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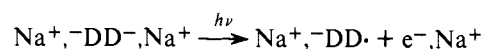
Dimerization of the Li, Na, K, and Cs Salts of Diphenylethylene Radical Anions and the Equilibria and Kinetics of Their Formation by Attachment of Electron–Cation Pairs. The Nature of Electron–Cation Aggregates

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Abstract: Flash photolysis of $\text{Cat}^+, \bar{\text{C}}(\text{Ph})_2\text{CH}_2\text{CH}_2\bar{\text{C}}(\text{Ph})_2$, $\text{Cat}^+ = \text{Cat}^+, -\text{DD}^-, \text{Cat}^+$, results in electron photoejection and yields $\text{C}(\text{Ph})_2\text{CH}_2^{\cdot-}, \text{Cat}^+ = \text{D}^{\cdot-}, \text{Cat}^+$, the unreduced hydrocarbon D, and the electron–cation pair e^-, Cat^+ . The latter two products react and form $\text{D}^{\cdot-}, \text{Cat}^+$ radical anions: $\text{D} + e^-, \text{Cat}^+ \rightleftharpoons \text{D}^{\cdot-}, \text{Cat}^+$ (k_1, k_{-1}). The radical anions combine and reform the original dimer, $\text{Cat}^+, -\text{DD}^-, \text{Cat}^+$: $2\text{D}^{\cdot-}, \text{Cat}^+ \rightarrow \text{Cat}^+, -\text{DD}^-, \text{Cat}^+$ (k_2). Kinetic studies of the reactions ensuing after a flash allow us to determine k_1, k_{-1}, k_2 , and the equilibrium constant $K_1 = k_1/k_{-1}$. Their values depend on the cations' nature, namely, for Li, $k_1 = 0.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, $k_{-1} = 15 \text{ s}^{-1}$, $K_1 = 6 \times 10^4 \text{ M}^{-1}$, and $k_2 = 1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$; for Na, $k_1 = 1.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, $k_{-1} = 33 \text{ s}^{-1}$, $K_1 = 6 \times 10^5 \text{ M}^{-1}$, and $k_2 = 3.5 \times 10^8$; for K, $k_1 = 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $k_{-1} \leq 20 \text{ s}^{-1}$, $K_1 \geq 2 \times 10^8 \text{ M}^{-1}$, and $k_2 = 10 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$; and for Cs, $k_1 \gg 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $K_1 \gg 10^8 \text{ M}^{-1}$, and $k_2 = 30 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The significance of these findings is discussed. The striking increase in k_1 and K_1 as the cation is varied from Li^+ to Cs^+ is noteworthy and may shed light on the nature of electron–cation aggregate.

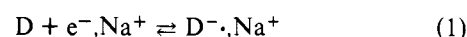
The results of our studies of flash photolysis of the sodium salt of the dimeric dianions of 1,1-diphenylethylene in tetrahydrofuran¹ ($\text{Na}^+, \bar{\text{C}}(\text{Ph})_2\text{CH}_2\text{CH}_2\bar{\text{C}}(\text{Ph})_2\text{Na}^+ = \text{Na}^+, -\text{DD}^-, \text{Na}^+$) demonstrated that the absorption of visible light results in electron photoejection



and not in photodissociation of the dimer into two radical anions:



The dimeric radical anions $\text{Na}^+, -\text{DD}^{\cdot-}$ decompose within $\sim 1 \mu\text{s}$ into the hydrocarbon D and its radical anion $\text{D}^{\cdot-}, \text{Na}^+$. Whenever the excess of D is large, electron capture is rapid and virtually quantitative



and the simple dimerization



is observed in the dark period, i.e., the reciprocal of $\Delta(\text{OD})$ monitored at any wavelength is linear with time.

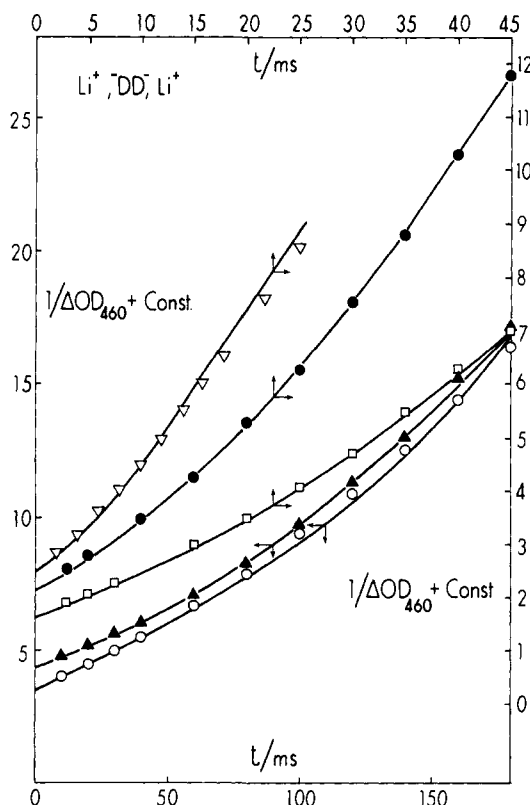


Figure 1. Plots of $1/\Delta OD_{460}$ vs. time in the photolysis of $\text{Li}^+, \text{-DD}^-, \text{Li}^+$: ∇ , run 16, exc. $D = 260 \times 10^{-6} \text{ M}$, const = 0; \bullet , run 12, exc. $D = 100 \times 10^{-6} \text{ M}$, const = 1; \square , run 4, exc. $D = 50 \times 10^{-6} \text{ M}$, const = 0; \blacktriangle , run 13, exc. $D = 17 \times 10^{-6} \text{ M}$, const = 2; \circ , run 14, exc. $D = 15 \times 10^{-6} \text{ M}$, const = 0. The lines are the theoretical ones, and well fit the experimental points.

Kinetics of the re-formation of the dimers becomes more complex when the excess of D is low. The available data show² that not all of the ejected electrons are recombined with the hydrocarbon under such conditions. The reaction is governed then by the reversible step 1 and the irreversible step 2. Kinetics of such a process was solved² on the assumption of stationary concentration of D^- , Na^+ and the results allowed us to determine the rate constants of electron attachment, k_1 , and detachment, k_{-1} .

This work was expanded now to the Li^+ , K^+ , and Cs^+ salts. We improved also our calculations, abandoning the stationary-state approximation and computer solving the two simultaneous differential equations. The nature of the cation greatly affects the rates of the dimerization, of the electron-cation pairs attachment to 1,1-diphenylethylene, as well as the rate of their detachment. These results shed some light on the nature of the electron-cation pairs.

Experimental Section

Preparation and purification of 1,1-diphenylethylene was reported elsewhere.³ The hydrocarbon was free of benzophenone and dibenzyl. Its reduction to the dimeric dianions was performed in tetrahydrofuran on a high vacuum line using mirrors of the respective metals as the reducing agents (specially purified chunks of lithium having a shiny surface free of oxides were utilized in the preparation of the lithium salt). Salts sharing a common cation with the dimeric dianions, namely, $\text{Li}^+, \text{BPh}_4^-, \text{Na}^+, \text{BPh}_4^-, \text{K}^+, \text{BPh}_3\text{-CN}^-$, and $\text{Cs}^+, \text{BPh}_3\text{-CN}^-$, were added to the solutions of the dianion's salt to prevent their dissociation into $\text{Cat}^+, \text{-DD}^-$ or -DD^- . The technique of the dianion's dilution to $\sim 10^{-6} \text{ M}$ concentration, and the details of the flash-photolytic procedure, were described previously.⁴ Only visible light reached the 10-cm long cylindrical cell containing the solution to be photolyzed. The spectra of the dimeric dianion's salts were recorded on a Beckman Acta VI spectrometer and the molar absorbances at

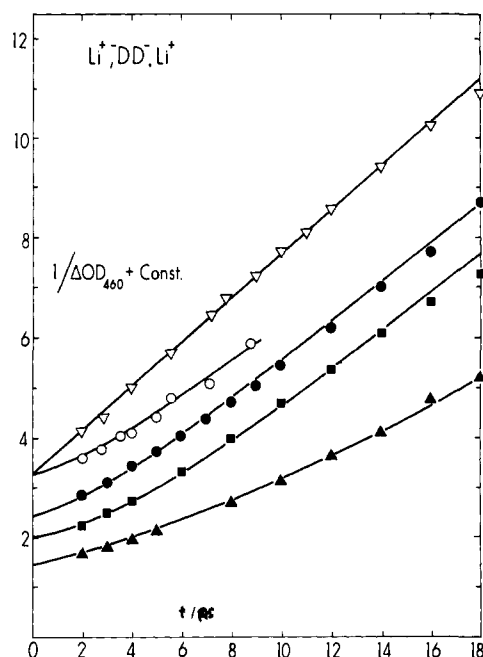


Figure 2. Plots of $1/\Delta OD_{460}$ vs. time in the photolysis of $\text{Li}^+, \text{-DD}^-, \text{Li}^+$: ∇ , run 11, exc. $D = 2000 \times 10^{-6} \text{ M}$, const = 0; \circ , run 15, exc. $D = 710 \times 10^{-6} \text{ M}$, const = 2; \bullet , run 10, exc. $D = 580 \times 10^{-6} \text{ M}$, const = 0; \blacksquare , run 9, exc. $D = 400 \times 10^{-6} \text{ M}$, const = 0; \blacktriangle , run 8, exc. $D = 180 \times 10^{-6} \text{ M}$, const = 0. The lines are the theoretical ones, and well fit the experimental points.

the respective λ_{max} were determined by converting $\text{Cat}^+, \text{-DD}^-, \text{Cat}^+$ into equivalent amounts of perylene salts. The spectra and molar absorbances of the latter are known (λ_{max} 578 nm, $\epsilon 5.9 \times 10^4$). The λ_{max} of $\text{Cat}^+, \text{-DD}^-, \text{Cat}^+$ is at 460 nm ($\epsilon 5.4 \times 10^4$) for the Li^+ , 470 nm ($\epsilon 5.2 \times 10^4$) for the Na^+ , 475 nm ($\epsilon 5.2 \times 10^4$) for the K^+ , and 475 nm ($\epsilon 5.4 \times 10^4$) for the Cs^+ salts, respectively.

After each flash the investigated systems eventually returned to their initial state; at any wavelength the optical density measured long after a flash was identical with its initial value determined before a flash. In most runs the reaction was monitored at λ_{max} of the dimeric dianions.

The stock solution was relatively concentrated, about 10^{-2} – 10^{-3} M in $\text{Cat}^+, \text{-DD}^-, \text{Cat}^+$, and in addition it contained the desired amount of unreduced hydrocarbon, D. In the process of distillation of the solvent from the storage vessel into the optical cell the hydrocarbon, but not the dianions, was distilled, too. The distilled-over hydrocarbon formed "the excess of D" and its concentration was determined spectrophotometrically (λ_{max} 248 nm, $\epsilon 1.09 \times 10^4$). Thereafter, a drop of the stock solution was transferred into the cell to attain $\sim 10^{-6} \text{ M}$ solution of $\text{Cat}^+, \text{-DD}^-, \text{Cat}^+$. Some additional D was transferred with this drop; however, this hardly affected "the excess of D" because its concentration in the stock solution was lower than that of the dianions.

Results

The dark reaction in the Li or Na systems was monitored at λ_{max} of the respective dimeric dianions. The results are presented in Figures 1–3 as a set of points giving the reciprocal of optical density difference, $1/\Delta(\text{OD})$, as a function of time. The experimental points define curves of increasing curvature for decreasing concentration of the excess of D.

In contrast, when K or Cs salts were photolyzed the plots of $1/\Delta(\text{OD})$ vs. time were linear, their slopes virtually independent of the concentration of the excess of D. At constant [D] the ratios of the slopes obtained from experiments performed at different wavelength were constant, and in this respect the K and Cs salts differ again from those of Li or Na.

In all the systems the dark reaction was faster in the absence of the boride salts than in their presence. Apparently the free D^- radical anions dimerize faster than their D^-, Cat^+ pairs.

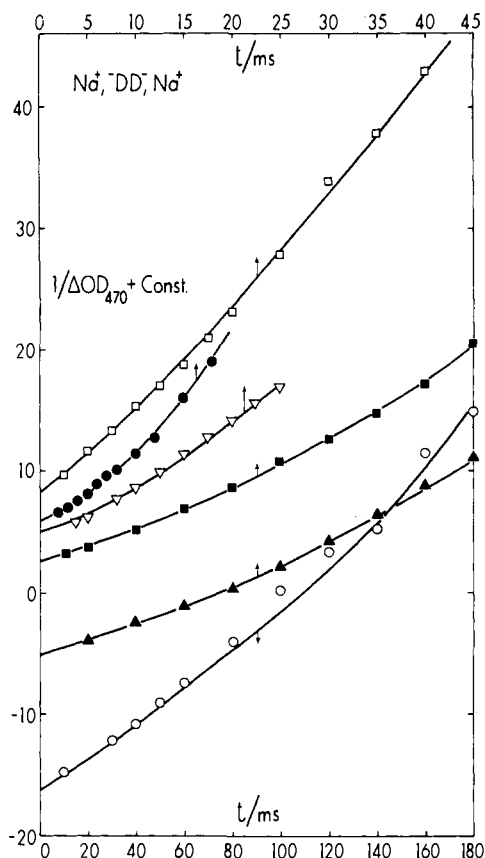
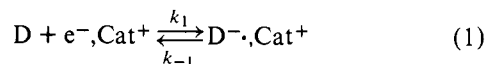


Figure 3. Plots of $1/\Delta OD_{470}$ vs. time in the photolysis of $\text{Na}^+, -\text{DD}^-, \text{Na}^+$: \square , run 34, exc. $D = 24.4 \times 10^{-6} \text{ M}$, const = 5; \bullet , run 33, exc. $D = 13.3 \times 10^{-6} \text{ M}$, const = 3; ∇ , run 35, exc. $D = 8.0 \times 10^{-6} \text{ M}$, const = 1; \blacksquare , run 36, exc. $D = 4.7 \times 10^{-6} \text{ M}$, const = 0; \blacktriangle , run 37, exc. $D = 2.7 \times 10^{-6} \text{ M}$, const = -9; \circ , run 32, exc. $D = 0.9 \times 10^{-6} \text{ M}$, const = -25. The lines are the theoretical ones and well fit the experimental points.

Kinetics of the Reaction Observed in the Li and Na Systems.

Variations of OD at λ_{max} of the $\text{Cat}^+, -\text{DD}^-, \text{Cat}^+$ arise entirely from changes in the concentration of the dimeric dianions, provided that neither D^-, Cat^+ nor e^-, Cat^+ absorbs in this region. In that case $\Delta(\text{OD})$ at $\lambda_{\text{max}} \sim$ concentration of the photolyzed $\text{Cat}^+, -\text{DD}^-, \text{Cat}^+$. Denoting the momentary concentrations of the bleached dianions and of D^-, Cat^+ by $1/2x$ and y , respectively, we find the concentrations of e^-, Cat^+ to be $x - y$ and that of D formed by the photolysis to be equal to e^-, Cat^+ . The concentration of excess of D present before a flash is denoted by β , and hence the total concentration of D at time t is $\beta + x - y$.

The mechanism proposed for the dark reaction is



leading to the equations

$$-dx/dt = k_2 y^2$$

$$dy/dt = k_1(\beta + x - y)(x - y) - k_{-1}y - k_2 y^2$$

Values of $1/2x_0$ and y_0 , the initial concentrations of the bleached $\text{Cat}^+, -\text{DD}^-, \text{Cat}^+$ and of the formed D^-, Cat^+ , are needed for numerical solution of the differential equations. Extrapolation of the experimental data to zero time provides x_0 ; however, the value of y_0 has to be assumed. Had the flash been instantaneous and the onset of our monitoring coinciding with the flash time, then y_0 would be equal to $1/2x_0$ because 1

mol of D^-, Cat^+ and of D is formed for each mol of the bleached $\text{Cat}^+, -\text{DD}^-, \text{Cat}^+$. This is assumed for the Li system since the electron capture, $\text{D} + \text{e}^-, \text{Li}^+ \rightarrow \text{D}^-, \text{Li}^+$, is relatively slow. A somewhat lower value of y_0 was chosen for the sodium system. Fortunately, variation of the y_0/x_0 ratio negligibly affects the results when β is large, and the deviations are still marginal as long as β/x_0 is not smaller than 2 or 3.

The values of k_2 are derived from experiments performed with large excess of D(β); under these conditions $1/\Delta(\text{OD})$ is linear with time, the slope of the line giving k_2 . It is worth noting that β needed to ensure the linearity of plots of $1/\Delta(\text{OD})$ vs. time is substantially larger for the Li system than for the Na one. Using a computer program with k_1 and k_{-1} as adjustable parameters we find their values by matching the calculated curves to the experimental points. The results are summarized in Tables I and II and the degree of agreement may be judged from inspection of Figures 1-3, or it is indicated by the $R\%$ values given in the last columns of the tables. These represent the relative mean square-roots deviations of the calculated and observed $1/x$ values in each run. The reported k_1 's and k_{-1} 's are reliable within 50%.

Kinetics of Dimerization in the K^+ and Cs^+ Systems. For the excess of D, denoted by β , greater than $1 \times 10^{-6} \text{ M}$ the plots of $1/\Delta(\text{OD})$ vs. time are linear for both systems. All the e^-, Cat^+ pairs are captured by D before the reaction is monitored and the D^-, Cat^+ 's are the sole transient intermediates present during the period of our observations. From these experiments only the k_2 values can be deduced and these are listed in Table III.

In one set of experiments performed with the potassium salt, β was smaller than $0.6 \times 10^{-6} \text{ M}$ and the plot of $1/\Delta(\text{OD})$, 475 nm vs. time showed then a definite curvature. Assuming that $\beta = 0.6 \times 10^{-6} \text{ M}$, the values of $k_1 \sim 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{-1} = 20 \text{ s}^{-1}$ were deduced. The former constant is only slightly affected by the value of β , while the latter one decreases with decreasing β . Hence, $K_1 \geq 2 \times 10^8 \text{ M}^{-1}$.

The incompleteness of the electron attachment in these experiments is revealed by the oscilloscope tracers shown in Figure 4 (monitored at 850 nm) and Figure 5 (monitored at 390 nm). The fast decay of the transient seen in Figure 4 is attributed to the initial e^-, K^+ attachment to D and the subsequent slow decay to the effect of D^-, K^+ dimerization on the electron attachment equilibrium. At this wavelength the absorbance of e^-, K^+ is strong ($\epsilon 2.5 \times 10^4$) and that of D^-, K^+ is weaker ($\epsilon 0.6 \times 10^4$).

At 390 nm the absorbance of D^-, K^+ ($\epsilon \sim 1.2 \times 10^4$) is twice as strong as $1/2$ of the absorbance of $\text{K}^+, -\text{DD}^-, \text{K}^+$, while the absorbance of e^-, K^+ is negligible. The increase of the absorbance during the first 250 μs revealed by Figure 5 demonstrates the initial rapid formation of D^-, K^+ , and its following decrease is due to the dimerization that consumes more D^-, K^+ than are formed by the electron attachment.

Quantitative treatment of these data is difficult but semi-quantitative calculations support our estimates of k_1 and k_{-1} .

In the Cs^+ system the plots of $1/\Delta(\text{OD})$ vs. time did not show any deviation from linearity even at the lowest practically attainable concentrations of the excess of D. It seems therefore that the reaction $\text{D} + \text{e}^-, \text{Cs}^+ \rightleftharpoons \text{D}^-, \text{Cs}^+$ is characterized by $k_1 > 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $K_1 \gg 10^8 \text{ M}^{-1}$.

Discussion

Our final results, summarized in Table III, lead to the following conclusions.

(1) The dimerization constant of D^-, Cat^+ pairs depends on the cation's nature, being the largest for the Cs^+ pairs and the smallest for the Li^+ . Hückel calculations show that the density of the odd electron in D^- radical anion is the greatest

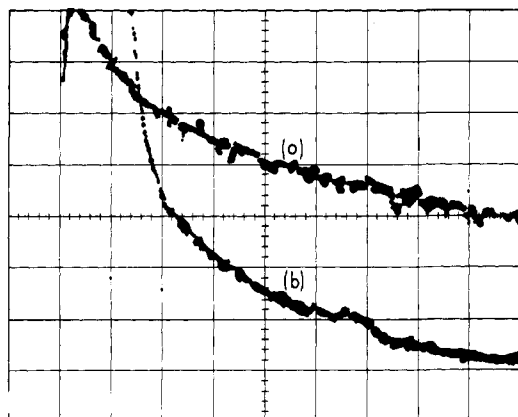


Figure 4. Oscilloscope tracers in flash photolysis of $K^+, -DD^-, K^+$ monitored at λ 850 nm. Curve (a), time scale 100 μ s/div; vertical scale 20 mV/div. Curve (b), time scale 1 ms/div; vertical scale 20 mV/div.

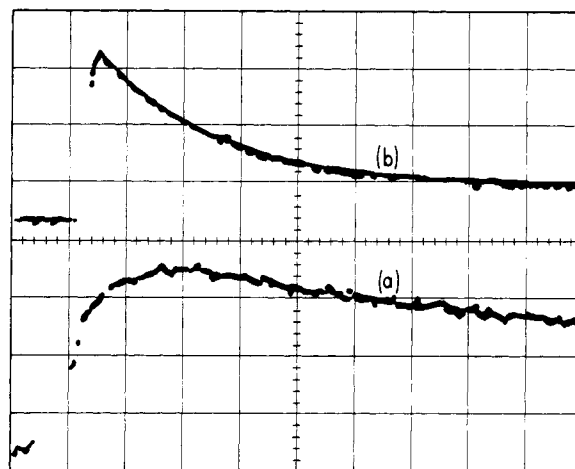


Figure 5. Oscilloscope tracers in flash photolysis of $K^+, -DD^-, K^+$ monitored at λ 390 nm. Curve (a), time scale 100 μ s/div; vertical scale 20 mV/div. Curve (b), time scale 1 ms/div; vertical scale 20 mV/div.

Table I. Photolysis of $Li^+, -DD^-, Li^+$ in THF with Added Li^+, BPh_4^- .

run	$10^6[D]/M$	$10^6[-DD^-]/M$	$10^{-6}k_1$ M s	k_{-1} s	$10^{-8}k_2$ M s	$R, \%^a$
11	2000	2.7	≥ 1.1	≤ 20	1.2	1.9
15	710	2.4	0.81	16	1.2	0.6
10	580	1.8	0.84	15	1.2	0.9
9	405	2.2	0.81	20	1.2	0.5
16	260	1.4	0.81	20	1.2	1.2
8	180	2.9	0.81	14	1.2	0.8
12	100	2.6	1.05	16	1.2	0.4
4	50	1.1	1.08	10	1.2	0.8
13	17	1.7	0.97	10	1.1	0.4
14	15	1.1	1.03	10	1.2	0.6
		average	0.93 ± 0.13	15 ± 4	$K_1 = 6 \times 10^4$	

^a R is defined as $\{\sum[(X_{exp} - X_{cal})/X_{exp}]^2\}^{1/2}/n$ and measures the reliability of the fit of the experimental points to the calculated curve.

Table II. Photolysis of $Na^+, -DD^-, Na^+$ in the THF with Added Na^+, BPh_4^- .

run	$10^6[D]/M$	$10^6[-DD^-]/M$	$10^{-7}k_1$ M s	k_{-1} s	$10^{-8}k_2$ M s	$R, \%^a$
34	24.4	1.4	1.6	40	3.1	2.7
33	13.3	1.7	1.9	40	3.5	1.6
35	8.0	1.9	1.8	40	4.0	1.1
36	4.7	2.6	1.9	33	3.5	0.5
37	2.7	1.4	2.0	20	4.0	0.3
32	0.9	1.0	2.0	26	4.0	1.1
		average	1.9 ± 0.2	33 ± 9	$K_1 = 6 \times 10^5$	

^a R is defined as $\{\sum[(X_{exp} - X_{cal})/X_{exp}]^2\}^{1/2}/n$ and measures the reliability of the fit of the experimental points to the calculated curve.

Table III. Effect of Cation on the Rates and Equilibria of Electron Attachment and on the Rate of Dimerization of D^-, Cat^+ .

system	k_1 M s	k_{-1} s	K_1 M	k_2 M s
Li^+	0.9×10^6	15	6×10^4	1.2×10^8
Na^+	1.9×10^7	33	6×10^5	3.5×10^8
K^+	4×10^9	≤ 20	$\geq 2 \times 10^8$	$10. \times 10^8$
Cs^+	$> 10^{10}$		$\gg 10^8$	$30. \times 10^8$

on the CH_2 carbon, implying that the cation is associated with that carbon atom. However, in their aggregates with $-DD^-$ the cations are associated with the $-CPh_2$ groups and hence they have to move from one position to the other during the act of dimerization. The observed gradation, $Cs^+ > K^+ > Na^+ > Li^+$, suggests that the aggregates are tight (not solvent separated) and then the reported gradation is expected because Li^+ is the most strongly bonded while Cs^+ is the least strongly bonded. This is, e.g., the trend observed in anionic polymerization of styrene carried out in dioxane⁵ where the reaction is due to tight pairs.

The high rate of dimerization makes insignificant the contribution of the loose pairs to the overall process. In this respect the dimerization differs from anionic polymerization of styrene carried out in tetrahydrofuran. Dimerization of free $D^{\cdot-}$ ions seems to be even faster than that of $D^{\cdot-}, Cat^+$ because the reaction proceeds slower in the presence of salts that depress the ionic dissociation.

(2) The most striking is the effect of the cation's nature on the rate and equilibrium of the electron attachment process. The nature of $e^{\cdot-}, Cat^+$ is still unknown. Although our symbolism implies that the solvated electron forms an ion pair with a presumably solvated cation, other structures are also possible, e.g., an expanded alkali atom.⁶⁻⁸ In fact, our present results favor the latter suggestion.¹³ Conversion of expanded atom into cation with simultaneous transfer of an electron to the hydrocarbon acceptor may be affected by the ionization potential of the donor. Provided that the ionization potentials of expanded atoms follow the same trend as the ionization potentials of gaseous alkali atoms, the observed trend reported here for k_1 could be rationalized.

Finally, the slowness of the electron capture process in the Li and Na systems calls for some comments. The slowness of capture of e^- , Na^+ pairs by D was confirmed by utilizing pulse-radiolysis technique. These experiments were performed in the laboratory of Professor Dorfman, using his standard technique, with the help of Dr. B. Bockrath, and we thank them for their cooperation. The results showed that the attachment constant of e^- , Na^+ had to be $<10^7 M^{-1} s^{-1}$. However, the virtually irreversible capture of e^- , Na^+ by other aromatic hydrocarbons is fast and approaches the diffusion-controlled limit.^{9,10} Reversible electron capture was reported by Bøddeker et al.¹¹ for the system benzene in liquid ammonia-methylamine mixtures at $-78^\circ C$, and by Farhataziz and Perkey¹² for biphenyl in liquid ammonia at room temperature. In spite of its reversibility the latter electron capture process was found to be very rapid, its bimolecular rate constant greater than $10^{10} M^{-1} s^{-1}$. However, this reaction probably refers to the solvated electron and not to e^- , Na^+ aggregate.

It is probable that capture by biphenyl of the electron-sodium pair is reversible even in tetrahydrofuran; nevertheless, the rate of capture is still fast.^{9b} The slowness of the capture of e^- , Na^+ and e^- , Li^+ by 1,1-diphenylethylene is therefore puzzling.

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Appendix

The electron photoejection from Cat^+ , $^-DD^-$, Cat^+ could lead to some intermediate, e.g., a cyclobutane derivative, that would become converted back into the dianion after acquiring the ejected electrons. Such a suggestion might account for the peculiarities observed in the absence of D. To demonstrate the direct or indirect dissociation of $^-DD^-$ into D^- radical anions, the following experiments were performed.

Starting with C_6D_5Br and acetophenone we prepared $(C_6H_5)(C_6D_5)C=CH_2$ that was converted into $^-DD^-$ possessing 10 deuterons. Its solution was mixed with the solution of the nondeuterated dimeric dianion and exposed to *one flash*. Thereafter the products were protonated by adding methanol, and the hydrocarbons were isolated and analyzed by mass spectroscopy.

The mass spectra of nondeuterated and deuterated tetraphenylbutane follow: $C_{28}H_{24}$, m/e 362 (73.3%), 363 (23.0%), 364 (3.7%); $C_{28}H_{14}D_{10}$, m/e 371 (5.6%), 372 (68.5%), 373 (21.81%), 374 (4.1%).

The mass spectra of the mixture follow:

m/e 362, 363, 364, 366, 367, 368, 369, 371, 372, 373, 374 before the flash

% 40.6, 13.2, 2.1, 0, 0.8, 0.2, 0, 2.2, 29.3, 10.1, 1.5 after a flash

% 31.2, 9.7, 1.6, 0.8, 20.2, 6.1, 1.1, 1.5, 20.3, 6.3, 1.1.

The photolysis bleached 57% of the dimers which eventually were re-formed. The ratios of the nondeuterated, half-deuterated (five deuterons), and fully deuterated (ten deuterons) tetraphenylbutanes calculated from the mass spectra are 0.425:0.282:0.292. The ratio of the nondeuterated to deuterated butane in the nonphotolyzed mixture was 0.57:0.43 = $(1-p):p$. Hence, the fraction of f of photolyzed hydrocarbons calculated from

$$(1-f)p + fp^2 = 0.425 \text{ is } f = 0.55$$

$$2fp(1-p) = 0.282 \text{ is } f = 0.57$$

$$(1-f)(1-p) + f(1-p)^2 = 0.292 \text{ is } f = 0.60$$

compared to that determined from the degree of bleaching $f = 0.57$. It is concluded that all the photolyzed $^-DD^-$ yielded D^- radical anions which recombined randomly.

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- (13) The problem may be reduced to the question: Is an electron moving in a field concentric or eccentric with the cation's nucleus?