

## ELECTRON-PHOTOEJECTION IN SOLUTIONS OF RADICAL-ANIONS AND DIANIONS\*

M. SZWARC and G. LEVIN

*Department of Chemistry, State University of New York, College of Environmental Science and Forestry, Syracuse, N.Y. 13210 (U.S.A.)*

### Abstract

Kinetics of electron photoejection and electron-capture processes in solutions of radical anions and dianions was investigated. The effect of counterions and solvents upon the equilibria and kinetics of these processes was stressed and it was shown that these effects could lead, in some systems, to changes greater than  $10^{10}$  of the respective rate or equilibrium constants.

The following classes of reactions were studied: electron or  $e^-$ ,  $Na^+$  capture by aromatic hydrocarbons and by radical ions — the latter reaction yields dianions, electron transfers like  $A^- + B \rightleftharpoons A + B^-$ , the reversible disproportionation of radical anions to dianions, the electron transfer initiated *cis-trans* isomerization, and some reactions involving radical cations.

A flash of visible light ejects electrons from a variety of radical anions or the corresponding dianions dissolved in ethereal solvents [1 - 3]. The course and mechanism of the dark reactions initiated by such photochemical events are the subject of the present review.

The mechanism of the electron photoejection process will not be discussed here. However, it is worth stressing that its efficiency for a particular electron donor,  $A^-$  or  $A^{2-}$ , may be dramatically affected by the nature of solvent and of the cation. The latter is present in the solution in a concentration equimolar with the anions. In ethereal solvents the anions and cations form associates such as  $A^-, Cat^+$  or  $A^{2-}, 2Cat^+$  which are in equilibrium with the free ions, *e.g.*,  $A^-, Cat^+ \rightleftharpoons A^- + Cat^+$  or  $A^{2-}, 2Cat^+ \rightleftharpoons A^{2-}, Cat^+ + Cat^+$ . The degree of their dissociation depends on their nature and concentration, the nature of the solvent, and the temperature of solution. The dissociation may be depressed by the addition of a salt inac-

---

\*Invited lecture delivered to the VIII International Symposium on Photochemistry, Alberta, August 1975.

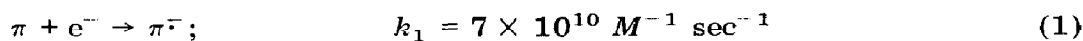
tive in the photochemical process but easily dissociated and sharing common cation with the investigated associate. This has been often done in our experiments.

The kind of aggregation of a particular associate, *e.g.*  $A^-, Cat^+$ , is affected by the solvent, since such species may exist in a variety of forms, *e.g.* ion pairs may be classified as loose — separated by a molecule of solvent or solvating agent, or tight — virtually in contact with each other. Alternative structural differences are also possible. The different kinds of associates behave differently in electron photoejection. Two examples show such a behavior. The ejection of electrons from sodium pyrenide ( $\pi^-, Na^+$ ) is 15 times as efficient when this species is dissolved in tetrahydrofuran than when tetrahydropyran solution is photolyzed under the same conditions [3]. A single flash photolyzed 40% of sodium salt of tetraphenylethylene dianions dissolved in tetrahydrofuran; however, a flash of the same intensity does not eject electrons at all when the salt is dissolved in dioxane [4].

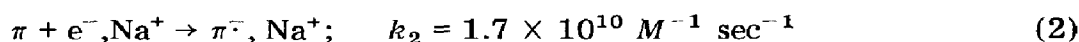
Electron-photoejection yields solvated electrons which subsequently become rapidly associated with cations into electron-cation pairs,  $e^-, Cat^+$ . Their presence is revealed by their characteristic absorption spectra and, for the sake of illustration, the spectra of  $e^-, Na^+$ ,  $e^-, K^+$ , and  $e^-, Cs^+$  in tetrahydrofuran are shown in Fig. 1. The association is faster than diffusion controlled, its rate has been determined to be  $> 10^{11} M^{-1} sec^{-1}$ , mainly by pulse radiolysis technique [5]. The equilibrium constant of  $e^-, Na^+ \rightleftharpoons e^- + Na^+$  is estimated [3] to be  $0.5 \times 10^{-7} M$ , being slightly lower than the dissociation constant of sodium naphthalenide in the same medium ( $\sim 1 \times 10^{-7} M$ ).

Solvated electrons, or the electron-cation pairs, may be scavenged by a variety of aromatic hydrocarbons or by some other suitable electron acceptors. The kinetics of such reactions was studied by flash-photolysis technique [3] and, more extensively, by pulse-radiolysis [6]. For example, flash photolysis of  $\sim 10^{-6} M$  solution of sodium pyrenide ( $\pi^-, Na^+$ ) in tetrahydrofuran leads to bleaching of the 493 nm absorption band due to  $\pi^-, Na^+$  and to the appearance of a transient absorption at 650 or 750 nm attributed to  $e^-, Na^+$  pairs. In the dark period following the flash the system returns to its initial state, *i.e.*, the spectrum of the solution recorded a few minutes after a flash is identical with that observed before flashing. This feature is encountered in many of the systems studied in our laboratory. It greatly facilitates the investigation because the composition of the photolyzed solution remains unaffected even by numerous flashes — a point especially important when the spectra of the transient have to be established.

Using this approach, we determined [3] the bimolecular rate constants of the reactions



and



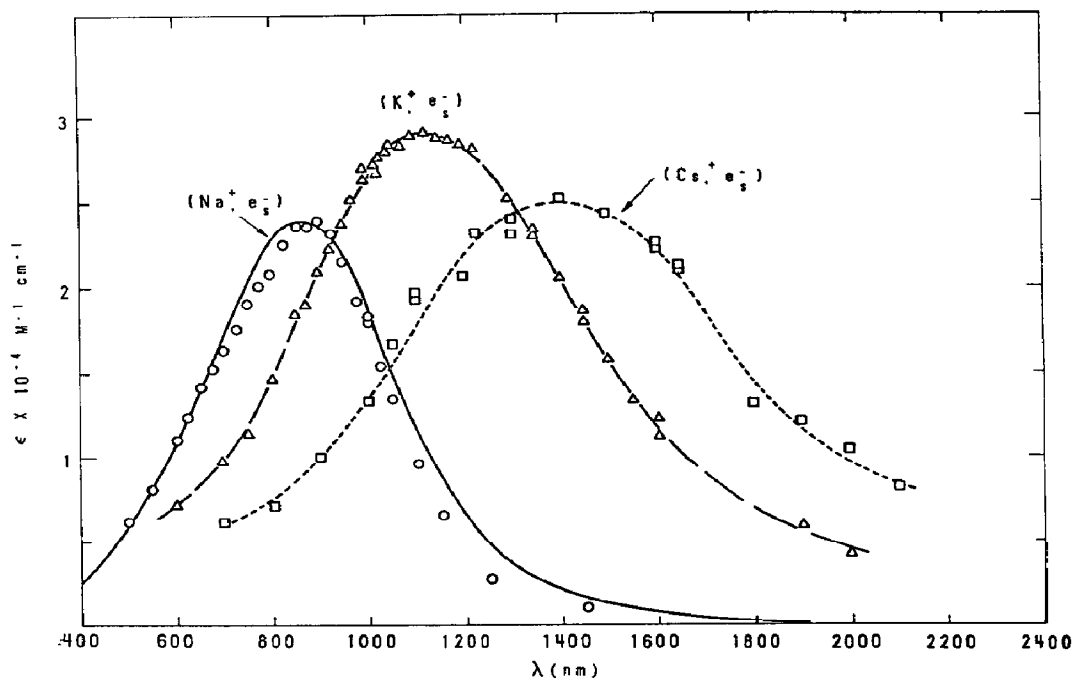


Fig. 1. Absorption spectra of  $e^-$ ,  $Na^+$ ,  $e^-$ ,  $K^+$ , and  $e^-$ ,  $Cs^+$  pairs in THF.

proceeding in THF. Since mixtures of  $\pi$  and  $\pi^-$  were flash-photolyzed, the return of the 493 nm absorption followed a pseudo-first order kinetics ( $[\pi] \gg [e^-]$ ) with a pseudo-first order rate constant proportional to the concentration of pyrene. These bimolecular rate constants compare favorably with those obtained by pulse radiolysis [6] and show that the free solvated electrons are captured 4 times faster than the  $e^-$ ,  $Na^+$  pairs.

A subtle point needs consideration. An ejected electron and the residue A produced by its ejection are initially in the vicinity of each other. In the early stage of the electron-capture reaction the combination of these neighbors is favored, and such a "cage" reaction imparts a first-order kinetic character on the overall process. However, the "cage" type combination is over in an extremely short time, while those partners that did not recombine diffuse away from each other and rapidly become scrambled. In our experiments we start to monitor the reaction at 50  $\mu$ sec after a flash and by then the process is truly bimolecular the cage reaction being over.

The most convincing evidence demonstrating electron photoejection is provided by the following experiment. Consider a solution of radical anions derived from an electron acceptor of high electron affinity mixed with a large excess of another electron acceptor whose electron affinity is relatively low, for example pyrenide,  $\pi^-$ , mixed with an excess of biphenyl, B. The difference of electron affinities of pyrene,  $\pi$ , and biphenyl, B, is greater than 0.5 V [7], and hence even for a 100-fold excess of B the equilibrium concentration of  $B^-$ ,



is too low for its detection. With a flash of visible light electrons are ejected from  $\pi^-$ , and since the electron capture process is virtually indiscriminate most of them are captured by B forming  $B^-$ . Thus the concentration of  $\pi^-$  is decreased immediately after a flash and the concentration of  $B^-$  increased accordingly. This is seen by observing the partially bleached absorbance at 493 nm, *i.e.*, at  $\lambda_{\max}$  of  $\pi^-$ , and the suddenly appearing absorbance at 400 nm ( $\lambda_{\max}$  of  $B^-$ ). Figure 2 illustrates such findings. The spectrum of the investigated solution recorded before a flash, or a few minutes after, is drawn in a solid line, while the dotted lines depict the spectrum observed at 50  $\mu\text{sec}$  and 100  $\mu\text{sec}$ , respectively, after a flash [3].

The equilibrium (3) was perturbed by a flash and the system has to return to its equilibrium state in the dark period following the flash. The kinetics of this reaction,



can be investigated by the conventional techniques, following on an oscilloscope the decay of the transient absorbance at 400 nm, or the decrease of the bleaching at 493 nm. Both approaches give concordant results from which we calculated  $k_4$  to be  $4.8 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ . By adding sodium tetraphenyl boride to the dilute THF solution of  $\pi^-$  and B one converts all the radical anions to the respective ion pairs. Under such conditions the bimolecular rate constant of reaction (5)

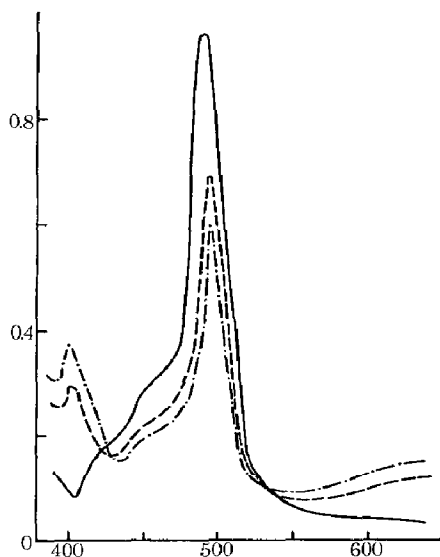
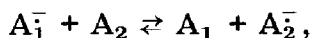


Fig. 2. Absorption spectra of a solution of  $\pi^-$ ,  $\text{Na}^+$  mixed with an excess of B before a flash (solid line) and at 50 and 100  $\mu\text{sec}$  after a flash.  $\lambda_{\max}$  of  $\pi^-$ ,  $\text{Na}^+$  = 493 nm;  $\lambda_{\max}$  of  $B^-$ ,  $\text{Na}^+$  = 400 nm. A few minutes after a flash the absorption spectrum is identical with that recorded before a flash.



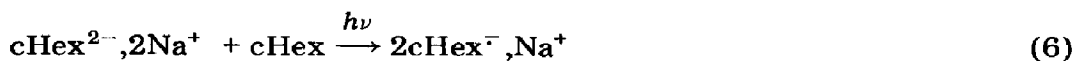
could be determined. The latter rate constant was found to be  $0.5 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ , indicating that the investigated electron transfer becomes about 10 times slower when a  $\text{Na}^+$  cation has to accompany the electron. This phenomenon was observed previously in electron exchange processes studied by the ESR technique [8, 9].

Electron transfer reactions,



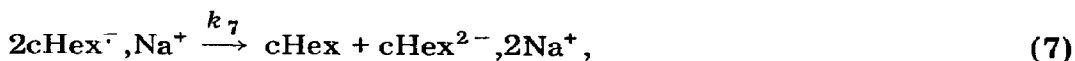
involving several pairs of aromatic hydrocarbons were investigated by Dorfman and his associates [6] who applied in their studies the pulse-radiolysis technique. The agreement between the results obtained by flash-photolysis and pulse-radiolysis is satisfactory.

Alkali reduction of some aromatic hydrocarbons yields their dianions, and the concentration of the intermediate radical anions could be below their detection even at the early stages of the reduction when the unreduced hydrocarbon is still in a large excess. Diphenyl-1,2-cyclohexene (cHex) exemplifies such a case. Nevertheless, the spectrum and the extinction coefficient of the elusive  $\text{cHex}^{\cdot-}$  radical anions were determined by utilizing flash-photolysis technique [10]. Electrons photoejected from  $\text{cHex}^{2-}, 2\text{Na}^+$  dianions were captured by cHex present in excess in the irradiated solution and thus the transient absorbance of  $\text{cHex}^{\cdot-}$  appeared after a flash.



The spectra of the radical anion and dianion are shown in Fig. 3. The extinction coefficient of the former was determined by comparing the transient absorbance at 560 nm with the extent of bleaching at 470 nm ( $\lambda_{\text{max}}$  of  $\text{cHex}^{2-}, 2\text{Na}^+$ ); the calculations were performed by assuming that the absorbance of  $\text{cHex}^{\cdot-}$  is negligible at the absorption peak of  $\text{cHex}^{2-}$ .

Thus formed  $\text{cHex}^{\cdot-}, \text{Na}^+$  radical anions disproportionate in the dark period of the reaction and the kinetics of decay of the transient absorbance, or of the bleaching, allows us to calculate the rate constant of the disproportionation [10],



namely  $k_7 = 1 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ . Other examples of radical anions disproportionation will be discussed later.

Another example of the approach outlined above is provided by our studies of radical anions of *cis*- and *trans*-stilbene. The radical anions of *trans*-stilbene,  $t\text{-St}^{\cdot-}$ , were prepared and identified by their optical [11] and ESR [12] spectra. However, all the attempts to characterize the *cis*-stilbene radical anions,  $c\text{-St}^{\cdot-}$ , were in vain [12]; *e.g.*, the reduction of *cis*-stilbene, whether by alkali metal [12] or by sodium biphenylide [13],

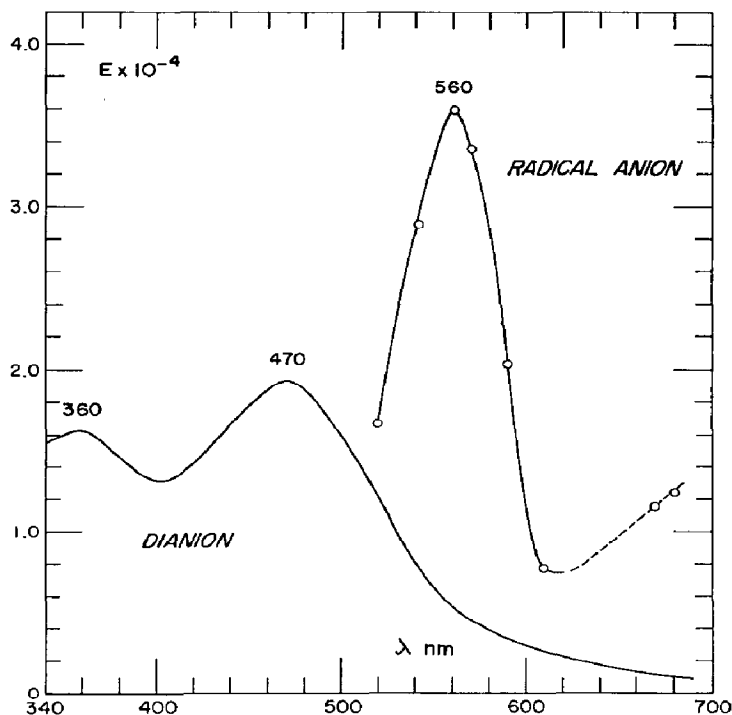
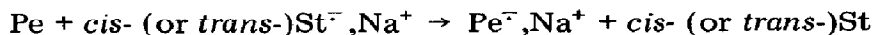


Fig. 3. Absorption spectra of  $cHex^- , Na^+$  and  $cHex^{2-} , 2Na^+$ . The former derived from the results of flash photolysis.

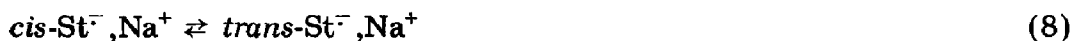
resulted in a species with the characteristic ESR spectrum of the *trans*-stilbene radical anion. In fact, the isomerization of *cis*-stilbene into its *trans*-isomer may be catalyzed by electron transfer [14], e.g., the isomerization in THF takes place in less than 1 sec if *trans*-stilbene radical anion is used as the catalyzing agent.

Addition of sodium perylenide,  $Pe^- , Na^+$ , to tetrahydrofuran solution of *cis*-stilbene does not induce any measurable isomerization of that hydrocarbon. The difference of electron affinities of perylene and *cis*-stilbene is much too great, and no detectable electron transfer could be observed in this system. However, irradiation of a solution of  $Pe^- , Na^+$  containing an excess of *cis*-stilbene leads to the transient formation of *cis*-stilbenide and, by using the stratagem adopted in the study of  $cHex^-$  radical anions, the optical spectrum and the extinction coefficient of that radical anion were determined [15]. The reliability of this procedure was checked by repeating these experiments with *trans*-stilbene and successfully redetermining its known optical spectrum and the extinction coefficient.

The lifetime of stilbene radical anions formed by this technique is very short, about 500  $\mu$ sec, because the reaction



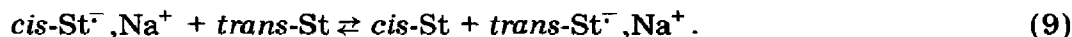
converts them into the respective hydrocarbons. Consequently, no detectable isomerization



takes place in these experiments. Nevertheless, the exchange such as



may occur provided the concentration of the hydrocarbon is relatively high. Hence, it has become possible to study the equilibrium such as



Flash-photolysis of tetrahydrofuran solution of  $Pe^{\cdot-}, Na^+$  was investigated in the presence of a large excess of a *cis*- and *trans*-stilbene mixture. The photoejected electrons were captured by the stilbenes forming a mixture of *cis*- $St^{\cdot-}$  and *trans*- $St^{\cdot-}$ . In the period of 100 to 500  $\mu$ sec the ratio of the transient absorbance at 500 nm ( $\lambda_{max}$  of *trans*- $St^{\cdot-}, Na^+$ ) and at 577 nm ( $\lambda_{max}$  of  $Pe^{\cdot-}, Na^+$ ) was constant, although the extinction coefficients of *cis*- and *trans*- $St^{\cdot-}$  are very different at 500 nm. This implies that equilibrium (9) was established in 100  $\mu$ sec, *i.e.*, the ratio  $[cis-St^{\cdot-}, Na^+]/[trans-St^{\cdot-}, Na^+]$  was constant and independent of time, provided  $t > 100 \mu$ sec. The latter ratio was found to be proportional to the ratio  $[cis-St]/[trans-St]$  present in the cell, and thus the equilibrium constant  $K_9$  could be calculated, the results [15] giving  $K_9 = 5$ .

We intend to perform these experiments again using, however, laser photolysis. The initial ratio  $[cis-St^{\cdot-}, Na^+]/[trans-St^{\cdot-}, Na^+]$  will then determine the relative efficiencies of electron capture by the two isomers. Moreover, if the initial composition of the irradiated solution would differ appreciably from its equilibrium composition, the approach to equilibrium could be observed and its relaxation time determined.

Flash-photolysis of an equilibrated solution of an aromatic hydrocarbon A, its radical anions,  $A^{\cdot-}, Cat^+$ , and dianions,  $A^{2-}, 2Cat^+$ , leads to ejection of electrons from the radical anions (quantum yield  $\Phi^-$ ) and the dianions (quantum yield  $\Phi^{2-}$ ). The ejected electrons could be captured by A (the rate constant  $k^0$ ) and by  $A^{\cdot-}, Cat^+$  (the rate constant  $k^-$ ), whereas we shall assume that  $A^{2-}, 2Cat^+$  is incapable to capture electrons. Which of the three species will be formed in an excess, over and above its equilibrium concentration, *after* all the ejected electrons had been captured?

Let us denote by  $\Delta^{2-}$  the excess of the  $A^{2-}, 2Cat^+$  concentration at the end of the above process. The calculation shows that  $\Delta^{2-}$  is

$$\Delta^{2-} = (k^- \Phi^- - k^0 \Phi^{2-} K_{dispr}) [A^{\cdot-}, Cat^+]_e^2 / (k^0 [A]_e + k^- [A^{2-}, 2Cat^+]_e),$$

where  $K_{dispr}$  denotes the equilibrium constant of disproportionation, *i.e.*,



and the square brackets give the equilibrium concentrations of the reagents. It follows that  $\Delta^{2-}$  is positive, *i.e.*, the concentration of the dianions would rise above their equilibrium value *after all the photoejected electrons had been captured*, when  $k^- \Phi^- - k^0 \Phi^{2-} K_{dispr} > 0$ , but for  $k^- \Phi^- - k^0 \Phi^{2-} K_{dispr}$

$< 0$ , the concentration of dianions would decrease and of the radical anions increase. Let us stress that these results are independent of the composition of the irradiated solution, *e.g.*, they are not affected by the  $[A^{\cdot-}, Cat^+]/[A^{2-}, 2Cat^+]$  ratio, provided that the system to be irradiated was at equilibrium before flashing and that all the ejected electrons were captured in time much shorter than the relaxation time of the perturbed system.

We may conclude therefore that the irradiation should lead to bleaching of the absorbance of  $A^{\cdot-}, Cat^+$  and the appearance of an enhanced absorbance of  $A^{2-}, 2Cat^+$  whenever  $K_{dispr}$  is sufficiently small, but the reverse should be observed when  $K_{dispr}$  is sufficiently large. Stoichiometry demands that the excess or deficiency of A would be equal to that of  $A^{2-}, 2Cat^+$ .

After a flash the perturbed system returns to its state of equilibrium and the kinetics of this process could be studied by the conventional technique. Denoting by  $X$  the deviation from the equilibrium concentration of  $A^{2-}, 2Cat^+$ , or of A, at time  $t$ , we find that

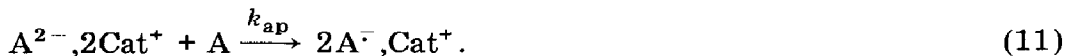
$$\ln\{[A]_e + [A^{2-}, 2Cat^+]_e + 4K_{dispr}[A^{\cdot-}, Cat^+]_e - (1 - K_{dispr})X\}/X = k_{ap}\{[A]_e + [A^{2-}, 2Cat^+]_e + 4K_{dispr}[A^{\cdot-}, Cat^+]_e\}t + \text{const.}$$

For systems for which  $K_{dispr}$  is very low, this relation may be simplified, *viz.*,

$$\ln(a + X)/X = k_{ap}at$$

where  $a = [A]_e$  while  $[A^{2-}, 2Cat^+]_e \approx 0$  or  $a = [A^{2-}, 2Cat^+]_e$  while  $[A]_e \approx 0$ .

In either expression  $k_{ap}$  denotes the rate constant of



Using this approach we investigated the kinetics of disproportionation of tetracene radical ions,  $Te^{2-}$ , associated with  $Li^+$ ,  $Na^+$ ,  $K^+$ , or  $Cs^+$  in a variety of solvents, namely tetrahydrofuran, THF, dioxane, DOX, and diethylether, DEE. In THF the disproportionation constant is extremely low, its value being determined by potentiometric techniques [16]. Hence, the approximate expression could be used and the values of  $k_{ap}$  are derived from the slopes of  $\ln(a + X)/X$  versus  $t$ .

The disproportionation leads to a non-negligible concentration of the dianions when the equilibrium was studied in DOX or DEE. In these systems  $K_{dispr}$  was determined by spectrophotometric technique [17] and  $k_{ap}$  from plots of  $k_{obs}$  versus  $r$  where  $k_{obs}$  is the slope of a line determined by plotting  $\ln(r + sX)/X$  versus time,

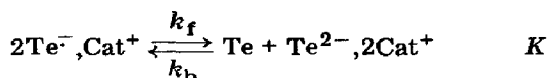
$$r = [Te]_e + [Te^{2-}, 2Cat^+]_e + 4K_{dispr}[T^{\cdot-}, Cat^+]_e, \text{ and } s = 1 - 4K_{dispr}.$$

The pertinent results [17] are collected in Table 1. They show the enormous effect of solvent on the equilibrium and rate constants of these disproportionations, *e.g.*,  $K_{dispr}$  of  $Te^{\cdot-}, Li^+$  increases by more than 10 orders of magnitude when THF is substituted by DEE.



TABLE 1

Disproportionation of tetracene radical anions at 25 °C



Solvent	Cation	K	$k_f$ M sec	$k_b$ M sec
THF	Li <sup>+</sup>	$5.8 \times 10^{-9}$	$3.6 \times 10$	$6.3 \times 10^9$
THF	Na <sup>+</sup>	$1.0 \times 10^{-5}$	$5.5 \times 10^4$	$5.5 \times 10^9$
THF	K <sup>+</sup>	$4.6 \times 10^{-6}$	$3.0 \times 10^4$	$6.5 \times 10^9$
THF	Cs <sup>+</sup>	$3.2 \times 10^{-6}$	$2.5 \times 10^4$	$7.8 \times 10^9$
DOX	Li <sup>+</sup>	$6.6 \times 10^{-2}$	$6.0 \times 10^6$	$1.1 \times 10^8$
DOX	Na <sup>+</sup>	$6.5 \times 10^{-2}$	$2.0 \times 10^7$	$3.1 \times 10^8$
DOX	K <sup>+</sup>	$1.1 \times 10^{-2}$	*	*
DOX	Cs <sup>+</sup>	$0.65 \times 10^{-2}$	*	*
DEE	Li <sup>+</sup>	$2.7 \times 10$	$7.0 \times 10^7$	$2.6 \times 10^6$
DEE	Na <sup>+</sup>	$1.2 \times 10^{-1}$	$2.4 \times 10^8$	$2.0 \times 10^9$

\*A flash of visible light ( $\lambda > 400$  nm) does not lead to any observable bleaching. Monitoring starts 25  $\mu$ sec after a flash.

The large variations of the rate and equilibrium constants of disproportionation result from modification of structure of the  $\text{Te}^{\cdot-}, \text{Cat}^+$  ion pairs and  $\text{Te}^{2-}, 2\text{Cat}^+$  aggregates caused to a great extent by changing the solvent. The solvating power towards cations decreases in the series THF, DOX, and DEE and this is the decisive factor affecting the tightness of these ionic associates.

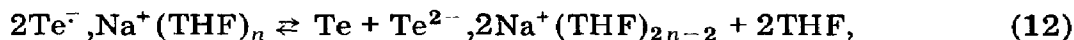
Direct participation of a solvent in disproportionation is well illustrated by studies of  $\text{Te}^{\cdot-}, \text{Na}^+$  disproportionation in benzene to which variable amounts of THF was added [18]. The spectrophotometrically determined disproportionation ratio,

$$[\text{Te}][\text{Te}^{2-}, 2\text{Na}^+]/[\text{Te}^{\cdot-}, \text{Na}^+]^2,$$

decreases with increasing THF concentration, being inversely proportional to  $[\text{THF}]^2$ , i.e.,

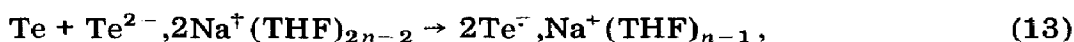
$$[\text{Te}][\text{Te}^{2-}, 2\text{Na}^+]/[\text{Te}^{\cdot-}, \text{Na}^+]^2 [\text{THF}]^2 = \text{const.}$$

This implies that the disproportionation proceeds according to the equation,

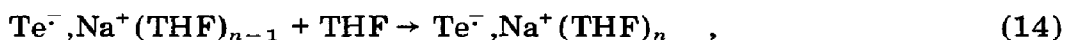


the cations in those ion pairs being more extensively solvated by THF than in  $\text{Te}^{2-}, 2\text{Na}^+$  aggregates. Although the number of THF molecules solvating the  $\text{Na}^+$  is not known, it is probable that  $n = 2$ .

Using again the flash photolytic approach, we investigated the kinetics of their disproportionation [18]. The results indicate that the rate determining step of the reverse reaction is



followed by a rapid solvation of the not yet fully solvated radical anions,



Disproportionation of barium salt of tetracene radical anions may involve reaction (15) or (16)



The equilibrium of this disproportionation was studied [22] in THF at low concentration of the salt ( $\sim 10^{-6} M$ ). Spectrophotometric data showed that the ratio

$$[\text{Ba}^{2+}, \text{Te}^{2-}][\text{Te}]/[\text{Te}^{\cdot-}]_{\text{total}}^2 \approx 500$$

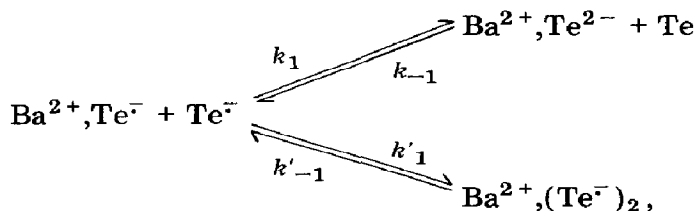
was independent of dilution implying that reaction (15) correctly describes this process. Indeed, the conductance data demonstrated that the dissociation



is virtually quantitative at these concentrations,  $K_{17}$  being  $6 \times 10^{-6} M$ .

Kinetics of this disproportionation was investigated by flash-photolyzing dilute ( $\sim 2 \times 10^{-6} M$ ) THF solutions of  $\text{Ba}^{2+}, \text{Te}^{2-}$  mixed with an excess of Te, containing only a very small fraction of radical anions. The high dilution of the latter results in their nearly complete dissociation into  $\text{Ba}^{2+}, \text{Te}^{\cdot-}$  and  $\text{Te}^{\cdot-}$ . Electrons are ejected mainly from  $\text{Ba}^{2+}, \text{Te}^{2-}$  and most of them are captured by Te. The ejection converts  $\text{Ba}^{2+}, \text{Te}^{2-}$  into  $\text{Ba}^{2+}, \text{Te}^{\cdot-}$  and the capturing process results in the formation of an equivalent amount of  $\text{Te}^{\cdot-}$ .

The dark process involves a very fast reaction consuming 40 - 50% of the photo-products and regenerating equivalent amount of  $\text{Ba}^{2+}, \text{Te}^{2-}$ , followed by a much slower reaction producing the remaining dianions. This behavior of the system is clearly recognized by inspecting the oscilloscope tracing seen in Fig. 4. Since no other transients than radical anions are observed in the formation of  $\text{Ba}^{2+}, \text{Te}^{2-}$ , it has to be concluded that the latter reaction proceeds through two parallel routes — a fast and a slow one. The following mechanism accounts for all the observations. A successful encounter of  $\text{Ba}^{2+}, \text{Te}^{\cdot-}$  with  $\text{Te}^{\cdot-}$  leads to two outcomes:



the former representing a direct electron transfer process while the latter forms the associate of the oppositely charged ions which eventually decomposes as shown below:

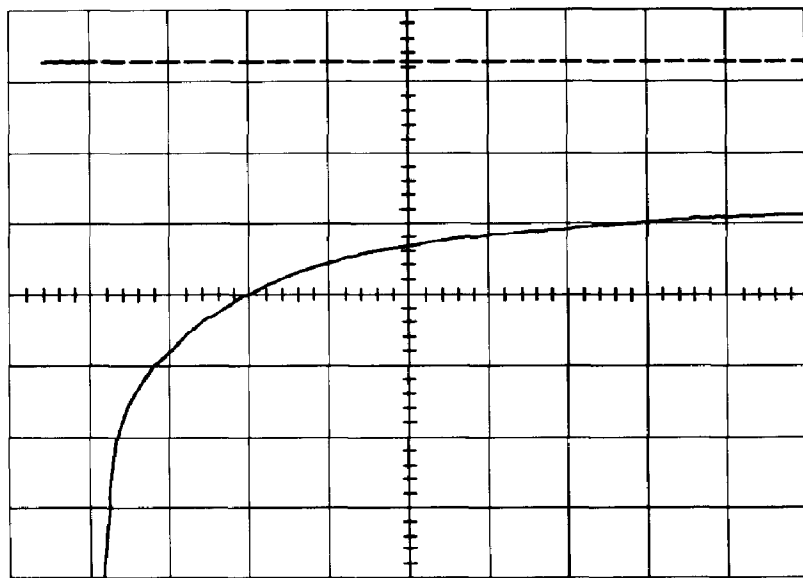
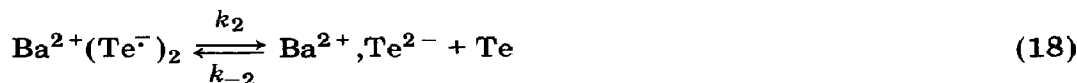


Fig. 4. Oscilloscope tracing at 630 nm of flash-photolysis of  $\text{Ba}^{2+}$ ,  $\text{Te}^{2-} + \text{Te}$  in THF,  $50 \mu\text{sec}/\text{div}$ . Optical density before flashing and a few seconds after a flash is given by the horizontal line (dashed). Note the rapid increase in the optical density during the first 200  $\mu\text{sec}$  and the extremely slow return thereafter.



Let us denote by  $a$ ,  $b$ , and  $c$  the equilibrium concentration of  $\text{Ba}^{2+}, \text{Te}^-$ , of  $\text{Ba}^{2+}, (\text{Te}^-)_2$  and of  $\text{Ba}^{2+}, \text{Te}^{2-}$ , respectively, and by  $T$  the concentration of  $\text{Te}$  which is always in large excess. The flash initially increases the concentration of  $\text{Ba}^{2+}, \text{Te}^-$  and  $\text{Te}^-$  by  $x_0$ , decreasing the concentration of  $\text{Ba}^{2+}, \text{Te}^{2-}$  by the same amount, while the concentration of  $\text{Ba}^{2+}, (\text{Te}^-)_2$  initially remains unchanged.

The proposed kinetic scheme leads to the relation

$$x = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t)$$

giving the time dependence of the excess concentration  $x$  of  $\text{Ba}^{2+}, \text{Te}^-$  or  $\text{Te}^-$  over and above their equilibrium concentration. The constants  $\lambda_1$  and  $\lambda_2$  are the roots of the quadratic,  $\lambda^2 - (\alpha + \delta)\lambda + \alpha\delta + \beta\gamma = 0$ , with the coefficients  $\alpha = 2(k_1 + k'_1)a + k_{-1}T$ ,  $\beta = k_{-1}T - k'_1$ ,  $\gamma = k_{-2}T - 2k'_1a$ , and  $\delta = k'_{-1} + k_2 + k_{-2}T$ . Only qualitative estimates of the rate constants have been possible. It seems that

$$k_1 \approx 2 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}, k'_1 < k_1$$

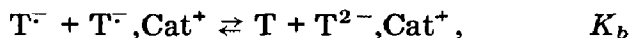
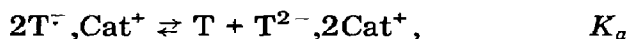
$$k_{-1}T \ll k_1a \text{ and } k_{-2}T \ll k_2.$$

Less extensive studies of disproportionation of perylene radical anions,  $\text{Pe}^-, \text{Na}^+$ , led to the rate constant of reaction (19) proceeding in THF,



The measurements based on the decay of the 437 nm peak ( $\lambda_{\max}$  of Pe) led to  $k_{19} = 1.3 \times 10^{10} M^{-1} \text{ sec}^{-1}$ , while the monitoring of the 577 peak gave  $k_{19} = 0.8 \times 10^{10} M^{-1} \text{ sec}^{-1}$ . These values agree within the experimental uncertainties of this study.

Disproportionation of radical anions of tetraphenylethylene, T, provided an opportunity to investigate the effect of the degree of ionic aggregation on the rate and equilibrium of this reaction. Three reactions should be considered, namely,



and



Studies of the sodium [20] and lithium [21] salts in tetrahydrofuran allowed us to determine  $K_a$  and  $K_b$  for these systems by combining spectrophotometric and conductance data. The former provided the ratios

$$K_{\text{ap}} = [\text{T}] [\text{T}^{2-}_{\text{total}}] / [\text{T}^{\cdot-}_{\text{total}}]^2$$

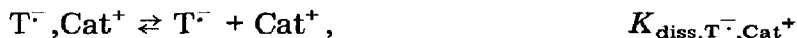
where  $[\text{T}^{2-}_{\text{total}}] = [\text{T}^{2-}, 2\text{Cat}^+] + [\text{T}^{2-}, \text{Cat}^+]$  and  $[\text{T}^{\cdot-}_{\text{total}}] = [\text{T}^{\cdot-}, \text{Cat}^+] + [\text{T}^{\cdot-}]$ . Since the dilution of the investigated solution increases the ratios  $[\text{T}^{2-}, \text{Cat}^+] / [\text{T}^{2-}, 2\text{Cat}^+]$  and  $[\text{T}^{\cdot-}] / [\text{T}^{\cdot-}, \text{Cat}^+]$ , the value of  $K_{\text{ap}}$  varies. The mathematical solution of this problem leads to the relation

$$K_{\text{ap}} = K_a (1 + K_{\text{diss}, \text{T}^{2-}, 2\text{Cat}^+} / [\text{Cat}^+]) / (1 + K_{\text{diss}, \text{T}^{\cdot-}, \text{Cat}^+} / [\text{Cat}^+])^2$$

where  $K_{\text{diss}, \text{T}^{2-}, 2\text{Cat}^+}$  and  $K_{\text{diss}, \text{T}^{\cdot-}, \text{Cat}^+}$  refer to the equilibria of the respective ionic dissociations, namely,



and



The latter two constants were determined from conductance data and their knowledge permits the calculation of the concentrations of cations for any composition of the solution, *i.e.* for any  $[\text{T}^{2-}_{\text{total}}]$  and  $[\text{T}^{\cdot-}_{\text{total}}]$ . Whenever  $K_{\text{diss}, \text{T}^{2-}, 2\text{Cat}^+} / [\text{Cat}^+] \ll 1$  an approximation leads to a simpler relation, *viz.*,

$$1/K_{\text{ap}}^{1/2} = 1/K_a^{1/2} + (K_{\text{diss}, \text{T}^{\cdot-}, \text{Cat}^+}^{1/2} / K_a^{1/4}) \{[\text{T}] [\text{T}^{2-}_{\text{total}}]\}^{-1/4}.$$

Thus, the plot of  $1/K_{\text{ap}}^{1/2}$  versus  $\{[\text{T}] [\text{T}^{2-}_{\text{total}}]\}^{-1/4}$  results in a straight line, its intercept and slope providing the value of  $K_a$  and an independent check for  $K_{\text{diss}, \text{T}^{\cdot-}, \text{Cat}^+}$ . This approximation is valid for the system T,  $\text{T}^{\cdot-}, \text{Na}^+$ , and  $\text{T}^{2-}, 2\text{Na}^+$  in THF. The dissociation constant of  $\text{T}^{2-}, 2\text{Li}^+$  is too high for the approximate approach, and hence for the lithium system the concentration of  $\text{Li}^+$  cations had to be calculated for each composition and  $K_a$  was found from the non-approximated relation.

The value of  $K_b$  was then calculated from an obvious relation

$$K_a/K_b = K_{\text{diss},\text{T}^{\cdot-},\text{Cat}^+} / K_{\text{diss},\text{T}^{2-},2\text{Cat}^+},$$

whereas the disproportionation of  $\text{T}^{\cdot-}$  free ions into  $\text{T}^{2-}$  free dianions could be neglected since the concentration of the latter dianions is vanishingly small in tetrahydrofuran under our experimental conditions.

The results of these studies are summarized in Table 2. The disproportionation of both salts is endothermic and the reaction is driven by the increase of entropy arising from the desolvation of cations when they become associated with  $\text{T}^{2-}$ . The change in the geometry of the reacting species arising from rotation around the central C—C bond is an important factor accounting for the behavior of this system.

Comparison of the reaction involving two  $\text{T}^{\cdot-},\text{Cat}^+$  with that arising from the interaction of  $\text{T}^{\cdot-}$  and  $\text{T}^{\cdot-},\text{Cat}^+$  is most instructive. It demonstrates how effective is the stronger interaction of the  $\text{Cat}^+$  with  $\text{T}^{2-}$  in shifting the equilibrium towards dianions. In the absence of  $\text{Cat}^+$  the disproportionation is negligible. For example, in hexamethylphosphorictriamide, a solvent conducive to dissociation of the ionic aggregates,  $K_c = [\text{T}][\text{T}^{2-}] / [\text{T}^{\cdot-}]^2 = 10^{-8}$  and the respective constant in THF is estimated to be  $\sim 10^{-12}$  or less [22].

TABLE 2

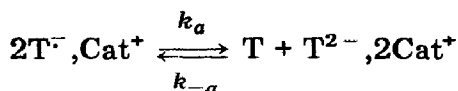
Disproportionation of sodium and lithium salts of tetraphenyl ethylene radical anions in THF

	Sodium salt	Lithium salt
$K_a$ at 25 °C	400	8.7
$\Delta H_a$	19 kcal/mole	6.6 kcal/mole
$\Delta S_a$	+75 eu	+27 eu
$k_{af}$	$< 160 \times 10^5 M^{-1} \text{sec}^{-1}$	$11 \times 10^5 M^{-1} \text{sec}^{-1}$
$K_b$ at 25 °C	3.3	0.7
$\Delta H_b$	13 kcal/mole	6.7 kcal/mole
$\Delta S_b$	+45 eu	+22 eu
$k_{bf}$	$100 \times 10^5 M^{-1} \text{sec}^{-1}$	$1.8 \times 10^5 M^{-1} \text{sec}^{-1}$

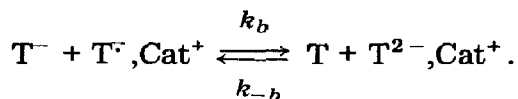
$k_{af}$  denotes the rate constant of  $2\text{T}^{\cdot-},\text{Cat}^+ \rightarrow \text{T} + \text{T}^{2-},2\text{Cat}^+$ .

$k_{bf}$  denotes the rate constant of  $\text{T}^{\cdot-} + \text{T}^{\cdot-},\text{Cat}^+ \rightarrow \text{T} + \text{T}^{2-},\text{Cat}^+$ .

The kinetics of disproportionation of the salt of  $\text{T}^{\cdot-}$  was studied [21, 23], again by flash photolysis technique. In tetrahydrofuran two reversible reactions proceed simultaneously



and



Since the observed reaction is relatively slow, having relaxation time  $\sim 1$  sec, one may assume that the ionic equilibria,  $\text{T}^{\cdot-}, \text{Cat}^+ \rightleftharpoons \text{T}^- + \text{Cat}^+$  and  $\text{T}^{2-}, 2\text{Cat}^+ \rightleftharpoons \text{T}^{2-}, \text{Cat}^+ + \text{Cat}^+$ , are maintained all the time. Under these conditions the excess of  $\text{T}^-_{\text{total}}$ , denoted by  $x$ , decays with a kinetics given by

$$-dx/dt = (k_{-a} + k_{-b} K_{\text{diss}, \text{T}^{2-}, 2\text{Cat}^+} / [\text{Cat}^+]) (\alpha x + \beta)$$

where  $\alpha = 2K_a(1 + K_{\text{diss}, \text{T}^{\cdot-}, \text{Cat}^+} / [\text{Cat}^+])^2 [\text{T}^-_{\text{total}}]_e +$

$$1/2(1 + K_{\text{diss}, \text{T}^{2-}, 2\text{Cat}^+} / [\text{Cat}^+]) ([\text{T}^{2-}_{\text{total}}]_e + [\text{T}]_e)$$

and  $\beta = K_a(1 + K_{\text{diss}, \text{T}^{\cdot-}, \text{Cat}^+} / [\text{Cat}^+])^{-2} - 1/4(1 + K_{\text{diss}, \text{T}^{2-}, 2\text{Cat}^+} / [\text{Cat}^+])^{-1}$ .

Integration leads then to the relation

$$\alpha^{-1} \ln \{(\alpha + \beta x)/x\} = (k_{-a} + k_{-b} K_{\text{diss}, \text{T}^{2-}, 2\text{Cat}^+} / [\text{Cat}^+]) t$$

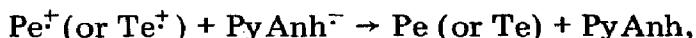
provided that the concentration of the  $\text{Cat}^+$  remains constant in each run. The concentration of  $\text{Cat}^+$  could be varied by adding to the solution under investigation an easily dissociated salt sharing the same cation as the  $\text{T}^-$  salt, e.g.  $\text{Cat}^+(\text{BPh}_4)^-$ .

The experimental results led to a series of straight lines when  $\ln \{(\alpha + \beta x)/x\} / \alpha$  was plotted *versus* time. Their slopes were found to be linear with  $1/[\text{Cat}^+]$ , and the latter linear relation yielded  $k_{-a}$  as an intercept and  $k_{-b} K_{\text{diss}, \text{T}^{2-}, 2\text{Cat}^+}$  as the slope. The pertinent  $k_a$  and  $k_b$  are given in Table 2. It is surprising that the rate of disproportionation of the lithium salts is substantially slower than of that the sodium. Apparently the lithium cations are more strongly bonded to  $\text{T}^-$  than the sodium, although there are systems when the reverse is true.

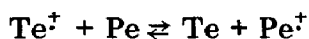
The behavior of sodium salt of tetraphenyl ethylene dianions was also investigated by picosecond spectroscopy [22]. In tetrahydrofuran the bleaching of the 485 nm band due to  $\text{T}^{2-}$  was not accompanied by the appearance of the absorbance at 660 nm arising from the formation of  $\text{T}^{\cdot-}$ . It was speculated that the electron ejection leaves the residue in a twisted form, different from the equilibrium geometry of  $\text{T}^-$ , and the internal rotation is too slow to produce the equilibrium form in 60 psec (time of observation). This statement is still debatable and needs further verification. However, it is interesting that the photolysis of dioxane solution led to the regeneration of the original absorbance in about 6 - 10 psec. This event could be treated as a kind of cage-reaction.

Recently our work was extended to electron-transfer processes yielding radical-cations [23]. As shown by one of us (G.L.), flash photolysis of perylene or tetracene mixed in acetonitrile with about 50-fold excess of pyromeliticdianhydride yields the radical cations of the hydrocarbon ( $\text{Pe}^{\cdot+}$

or  $\text{Te}^+$ ) and the radical anions of pyromelitic dianhydride ( $\text{PyAnh}^-$ ). Their recombination,



proceeds cleanly without formation of any new products and the bimolecular rate constant for the reaction involving  $\text{Pe}^+$  was found to be  $7.6 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ . Photolysis of a mixture of Pe and Te with  $\text{PyAnh}$  yields a mixture of  $\text{Pe}^+$  and  $\text{Te}^+$ , their ratio, determined by the ratio of  $[\text{Pe}]/[\text{Te}]$  in the original solution was constant during each run. This implies that the equilibrium.

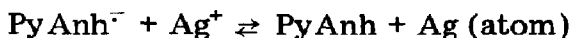


is established after the flash and maintained during the recombination period. The equilibrium constant was determined to be about 15, in a satisfactory agreement with the value of 21 determined by electrochemical methods [24].

Addition of  $\text{Fe}^{3+}(\text{ClO}_4^-)_3$  to the solution of Pe and  $\text{PyAnh}$  yields after a flash a relatively stable  $\text{Pe}^+$  (10% decay per msec), while  $\text{PyAnh}^-$  is destroyed within  $\sim 30 \mu\text{sec}$ . The stability of  $\text{Pe}^+$  should allow to study the kinetics of  $\text{Pe}^+$  reaction with a variety of nucleophiles.

Interestingly,  $\text{PyAnh}^-$  formed in flash photolysis is not destroyed by  $\text{Ag}^+, \text{ClO}_4^-$ .

Apparently the equilibrium



yields a very low concentration of Ag atoms. Under other conditions the aggregation of silver atoms into silver particles takes place and this shifts the reaction to the right; however, under conditions of flash photolysis (high dilution  $\sim 10^{-7} \text{ M}$ , and short lifetime) the aggregation does not take place and  $\text{PyAnh}^-$  is instead oxidized by  $\text{Pe}^+$ .

It is hoped that these examples illustrate the scope of our studies and point to the future goals.

## Acknowledgement

The financial support of these investigations by the National Science Foundation is gratefully acknowledged.

## References

- 1 J. Eloranta and H. Linschitz, *J. Chem. Phys.* 38 (1963) 2214.
- 2(a) L. J. Giling, J. G. Kloosterboer, R. P. H. Rettschnick and J. D. W. van Voorst, *Chem. Phys. Lett.*, 8 (1971) 309.
- (b) J. G. Kloosterboer, L. J. Giling, R. P. H. Rettschnick, and J. D. W. van Voorst, *Chem. Phys. Lett.*, 8 (1971) 462.

- 3(a) R. Rämme, M. Fisher, S. Claesson, and M. Szwarc, *Proc. Roy. Soc. London*, A327 (1972) 467.  
(b) M. Fisher, G. Rämme, S. Claesson and M. Szwarc, *Proc. Roy. Soc. London*, A327 (1972) 481.
- 4 G. Levin, S. Claesson and M. Szwarc, *J. Am. Chem. Soc.*, 94 (1972) 8672.
- 5(a) B. Bockrath and L. M. Dorfman, *J. Phys. Chem.*, 77 (1973) 1002.  
(b) I. A. Taub, D. A. Harter, M. C. Sauer, and L. M. Dorfman, *J. Chem. Phys.*, 41 (1964) 979.
- 6(a) S. Arai and L. M. Dorfman, *J. Chem. Phys.*, 41 (1964) 2190.  
(b) S. Arai, D. A. Brev and L. M. Dorfman, *J. Chem. Phys.*, 46 (1967) 2572.  
(c) J. R. Brandon and L. M. Dorfman, *J. Chem. Phys.*, 53 (1970) 3849.
- 7 J. Jagur-Grodzinski, M. Feld, S. L. Yang, and M. Szwarc, *J. Phys. Chem.*, 69 (1965) 628.
- 8 For summary of the available data, see M. Szwarc and J. Jagur-Grodzinski, in M. Szwarc, (ed.), *Ions and Ion Pairs in Organic Reactions*, John Wiley, 1974, Vol. II, p. 57-71.
- 9 J. Chaudhuri, J. Jagur-Grodzinski and M. Szwarc, *J. Phys. Chem.*, 71 (1976) 3063.
- 10 G. Levin and M. Szwarc, *Chem. Phys. Lett.*, 35 (1975) 323.
- 11(a) E. R. Zabolotny and J. F. Garst, *J. Am. Chem. Soc.*, 86 (1964) 1645.  
(b) S. Sorensen, G. Levin and M. Szwarc, *J. Am. Chem. Soc.*, 97 (1975) 2341.
- 12(a) C. S. Johnson and R. Chang, *J. Chem. Phys.*, 43 (1965) 3183.  
(b) N. M. Atherton, F. Gerson, and J. N. Oakwell, *J. Chem. Soc. A*, (1966) 109.
- 13 See Ref. 11b.
- 14 G. Levin, T. A. Ward and M. Szwarc, *J. Am. Chem. Soc.*, 270 (1974) 96.  
T. A. Ward, G. Levin and M. Szwarc, *J. Am. Chem. Soc.*, 97 (1975) 258.
- 15 P. K. Wong, G. Levin and M. Szwarc, to be published.
- 16 A. Rainis and M. Szwarc, *J. Am. Chem. Soc.*, 96 (1974) 3008.
- 17 G. Levin and M. Szwarc, *J. Am. Chem. Soc.*, 98 (1976) 000.
- 18 J. Pola, G. Levin and M. Szwarc, *J. Phys. Chem.*, 80 (1976) 000.
- 19 B. De Groof, G. Levin, and M. Szwarc, to be published.
- 20(a) J. F. Garst and E. R. Zabolotny, *J. Am. Chem. Soc.*, 87 (1965) 495.  
(b) R. C. Roberts and M. Szwarc, *J. Am. Chem. Soc.*, 87 (1965) 5542.
- 21 B. Lundgren, G. Levin, S. Claesson and M. Szwarc; *J. Am. Chem. Soc.*, 97 (1975) 262.
- 22 W. S. Struve, T. L. Netzel, P. M. Rentzepis, G. Levin and M. Szwarc, *J. Am. Chem. Soc.*, 97 (1975) 3310.
- 23 G. Levin, *J. Am. Chem. Soc.*, in press.
- 24 E. S. Pysh and N. C. Yang, *J. Am. Chem. Soc.*, 85 (1965) 2125.