

Ionic Aggregation of the Solvated Electron
with Lithium Cation in Tetrahydrofuran Solution

Bradley Bockrath and Leon M. Dorfman

Department of Chemistry, The Ohio State University,
Columbus, Ohio 43210

Abstract

Aggregation of the solvated electron with lithium cation in tetrahydrofuran forms ionic species which have been investigated by the pulse radiolysis method. The ion pair (Li^+, e_s^-) has a near infra-red absorption band with $\lambda_{\text{max}} = 1175 \text{ nm}$ and a molar extinction coefficient of $2.28 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ at the maximum. A higher aggregate, suggested to be the dilithium cation-electron triple ion, $\{(\text{Li}^+)_2, e_s^-\}$ has an optical absorption band with $\lambda_{\text{max}} = 890 \text{ nm}$ and an extinction coefficient of $5400 \text{ M}^{-1}\text{cm}^{-1}$ at the maximum. Absolute rate constants have been determined for reactions of these species with anthracene, biphenyl and dibenzylmercury. The reactivities of these two species are compared along with the reactivities of (Na^+, e_s^-) and e_s^- in THF solution.

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with Lithium Cation in Tetrahydrofuran Solution¹

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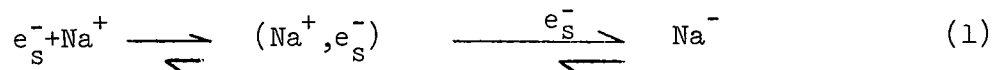
Department of Chemistry, The Ohio State University,
Columbus, Ohio 43210

Introduction

Aggregation of the solvated electron with alkali metal cations forms a variety of species in a number of weakly polar liquids. The sodium cation-electron pair, (Na^+, e_s^-) , has been observed in diglyme^{2,3} and in tetrahydrofuran⁴. The species Na^- , formed by reaction of two solvated electrons with sodium cation, has been observed in ethylenediamine⁵⁻⁷ and in tetrahydrofuran^{8,9}. Optical absorption spectra have been determined. The kinetics^{4,7,10} of both the formation of such species and the reactions they undergo have been studied.

In some solvents, the optical absorption spectrum of the solvated electron is very greatly altered upon ion pair formation. Thus, the absorption maximum for (Na^+, e_s^-) in THF is 890 nm⁴ compared with a maximum at 2120 nm for e_s^- in THF^{11,12}, corresponding to a change of 0.8 e.V. in the transition energy. Rate constants for the attachment of the electron to various substrates are substantially diminished^{4,10} upon ion pair formation with sodium cation.

The reactions involved in this pairing:



are by no means unique to sodium cation. To obtain a broader knowledge of alkali metal-electron pairing, information has been obtained about the

pairing of the solvated electron with lithium cation in THF. The results have been obtained by pulse radiolysis of THF solutions of various dissociative lithium salts. We report here the optical absorption spectrum of the species (Li^+, e_s^-) as well as rate constants for the attachment of this species to anthracene and to biphenyl. Evidence has also been obtained for the subsequent formation of a higher ionic aggregate of e_s^- , thought to be $\{(\text{Li}^+)_2, e_s^-\}$, the dilithium cation-solvated electron triple ion. This species is found to be much less reactive than either e_s^- or (Li^+, e_s^-) in the attachment to biphenyl in THF.

Experimental

The source of the electron pulse, as in our earlier studies¹³, was a Varian V-7715A electron linear accelerator, delivering 3-4 MeV electrons at a pulse current of about 300 mA for pulse duration of 100-1500 nsec and about 600 mA for pulse duration less than 80 nsec. Electron pulses of 200 to 800 nsec duration were used in this work. The transient optical absorptions in the region from 600 to 1100 nm were observed using an RCA 7102 photomultiplier which has S-1 spectral response. Our infrared detector¹², a solid state diode employing a diffused junction of indium antimonide, manufactured by Barnes Engineering Co., was used for observation in the region from 900 to 2000 nm. The 10-90% rise time of the electronic detection systems is 80 nsec for the infrared detector and considerably less for the RCA 7102 photomultiplier. A Bausch and Lomb grating monochromator, type 33-86-25, f/3.5 was used. Corning filters were selected to eliminate second-order components from the analyzing light beam. Our standard reaction cells¹³, with high-purity silica windows

and a cell length of 20.0 mm, were used with a double pass of the analyzing light beam.

The THF was purified first by refluxing under argon, for several hours, a solution containing benzophenone and excess sodium metal. The solvent was then distilled through a glass bead-packed column, the middle fraction being retained. It was then degassed and vacuum distilled into a storage bulb containing a mirror of freshly distilled potassium. Solvent was vacuum distilled from this bulb into the reaction cells just prior to the runs.

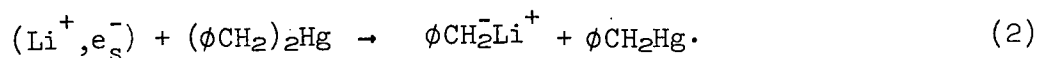
Anthracene and biphenyl (Aldrich) were zone refined, with a nominal purity of at least 99.9%. Dibenzylmercury (Alfa Inorganics) was recrystallized from ethanol, dried under vacuum, and stored in the dark until used. Lithium perchlorate (Alfa Products, 99.5%), lithium bromide (Matheson, Coleman and Bell, >99%) and lithium chloride (Baker, 99.8%) were used as supplied after thorough drying under vacuum. Lithium tetraphenylboron was prepared from sodium tetraphenylboron (Fisher reagent grade) and lithium chloride by cation exchange¹⁴. The freshly prepared salt was recrystallized three times by addition of cyclohexane to a dichloroethane solution. Solutions of lithium tetraphenylboron become discolored when exposed to the atmosphere. Precautions were taken to reduce contact with the atmosphere by conducting the preparation and recrystallization in a glove bag filled with argon and storing the salt under vacuum until immediately before weighing on a pan balance and transfer to the reaction cell.

Results and Discussion

Optical Absorption Spectrum of (Li^+, e_s^-)

The transient absorption band which we assign to the lithium cation-solvated electron ion pair, (Li^+, e_s^-) , was obtained by measuring the optical density, at different wavelengths, immediately after an electron pulse in THF solutions of several dissociative lithium salts. The data are shown in Fig. 1. The data combined in Fig. 1 were obtained in separate experiments using either LiCl, LiBr or LiClO₄ as the added salt. The salt concentration was sufficiently high so that the ion pairing reaction, $e_s^- + \text{Li}^+$, was essentially complete at the end of the electron pulse. This was readily verified by observations in the near infra-red which showed that e_s^- is not present after the pulse because of this effective scavenging. It may be readily seen that, when the optical densities obtained from the separate solutions of the three salts are normalized to the absorption maximum, the data define a common absorption band with the maximum at 1175 nm. Since the same band is obtained from the three lithium salts it is evident that the anion does not play a role in the formation of this transient which is indicated to be (Li^+, e_s^-) .

Further scavenger experiments indicate that this transient is composed of both the lithium cation and a solvated electron. When dibenzylmercury was used to scavenge the band at 1175 nm, formed in lithium perchlorate solutions, a new band with a maximum at 330 nm appeared. This new species is identified as benzyl lithium since the absorption band corresponds to that reported¹⁵ for $\phi\text{CH}_2^-\text{Li}^+$. Under our experimental conditions, this band could have arisen only by the reaction:



This conclusion is well-founded for several reasons. Firstly, we have

previously established that, in irradiated THF solutions of dibenzylmercury, the solvated electron is the precursor of free benzyl anion¹⁶. Secondly, the absorption spectrum of $\phi\text{CH}_2\text{Li}^+$ is readily distinguished from that of ϕCH_2^- or that of ϕCH_2^- paired with other alkali metal cations¹⁷, since the absorption maximum differs in each case. Finally it was shown that no significant amount of e_s^- could react directly with dibenzylmercury. To insure that the solvated electron reacted only with lithium cation, the solution was made with lithium perchlorate (0.028F) in rather large excess over dibenzylmercury ($2.5 \times 10^{-4}\text{M}$). Observation of the band at 1175 nm under these conditions shows only decay, as expected. Thus we may confidently rule out formation of benzyl lithium by the reaction sequence $e_s^- + (\phi\text{CH}_2)_2\text{Hg}$ followed by $\phi\text{CH}_2^- + \text{Li}^+$. Reaction (2) thus seems well established, providing assurance that the benzyl lithium precursor, with $\lambda_{\text{max}} = 1175 \text{ nm}$, is in fact (Li^+, e_s^-) .

Table I contains a comparison of the optical transition energies for the absorption bands of the solvated electron itself, the lithium-electron pair and the sodium-electron pair in THF. The change in transition energy for the solvated electron induced by pairing with lithium ion is considerably less than that induced by pairing with sodium ion. If this shift in transition energy is taken as an indication of the strength of the coupling in the ion pair, the relative effect for Li^+ and Na^+ is difficult to rationalize only on the basis of the ionic radii of the bare alkali metal cations. If ionic radius were the dominant parameter in determining the change in transition energy, the smaller lithium ion might be expected to induce the greater shift. Our contrary observation suggests that solvation of the alkali metal cation is the important phenomenon which determines the interionic distance in the pair; in short, we are dealing with a solvent-separated pair.

Table I.

Optical Absorption Spectrum of the Solvated Electron,
its Lithium Ion Pair and its Sodium Ion Pair in THF Solution

Species	Absorption Maximum	Transition Energy	Shift from e_s^-	Width at Half-Height
e_s^-	2120 nm ^a	0.58eV	--	3450 cm^{-1}
(Li^+, e_s^-)	1175	1.04	0.46eV	6270
(Na^+, e_s^-)	890 ^b	1.39	0.81	7000

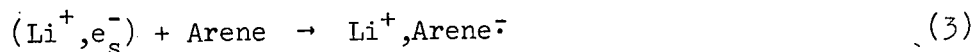
a) Data taken from ref. 11

b) Data taken from ref. 4

Any meaningful evaluation of the role of the solvent would require knowledge of the number and the geometric arrangement of solvent molecules in at least the first solvation shell. Such detailed microscopic information is lacking. Attention has, however, been drawn to the role of the solvent with these ions on the basis of other macroscopic properties. The limiting conductance^{14,18} of Li^+ in THF solution was found to be lower¹⁴ than that of Na^+ , a fact attributed to the relative size of the solvation shell of THF molecules bound to the metal cations. Of the two ions, Li^+ apparently has the larger solvation shell. The effect on the spectrum, which we observe and which we interpret as stronger coupling of the electron by sodium cation may be rationalized similarly on the basis that Li^+ is solvated to a greater degree than Na^+ in the ion pair, (M^+, e^-) , just as for the free ion in solution. A greater degree of solvation, together with the lesser effect of effective nuclear charge for Li^+ than for Na^+ , would reduce the coulombic attraction between the cation and the electron in the pair.

The shape of the absorption band of $(\text{Li}^+, \text{e}_s^-)$ conforms reasonably well to the same shape function as does the band for e_s^- and for $(\text{Na}^+, \text{e}_s^-)$, namely a Gaussian curve on the low energy side and a Lorentzian curve on the high energy side of the maximum. The fit of the data in the region to the right of the band maximum in Fig. 1 does not appear to be quite as close as for other cases. The total band width at half height, for the three spectra in THF, is also compared in Table I. Both metal cation-paired species have a considerably broader band than does e_s^- .

The molar extinction coefficient of (Li^+, e_s^-) at the band maximum was found to be $2.28 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$. This value was determined, as before⁴, by using aromatic compounds to scavenge the transient species:



The extent of growth or decay, after the electron pulse, of optical density at any given wavelength, depends upon the relative values of the extinction coefficient of (Li^+, e_s^-) and of $\text{Li}^+, \text{Arene}^-$. At wavelengths for which the extinction coefficients of these two species are equal, neither growth nor decay is observed. With anthracene as the scavenger, this wavelength of equivalence was found to be 720 nm, which happens to correspond to an absorption peak of anthracenide ion. With biphenyl as scavenger the wavelength of equivalent extinction coefficients was found to be 675 nm. The extinction coefficient of (Li^+, e_s^-) was then obtained from the two sets of data by using the known extinction coefficients of sodium anthracenide¹⁹ and sodium biphenylide¹⁹ in THF, $10,000 \text{ M}^{-1}\text{cm}^{-1}$ and $12,500 \text{ M}^{-1}\text{cm}^{-1}$ at the absorption peak, respectively. Good agreement was obtained, the average value being $2.28 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$.

The oscillator strength of the 1175 nm band was determined from the equation:

$$f = 4.32 \times 10^{-9} (1.065 W_{\frac{1}{2}}^G + 1.511 W_{\frac{1}{2}}^L) \epsilon_{\text{max}} \quad (4)$$

where $W_{\frac{1}{2}}^G$ and $W_{\frac{1}{2}}^L$ are the portions of the half-width on the Gaussian and Lorentzian side respectively. This gives a value of $f = 0.90$ for the band of (Li^+, e_s^-) , which is similar to the value found for other one-electron species, namely e_s^- in THF¹² ($f=0.85$) and (Na^+, e_s^-) in THF⁴ ($f=1.0$), as well as for e_s^- in a variety of liquids.

The optical absorption data thus indicate that ion-pairing of e_s^- in THF induces a shift in the absorption to higher transition energies. The magnitude of the shift depends upon the specific cation involved,

being greater for sodium than for lithium. The absorption band for e_s^- is considerably broadened by cation pairing, and the extinction coefficient reduced, while the oscillator strength remains roughly the same.

Reaction Kinetics of (Li^+, e_s^-) .

Table II contains absolute rate constants for elementary reactions of (Li^+, e_s^-) with three different substrates. Two are examples of electron attachment to aromatic compounds, reaction (3), and one of a dissociative electron attachment, reaction (2). Values of the rate constants for analogous reactions of e_s^- and of (Na^+, e_s^-) have been included for comparison.

These rate constants were determined in each case by observing the decay in the absorption at 1000 nm in the absence as well as in the presence of appropriate concentrations of the added reactants. This wavelength is near the absorption maximum of (Li^+, e_s^-) , but sufficiently far removed from the absorptions arising from the products (either the corresponding aromatic radical anions or benzyl lithium) so that there is no spectral overlap. In the absence of added substrate, the decay of (Li^+, e_s^-) in $LiClO_4$ solutions (0.03 to 0.06 F) followed a first order rate law with a half-life of about 3 μ secs. In the presence of anthracene (0.46 and $1.0 \times 10^{-4}M$) and of dibenzylmercury (1.3 and $2.4 \times 10^{-4}M$) the decay was again first order with a half life reduced to less than 300 nsecs. The rate constant for the reaction was then evaluated from the pseudo first order constant and each substrate concentration. The rate constants in Table II are the average of the two determinations at the indicated substrate concentrations. The separate values agree to within $\pm 15\%$. The uncertainty of the rate constant values in Table II is $\pm 20\%$. In the case of biphenyl, k_3 was obtained in an experiment using lithium tetraphenylboron

Table II.

Absolute Rate Constants for Reactions of (Li^+, e_s^-) ,
 (Na^+, e_s^-) and e_s^- in THF Solution at 25°C. ($\text{M}^{-1}\text{sec}^{-1} \times 10^{-10}$)

<u>Reactant</u>	<u>(Li^+, e_s^-)</u>	<u>(Na^+, e_s^-)</u>	<u>e_s^-</u>
Anthracene	2.65	--	--
Biphenyl	1.00	0.55 ^a	11.0 ^a
Dibenzylmercury	1.8	0.79 ^b	2.7 ^b

a) Data taken from ref. 4

b) Data taken from ref. 16

as the dissociative salt. Other aspects of the experiment with $\text{Li}\Phi_4\text{B}$, along with the details of experiments from which k_3 was determined, are described in detail in a following section.

These attachment rate constants for (Li^+, e_s^-) are all close to the diffusion controlled limit judging from the approximate value for k_{diff} calculated from the Smoluchowski equation²⁰:

$$k_{\text{diff}} = \frac{2RT}{3\eta} \frac{(r_a + r_b)^2}{r_a r_b} \quad (5)$$

where η , the viscosity is¹⁸ $4.61 \times 10^{-3} \text{P}$, and r_a and r_b are the interaction radii, which are taken, as an approximation, to be equal. We thus estimate $k_{\text{diff}} = 1.4 \times 10^{10} \text{M}^{-1} \text{sec}^{-1}$, quite comparable to the experimental values.

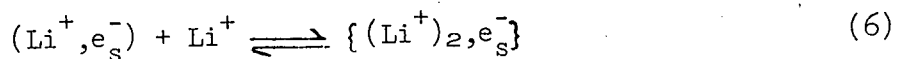
Two properties of the rate constants for the metal cation-coupled species, compared with those for e_s^- , are noteworthy. Firstly, the values for (M^+, e_s^-) are somewhat lower. Secondly, there is a difference in selectivity; the ratio $k_{\phi_2} / k_{(\phi\text{CH}_2)_2\text{Hg}}$ is less than unity for (M^+, e_s^-) , while it is 4 for e_s^- .

Optical Absorption Spectrum of $\{(\text{Li}^+)_2, e_s^-\}$.

Experiments with $\text{Li}\Phi_4\text{B}$ as the added dissociative salt lead to the observation of a second absorption band which we propose to be the dilithium cation-solvated electron triple ion. Fig. 2 shows the absorption spectrum obtained at the end of an 800 nsec pulse in a 0.023F solution of $\text{Li}\Phi_4\text{B}$ in THF. This figure contains the spectrum of (Li^+, e_s^-) along with the optical density points observed in the solution of $\text{Li}\Phi_4\text{B}$. The second band is obtained as a difference spectrum by subtracting the band assigned to (Li^+, e_s^-) after normalization to the 1175 nm maximum.

A similar band was obtained in solutions 0.10 and 0.18F in $\text{Li}\Phi_4\text{B}$. In such solutions the signal decays to a plateau within 2 μsec after the pulse. Optical densities measured at the plateau define an absorption band identical to that obtained by the foregoing difference method. Fig. 3 shows the combined data from the two methods; the band has an absorption maximum at 890 nm and a width at half-height of 5900 cm^{-1} .

We propose that this 890 nm band is to be identified as the species $\{(\text{Li}^+)_2, e_s^-\}$ on the basis of the following evidence. The 890 nm band is observed only with $\text{Li}\Phi_4\text{B}$ as the added salt. It is a unique property of this salt, in comparison with the others used, that it is far more dissociative ($K_{\text{diss}} = 7.9 \times 10^{-5}\text{M}^{-1}$)¹⁴ than LiClO_4 ($2.1 \times 10^{-8}\text{M}^{-1}$)²¹, LiBr ($2 \times 10^{-7}\text{M}^{-1}$)²² and very likely than the less soluble LiCl . Thus, $\text{Li}\Phi_4\text{B}$ solutions have over an order of magnitude higher concentration of free Li^+ and $\Phi_4\text{B}^-$. While the (Li^+, e_s^-) could, in principle, couple with either the cation or the anion (or indeed with the undissociated salt molecule), the over-all evidence favours coupling with Li^+ as the mode of formation of the 890 nm band:



The limiting factor in the formation of the 890 nm band is thus that $[\text{Li}^+]$ must be sufficiently high to make reaction (6) competitive with the normal decay of the precursor, (Li^+, e_s^-) in the irradiated solution. With LiClO_4 as the added salt, by contrast, there is no formation of the 890 nm band even at a salt concentration of 0.35F.

The decay of the (Li^+, e_s^-) band was observed at 1020 nm as a function of the $\text{Li}\Phi_4\text{B}$ concentration. At low salt concentration ($3.9 \times 10^{-4}\text{F}$) the band decays completely, in accord with a first-order rate law and a half-life of 1.0 μsec , and no 890 nm band is seen. Presumably this

decay is accounted for by reaction of (Li^+, e_s^-) with radiolysis products, including the solvent counterion. At progressively higher salt concentration the formation of a plateau is observed as the formation reaction, (6), becomes fast enough to convert (Li^+, e_s^-) to the species with a band at 890 nm. The decay of (Li^+, e_s^-) is still first-order, but with a progressively shorter half-life as $[\text{Li}\Phi_4\text{B}]$ is increased.

The data permit us to determine the kinetic order with respect to formal $\text{Li}\Phi_4\text{B}$ concentration, and to set a lower limit for k_6 . A plot of $\log k'_6$, the first-order constant, against $\log [\text{Li}\Phi_4\text{B}]$ in the concentration range 8.2×10^{-4} to $7.5 \times 10^{-2}\text{F}$, shows only a small degree of curvature, and is reasonably well-represented by a straight line with slope ~ 0.46 . This low kinetic order with respect to the salt indicates that a dissociative process is important and that free ion participates in the formation of the 890 nm band, as in reaction (6). The lifetime of the 890 nm band, as will be shown, is fully 3-fold greater than the lifetime of (Li^+, e_s^-) in irradiated solutions, which is also consistent with a net positive charge for the 890 nm species.

We may determine only a lower limit for k_6 , since at salt concentrations at which we observe reaction (6), only an upper limit for free Li^+ may be obtained. This upper limit for $[\text{Li}^+]$ is calculated from the equilibrium constant for the dissociation:



K_{diss} was determined at $[\text{Li}\Phi_4\text{B}] < 10^{-4}\text{F}$ since formation of triple ions becomes a complicating factor at higher concentrations¹⁴. On the basis of such an upper limit, we obtain $k_6 \geq 2 \times 10^9 \text{ M}^{-1}\text{sec}^{-1}$, which may be compared with a rate constant recently reported²¹ for an analogous reaction, the formation of a triple ion from the ion pair and free ion in THF solutions of LiClO_4 . This constant obtained

by ultrasonic relaxation methods, is $1.60 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$, similar to our lower limit for k_6 .

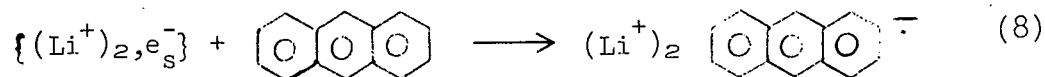
The molar extinction coefficient of $\{(\text{Li}^+)_2, e_s^-\}$ at the band maximum was found to be $5400 \text{ M}^{-1} \text{ cm}^{-1}$. This value was determined from rate curves observed at 890 nm in $\text{Li}\Phi_4\text{B}$ solutions in which a plateau in the rate curve was established as (Li^+, e_s^-) was completely scavenged. The value was calculated from the relative absorptions due to (Li^+, e_s^-) and $\{(\text{Li}^+)_2, e_s^-\}$, assuming material balance, namely that the amount of $\{(\text{Li}^+)_2, e_s^-\}$ at the plateau is equivalent to the amount of (Li^+, e_s^-) at the end of the pulse in solutions of high salt concentration. The value is thus based on the extinction coefficient for (Li^+, e_s^-) , $\epsilon^{1175} = 2.28 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.

The subsequent decay of the 890 nm band is first-order with a half-life of about 10 μsec , fully 3-fold longer than the half-life of (Li^+, e_s^-) when that ion pair is formed in solution of low $\text{Li}\Phi_4\text{B}$ concentration or in solutions of the other three lithium salts, i.e. at low $[\text{Li}^+]$. Since the mode of decay includes reaction with the solvent cation, THF^+ , formed in the radiolysis, the extended lifetime seems qualitatively in accord with the assignment of the 890 nm band to a species with net positive charge, which would undergo Coulombic repulsion. The observed lifetimes of both e_s^- and (Li^+, e_s^-) are shorter than for $\{(\text{Li}^+)_2, e_s^-\}$, in that order.

Our observations, considered together, are best rationalized by assignment of the 890 nm band to $\{(\text{Li}^+)_2, e_s^-\}$: rapid formation from (Li^+, e_s^-) only in the presence of a high concentration of Li^+ , with a rate constant similar in value to that for formation of a closely analogous triple ion, and exhibiting a somewhat extended lifetime consistent with a positively charged species in the presence of solvent cation.

Reactions of $\{(Li^+)_2, e_s^-\}$.

The absolute rate constant for the electron attachment to anthracene:



was determined by observation of the decay of the 890 nm band, at its maximum, in both the presence and the absence of anthracene. The decay, following a 600 nsec pulse in a 0.18F solution of $Li\Phi_4B$, in the absence of anthracene, conforms to a first-order rate law. In the presence of anthracene (0.42 to $3.6 \times 10^{-4}M$), the decay is also first-order, with a progressively shorter half-life. A plot of the first-order constants obtained at the various anthracene concentrations, against anthracene concentration, gives a straight line with slope $k_8 = (4.1 \pm 0.7) \times 10^9 M^{-1} sec^{-1}$. Thus the rate constant for attachment of $\{(Li^+)_2, e_s^-\}$ to anthracene is some 6-fold smaller than the rate constant for the analogous attachment of the ion pair, (Li^+, e_s^-) .

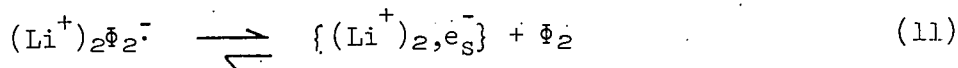
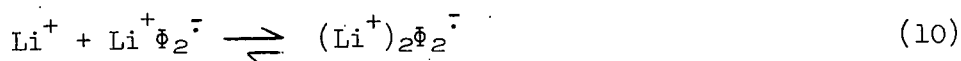
The reaction product which we observe is the anthracenide ion. This was verified from the close correspondence of the absorption spectrum taken over the range 500 to 800 nm, after the scavenging of the 890 nm band was complete, with the known long-wavelength absorption band of sodium anthracenide.²⁴

We have written the anthracenide ion, in reaction (8), in the form of the triple ion, but direct evidence concerning the state of aggregation requires further experimentation.

The subsequent decay of the anthracenide ion under our pulse conditions, is first-order with a half-life of about 20 μ secs.

The attachment to biphenyl shows quite different kinetic behaviour than the attachment to anthracene. In a solution of $Li\Phi_4B$ at high concentration with biphenyl present, the 890 nm band continues to grow in

after the pulse, reaching a maximum in several μsecs followed by a subsequent decay with a half-life greater than 20 μsecs . This observation of an increase in optical density at 890 nm following the pulse is quite unlike our observation of irreversible scavenging of $\{(\text{Li}^+)_{2}, e_{\text{S}}^{-}\}$ by anthracene. To account for these observations, we propose the reaction sequence:



The growing in at 890 nm occurs when the ratio $[\Phi_2]/[\text{Li}^+]$ is great enough to favour formation of $\text{Li}^+ \Phi_2^{-}$ in the competition between reactions (9) and (6). Thus, following pulse irradiation of a solution 0.021 M in Φ_2 and 0.051 F in $\text{Li}\Phi_4\text{B}$, absorption at 890 nm increases, reaching a maximum in about 10 μsec , while absorption at 630 nm (the long-wavelength peak of biphenylide) decays to a plateau during the same interval, in accord with a first order rate law.

The rate constant for attachment of $(\text{Li}^+, e_{\text{S}}^{-})$ to biphenyl, k_9 , referred to in an earlier section, was determined by observation of the decay at 890 nm in the absence as well as the presence of biphenyl in a 0.086F $\text{Li}\Phi_4\text{B}$ solution. In the absence of biphenyl we observe only reaction (6). In the presence of biphenyl (0.35 to $5.23 \times 10^{-4}\text{M}$) the decay, which is first order, becomes increasingly faster with increasing biphenyl concentration as biphenyl scavenges $(\text{Li}^+, e_{\text{S}}^{-})$ in competition with Li^+ . A plot of the pseudo first-order rate constants versus biphenyl concentration (at the fixed Li^+ concentration) is linear with slope $k_9 = (1.0 \pm 0.2) \times 10^{10} \text{M}^{-1}\text{sec}^{-1}$.

The rate constant for the first-order decay of biphenylide ion, observed at 630 nm, was found to be $(1.4 \pm 0.3) \times 10^5 \text{ sec}^{-1}$. This is an over-all rate constant for the decay which cannot, with the present data, be identified with a specific reaction in the sequence (9)-(11). This rate constant could also be estimated from observations, at 890 nm, of the formation of $\{(\text{Li}^+)_{2}, e_{\text{S}}^{-}\}$, a comparison which is of interest in testing the validity of the proposed reaction sequence. The value could not be accurately determined by simple direct kinetic analysis since a plateau in the rate curve was not well-defined because of the concurrent decay of $\{(\text{Li}^+)_{2}, e_{\text{S}}^{-}\}$. A good estimate of this formation rate constant was however obtained by measuring the time from the end of the pulse to the maximum of optical density, t_{max} , and using the following equation suitable for the case of consecutive first-order reactions²³:

$$t_{\text{max}} = \frac{1}{k_{\text{D}} - k_{\text{F}}} \ln \frac{k_{\text{D}}}{k_{\text{F}}} \left(1 + \frac{[\{(\text{Li}^+)_{2}, e_{\text{S}}^{-}\}]_0}{[\Phi_{2}^{-}]_0} - \frac{k_{\text{D}}}{k_{\text{F}}} \frac{[\{(\text{Li}^+)_{2}, e_{\text{S}}^{-}\}]_0}{[\Phi_{2}^{-}]_0} \right) \quad (12)$$

where the concentrations of the two transient species in equation (12) are determined at $t = 0$ after the pulse. Φ_{2}^{-} represents the biphenylide ion in either state of aggregation with Li^+ . k_{F} is the observed formation rate constant, and k_{D} is the measured first-order constant for the subsequent decay of $\{(\text{Li}^+)_{2}, e_{\text{S}}^{-}\}$ under our experimental conditions.

Graphical solution of equation (12) gives $k_{\text{F}} = (2.1 \pm 0.6) \times 10^5 \text{ sec}^{-1}$ in reasonable agreement with the value $1.4 \times 10^5 \text{ sec}^{-1}$ obtained from the decay of biphenylide ion. This agreement is supportive of the proposal that we are observing reactions (10) and (11).

Any quantitative analysis of the proposed sequence, (9)-(11), would require a good deal of additional data. However, the following

qualitative observation may be of interest. The rate constant for the appearance of the 890 nm band was independent of biphenyl concentration over the range 0.03 to 0.3 M. We infer from this that the reverse reaction (11r) is too slow to be observed on our time scale, which implies that $k_{11r} < 10^5 \text{M}^{-1} \text{sec}^{-1}$. This suggests an enormous difference in reactivity of anthracene and biphenyl as scavengers of $\{(Li^+)_2, e_s^-\}$, amounting to several orders of magnitude. The rate constant for the formation of the 890 nm band, k_F , was also found to increase with increasing $[Li \Phi_4B]$, which confirms that k_F is not to be identified with the elementary constant k_{11} , but must involve, as well, the other steps in the ionic aggregation process. Our primary interest at this stage, is in the observation that a higher ionic aggregate of e_s^- in THF, most likely $\{(Li^+)_2, e_s^-\}$ is formed, and is intermediate, in chemical stability between $(Li^+)_2\Phi_2^-$ and $(Li^+)_2An^-$.

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References

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Figure Legends

Figure 1. Spectrum of (Li^+, e_s^-) in THF at 25° obtained in solutions of: \bullet , LiClO_4 (0.035F); \square , LiCl (0.064F); and $+$, LiBr (0.12F). The absorption maximum is at 1175 nm with a molar extinction coefficient of 22,800 at the maximum and width at half-height of 6270 cm^{-1} . The line is calculated using a Gaussian curve on the low energy side of the maximum and a Lorentzian curve on the high energy side, and is not a best fit for the experimental points.

Figure 2. Absorption spectrum obtained at $t = 0$ following the pulse of a THF solution of $\text{Li}\Phi_4\text{B}$ (0.023F). The solid line is the spectrum of (Li^+, e_s^-) using the data contained in Figure 1, normalized to the experimental points, X, taken in the $\text{Li}\Phi_4\text{B}$ solution in the infrared region. The difference spectrum, \bullet , is proposed to be the dilithium-solvated electron triple ion, $\{(\text{Li}^+)_2, e_s^-\}$.

Figure 3. Absorption spectrum of the higher ionic aggregate proposed to be $\{(\text{Li}^+)_2, e_s^-\}$, determined with data obtained in $\text{Li}\Phi_4\text{B}$ solutions by recording the absorbance at the plateau region of the formation rate curve, when the formation of the band is complete: 0, 0.18F, \bullet , 0.1F, combined with the data obtained by difference in Figure 1, $+$. The absorption maximum is 890 nm, with a molar extinction coefficient of 5400 at this maximum.

