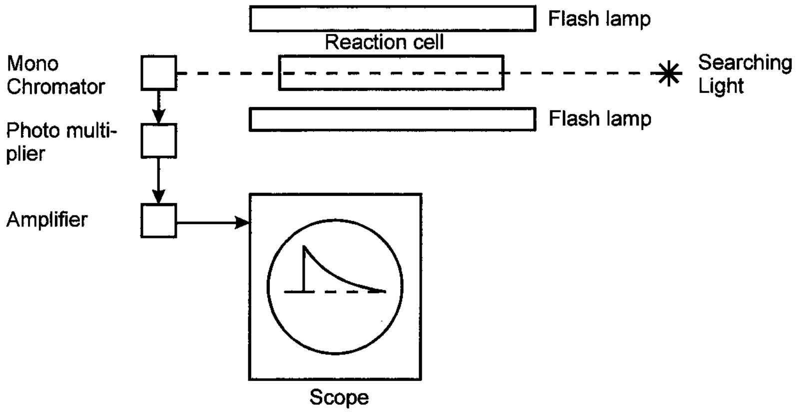

Fig. 1 Schematic representation of the flash photolysis equipment

The flash photolysis equipment applied in our studies is shown in Fig.1. A discharge of condensers through two parallel lamps results in flash of visible light (shorter UV light is absorbed by filters placed between the lamps and the cell containing the investigated solution). The intensity of monochromatic light of a desired wavelength, transmitted through the studied solution, is amplified by a photomultiplier whose outcome is recorded on a scope. This permits studies of the return of this system to its initial state.

Flash-photolysis of THF solution of sodium pyrenide radical anions ($\pi^{\bullet-}$, Na^+) containing large excess of biphenyl (B) exemplifies a typical experiment[1c,d]. Electron affinity of pyrene (π) is much higher than that of biphenyl[2]. Therefore, no detectable amount of sodium biphenylide ($B^{\bullet-}$, Na^+) is formed in such solution. However, the flash of light that partially bleaches the absorbance of $\pi^{\bullet-}$ produces a transient identified as $B^{\bullet-}$, Na^+. The spectrum of the transient is shown in Fig. 2. Its intensity fades with time without changing its shape, while that of the $\pi^{\bullet-}$ absorption intensifies. Eventually, the initial state of the system is restored, and then the absorption spectrum of the previously irradiated solution becomes identical with its initial spectrum. Hence, no persistent side products are formed.

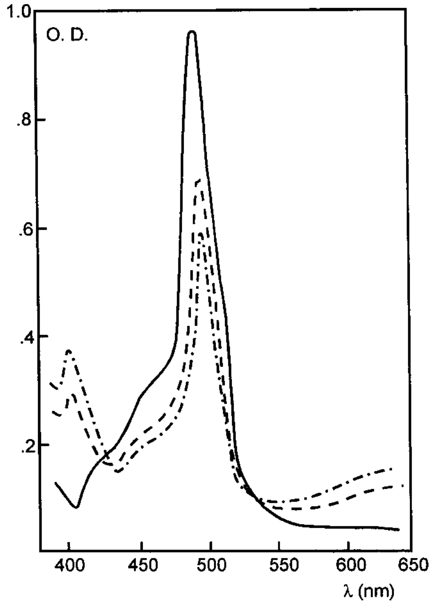

Fig. 2 The spectrum of the irradiated solution of pyrene radical anion in the presence of an excess of biphenyl

Clearly, the flash of light ejects an electron from $\pi^{\bullet-}$, and the ejected electron is captured by B yielding $B^{\bullet-}$:

$$\pi^{\bullet-}, \mathrm{Na}^+ \xrightarrow{h\nu} \pi + e^-, \mathrm{Na}^+$$

$$B + e^-, \mathrm{Na}^+ \rightarrow B^{\bullet-}, \mathrm{Na}^+$$

In the dark period following the flash the electron transfer

$$B^{\bullet-}, \mathrm{Na}^+ + \pi \rightarrow B + \pi^{\bullet-}, \mathrm{Na}^+$$

restores the initial state of the system. Changes of $\pi^{\bullet-}$, Na^+ concentration modify the proportion of free anions and their ion-pairs in the solution. Hence, their contributions to the rate of the overall electron transfer are altered. This allows determination of the rate constants of transfer by free ions and by ion-pairs. At ambient temperature the rate constant of transfer by free anions is $k_- = 2.10^{10}$ $M^{-1}s^{-1}$, and that due to ion-pairs is $k_\pm = 8.10^9$ $M^{-1}s^{-1}$ (this value seems too high).

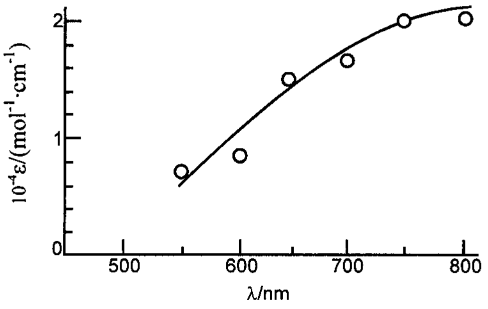

Fig. 3 The difference spectrum of the photolysed solution of pyrene radical anion in the absence of biphenyl

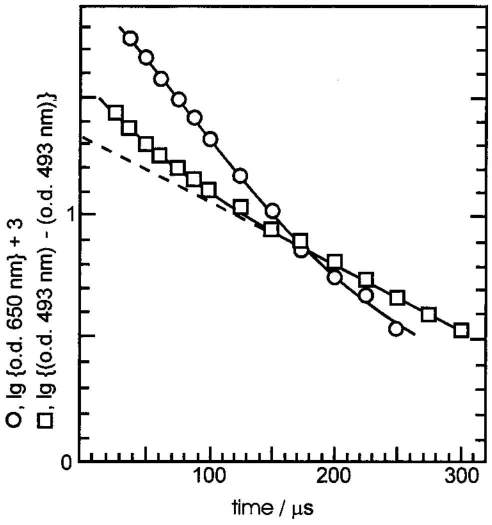

Fig. 4 Plot of log of optical densities at 650 and 493 nm of the flash photolysed solution of pyrene radical anion at 10^{-7} M concentration of π^- as function of time

Absorbance of $\pi^{\bullet-}$ is bleached by flash of light even in the absence of B[3]. However, a transient other than $B^{\bullet-}$ is then formed, apparently e^-, Na^+ (see Fig. 3). At high dilution of $\pi^{\bullet-}$, Na^+ (~10^{-7} M), the rate of the transient decay exceeds that of reformation of $\pi^{\bullet-}$ (see Fig. 4). It seems that e^-, Na^+ collapses into some invisible species, presumably an expanded sodium atom (Na^0), which reacts with π, regenerates $\pi^{\bullet-}$, Na^+, and thus contributes to the restoration of the initial state.

Collating all the available evidence the following constants were computed:

$e^- + \pi \rightarrow \pi^{\bullet -}$	$10.10^{10}\ M^{-1}s^{-1}$
$e^-, Na^+ + \pi \rightarrow \pi^{\bullet -}, Na^+$	$1.4.10^{10}\ M^{-1}s^{-1}$
$Na^0 + \pi \rightarrow \pi^{\bullet -}, Na^+$	$1.1.10^{10}\ M^{-1}s^{-1}$
$e^- Na^+ \rightarrow Na^0$	$\sim 10^4\ s^{-1}$
$e^-, Na^+ \Leftrightarrow e^- + Na^+$	$K_{diss}=5.10^{-8}\ M$

Electron photo-ejection is vividly illustrated by flash photolysis of perylenide radical-anion ($Pe^{\bullet -}$)[4]. The transient appearing while the absorbance of $Pe^{\bullet -}$ is bleached is identified as a neutral perylene (see Fig. 5).

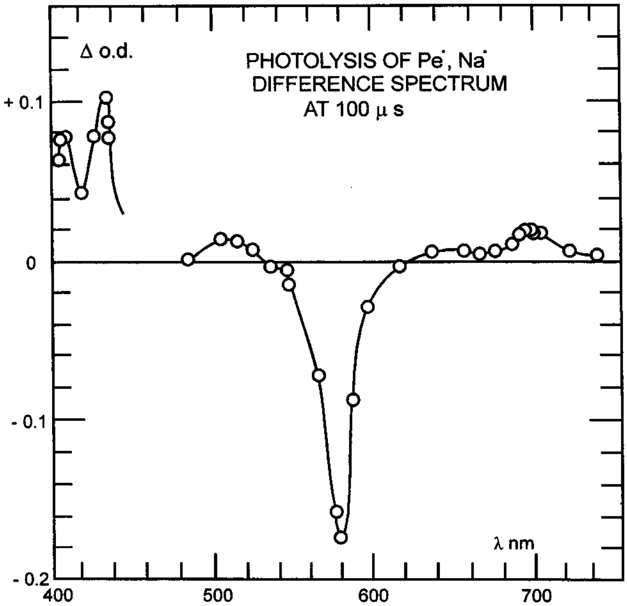

Fig. 5 The difference spectrum of the photolysed perylene radical anion solution revealing the formation of perylene after a flash of light

Flash photolysis of carbanion is exemplified by the photolysis of dimeric dianions of α-methyl styrene K^+, $^-C(CH_3)(Ph)CH_2CH_2C^-(CH_3)(Ph)$, K^+. The pertinent difference spectrum is shown by Fig. 6.

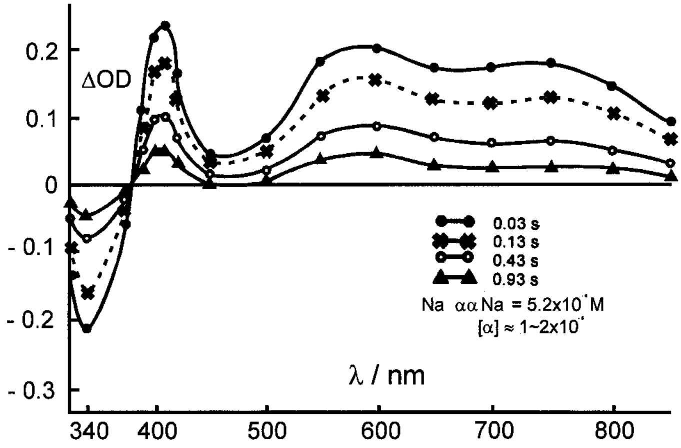

Fig. 6 The difference spectrum of the flash photolysed solution of the dimeric α-methyl styrene dianions

Conventional electron transfer to 1,2-cyclohexene (Hex) produces its dianion. The very rapid disproportionation of the expected radical anion

$$2\text{Hex}^{\overset{\bullet}{-}}, \text{Na}^{+} \quad \Leftrightarrow \quad \text{Hex} + \text{Hex}^{2-}, 2\text{Na}^{+} \qquad K_{\text{diss}}=\sim 1000$$

is virtually quantitative, even in the presence of excess of Hex. However, the spectrum of $\text{Hex}^{\overset{\bullet}{-}}$ radical anion appears (the dotted line in Fig. 7) when solution of Hex^{2-} containing some hexene is exposed to flash of light[5]. Obviously, electron ejected from Hex^{2-} is captured then by Hex. The unstable $\text{Hex}^{\overset{\bullet}{-}}$ radical-anion, formed momentarily, disproportionates in less than 1 ms into its dianion. The disproportionation of radical anions deserves closer examination:

$$2\text{A}^{\overset{\bullet}{-}}, \text{Cat}^{+} \quad \underset{k_2}{\overset{k_1}{\Leftrightarrow}} \quad \text{A} + \text{A}^{2-}, 2\text{Cat}^{+} \qquad K_{\text{dispr}}=k_1/k_2$$

For any aromatic hydrocarbon the disproportionation constant of its radical anion varies widely with the nature of cation and solvent, as exemplified by the data collected in Table I[6].

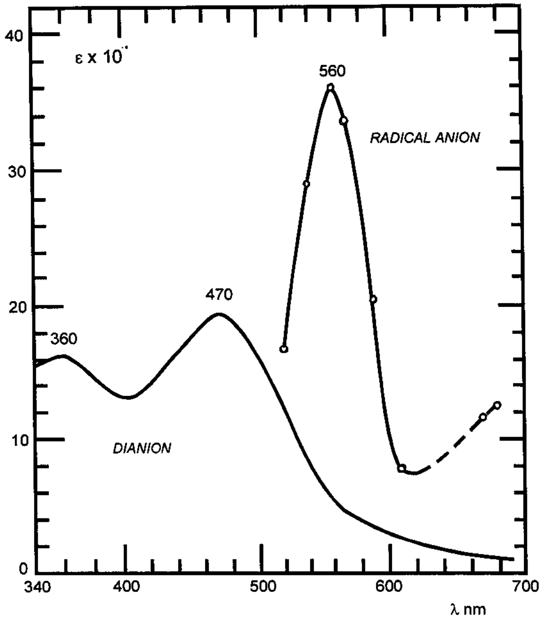

Fig. 7 The spectra of 1,2-diphenyl cyclohexene radical anion and its dianion

Table I. Disproportionation of tetracene radical anions coupled with various cations in a variety of solvents.

Solvent	Cation	K_{dispr}	k_1 Ms	k_2 Ms
THF	Li^+	$5.8.10^{-9}$	3.6.10	$6.3.10^9$
THF	Na^+	$1.0.10^{-5}$	$5.5.10^4$	$5.5.10^9$
THF	K^+	$4.6.10^{-6}$	$3.0.10^4$	$6.5.10^9$
THF	Cs^+	$3.2.10^{-6}$	$2.5.10^4$	$7.8.10^9$
DOX	Li^+	$6.6.10^{-2}$	$6.0.10^6$	$1.1.10^8$
DOX	Na^+	$6.5.10^{-2}$	$2.0.10^7$	$3.1.10^8$
DOX	K^+	$1.1.10^{-2}$	no bleaching by flash	
DOX	Cs^+	$0.6.10^{-2}$	no bleaching by flash	
DEE	Li^+	2.7.10	$7.0.10^7$	$2.6.10^6$
DEE	Na^+	$1.2.10^{-1}$	$2.4.10^8$	$2.0.10^9$
Benzene	Na^+	$\sim 10^4$	too slow	

Electron photo-ejection technique allows the determination of k_1 and k_2 governing the disproportionation. A flash of light upsets the equilibrium established between A, $A^{\bullet-}$, and A^{2-}. For example, the ejection of electron from A^{2-} and its capture by A decreases concentrations of these species, and increases the proportion of $A^{\bullet-}$. The kinetics of return to the initial state yields then the relaxation time of this equilibrium. Its value, combined with the independently determined K_{dispr}, leads to the values of k_1 and k_2. These constants listed also in Table I refer to the tetracene system.

Ionicity of the reagents affects rates of disproportionation. Disproportionation of tetraphenyl ethylene radical anions ($T^{\bullet-}$) in THF provides an example.

(1)	$2\,T^{\bullet-}, Na^{+}$	$\underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}}$	$T + T^{2-}, 2Na^{+}, K_1=400$	$k_1=8.10^6\ M^{-1}s^{-1}$ $k_{-1}=2.10^4\ M^{-1}s^{-1}$
(2)	$T^{\bullet-} + T^{\bullet-}, Na^{+}$	$\underset{k_{-2}}{\overset{k_2}{\Leftrightarrow}}$	$T + T^{2-}, Na^{+},\ K_2=3.3$	$k_2=1.10^7\ M^{-1}s^{-1}$ $k_{-2}=3.10^6\ M^{-1}s^{-1}$
(3)	$2\,T^{\bullet-}$	$\underset{k_{-3}}{\overset{k_3}{\Leftrightarrow}}$	$T + T^{2-}\quad K_3 \sim 10^{-8}$	too slow to measure

In spite of the low concentrations of $T^{\bullet-}$and T^{2-}, it is reaction (2) that governs the rate of the overall disproportionation. The high value of k_2 makes reaction (2) the most significant (note, k_2 refers to transfer of electron unassociated with cation).

The entropy of disproportionation varies with the nature of solvent and cation. A simple device developed in our laboratory[8)], shown Fig. 8, allows determination of the respective ΔH and ΔS as functions of temperature[9)]. A 50/50 solution of A and $A^{\bullet-}$, Cat^{+}, and again of $A^{\bullet-}$, Cat^{+} and A^{2-}, $2Cat^{+}$ are placed in the evacuated bulbs shown in Fig. 8. The bulbs are connected through a liquid junction filled with a concentrated solution of the respective tetraphenylboride salt. Two platinum electrodes immersed in the investigated solution are linked to a voltmeter. The bulbs are placed in a thermostat kept at a desired temperature. The ΔG of disproportionation at that temperature is given then by the read voltage. Slopes of the plots of ΔG versus 1/T or T, shown in Fig. 9, provide the respective ΔH and ΔS.

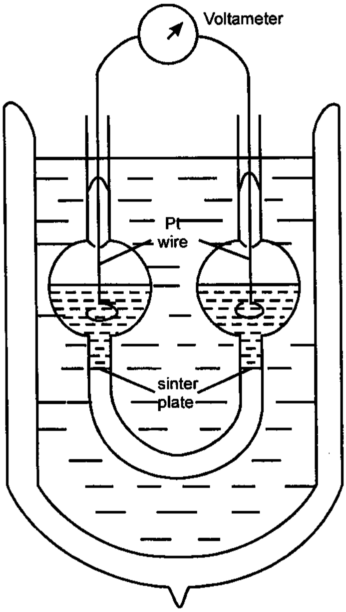

Fig. 8 The device determining the ΔG of disproportionation of radical anion as function of temperature

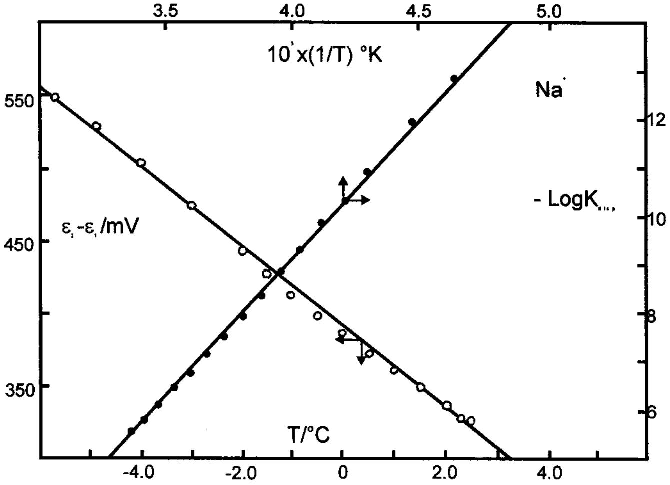

Fig. 9 Plots of the ΔG of disproportionation of radical anion as function of T and 1/T

The results listed in Table II are illuminating[10)].

Table II. ΔH and ΔS of the disproportionation of perylenide salts (Pe^-, Cat^+) in THF

Cation	Temperature range °C	ΔH/(kcal·mol^{-1})	ΔS/e. u.
Li^+	-55 to -40	13.6	0.0
Li^+	0 to +25	16.2	13.1
Na^+	-55 to +25	27.2	65.8
K^+	-55 to +25	14.2	22.2
Cs^+	-55 to +25	11.0	15.1

ΔS of disproportionation of tetracene radical-anion is low for its Li^+, K^+, or Cs^+ salts in THF, whereas it is large for the Na^+ salt. Small Li^+ cations seem capable to retain their solvation shell whether associated with radical anions or dianions. Therefore, the gain in entropy on disproportionation of Li^+, $\text{Te}^{\bullet-}$is relatively small. The large K^+ and Cs^+ cations are poorly solvated in either aggregates. Hence, not much gain in entropy of disproportionation of the K^+ or Cs^+ salts of $\text{Te}^{\bullet-}$may be expected. On the other hand, the Na^+ cations retain solvation shell when associated with radical anions, but lose much of it when combined with the more strongly attracting dianions. Hence, the disproportionation of Na^+, $\text{Te}^{\bullet-}$ releases some solvent molecules from its solvation shells, causing a large gain in entropy.

The effect of solvation is clearly revealed in the disproportionation of sodium tetracenide in benzene solution[11)]. Its solubility in that solvent is too low to allow a photometric study of disproportionation, but becomes sufficiently high on addition of small amounts of THF. The ratio

$$[\text{Ba}^{2+}\ \text{Te}^{\bullet-}{}_2]^2/[\text{Te}].[\text{Ba}^{2+}, \text{Te}^{2-}]$$

i.e., the formal disproportionation constant, was found to be linear with log[THF] (its slope = -2 as shown in Fig. 10) indicating the establishment of following equilibrium:

$$2\ \text{Te}^{\bullet-}, (\text{Na}^+, \text{THF}_{n+1}) \underset{k_b}{\overset{k_f}{\Leftrightarrow}} \text{Te} + \text{Te}^{2-}(\text{Na}^+, \text{THF}_n)_2 + 2\ \text{THF}$$

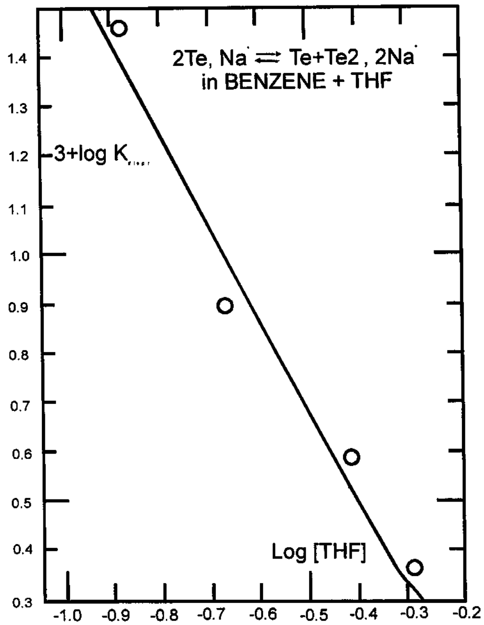

Fig. 10 Plot of log of the apparent equilibrium constant of disproportionation of sodium tetracene radical anions in benzene solution containing small amounts of THF as a function of log [THF]

Two distinct mechanisms may account for such equilibrium. It might arise from disproportionation of minute amounts of poorly solvated aggregates, $Te^{-\bullet}$, (Na^+, THF_n), being in equilibrium with the fully solvated ones, $Te^{-\bullet}$, (Na^+, THF_{n+1}). Such reaction directly yields the final Te^{2-}, (Na^+, THF_n)$_2$. Alternatively, the fully solvated aggregates, $Te^{-\bullet}$, (Na^+, THF_{n+1}) may disproportionate, yield the oversolvated dianions, Te^{2-}, (Na^+, THF_{n+1})$_2$. The latter, however, desolvate rapidly any thus the final dianion, Te^{2-}, (Na^+, THF_n)$_2$ and two molecules of THF are formed. The desolvation keeps the equilibrium concentration of the oversolvated dianions low.

The relaxation times of the solvation and desolvation processes are very short due to the relatively high concentration of THF. Hence, were the first alternative correct, then k_f would *decrease* on increasing [THF], leaving k_b unaffected. In the alternative case, k_b would *increase* on increasing [THF], whereas k_f would remain unaffected. The experiments have shown a decrease of k_f with increasing [THF]. Therefore, the prevalence of the poorly solvated radical anions, $Te^{-\bullet}$, (Na^+, THF_n), in this disproportionation process has been demonstrated.

A peculiar phenomenon was observed in the course of disproportionation of barium tetracenide radical anions in THF solution[12)]. The relevant disproportionation constant was found to be very high, ~10^6. Hence, the concentration of the paramagnetic radical anions, detected by ESR, was exceedingly low in this system, even in the presence of a large excess of Te. Not surprisingly, the radical anions Ba^{2+}, $Te^{\bullet -}_2$ were virtually quantitatively dissociated into Ba^{2+}, $Te^{\bullet}_{-}$ + $Te^{\bullet -}$. Therefore, the ratio $[\text{paramagnetic species}]^2/[Te]$. $[Ba^{2+}, Te^{2-}]$ was found to be constant, independent of the reagents concentrations, implying the following equilibrium:

$$Ba^{2+}, Te^{\bullet -} + Te^{\bullet -} \quad \Leftrightarrow \quad Te + Ba^{2+}, Te^{2-}$$

A flash of light bleaches the absorption of Ba^{2+}, Te^{2-} (λ_{max} = 630 nm), while a transient appears at λ_{max} = 715 nm (see Fig.11).

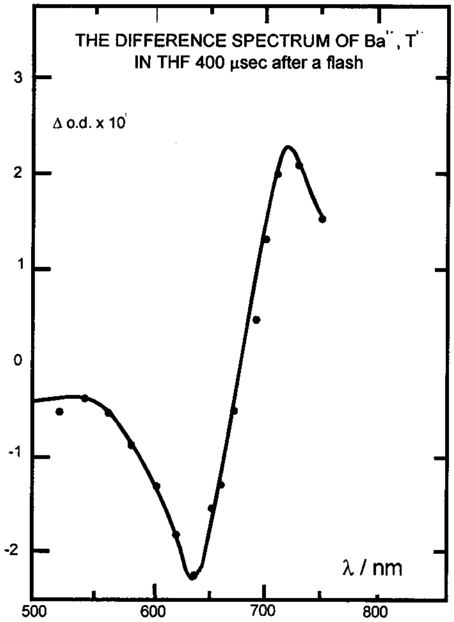

Fig. 11 The difference spectrum of flash photolysed solution of Ba salt of tetracene dianion in THF

Significantly, return to the initial state is very fast at the early stages of the reaction, but slows down thereafter (see Fig. 12).

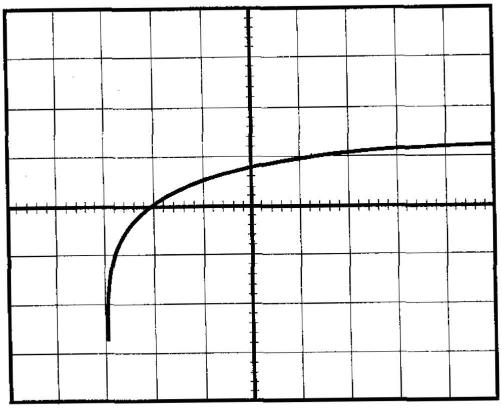

Fig. 12 Oscilloscope tracing of the absorbance of transient (630nm) formed in the flash photolysis of the solution of barium tetracene dianions in THF

It seems that two reactions participate in the observed process:

$\text{Ba}^{2+}, \text{Te}^{\bullet-} + \text{Te}^{\bullet-}$ (from the right) $\rightarrow$ $\text{Ba}^{2+}, \text{Te}^{2-} + \text{Te}$ (fast, second order)

but

$\text{Te}^{\bullet-} + \text{Ba}^{2+}, \text{Te}^{\bullet-}$ (from the right) $\rightarrow \text{Te}^{\bullet-}, \text{Ba}^{2+}, \text{Te}^{\bullet-}$ (still fast)

is followed by the relatively slow unimolecular "dissociation"

$\text{Te}^{\bullet-}, \text{Ba}^{2+}, \text{Te}^{\bullet-} \rightarrow \text{Te} + \text{Ba}^{2+}, \text{Te}^{2-}$ (first order)

The above examples illustrate the complexities of disproportionations of radical anions and the advantages offered by the electron photoejection technique in elucidating their behavior. There are other problems solved by this technique. For example, conventional electron transfer to *cis*-stilbene yields *trans*-stilbene radical anions. The *cis-trans* isomerization of stilbene radical anions is fast and virtually quantitative. However, flashing a solution of *cis*-stilbene containing some perylenide radical anions results in the formation of a transient - a *cis*-stilbene radical anion$^{13)}$ (see Fig. 13).

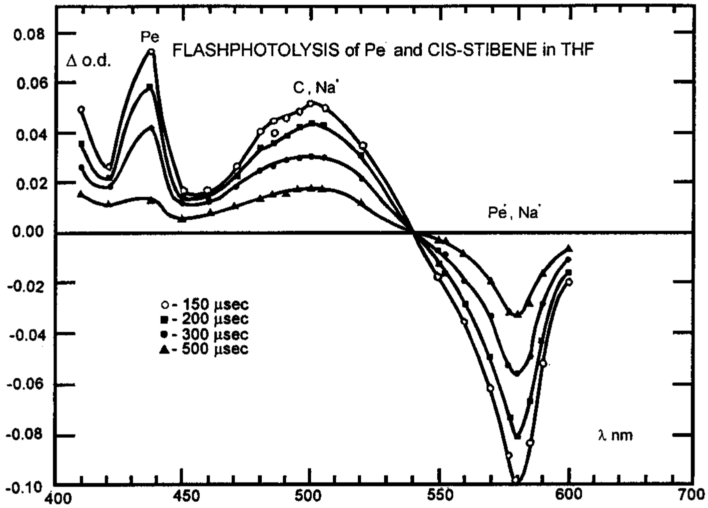

Fig. 13 The difference spectrum of flash photolysed perylene radical anions solution in the presence of *cis*-stilbene

A similar flash photolysis of *trans*-stilbene perylenide solution yields the known spectrum of *trans*-stilbene radical anion. Both spectra are shown in Fig. 14. They differ in the values of the extinction coefficients at λ_{max}. The identity of the spectrum of *trans*-stilbene produced by this procedure with the authentic one ascertains the reliability of the above procedure.

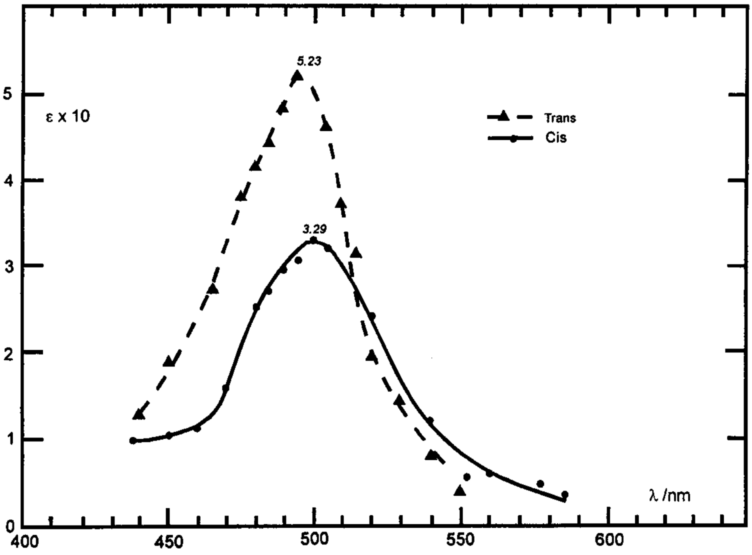

Fig. 14 Spectra of *cis*- and *trans*-stilbene radical anions

Analysis of spectra produced by flash photolysis of a mixture, say 50/50 of *cis*- and *trans*-stilbene, allows determination of the equilibrium constant:

cis-stilbenide + *trans*-stilbene ⇔ *cis*-stilbene + *trans*-stilbenide

Since the concentration of the stilbenes is much larger than that of the transients, the above equilibrium is established much faster than the decay of both spectra caused by the reformation of the perylenide. Therefore, the electron affinity of *cis*-stilbene could be computed from the value of the above equilibrium constant and the known electron affinity of *trans*-stilbene.

Now, I wish to discuss the application of the electron photoejection technique in the study of electron transfer initiation of anionic polymerization. This initiation involves three steps:

(1) Electron transfer from a suitable electron donor to a vinyl monomer, M, yielding monomer radical anions, $M^{\bullet-}$.
(2) Rapid dimerization of $M^{\bullet-}$'s yielding dimeric dianions $^{-}MM^{-}$.
(3) The conventional initiation of propagation of anionic polymerization by the carbanions of the dimeric dianions.

Although this scheme was proposed in 1956[14)], it took 20 years to acquire the techniques that allow determination of the relevant rate constants.

Consider for example 1,1-diphenylethylene (D), a vinyl "monomer"(α-phenyl-styrene) that undergoes electron transfer and yields monomeric radical anion $D^{\bullet-}$ that dimerize into $^{-}DD^{-}$. However, the propagation of polymerization is precluded by a steric strain expected in the potentially feasible polymer. Its high magnitude prevents $^{-}DD^{-}$ to react with added D, the reaction $^{-}DD^{-} + D \rightarrow {}^{-}DDD^{-}$ is prohibited.

Flash photolysis of THF solution of $^{-}DD^{-}$ salts performed in the presence of D yields a transient identified as $D^{\bullet-}$ (see Fig. 15)[15)]. Kinetics of its dimerization yielding $^{-}DD^{-}$ in the dark period following the flash obeys the second order law (see Fig. 16), allowing determination of the rate constant of dimerization.

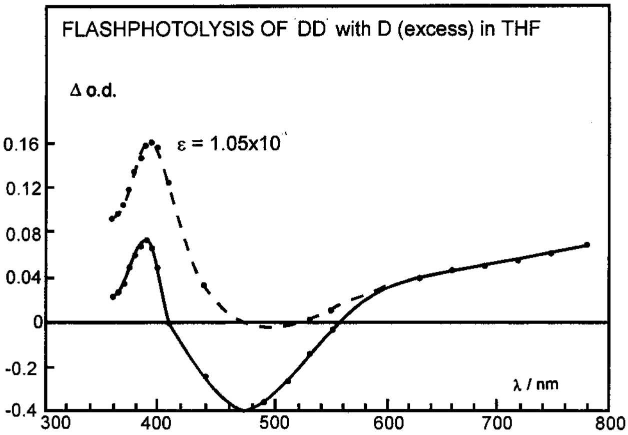

Fig. 15 The time dependence of the difference spectrum of flash photolysed solution of dimeric 1,1-diphenylethylene dianions mixed with a large excess of 1,1-diphenylethylene

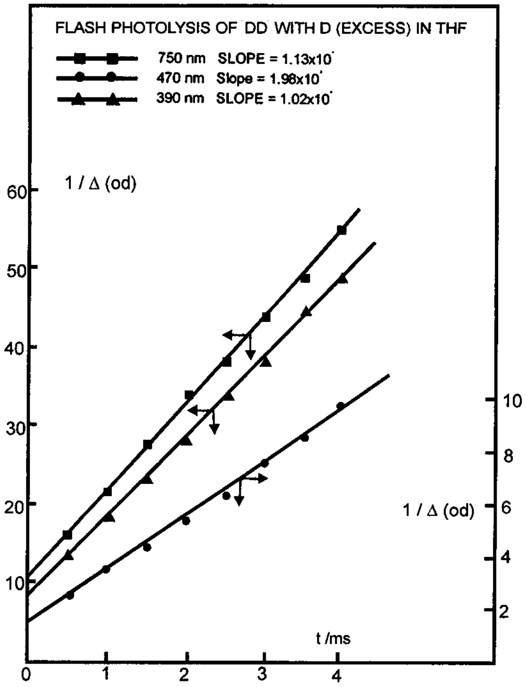

Fig. 16 Plots of optical density of the solution of flash photolysed dimeric dianions of 1,1-diphenylethylene mixed with an excess of 1,1-diphenylethylene as function of time

A question arises[16)]. Does the flash of light photodissociate $^{-}\mathrm{DD}^{-}$ into $2\mathrm{D}^{\bullet-}$, i.e.,

$$\mathrm{Cat^+,\ {}^{-}DD^{-},\ Cat^+} \xrightarrow{h\nu} 2\,\mathrm{D^{\bullet-},Cat^+}\ ?$$

Or does it lead to electron photoejection

$$\mathrm{Cat^+,\ {}^{-}DD^{-},\ Cat^+} \xrightarrow{h\nu} \mathrm{Cat^+,\ {}^{-}DD^{\bullet}\ e^{-},\ Cat^+}$$

followed by a rapid dissociation of the dimeric radical anion, $\mathrm{Cat^+,\ {}^{-}DD^{\bullet}}$ into $\mathrm{D^{\bullet-},Cat^+}$ and D?

Had light disassociated $^{-}\mathrm{DD}^{-}$into $2\mathrm{D}^{\bullet-}$, then the return to the initial state would result from a simple bimolecular association of the photo-produced radical anions, whether any D had been added or not. Moreover, the spectrum of the transient would be the same in the presence or absence of excess of D. However, this is not the case. The transient formed in the absence of D, shown in Fig. 17, is entirely different from the one formed in the presence of high concentration of D (see Fig. 15). Moreover, the kinetics of return of the system to its initial state is simple only when a sufficient amount of D is present in the irradiated solution. In its absence the kinetics becomes complex as exemplified by Fig. 18.

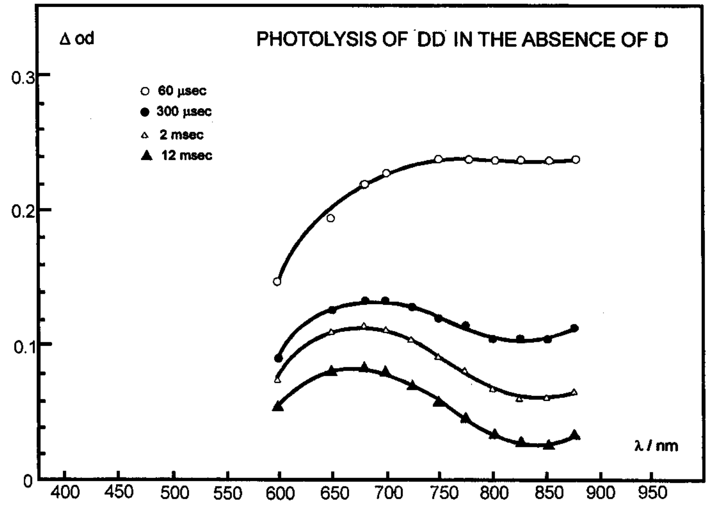

Fig. 17 The difference spectrum of the flash photolysed solution of the dimeric dianions of 1,1-diphenylethylene with no added 1,1-diphenylethylene

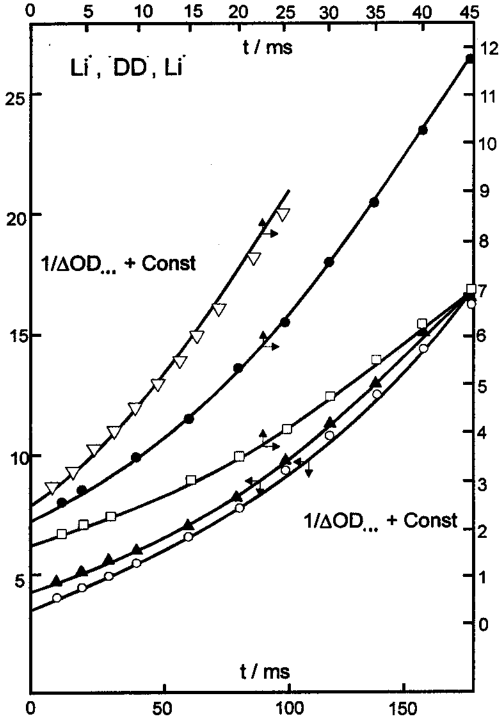

Fig. 18 Plots of the reciprocals of the optical density of a photolysed solution of lithium salt of dimeric dianions of 1,1-diphenylethylene, free of added1,1-diphenylethylene, as function of time

We conclude, therefore, that flash of light *does not* dissociate Cat$^+$, $^-$DD$^-$, Cat$^+$ into 2Cat$^+$, D$^{\bullet-}$, but ejects electrons from the dimers yielding then the respective dimeric radical anions, Cat$^+$, $^-$DD$^\cdot$, and e$^-$, Cat$^+$. The ejected electrons are rapidly captured by D whenever the latter is present at high concentration. Simple second order association of the resulting D$^{\bullet-}$,Cat$^+$ accounts then for the return of the system to its initial state. Therefore, the following mechanism was proposed to account for the return of the system to its initial state at very low concentration of D:

$$\mathrm{Cat^+, {}^-DD^\cdot} \quad \rightarrow \quad \mathrm{Cat^+, D^{\bullet-} + D}, \quad k \sim 10^5\ \mathrm{s^{-1}}$$

$$\mathrm{D + Cat^+, e^-} \quad \underset{k_i}{\overset{k_c}{\Leftrightarrow}} \quad \mathrm{Cat^+, D^{\bullet-}}$$

$$2\,D^{\bullet -},Cat^{+} \quad \xrightarrow{k_d} \quad Cat^{+}, {}^{-}DD^{-}, Cat^{+}$$

Fitting the intensities of the difference spectrum recorded at various times to the curves computed on the basis of the above mechanism (see Fig. 17) led to the values of k_c, k_i, and k_d listed in Table III. It was assumed in the computation that the dissociation of the dimeric radical ions, Cat^+, ${}^{-}DD^{-}$, has been completed at the observed onset of the dark reaction (i.e., 25 μs after a flash).

Table III.

$$D + e^{-}, Cat^{+} \quad \underset{k_i}{\overset{k_c}{\Leftrightarrow}} \quad D^{-}, Cat^{+} \qquad\qquad K_{diss} = k_i/k_c$$

$$2D^{-},Cat^{+} \quad \xrightarrow{k_d} \quad Cat^{+}, {}^{-}DD^{-}, Cat^{+}$$

Cation	k_c.M.s	k_i.s	K_{diss}.M	k_d.M.s
Li^+	$0.9.10^6$	15	6.10^4	$1.2.10^8$
Na^+	$1.9.10^7$	33	6.10^5	$3.5.10^8$
K^+	4.10^9	< 20	$> 2.10^8$	10.10^8
Cs^+	$> 10^{10}$		$>> 10^8$	30.10^8

The reversibility of electron capture was unexpected. However, for acceptors of low electron affinities the reversibility was observed. Namely, Boddeker *et al.*18) reported the reversibility of electron capture for benzene in a mixture of liquid ammonia and methyl amine at -78°C, and Fahataziz and Perkey19) observed it for biphenyl in liquid ammonia at ambient temperature. Significantly, electron affinity of 1,1-diphenylethylene is low (see Ref. 20).

Finally, let me describe another procedure permitting studies of some electron transfer process21). Consider a molecule possessing two identical groups kept close together which may act as a donor and as an acceptor. Its one electron reduction leads to an extra electron that oscillates then between these two groups. The frequency of such transfers may be determined by comparing the shape of ESR spectrum of such a radical anion with those computer drawn for various values of p - the frequency of exchange.

Keeping in mind this stratagem, we synthesized[22)] a chair-shaped cyclohexane having two α-naphthyl-CH_2– moieties attached to it by axial bonds, one below and the other above its center plane. These groups are ~ 9A apart. Reduction by metallic potassium (few % only) yields radical anions with an extra electron in one but none in the other naphthyl group. To avoid the interference of cations with the electron oscillation the investigated ESR spectrum was recorded for radical anions dissolved in HMPA (HMPA, hexamethylphosphorictriamide, is a solvent disassociating ion pairs). From the shape of the resulting ESR spectrum the frequency of electron transfer was found to be ~ 10^7/s at 15°C.

It should be possible to synthesize series of similar molecules having the naphthyl moieties separated by various distances and determine by the above procedure the frequency as function of the distance separating the naphthyl groups. Our to do it was unsuccessful[23)]. We investigated instead the electron transfer between two naphthyl moieties linked by a chain of $n$$CH_2$ groups as a function of n. However, in such systems the frequencies of the electron transfer is determined by the rate of folding and unfolding of the chains, a process distinct from the simple electron transfer[24)].

In conclusion, I wish to convey my thanks to my students and coworkers, mentioned in the references, their devoted and hard work which made these studies possible.

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