UTILIZATION OF ELECTRON-PHOTOEJECTION FOR CHARACTERIZATION OF LABILE SPECIES AND
STUDIES OF KINETICS OF THEIR REACTIONS

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Abstract – Photophysics of electron photo-ejection is briefly reviewed. Direct
photo-ionization, auto-ionization and biphotonic reactions are discussed. The
distinction is made between processes taking place in the gas phase and those
occurring in solution. In the latter case, the formation of solvated electrons
is contrasted with the formation of electron-cation pairs. The various ways
by which electron-photoejections provide information of spectroscopics ,
kinetic and thermodynamic nature are illustrated by examples. Spectra of
labile species were obtained by forming them in situ. This is illustrated
by examples involving 1,2-diphenylcyclohexene radical-anions, cis-stilbene
radical-anions, and radical-anions of 1,1-diphenylethylene·   Kinetics of
electron attachment and of electron-transfer processes are discussed, and it is
shown how the pertinent rate constants may be derived from experiments involving
electron photo-ejection. This method allows also to study the equilibria of
electron transfer involving labile radical anions, e.g. cis-stilbene$^-$,Na$^+$ +
trans-stilbene $\rightleftarrows$ cis-stilbene + trans-stilbene$^-$,Na$^+$ or 1,1-diphenylethylene
radical anions + biphenyl $\rightleftarrows$ 1,1-diphenyl ethylene + biphenyl$^-$. Finally,
dimerization of labile vinylidene radical anions is reviewed and the rate constants
of their dimerization determined. Electron attachment to 1,1-diphenylethylene
showed some interesting features. The rate of attachment is relatively slow and
equilibrium constant of attachment relatively low. Both the rate and equili-
brium of this process are strongly affected by the nature of the counter-ion.
The equilibrium constant of attachment of the electron-lithium cation pair to
1,1-diphenylethylene is lower by several orders of magnitude than that observed
for the electron-cesium cation pair.

Irradiation by visible light often leads to electron photoejection from photon-absorbing radical-anions, dianions, and carbanions. It is my intention to discuss briefly the principles of the electron-photoejection act and to show how this phenomenon could be utilized for characterization and for kinetic and thermodynamic studies of labile species as well as other elementary reactions.

ELECTRON PHOTOEJECTION

Light absorption is the prerequisite of any photochemical reaction. Therefore, the wavelength of actinic light must lie within an absorption band of investigated species. Ejection of an electron, if it results from absorption of light, may be either direct or indirect. The ionization of hydrogen atoms caused by absorption of light in the Rydberg region exemplifies a direct process,

$$H + h\nu \rightarrow H^+ + e^-,$$

whereas electron photoejection from many molecules, radical-anions, or carbanions may result from indirect processes, namely auto-ionization or multi-photon absorption. In auto-ionization, the irradiated species is excited to a quasi-bound state with energy exceeding that needed for an electron detachment. Such a metastable species loses its excitation energy either by radiating, i.e. through fluorescence, or in a radiationless transition, or through electron detachment. Since the latter process competes with the other two events, to be observable it has to be faster than, or at least comparable in rate to, the rate of fluorescence or radiationless transition. The common lifetime of fluorescence is 10^{-9}-10^{-8} sec, and the rate of radiationless transition is typically 10^6-10^8 sec^{-1}. Hence, the rate of observable auto-ionization has to be of the order of 10^{10} sec^{-1}.

Alternatively, light absorption may excite a molecule to a relatively long-lived state, typically a triplet reached through an intersystem crossing from the initially formed singlet, and then electron detachment may take place on absorption of a second photon. While the rate of electron photoejection caused by the direct process or by auto-ionization is proportional to light intensity, the rate of a biphotonic process increases as the square of the light intensity.

In the gas phase the total radiation energy needed for electron detachment must be equal or larger than the ionization energy of the irradiated species. Electron detachment from neutral molecules yields radical-cations,

$$M + h\nu \rightarrow M^{+\cdot} + e^-,$$
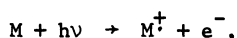
and typical ionization potentials of such species are in the range 6 - 10 V. Hence, visible light does not lead to direct photoionization or auto-ionization of such substrates. The ionization potential of organic radical-anions, equal to the electron-affinity of the parent compounds, is usually in the range 1 - 2 V, and therefore visible light could be effective in the direct or auto-ionization of those species. Since such a process yields neutral molecules from ions,

$$A^{-\cdot} + h\nu \rightarrow A + e^-,$$
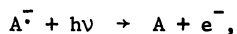
the term "photoionization" is awkward when applied to that event. Therefore, its description as an electron photoejection is preferred. Energy requirements for electron detachment from dianions are probably even lower, although they might be somewhat higher for electron photoejection from carbanions.

Electron detachment from a dissolved species is more complex than for a gaseous process. The transition may raise the bound electron into a conduction band of the solvent or lead to its tunneling into a nearby solvent cavity formed by thermal fluctuation. Usually the conduction bands are too high to be reached by absorption of a photon of visible light, and therefore most of the observed electron photoejections in solution involve transition to solvent cavities. This process yields solvated electrons, although the primary solvent cavity may be poorly organized and the relaxation into a thermodynamically stable cavity would take place later. Such a relaxation has been observed (ref. 1-3). It is manifested by a gradual change in the absorption spectrum of the solvated electron that shifts toward shorter wavelengths within a few picoseconds after the initial photochemical act.

The presence of cations causes further modification of the observed phenomena. Any solution of radical-anions, dianions, or carbanions must contain an equivalent amount of cations to secure its electrical neutrality. Depending on the nature of solutes and solvents the anions and cations could be free, moving independently of each other, or associated into various kinds of ion-pairs or still higher aggregates. The light absorption may produce therefore solvated electron-cation pairs either directly by transition of an electron from the irradiated anion to the adjacent cation, or indirectly by first forming a free solvated electron that subsequently combines with a cation. Electron-cation pairs are distinct from solvated electrons. Their absorption spectrum is shifted toward shorter wavelengths with respect to that of the solvated electrons, and under proper conditions electron coupling to the cation's nucleus may be revealed by the ESR spectrum.

In most of the systems investigated in my laboratory the ejected electrons eventually return to the parent molecules or ions from which they were ejected. Thus, long after the irradiation, the absorption spectrum of the investigated solution is identical with that recorded before the irradiation. However, such a return need not be direct. Interesting processes can take place during the intervening period and these will be discussed now.

ELECTRON ATTACHMENT PROCESS

Flash-photolysis with visible light of radical-anion solutions leads to the initial bleaching of their absorption. Examples are provided by flash-photolysis of sodium pyrenide (ref. 4), π^{-},Na^{+}, in tetrahydrofuran (THF) or tetrahydropyran (THP), of alkali tetracenides (ref. 5), Te^{-},Cat^{+} in a variety of ethereal solvents, and sodium perylenide (ref. 6), Pe^{-},Na^{+} in THF. In each case electron photoejection is responsible for the initial decrease in the concentration of radical-anions. At very high dilution ($< 10^{-6}$ M), the ejected electrons may be formed as the free solvated species or as the electron-cation pairs, provided that the concentration of any molecules capable of capturing them is sufficiently low. In the dark period following a flash, the electron attachment process can be observed. It is manifested by the increase of the absorbance of the bleached radical-anions or by the decrease of the absorbance of the electron-cation pairs. Indeed, both methods were employed in studies of flash-photolysis of π^{-},Na^{+}. The results (ref. 4) seem to indicate that the attachment process in THF, namely

$$\pi + e^{-} \rightarrow \pi^{-},$$
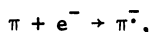
proceeds with bimolecular rate constant $\sim 7 \times 10^{10}$ M^{-1} sec^{-1}, whereas the reaction

$$\pi + e^{-},Na^{+} \rightarrow \pi^{-},Na^{+}$$
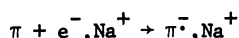
is about 5 times slower. These electron attachment processes were studied more extensively by pulse radiolysis, notably by Dorfman and his associates (ref. 7). For example, the rate constants of attachment of electrons solvated by alcohol varies from .4 to 1.0 x 10^{10} M^{-1} sec^{-1}. It seems that the electron attachment is only slightly affected by the nature of the capturing species, while the slower attachment of e^{-},Cat^{+} is more affected by the nature of cation than by the nature of the acceptor.

The quantum yield of electron detachment for the same donor depends on the nature of the solvent. Thus, while flash-photolysis of π^{-},Na^{+} in THF resulted in 70-80% of bleaching, only 5% of bleaching was observed in THP under the same conditions (ref. 4). Typical flash photolysis of the sodium salt of tetraphenylethylene dianion (ref. 8) results in about 20% of bleaching in THF. However, in dioxan bleaching was not observed, i.e. electron photodetachment did not take place, although the flash intensity was even higher than in the experiments performed in THF. The anion-cation aggregates are tighter in THP or dioxan than in THF. Apparently their tightness affects the electron detachment by increasing the strength of the electric field attracting the electron. It is tempting to suggest that the electron is transferred to the cation and the system relaxes to its initial state within a few picoseconds, because the e^{-},Cat^{+} pair and the formed acceptor remain in the vicinity of each other. Thus we deal here with a kind of cage reaction and its further study should be most interesting.

Somewhat similar behavior was noted in the flash photolysis of tetracene radical-anions (ref. 5). Bleaching was observed in the photolysis of Te^{-},Li^{+}, Te^{-},Na^{+}, Te^{-},K^{+} and Te^{-},Cs^{+} in THF, whereas in diethyl ether the flash led to bleaching of the Li^{+} and Na^{+} salts but not of the K^{+} and Cs^{+} salts.

OPTICAL SPECTRA OF LABILE SPECIES

Although many radical-anions are stable and their optical or ESR spectra could be easily recorded, some are intrinsically labile. For example, radical-anions of 1,2-diphenyl-cyclohexene-1, Hex, cannot be observed directly because the reduction of the parent hydrocarbon, that presumably should yield them, is followed by a rapid and nearly quantitative disproportionation yielding the respective dianions. The equilibrium constant of this

disproportionation is very high (ref. 9), greater than 10^3, and hence hardly any radical anions are formed on addition of the unreduced hydrocarbon to its dianion. The reason for such a high disproportionation constant is not clear. Interestingly, disproportionation constants of 1,2-diphenylcyclopentene and 1,2-diphenylcyclobutene are smaller, namely $\sim$ 100 and $\sim$ 1, respectively (ref. 10). In spite of the high degree of disproportionation, the spectrum of 1,2-diphenylcyclohexene radical anions could be recorded. Flash-photolysis of $Hex^{2-},2Na^+$ in the presence of an excess of the parent hydrocarbon leads to ejection of electrons,

$$Hex^{2-},2Na^+ + h\nu \rightarrow Hex^{\cdot -},Na^+ + e^{\cdot -},Na^+,$$
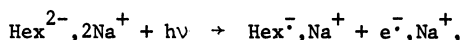
followed by their attachment to Hex,

$$Hex + e^{-},Na^+ \rightarrow Hex^{\cdot -},Na^+.$$
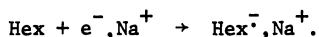
Thus, the destruction of one $Hex^{2-},2Na^+$ yields two $Hex^{\cdot -},Na^+$. The difference spectrum recorded in the dark period following a flash results from bleaching of the absorbance of $Hex^{2-},2Na^+$ and from absorbance of $Hex^{\cdot},Na^+$ formed in the above process. Assuming negligible absorbance of $Hex^{\cdot},Na^+$ at λ_{max} of $Hex^{2-},2Na^+$, the spectrum of the former and its molar absorbance could be computed from the observed difference spectrum. The results are shown in Fig. 1.
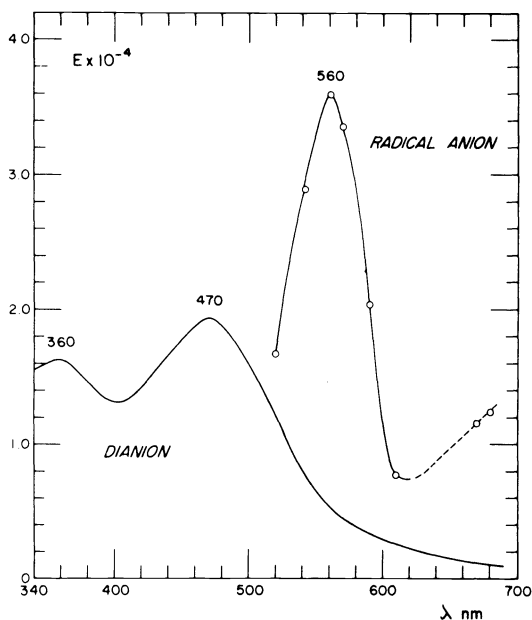

Fig. 1. Spectrum of $CH^{2-},2Na^+$ in THF recorded by a Cary-14 spectrophotometer (solid line). Spectrum of $CH^{\cdot -},Na^+$ recorded in a flash-photolysis spectrophotometer 40 μs after the flash.

The problem of cis-stilbene radical-anion, $C^{\cdot -},Na^+$, provides another example of utilization of electron photoejection as a means for determining spectra of labile species. In THF these radical anions extremely rapidly isomerize into trans-stilbene radical-anions, $T^{\cdot -},Na^+$. The mechanism of their isomerization is discussed elsewhere (ref. 11), but whatever its nature we face again the same difficulty in an attempt to record their spectrum. To reach this goal, we flash-photolyzed a solution of sodium perylenide, $Pe^{\cdot -},Na^+$, mixed with a large excess of cis-stilbene, C. Electrons ejected from $Pe^{\cdot -},Na^+$ were captured by C and thus in a short period following the flash (100-300 μsec) we observed the difference spectrum resulting from the partial destruction of $Pe^{\cdot -},Na^+$, and the formation of Pe and $C^{\cdot -},Na^+$. The change in optical density, $\Delta(od)$, at λ_{max} of Pe (437 nm) and $Pe^{\cdot -},Na^+$ (580 nm) confirmed the expected 1:1 stoichiometry $Pe:Pe^{\cdot -},Na^+$ (see Fig. 2). Hence, the unaccounted absorbance at $\sim$ 500 nm was ascribed to $C^{\cdot -},Na^+$. The difference spectrum decays in time without changing its shape, this being the result of the electron transfer, $C^{\cdot -},Na^+ + Pe \rightarrow C + Pe^{\cdot -},Na^+$ that restores the original state of the system. From such results the spectrum and molar absorbance of $C^{\cdot -},Na^+$ were deduced. To ascertain the reliability of this technique, the absorption spectrum of the trans-stilbenide was obtained by the same approach and it compared satisfactorily with the directly determined one. Both spectra, of $C^{\cdot -},Na^+$ and $T^{\cdot -},Na^+$, deduced from experiments based on electron photoejection are shown in Fig. 3.

Radical-anions derived from vinyl or vinylidene hydrocarbons are intrinsically unstable because they rapidly recombine into the respective dimeric dianions, e.g.,
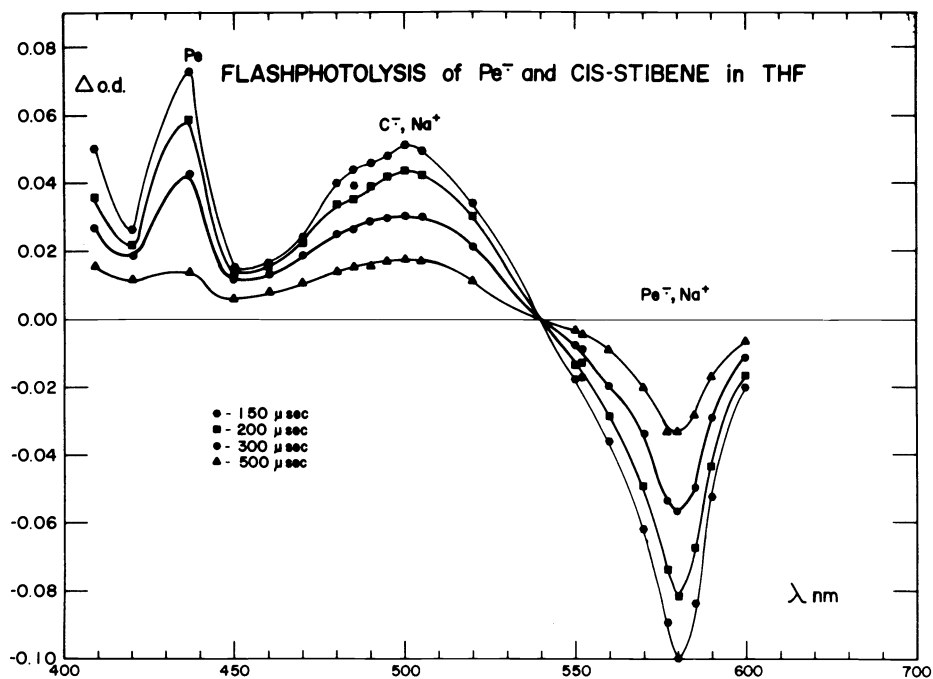
Figure 2. Difference spectrum of flash-photolyzed solution of Pe⁻·,Na⁺ and C in THF, 100 μs after flash. The bleaching at 580 nm arises from the temporary destruction of Pe⁻·,Na⁺, the absorbance at 437 nm manifests the formation of Pe, and the absorbance at 500 nm is attributed to C⁻·,Na⁺.
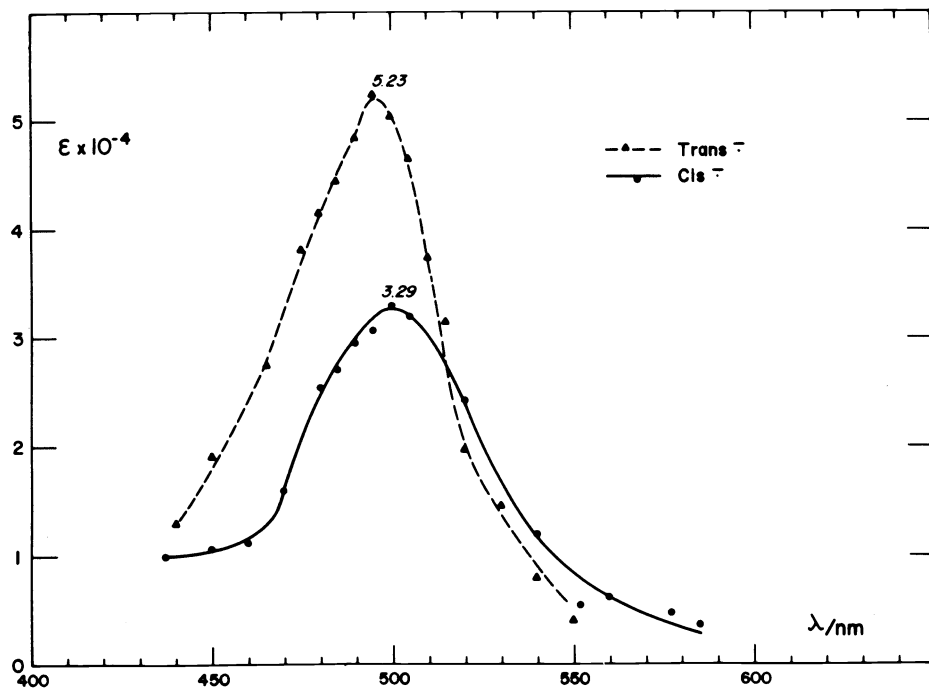
Figure 3 The absorption spectra of C⁻·,Na⁺ and T⁻·,Na⁺ in THF.

$$2CH_2 = C(Ph)_2^{\bar{\cdot}} \;\rightarrow\; \bar{C}(Ph)_2CH_2CH_2\bar{C}(Ph)_2.$$
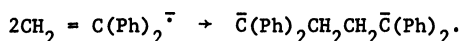
Again, flash-photolysis techniques allowed us to record their spectrum. The irradiation of the stable solution of the dimeric dianions eventually yields the monomeric radical-anions. The mechanism of this reaction will be discussed later; hence, whatever it's course, we have the opportunity to record the difference spectrum resulting from bleaching of the absorbance of the original dimer and the absorption of the monomeric radical-anions formed by photolysis. This approach was successful in studies of spectra of radical-anions derived from 1,1-diphenylethylene (ref. 12) and α-methylstyrene (ref. 13).

RATES OF ELECTRON-TRANSFER REACTIONS

Electron photoejection is useful in studies of electron-transfer reactions. The following example illustrates the approach. In a solution of sodium pyrenide, $\pi^{\bar{\cdot}},Na^+$ and biphenyl, B, the equilibrium,

$$\pi^{\bar{\cdot}},Na^+ + B \;\rightleftharpoons\; \pi + B^{\bar{\cdot}},Na^+,$$
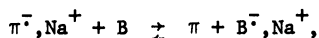
lies so far to the left that no $B^{\bar{\cdot}},Na^+$ could be detected even when the concentration of B was 100 times, or more, greater than that of $\pi^{\bar{\cdot}},Na^+$. This is the consequence of the much higher electron affinity of pyrene than of biphenyl. A flash of visible light ejects electrons from $\pi^{\bar{\cdot}},Na^+$, and then biphenyl, being in large excess, has the chance to capture them and to be reduced to $B^{\bar{\cdot}},Na^+$. Hence, immediately after a flash, the concentration of $\pi^{\bar{\cdot}},Na^+$ is diminished and an equivalent amount of $B^{\bar{\cdot}},Na^+$ is formed. The equilibrium between $\pi^{\bar{\cdot}},Na^+$, B, π, and $B^{\bar{\cdot}},Na^+$ is upset and, in the dark period following a flash, the relaxation to the equilibrium state is observed, i.e.

$$B^{\bar{\cdot}},Na^+ + \pi \;\rightarrow\; B + \pi^{\bar{\cdot}},Na^+.$$
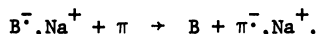
The progress of this electron-transfer reaction is reflected by the decay of the transient absorbance of $B^{\bar{\cdot}},Na^+$ (λ_{max} = 400 nm) and the reappearance of the absorbance of $\pi^{\bar{\cdot}},Na^+$ (λ_{max} = 493 nm). This may be seen by inspecting Fig. 4. The results allowed us to
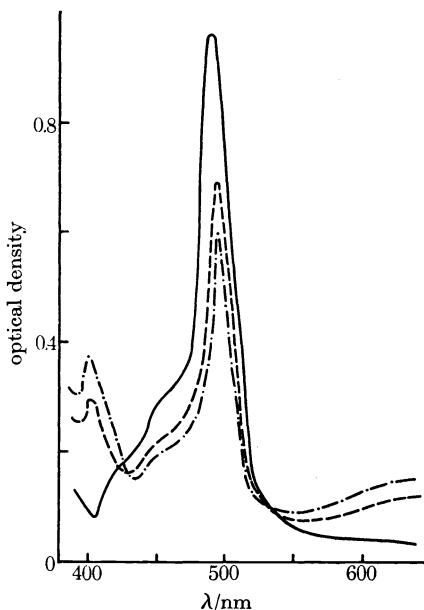

FIGURE 4. Visible spectrum of the solution of $\pi^{\bar{\cdot}}$ + B before flash photolysis and at $t > 1000$ μs after the flash (the solid line). The appearance of the transient at 400 nm and the bleaching of the absorbance at 493 nm at 50 μs(−·−·−·−) and 100 μs(− − −), respectively, after the flash. Solvent, THF.
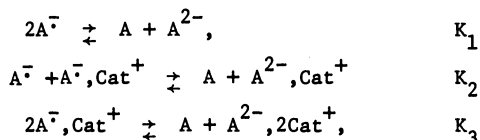
calculate the bimolecular rate constant of the above electron-transfer process (ref. 4) ($\underline{k}$ = 4 x 10^{10} M^{-1} sec^{-1} for the free ions, and about 10 times less for the Na^+ ion-pairs). More extensive studies of these reactions were reported by Dorfman and his colleagues (ref. 14) who utilized pulse-radiolysis in their work.

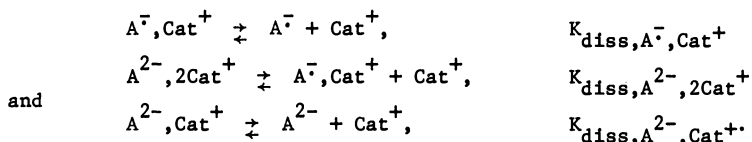### RATES OF DISPROPORTIONATION AND APROPORTIONATION OF RADICAL-ANIONS

In solution radical-anions have to be in equilibrium with dianions and the parent molecules, i.e.,

$$2A^{-},Cat^{+} \rightleftarrows A + A^{2-},2Cat^{+}.$$
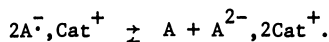
The disproportionation equilibrium constant depends not only on the nature of the substrate, A, but it is affected, often to a very large extent, by the nature of cation and of the solvent. In fact, three distinct equilibria c a n be distinguished, namely,

$$2A^{-} \rightleftarrows A + A^{2-}, \qquad\qquad K_1$$

$$A^{-} + A^{-},Cat^{+} \rightleftarrows A + A^{2-},Cat^{+} \qquad K_2$$

$$2A^{-},Cat^{+} \rightleftarrows A + A^{2-},2Cat^{+}, \qquad K_3$$

The individual constants can be determined experimentally by studying the effect of dilution on the overall equilibrium, and determining by independent methods, e.g. by conductance, the dissociation constants

$$A^{-},Cat^{+} \rightleftarrows A^{-} + Cat^{+}, \qquad\qquad K_{diss,A^{-},Cat^{+}}$$

$$A^{2-},2Cat^{+} \rightleftarrows A^{-},Cat^{+} + Cat^{+}, \qquad K_{diss,A^{2-},2Cat^{+}}$$

and

$$A^{2-},Cat^{+} \rightleftarrows A^{2-} + Cat^{+}, \qquad\qquad K_{diss,A^{2-},Cat^{+}}.$$

It is easy to prove that

$$K_3/K_2 = K_{diss,A^{-},Cat^{+}}/K_{diss,A^{2-},2Cat^{+}}$$

and

$$K_2/K_1 = K_{diss,A^{2-},2Cat^{+}}/K_{diss,A^{2-},Cat^{+}}.$$

Examples of such studies were reported by Roberts and Szwarc (ref. 15) and by Lundgren, Levin, Claesson, and Szwarc (ref. 16). For the sake of illustration, their results are collected in Table L

TABLE 1. The disproportionation equilibria for the tetraphenylethylene system, TP, in tetrahydrofuran at 20°C

$2TP^{-} \rightleftarrows TP + TP^{2-}$;	K_1
$TP^{-} + TP^{-},Cat^{+} \rightleftarrows TP + TP^{2-},Cat^{+}$;	K_2
$2TP^{-},Cat^{+} \rightleftarrows TP + TP^{2-},2Cat^{+}$;	K_3

Cations	K_1*	K_2	K_3
Li^+	$\sim 10^{-12}$	0.7	8.7
Na^+	$\sim 10^{-12}$	3.3	400

* Estimated value; $K_1 \sim 10^{-4}$ in hexamethylphosphorictriamide.

Cation	ΔH_2	ΔS_2	ΔH_3	ΔS_3
Li^+	6.7	2.2	6.6	27
Na^+	13.0	45	19	75

ΔH in kcal/mole; ΔS in cal /degree.

The kinetics of disproportionation can be studied by flash-photolysis. Let us consider, for example, an equilibrated solution of A, A^{-},Cat^{+}, and A^{2-},Cat^{+} where A^{-},Cat^{+} is in a large excess over A and $A^{2-},2Cat^{+}$, i.e. the disproportionation equilibrium constant is very low. A flash of visible light ejects electrons mostly from A^{-},Cat^{+} and some of the ejected electrons are captured then by the unphotolyzed A^{-},Cat^{+}. Thus, for $2A^{-},Cat^{+}$'s lost, one by photo-oxidation,

$$A^{-},Cat^{+} \xrightarrow{h\nu} A + e^{-},Cat^{+},$$
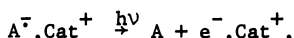
the other by reduction,

$$A^{-},Cat^{+} + e^{-},Cat^{+} \rightarrow A^{2-},2Cat^{+},$$
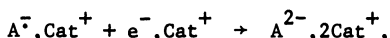
one A and one $A^{2-},2Cat^{+}$ are formed. The equilibrium,

$$2A^{-},Cat^{+} \; \underset{k_b}{\overset{k_f}{\rightleftarrows}} \; A + A^{2-},2Cat^{+}$$
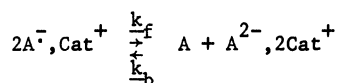
is upset and the system relaxes back to the state of equilibrium in the dark period following a flash. The kinetics of this relaxation, augmented by the knowledge of the respective equilibrium constant, $K = k_f/k_b$, allows one to calculate k_f and k_b. Figure 5 illustrates the difference spectrum of a flash-photolyzed solution of sodium perylenide in tetrahydro-
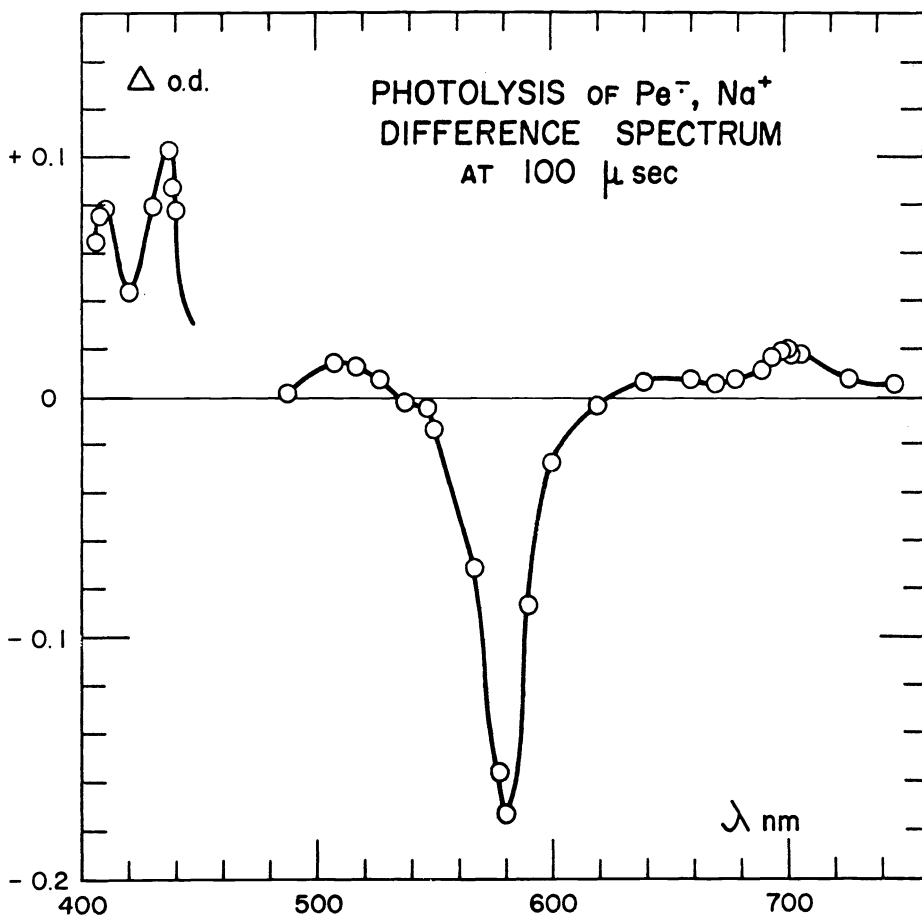

Fig. 5. The difference spectrum recorded at 100 μs after flashing a solution of Pe^{-},Na^{+} in THF.

furan. The degree of bleaching of the absorbance of the perylenide (λ_{max} = 580 nm) decreases with time simultaneously with the decay of the transient absorbances due to the formation of perylene, Pe, (λ_{max} = 408 nm and 437 nm) and its dianions, $Pe^{2-},2Na^{+}$.

In a system with A^{-},Cat^{+} and $A^{2-},2Cat^{+}$ in large excess of A, this again being possible when the disproportionation equilibrium constant is low, the flash of light would decrease the concentration of A^{-},Cat^{+} by forming A and $A^{2-},2Cat^{+}$. The photo-oxidation of $A^{2-},2Cat^{+}$ does not lead to a change of the system because, due to the exceedingly low concentration of A, the ejected electron would be captured by A^{-},Cat^{+} and regenerate $A^{2-},2Cat^{+}$. On the other hand, when the disproportionation equilibrium is high, the solution composed of A and $A^{2-},2Cat^{+}$ has a very low proportion of A^{-},Cat^{+}. In such a system the electrons are ejected mainly from $A^{2-},2Cat^{+}$, oxidizing it to A^{-},Cat^{+}, and become captured by A, reducing it to A^{-},Cat^{+}. After a flash the concentration of A^{-},Cat^{+} increases and that of A and $A^{2-},2Cat^{+}$ decreases. In each case the equilibrium is upset and the kinetics of the relaxation to the state of equilibrium provides the data needed for calculation of the forward and backward rate constants.

This approach was utilized in studies of the kinetics of disproportionation of lithium,

sodium, potassium, and cesium salts of tetracenides in a variety of solvents (ref. 5). The pertinent results are collected in Table 1. The equilibrium constant of disproportionation

TABLE 2. The effect of solvents and cations on the equilibrium and rates of tetracenide disproportionation at ambient temperature

$$2Te^{-},Cat^{+} \; \overset{k_f}{\underset{k_b}{\rightleftarrows}} \; Te + Te^{2-},2Cat^{+} \qquad K = k_f/k_b$$

| Solvent	Cation	K	k_f M sec.	k_b M sec
DME	Li^+	2.5×10^{-10}	–	–
DME	Na^+	2.2×10^{-9}	–	–
DME	K^+	9.4×10^{-8}	–	–
DME	Cs^+	6.7×10^{-7}	–	–
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	7.8×10^8
DOX	Li^+	6.6×10^{-2}	8.0×10^6	1.1×10^8
DOX	Na^+	6.5×10^{-2}	2.0×10^7	3.1×10^8
DOX	K^+	1.1×10^{-2}	–	–
DOX	Cs^+	6.5×10^{-3}	–	–
DEE	Li^+	1.6×10	5.9×10^7	3.6×10^6
DEE	Na^+	1.2×10^{-1}	2.4×10^8	2.0×10^9

can be determined by several methods. When it is low, the polarographic or potentiometric methods are most useful. The difference between the first and second redox potential yields $(RT/F)\ell nK_{disproportionation}$. For $K_{disproportionation}$ between $10^{-2} - 100$, the spectrophotometric technique is utilized for its determination, whereas ESR spectroscopy is applicable for systems with $K_{disproportionation}$ very high, up to 10^6.

I cannot discuss here the reasons for the large variation in the disproportionation constant for a fixed A when cation and solvents are varied. Discussion of this problem is given elsewhere (refs. 17 and 18), and it suffices to say that the cation-anion Coulombic interaction, and the nature of ion-pairs and $A^{2-},2Cat^+$ aggregates are the basic causes of these variations that result in variation of the constant often by a factor as large as 10^{20}.
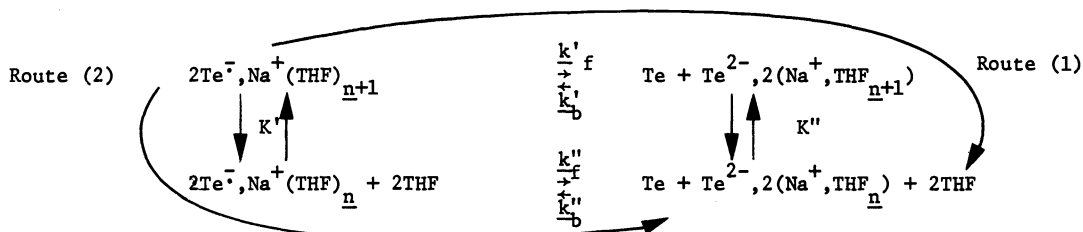
The possible complexity of disproportionation is illustrated by two systems. The apparent disproportionation constant of sodium tetracenide, Te^{-},Na^+, in benzene containing a small amount of tetrahydrofuran, THF, depends on the concentration of that ether (ref. 19), namely

$$\log K_{apparent\ dispr} = -2 \log[THF] + const.$$

This implies that the degree of solvation by THF is different for Te^{-},Na^+ and $Te^{2-},2Na^+$, the equilibrium referring to this reaction acquires therefore the following form,

$$2Te^{-},Na^+(THF)_{n+1} \; \rightleftarrows \; Te + Te^{2-},2(Na^+,THF_n) + 2THF,$$
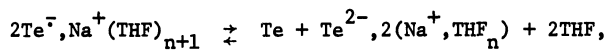
with n most probably equal to 1. Two routes are available for the disproportionation,

Route (2) $2Te^-,Na^+(THF)_{\underline{n}+1}$ $\overset{k'_f}{\underset{k'_b}{\rightleftarrows}}$ $Te + Te^{2-},2(Na^+,THF_{\underline{n}+1})$ Route (1)

$\downarrow\uparrow K'$ $\downarrow\uparrow K''$

$2Te^-,Na^+(THF)_{\underline{n}} + 2THF$ $\overset{k''_f}{\underset{k''_b}{\rightleftarrows}}$ $Te + Te^{2-},2(Na^+,THF_{\underline{n}}) + 2THF$

In view of the relatively large concentration of THF, ranging from 0.1 to 1.0 M, the relaxation time of the solvation-desolvation equilibria has to be exceedingly short, and therefore these equilibria are maintained all the time. The observed rate of disproportionation is governed by k'_f and k'_b for a reaction proceeding through route (1), or by k''_f and k''_b if it follows route (2). Hence, the observed rate constant of the forward process is given by $k_f = k'_f$ when route (1) represents its course, whereas $k_b = (k'_b/K'')(THF)^2$, i.e., the observed backward rate constant <u>increases</u> with increasing THF concentration while the observed forward constant remains independent of THF concentration. For a reaction following route (2) the observed forward rate constant <u>decreased</u> on increasing the THF concentration, i.e. $k_f = (k''_f K')/(THF)^2$, whereas the observed backward rate constant is unaffected by THF concentration. Hence, experiments allow us to discriminate between these two routes and demonstrate that the reaction follows route (2), the rate of return to equilibrium was retarded by an increase of THF concentration.

Another complex feature of the disproportionation process is illustrated by the behavior of barium tetracenide in THF. The barium salt of tetracene dianion, Ba^{2+},Te^{2-} is hardly soluble in THF, and its concentration could not exceed 10^{-6} M. Moreover, the pertinent disproportionation constant is high, so that the concentration of radical anions is lower than 10^{-7} M even in the presence of an excess of Te. Not surprisingly, nearly all the barium tetracenide is dissociated, and the disproportionation equilibrium is therefore represented by the scheme

$$Te^- + Ba^{2+},Te^- \rightleftarrows Te + Ba^{2+},Te^{2-},$$
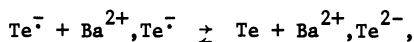
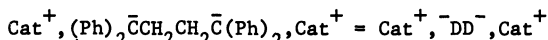according to which the degree of disproportionation is unaffected by dilution (ref. 20).

A flash of light perturbs the equilibrium, the concentration of radical anions increases, whereas those of Te and Ba^{2+},Te^{2-} decrease. Two routes are again available for its relaxation.
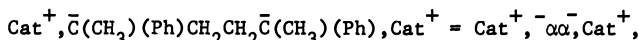
$$Te^- + Ba^{2+},Te^- \rightarrow Ba^{2+},Te^{2-} + Te$$
$$\searrow Te^-,Ba^{2+},Te^- \nearrow$$
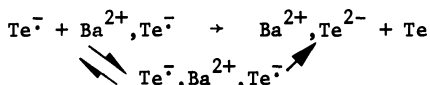
One alternative represents a direct, bimolecular electron transfer from Te^- to Ba^{2+},Te^-, a reaction naively anticipated if in the encounter Te^- approaches Ba^{2+},Te^- from the side of Te^- associated with Ba^{2+}. The other alternative leads to the transient neutral species Te^-,Ba^{2+},Te^- followed by <u>intramolecular</u> electron transfer. Kinetic studies showed that both processes contribute to the overall reaction (ref. 20).
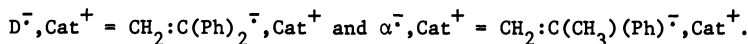
### RATE OF DIMERIZATION OF VINYLIDENE RADICAL-ANIONS

The stable dimeric dianions,

$$Cat^+,(Ph)_2\bar{C}CH_2CH_2\bar{C}(Ph)_2,Cat^+ = Cat^+,^-DD^-,Cat^+$$

and

$$Cat^+,\bar{C}(CH_3)(Ph)CH_2CH_2\bar{C}(CH_3)(Ph),Cat^+ = Cat^+,^-\alpha\alpha^-,Cat^+,$$

are dissociated by a flash of light into the respective radical anions,

$$D^-,Cat^+ = CH_2{:}C(Ph)_2^-,Cat^+ \text{ and } \alpha^-,Cat^+ = CH_2{:}C(CH_3)(Ph)^-,Cat^+.$$

The dissociation does not result from a direct photolytic act (refs. 12,21), but it is a consequence of electron photoejection followed by the dissociation of the resulting dimeric radical-anion, e.g.

$$Cat^+,^-DD^-,Cat^+ \overset{h\nu}{\rightarrow} Cat^+,^-DD\cdot + e^-,Cat^+$$
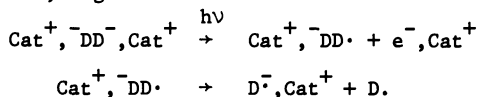
$$Cat^+,^-DD\cdot \rightarrow D^-,Cat^+ + D.$$

In an experiment performed in the presence of excess of D (note that D does not add to $^-DD^-$; no trimer $^-DDD^-$ is formed), the ejected electrons are captured,

$$D + e^-, Cat^+ \rightarrow D^{\cdot-}, Cat^+$$
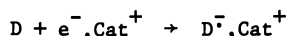
and thus $2D^{\cdot-}, Cat^+$ are formed from $Cat^+, {}^-DD^-, Cat^+$.

In the dark period the radical-anions reform the $Cat^+, {}^-DD^-, Cat^+$, i.e.
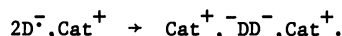
$$2D^{\cdot-}, Cat^+ \rightarrow Cat^+, {}^-DD^-, Cat^+.$$

Their dimerization is monitored either by the increased absorbance at 470 nm (λ_{max} of $Cat^+, {}^-DD^-, Cat^+$) or by the decrease of the transient absorbance at 390 nm (λ_{max} of $C^{\cdot-}, Cat^+$). In either case, as expected, $1/\Delta(od)$ increases linearly with time (refs. 12,21). Since the effective molar absorbances are known, the bimolecular rate constant of dimerization could be determined. The results are summarized in Table 3. they refer to the reaction proceeding in THF at ambient temperature. The large effect of cation on the rate is noteworthy. A similar study led to determination of the dimerization constant of the radical-anions of α-methylstyrene (ref. 13).

TABLE 3. Rate constant of dimerization of radical-anions derived from 1,1-diphenylethylene, D, and α-methylstyrene, α, in THF at $\sim$ 20°C

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

Cation	Li^+	Na^+	K^+	Cs^+
$10^{-8} \times \underline{k}_d$ M sec	1.2	3.5	10.	30.

$$2\alpha^{\cdot-}, Cat^+ \xrightarrow{k_d} Cat^+, {}^-\alpha\alpha^-, Cat^+$$

Cation	Na^+	K^+
$10^{-6} \times \underline{k}_d$ M sec	2	12

REDOX POTENTIAL OF ACCEPTORS FORMING LABILE RADICAL ANIONS

Conventional polarographic or potentiometric reduction of an acceptor yielding labile radical anions may be unreliable if the reaction of the formed radical anions upsets the electro-chemical equilibrium. Our technique provides ways to obtain such results, as illustrated by the following examples.

Cis-stilbene radical anions in THF are rapidly converted into dianions (ref. 11a) and eventually into trans-radical anions. Nevertheless, a simple technique, described in the previous section of this paper, allows us to record their optical spectrum and molar absorbance (ref. 11b). Flash photolysis of sodium perylenide ($Pe^{\cdot-}, Na^+$) at about 10^{-6} M concentration performed in the presence of an excess of cis-stilbene leads to oxidation of the former and reduction of the latter. At 100 μsec after a flash, we observe bleaching of the absorption of $Pe^{\cdot-}, Na^+$ (at λ = 580 nm), revealing the concentration of the ejected electrons that were captured by cis-stilbene, and an equivalent absorbance of cis-stilbene radical-anions at 500 nm. The same experiment performed with a mixture of cis and trans-stilbene, say in 1:1 proportion, with both hydrocarbons in excess, yields a mixture of cis- and trans-stilbenides. Since the concentration of hydrocarbons is high (say 10^{-3} M) the equilibrium, $K_{c,tr}$,

Cis-stilbene + trans-stilbene$^{\cdot-}, Na^+ \rightleftharpoons$ cis-stilbene$^{\cdot-}, Na^+$ + trans-stilbene,
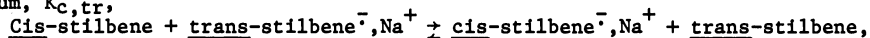
would be established in about 1 μsec and maintained during the experiment. The absorbance at 500 nm recorded 100 μsec after a flash results from the presence of both radical anions, and since their molar absorbances are known from previous work, and their total concentration from the extent of $Pe^{\cdot-}, Na^+$ bleaching, their proportion can be determined (ref. 11b). The redox potential of cis-stilbene is deduced from the value of $K_{c,tr}$ because the redox potential of trans-stilbene is known, being derived by the conventional electrochemical technique.

The radical anions of 1 1-diphenylethylene, D, rapidly dimerize and therefore the conventional electrochemical technique cannot be applied to determine the redox potential of that hydrocarbon. In the preceding section I showed how the absolute rate constant of the dimerization

$$2D^{\cdot-}, Cat^+ \rightarrow Cat^+, {}^-DD^-, Cat^+$$

was determined. A flash of light shined on a solution of $Cat^+, {}^-DD^-, Cat^+$ containing excess of D yields $D^{\cdot-}, Cat^+$ and their dimerization is followed, e.g., by the increase of the

absorbance of the partially bleached $Cat^+, ^-DD^-, Cat^+$. Such an experiment may be performed in the presence of an excess of D and, say, triphenylene, Tr, the latter having a higher electron affinity than D. Due to their relatively high concentration, say 10^{-4}-10^{-3} M (the concentration of the dimeric dianions is only about 10^{-6} M) the equilibrium

$$D^-, Cat^+ + Tr \; \overset{\rightarrow}{\leftarrow} \; D + Tr^-, Cat^+, \qquad K_{Tr,D},$$
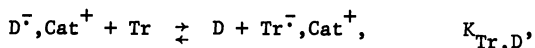
is established and maintained during that experiment. The dimerization of D^-, Cat^+ radical-anions is slower than that observed in the absence of Tr, because their concentration is lower, being given by

$$D^-, Cat^+ = 2\Delta[Cat^+, ^-DD^-, Cat^+]_{bleached} / \{ 1 + K_{Tr,D}[Tr]/[D] \}.$$

Hence, the slope of $1/\Delta(od, 470 \text{ nm})$, i.e. at λ_{max} of the dimeric dianions, is given by the absolute rate constant of D^-, Cat^+ dimerization, known from the previous experiments, divided by $\{ 1 + K_{Tr,D}[Tr]/[D] \}^2$. The ratio of the slopes of the reciprocal plots of $1/\Delta(od \; 470)$, determined in the absence and presence of Tr, gives $\{ 1 + K_{Tr,D}[D]/[Tr] \}^2$ from which K_{Tr} is calculated (ref. 12). The redox potential of Tr is determined by electrochemical techniques, and having $K_{Tr,D}$ we calculated the redox potential of D.

A similar approach was used in determining the redox potential of α-methylstyrene, α, the radical anions of which also rapidly dimerize. They may be formed by flash photolyzing the respective dimeric dianions, $Cat^+, ^-\alpha\alpha^-, Cat^+$ and the determination of the absolute rate constant of their dimerization was described previously (ref. 13). In the presence of excess of biphenyl, and in the absence of α, the equilibrium

$$\alpha^-, Cat^+ + B \; \overset{\rightarrow}{\leftarrow} \; \alpha + B^-, Cat^+, \qquad 1/K_{\alpha,B}$$
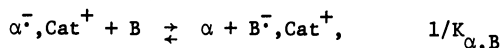
maintains only a minute concentration of α^-, Cat^+, i.e. at any time after a flash $[\alpha] = [B^-, Cat^+]$ and $[\alpha^-, Cat^+] = K_{\alpha,B}[B^-, Cat^+]^2/[B]$. Under these conditions the recombination, monitored by the absorbance of B^-, Cat^+, $\lambda_{max} = 400$ nm, appears to be a fourth-order reaction (ref. 13),

$$-d[B^-, Cat^+]/dt = k_\alpha K_{\alpha,B}^2 [B^-, Cat^+]^4/[B]^2,$$

with [B] being virtually constant. A plot of $\{ 1/\Delta(od \; 400) \}^3$ versus time is shown in Fig. 6.
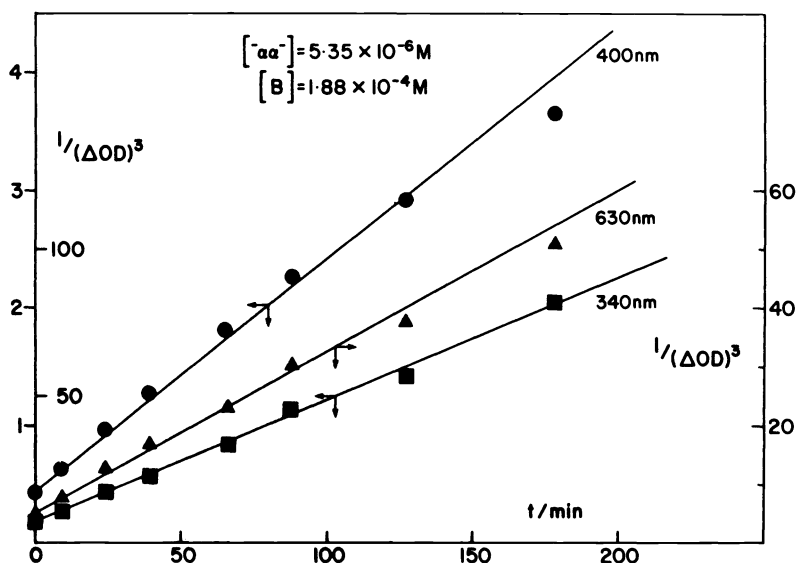

Fig. 6. Plot of $1/(\Delta od)^3$ for the return of the flash photolyzed $K^+, ^-\alpha\alpha^-, K^+$ performed in the presence of biphenyl (B) to its initial state. Monitored at 340, 400, and 640 nm, respectively.

From its slope we calculate $\underline{k}_d K^2_{\alpha,B}$, and having the value of $\underline{k}_d$ we find $K_{\alpha,B}$. The redox potential of biphenyl is determined by electrochemical techniques and then the redox potential of α is calculated from the value of $K_{\alpha,B}$.

PHOTO-DISSOCIATION OR ELECTRON PHOTO-EJECTION

Formation of two 1,1-diphenylethylene radical anions, D^-,Cat^+, by flash-photolysis of their dimer, $Cat^+,^-DD^-,Cat^+$, was discussed in earlier sections. How do we prove that the process involves electron photo-detachment and not photo-dissociation? In the latter process two D^-,Cat^+'s are formed and they recombine in the dark period. The difference spectrum is due to bleaching the absorbance of the dimer (λ_{max} = 470 nm) and the transient absorbance of D^-,Cat^+ (λ_{max} = 390 nm) should have a time-invariant shape, its intensity decaying according to the reciprocal law, i.e. $1/\Delta(od)$ at any wavelength should be linear with time. This kind of behavior should be observed whether some unreduced 1,1-diphenylethylene, D, is present in excess or is absent. However, this is not the case (refs. 12,21). The above characteristic of the dark reaction was observed in the presence of ten fold, or still greater excess of D; however, when the excess of D was low the return to the initial state became very slow, the plot of $1/\Delta(od)$ versus time became curved (see, e.g., Fig. 7), and the shape of the difference spectrum varied with time.
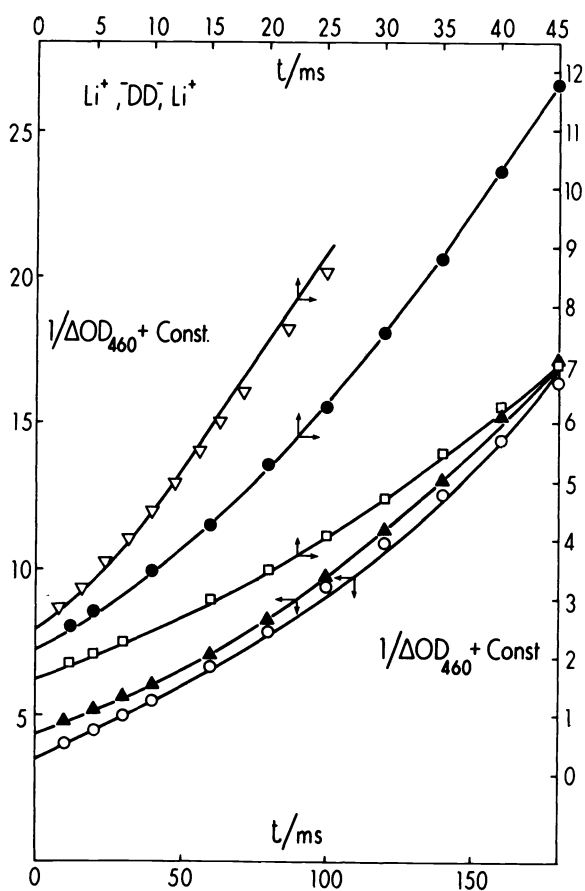

Fig. 7: Plots of $1/\Delta$(od, 400 nm) for the $Li^+,^-DD^-,Li^+$ system. The points are experimental for runs performed with different excess D = β. The lines are calculated by using the values of $\underline{k}_1$ and $\underline{k}_{-1}$ given below.

Points:	○	▲	□	●	▽
$10^6 \beta$/M	15	17	50	100	260
$10^{-6}\underline{k}_1$ Msec	1.03	0.97	1.08	1.05	0.81
$\underline{k}_{-1}$ sec	10	10	10	16	20

Obviously, the primary process does not result from photo-dissociation. Does electron photo-detachment account for all the observations? This route is composed of four elementary reactions:

(a) The photochemical act; $Cat^+, ^-DD^-, Cat^+ \xrightarrow{h\nu} Cat^+, ^-DD\cdot + e^-, Cat^+$,

(b) unimolecular, irreversible dissociation; $Cat^+, ^-DD\cdot \xrightarrow{k_{11}} D^{\overline{\cdot}}, Cat^+ + D$,

(c) reversible electron attachment; $D + e^-, Cat^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} D^{\overline{\cdot}}, Cat^+$; $K_1 = k_1/k_{-1}$,

(d) irreversible dimerization; $2D^{\overline{\cdot}}, Cat^+ \xrightarrow{k_d} Cat^+, ^-DD^-, Cat^+$.

The photochemical process occurs only during the flash (~ 25 μsec). The unimolecular disso-ciation of $Cat^+, ^-DD\cdot$ proceeds with a rate constant of about $10^5 - 10^6$ sec^{-1}, this being demonstrated by independent studies (ref. 22). Thus, at 100 μsec after a flash only the last two steps contribute to the return of the system to its initial state.

Let us denote by β the concentration of the excess of D, initially present, and the momen-tary concentrations of the bleached dianions and of the formed $D^{\overline{\cdot}}, Cat^+$ by $x/2$ and y, respectively. Then, the momentary concentration of e^-, Cat^+ is $x-y$ and of the unreduced D is $\beta + x-y$. The following differential equations describe the kinetics of the overall reaction,

$$-dx/dt = k_d y^2$$

$$dy/dt = k_1(\beta + x-y)(x-y) - k_{-1}y - k_d y^2.$$

The initial values of x and y were obtained by extrapolation to zero time and the equations were solved numerically (ref. 21). The value of k_d was obtained from the experiments per-formed at large excess of D ($\beta > 10^4$ M for the sodium system, and $> 10^3$ M for the lithium salt). The values of k_1 and k_{-1} were determined by fitting the theoretical curves to experimental points. As seen from Fig. 7, the agreement is good, although the reliability of that method is poorer for larger β's.'

The average values of k_1, k_{-1} and K_1 are collected in Table 4. It is interesting to note the substantial increase of k_1 and K_1 with increasing size of the cation from Li$^+$ to Na$^+$, K$^+$, and Cs$^+$. The slowness of the electron-cation pair attachment to 1,1-diphenyl ethylene is puzzling and further studies of this problem are contemplated.

TABLE 4. Kinetic data on attachment and detachment of electron-cation pairs to 1,1-diphenylethylene, D

$$D + e^-, Cat^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} D^{\overline{\cdot}}, Cat^+ \qquad K_1 = k_1/k_{-1}$$

| Cation	k_1 Msec	k_{-1} sec	K_1 M
Li$^+$	0.9×10^6	15	6×10^4
Na$^+$	1.9×10^7	33	6×10^5
K$^+$	4×10^9	< 20	$> 2 \times 10^8$
Cs$^+$	$> 10^{10}$		$\gg 10^8$

FLASH-PHOTOLYSIS OF TRIMERIC DIANIONS OF α-METHYLSTYRENE

In the presence of a small excess of α-methylstyrene, α, its dimeric dianions $K^+, ^-\alpha\alpha^-, K^+$ form trimers $K^+, ^-\alpha\alpha\alpha^-, K^+$. This reaction was studied in our laboratory by the stirred-flow reactor technique (ref. 23). Flash-photolysis of the trimer differs greatly from that of the dimer. In the latter case, one observes the formation of two $\alpha^{\overline{\cdot}}, K^+$ radical-anions that eventually recombine (ref. 13), the bimolecular rate constant being 1.2×10^7 M^{-1} sec^{-1} (see Table 3). Flash-photolysis of the trimer performed in the presence of the unreduced α-methylstyrene results in a difference spectrum distinct from that recorded in flash-photolysis of the dimer, and the system returns again to its initial state but much faster (ref. 24). The bimolecular rate constant determined from the $1/\Delta(od)$ versus time plot is 2×10^9 M^{-1} sec^{-1}. We interpret these results in terms of electron transfer

$$K^+\alpha\alpha\alpha^{\overline{\cdot}} + \alpha^{\overline{\cdot}}, K^+ \rightarrow K^+, ^-\alpha\alpha\alpha^-, K^+ + \alpha$$

following the initial electron photo-ejection,

$$K^+, {}^-\alpha\alpha\alpha^-, K^+ \overset{h\nu}{\rightarrow} K^+, {}^-\alpha\alpha\alpha\cdot + e^-, K^+,$$
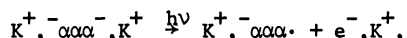
and its attachment to the unreduced α

$$e^-, K^+ + \alpha \rightarrow \alpha^{\bar{\cdot}}, K^+.$$
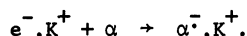
In contrast to the dimeric dianion, $K^+, {}^-\alpha\alpha\cdot$, the trimeric species $K^+, {}^-\alpha\alpha\alpha\cdot$ does not decompose. The decomposition of $K^+, {}^-\alpha\alpha\cdot$ is now being investigated by utilizing nitrogen laser pulses.

In conclusion, it is hoped that this report shows how electron photo-ejection can be utilized in the characterization of some labile species and in kinetic studies of their reaction.

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