Disproportionation of the Lithium Salt of Tetraphenylethylene Radical Anions in THF. Equilibrium and Kinetic Study

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Abstract: The behavior of the lithium salts of tetraphenylethylene radical anions ($T\cdot^-,Li^+$) and dianions ($T^{2-},2Li^+$) in THF was investigated. The spectroscopic study revealed a strong absorption band at 385 nm in the spectrum of $T^{2-},2Li^+$ which does not appear in the spectrum of $T^{2-},2Na^+$. This band is tentatively attributed to charge-transfer transition involving a partially desolvated and tightly bound Li^+ ion. The dissociation of $T\cdot^-,Li^+$ and $T^{2-},2Li^+$ was studied by conductometric method within a temperature range of −70 to +20°, and the disproportionation equilibria for the reactions $2T\cdot^-,Li^+ \rightleftarrows T + T^{2-},2Li^+$ (1) and $T\cdot^- + T\cdot^-,Li^+ \rightleftarrows T + T^{2-},Li^+$ (2) were investigated spectrophotometrically over the same temperature range. Finally, the kinetics of reactions 1 and 2 were investigated by applying the flash-photolytic technique. The various features of the lithium system were compared with those pertaining to the corresponding sodium system. The differences and the similarities were discussed.

Disproportionation of the sodium salt of tetraphenylethylene radical anion was investigated previously in our laboratory.[1,2] Since the lithium salts often behave differently from those of the other alkali metals, we decided to extend these studies to the lithium tetraphenylethylene radical anion, $T\cdot^-,Li^+$. The disproportionation was investigated in THF over temperatures ranging from −70 to 20° and the results show that in several respects this reaction of lithium salts substantially differs from that involving sodium cations.

The spectra of THF solutions of lithium and sodium salts of $T\cdot^-$ are virtually identical, their shape being shown in Figure 1. Two flat absorption maxima appear at 495 and 660 nm and the respective absorption coefficients are given in Table I. In contrast, surprisingly large differences appear when the spectrum of the lithium salt of tetraphenylethylene dianion, $T^{2-},2Li^+$, is compared with that of the sodium salt. The absorbance at λ_{max} = 485 nm, pronounced for the latter, is drastically lower and shifted by 10 nm toward red in the spectrum of the former, namely, the absorption coefficient, being 3.7×10^4 for $T^{2-},2Na^+$, is reduced to 2.64×10^4 for $T^{2-},2Li^+$. In addition, a strong new absorption band appears at λ_{max} = 385 nm in the spectrum of the lithium salt of the dianion ($\epsilon = 2.98 \times 10^4$), its position being close to that of the characteristic band of the radical anion (λ_{max} = 375 nm, $\epsilon \sim 2.35 \times 10^4$). However, it is not residual radical anion that causes this absorption because the esr signal obtained from a 10^{-3} *M* solution of $T^{2-},2Li^+$ in THF shows that the concentration of paramagnetic species is lower than 10^{-6} *M*. We proved also that the 385-nm band cannot be attributed to any impurities, contrary to the suggestion by Garst,[3] since it appears when LiCl is added to a solution of $T^{2-},2Na^+$ which exhibits its usual spectrum.

The relative intensities of the 385- and 495-nm absorption bands of $T^{2-},2Li^+$ are not affected by dilution from 5×10^{-3} to 1×10^{-5} *M*, nor by temperature varying from −70 to 20°. The addition of Li^+,BPh_4^- also had no effect on the spectrum; however, the intensity of the 385-nm band gradually diminishes on the addition of increasing amounts of tetraglyme. These spectral changes are under investigation and will be reported elsewhere.

The spectra of all the pertinent species are shown in Figure 1 and the required absorption coefficients are listed in Table I. We determined also their temperature dependence corrected for the contraction of volume. The absorption coefficients of the radical anion are virtually temperature independent, while those of the dianion increase by ~10% as the solution is cooled from 20 to −60°.

Conductance Studies

At least two distinct reactions participate in the disproportionation of the $T\cdot^-,Li^+$ radical anions, namely

$$2T\cdot^-,Li^+ \rightleftarrows T + T^{2-},2Li^+ \qquad (1)$$

and

$$T\cdot^- + T\cdot^-,Li^+ \rightleftarrows T + T^{2-},Li^+ \qquad (2)$$

Reaction 3, $2T\cdot^- \rightleftarrows T + T^{2-}$, can be omitted because the concentration of the free T^{2-} dianions is vanishingly small under our experimental conditions. The treatment of such a system requires the knowledge of the pertinent dissociation constants

$$T\cdot^-,Li^+ \rightleftarrows T\cdot^- + Li^+ \qquad K_{D1}$$

and

$$T^{2-},2Li^+ \rightleftarrows T^{2-},Li^+ + Li^+ \qquad K_{D2}.$$

and these were obtained from conductance studies using the technique described elsewhere.[4,5] The concentrations of the organic ions were determined spectrophotometrically at room temperature and corrected for contraction of volume at lower temperatures. A 60-fold excess of the unreduced parent hydrocarbon was added to the solutions of $T\cdot^-,Li^+$ to suppress the formation of the T^{2-} dianions, whereas the solutions of the dianions were kept in contact with metallic lithium to ensure the reduction of any residual radical anions to dianions. The absence of radical anions in the solutions of $T^{2-},2Li^+$ was ascertained by esr technique.

The conductance studies covered the range of concentrations from 1×10^{-5} to 2×10^{-4} *M*, and all the plots of $1/\Lambda$ *vs.* $c\Lambda$ were linear in this range. The results led to the values of Λ_0 and K_{Diss} collected in Table II. The Walden products, listed in the third column, show the usual slight decrease with decreasing temperature.

The van't Hoff plots for K_{D1} and K_{D2} are shown in Figure 2. They are linear and the relevant values of ΔH_{D_1} and ΔH_{D2} are low, *viz.*, −0.9 and −0.8 kcal/mol, respectively. This implies that in either aggregate the dissociating Li^+ ion is extensively solvated over the whole temperature range; *i.e.*, it is loosely bonded even to the dianion.

In this respect the $T^{2-},2Li^+$ aggregate again substantial-

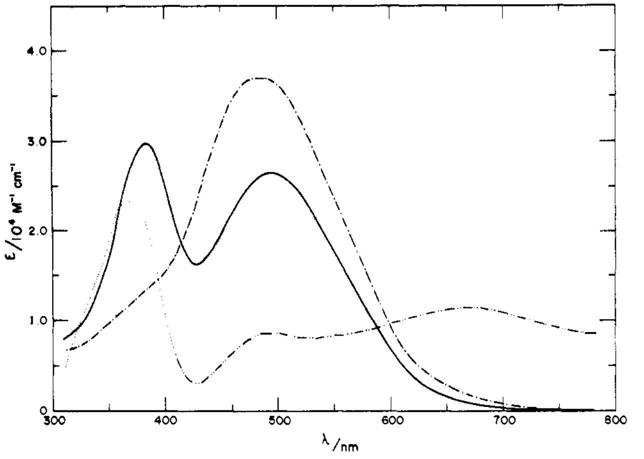

Figure 1. Absorption spectrum of tetraphenylethylene dianions and radical anions; (—) T^{2-},$2Li^+$; (- - -) T^{2-},$2Na^+$; (• • •) and (- • • •) $T^{\cdot -}$,Li^+ and $T^{\cdot -}$,Na^+.

Table I. Decimal Absorption Coefficients ($\epsilon \times 10^{-4}$) in THF at 20° [a]

	λ, nm					
Species	309	375	385	495	660	700
T	*1.46*	0.34	0.008			
$T^{\cdot -}$, Li^+	0.43	*2.35*	2.20	*0.85*	*1.13*	1.08
T^{2-}, $2Li^+$	0.80	2.85	*2.98*	*2.64*	0.11	0.037

[a] The italic values correspond to absorption coefficients at λ_{max} of the respective species.

ly differs from T^{2-},$2Na^+$. The van't Hoff plot for the latter salt shows a significant curvature, and at ambient temperature ΔH_{D2} is −7.2 kcal/mol; *i.e.*, the dissociating sodium ion is then tightly bonded to T^{2-} and to a large extent desolvated. At lower temperatures the T^{2-},$2Na^+$ changes from a tight aggregate to a loose one, its dissociation constant greatly increases, and $-\Delta H_{D2}$ decreases to about 0.9 kcal/mol. Therefore, at ambient temperature the ratio K_{D1}/K_{D2} is large for T^{2-},$2Na^+$ (about 100) but relatively small (about 10) for T^{2-},$2Li^+$.

Table II. Conductance Data in THF [a]

Temp, °C	Λ_0, Ω^{-1} cm^2 mol^{-1}	$\eta \times \Lambda_0$	slope = $1/\Lambda_0^2 K_D$	K_D, 10^{-6} *M*
		$T^{\cdot -}$, Li^+		
20	75	0.366	3.29	54
10	67	0.363	3.82	58
0	59	0.359	4.57	63
−10	52	0.359	5.58	66
−20	45.5	0.359	6.72	72
−30	39.0	0.357	8.17	80
−40	32.8	0.353	10.4	89
−50	27.5	0.352	13.8	96
−60	22.5	0.349	20.0	98
−70	18.0	0.344	30.5	101
		T^{2-}, $2Li^+$		
20	125	0.610	14.0	4.6
10	112	0.607	16.7	4.8
0	100	0.608	20.2	5.0
−10	88	0.607	24.7	5.2
−20	76.5	0.605	30.5	5.6
−30	65	0.595	38.0	6.2
−40	54.5	0.586	50.5	6.7
−50	45.5	0.582	70.0	6.9
−60	37.5	0.581	102	7.1
−70	28.5	0.544	153	8.0

[a] The limiting conductance is larger for the T^{2-},Li^+ + Li^+ system than $T^{\cdot -}$ + Li^+ and the same relation was found for the sodium salts. We do not offer at present any explanation for these findings.

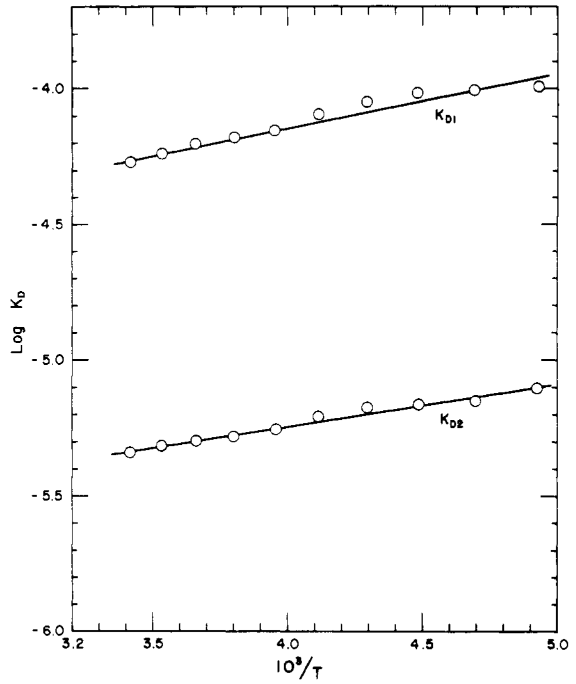

Figure 2. Van't Hoff plot of the dissociation constants K_{D1} and K_{D2}.

Determination of the Equilibrium Constants of the Disproportionation

As remarked in the preceding section, two equilibria govern the disproportionation, *viz.*

$$2T^{\cdot -}, Li^+ \rightleftarrows T + T^{2-}, 2Li^+ \qquad K_1$$

$$T^{\cdot -} + T^{\cdot -}, Li^+ \rightleftarrows T + T^{2-}, Li^+ \qquad K_2$$

The apparent equilibrium constant, K_{ap}, defined as

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

is related to K_1 and K_2 through the equations[1]

$$K_{ap} = K_1(1 + K_{D2}/[Li^+])/(1 + K_{D1}/[Li^+])^2$$

and

$$K_1/K_2 = K_{D1}/K_{D2}$$

Here $[T^{2-}_{total}] = [T^{2-},2Li^+] + [T^{2-},Li^+]$, $[T^{\cdot -}_{total}] = [T^{\cdot -},Li^+] + [T^{\cdot -}]$, and [T] and $[Li^+]$ denote the concentrations of the unreduced tetraphenylethylene and of the free Li^+ ions, respectively.

It is assumed that the λ_{max} and the respective absorption coefficients of $T^{\cdot -}$,Li^+ and $T^{\cdot -}$ are identical, an assumption supported by the temperature invariance of their spectrum. A similar assumption pertains to T^{2-},$2Li^+$ and T^{2-},Li^+, the latter being justified by the invariance of the spectrum to dilution. On this basis $[T^{\cdot -}_{total}]$ and $[T^{2-}_{total}]$ in the investigated mixtures were determined from the absorbances at 495 and 660 or 700-nm, respectively, using the absorption coefficients given in Table I.

The concentration of the unreduced hydrocarbon was determined from the absorbance at 309 nm. The results were checked through the relation $\{[T] + [T^{\cdot -}_{total}] + [T^{2-}_{total}]\}/\{[t^{\cdot -}_{total}] + 2[T^{2-}_{total}]\}$ = const.

The solutions to be investigated were prepared by complete reduction of a known amount of T in THF and thereafter by adding to it a weighed and vacuum sublimed amount of T enclosed in an ampoule equipped with a breakseal. Thus, the total amounts of T, in whatever form, and of Li^+ were predetermined by this procedure. All these operations were performed on a vacuum line in all glass equipment.

Three different stock solutions were prepared and these could be diluted, without introducing any additional solvent, by adopting the technique described by Bhattacharyya, *et al.*[4] At each stage of dilution the concentrations of the reagents were determined spectrophotometrically at 25° and thereafter the solution was progressively cooled and the concentrations redetermined at chosen temperatures. Finally, the solution was brought back to 20°, its spectrum rechecked and then it was diluted further.

The results of these experiments are summarized in Table III. For the sake of brevity, this table gives only the data obtained at 20°. The calculation of K_1 from the known values of K_{ap}, K_{D1}, and K_{D2} required determination of the concentration of the free Li^+ cations. This was done by applying the method of successive approximations. (The approach used in ref 1 is not applicable in our case since the factor $1 + K_{D2}/[Li^+]$ could not be approximated by 1.) Denoting by x and y the concentrations of $T\cdot^-$ and T^{2-},Li^+, we find $x[Li^+] = K_{D1}\{[T\cdot^-_{total}] - x\}$, $y[Li^+] = K_{D2}\{[T^{2-}_{total}] - y\}$, and $x + y = [Li^+]$. The solution of these equations can usually be achieved with three iterative operations.

Table III. The Effect of Dilution on K_{ap} at 20°

$[T^{2-}]$, 10^{-4} M	$[T\cdot^-]$, 10^{-4} M	[T], 10^{-4} M	$[Li^+]_f$, 10^{-4} M	K_{ap}	K_1
8.45	6.35	22.6	1.73	4.73	7.93
1.69	1.51	4.14	0.737	3.06	8.65
0.705	0.752	1.98	0.466	2.35	9.97
0.232	0.367	0.699	0.276	1.20	9.00
0.122	0.227	0.408	0.191	0.97	11.4
8.08	8.90	47.9	2.04	4.89	7.65
1.33	1.98	8.00	0.842	2.72	6.95
0.638	1.18	4.66	0.603	2.13	7.11
0.289	0.630	2.35	0.394	1.72	8.66
0.160	0.455	1.49	0.310	1.15	8.12
7.15	10.4	68.3	2.20	4.51	6.85
1.59	2.70	17.0	1.01	3.71	8.36
0.804	1.56	9.79	0.718	3.23	9.32
0.254	0.645	3.24	0.398	1.98	9.87
0.108	0.359	1.69	0.259	1.41	11.4
				Av 8.75 ±	1.4

Thus obtained values of K_1 and K_2 are listed in Table IV and presented in the form of van't Hoff plots in Figure 3. The values of ΔH_1 and ΔH_2 are 6.6 and 6.7 kcal/mol, respectively, while $\Delta S_1 = 27$ cal $°K^{-1}$ and $\Delta S_2 = 22$ cal $°K^{-1}$. As in the sodium system, the disproportionation is endothermic but leads to entropy gain arising from partial desolvation of Li^+ ions.

Table IV. Calculated Values of K_1 and K_2[a]

$2T^-,Li^+ \rightleftarrows T + T^{2-},2Li^+$ K_1

$T\cdot^- + T\cdot^-,Li^+ \rightleftarrows T + T^{2-},Li^+$ K_2

Temp, °C	K_1	K_2
20	8.75	0.74
0	4.0	0.32
−20	1.5	0.12
−40	0.59	0.045
−70	0.079	0.0063

[a] All these constants are reliable within ±20%.

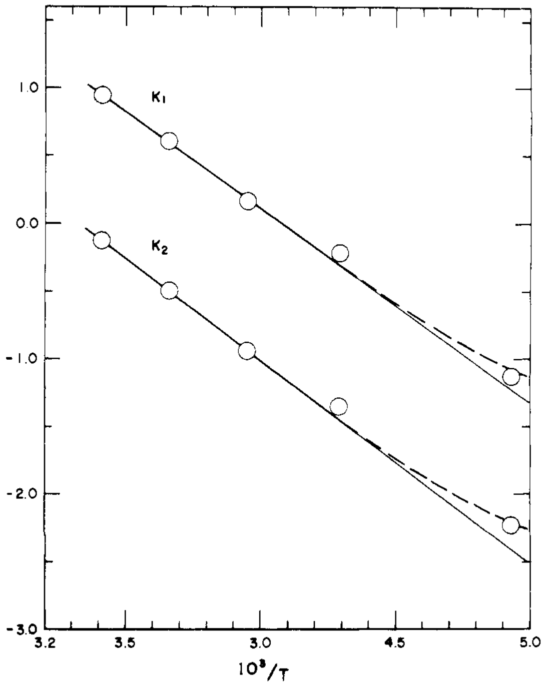

Figure 3. Van't Hoff plot of the disproportionation constants K_1 and K_2.

Kinetics of Disproportionation

The approach developed in the kinetic studies of the sodium salt disproportionation[2] has been adopted for the present investigation. The equilibrium maintained in the mixture of T and the lithium salts of $T\cdot^-$ and T^{2-} is perturbed by a flash of light (~25 μsec) ejecting electrons from the dianions. The loss of the photoejected electrons and their capture by T increases the concentration of $T\cdot^-$ over and above its equilibrium concentration. Simultaneously the concentrations of T and T^{2-} decrease by an equivalent amount. The return of the system to its equilibrium is then monitored spectrophotometrically by recording in the conventional way the time dependence of the absorbance at 495 nm (the reappearance of T^{2-}) or at 700 nm (the decay of $T\cdot^-$).

The stoichiometry of that process demands that

$$[T]_e - [T]_t = [T^{2-}{}_{total}]_e - [T^{2-}{}_{total}]_t = \frac{1}{2}\{[T\cdot^-{}_{total}]_t - [T\cdot^-{}_{total}]_e\} = X$$

where the subscripts e and t refer to the equilibrium and momentary concentrations of the respective reagents. These relations have been verified by the observation of an isosbestic point at 553 nm, the wavelength at which $\epsilon(T^{2-}) = 2\epsilon(T\cdot^-)$.

The kinetics of the relaxation process following the flash seems to be governed by two reversible reactions

$$2T\cdot^-, Li^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} T + T^{2-}, 2Li^+ \tag{1}$$

and

$$T\cdot^- + T\cdot^-, Li^+ \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} T + T^{2-}, Li^+ \tag{2}$$

provided it is assumed that the ionic equilibria

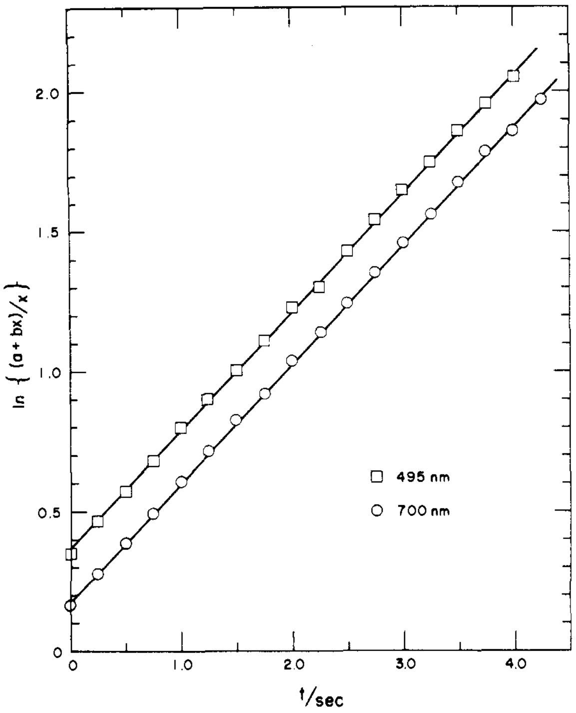

Figure 4. Plot of ln $\{(a + bX)/X\}$ *vs.* time, t: (□) the disappearance of T^{2-} and (○) the appearance of $T\cdot^-$ both under the same experimental conditions. The upper line is shifted by 0.2 units.

$$T\cdot^-, Li^+ \rightleftharpoons T\cdot^- + Li^+ \qquad K_{D1}$$

and

$$T^{2-}, 2Li^+ \rightleftharpoons T^{2-}, Li^+ + Li^+ \qquad K_{D2}$$

are maintained at any stage of the process. This assumption is justified because the disproportionation is relatively slow (0.5–10 sec) whereas the relaxation time of the ionic dissociation–association reactions is very short. On this basis the following relation is derived:

$$a^{-1} \ln\{(a + bX)/X\} = \{k_{-1} + k_{-2}K_{D2}/[Li^+]\}t + \text{const}$$

The coefficients a and b are defined by the equations

$$a = 2K_1(1 + K_{D1}/[Li^+])^{-2}[T\cdot^-{}_{total}]_e + \tfrac{1}{2}(1 + K_{D2}/[Li^+])^{-1}([T^{2-}{}_{total}]_e + [T]_e)$$

and

$$b = K_1(1 + K_{D1}/[Li^+])^{-2} - \tfrac{1}{4}(1 + K_{D2}/[Li^+])^{-1}$$

Table V. Equilibrium Concentrations of the Reagents in Flash Photolysis Experiments

$[T\cdot^-{}_{total}]$, 10^{-6} *M*	$[T^{2-}{}_{total}]$, 10^{-6} *M*	[T], 10^{-6} *M*	$[Li^+,-BPh_4^-]$, 10^{-6} *M*	$[Li^+]_f$, 10^{-6} *M*	k_{obsd}, 10^5 sec^{-1}
1.74	0.730	0.292	0	2.17	5.90
2.18	1.04	0.407	0	2.73	4.96
3.39	2.03	0.924	0	4.20	4.02
5.39	3.68	1.70	0	6.36	3.23
1.09	0.713	0.400	7.10	7.48	2.83
1.44	1.09	0.614	9.75	9.84	2.27
1.72	1.45	0.720	11.1	11.10	2.05
2.06	1.71	0.924	14.2	13.5	2.04
2.72	2.76	1.50	20.8	18.0	1.86
3.59	4.22	2.27	29.0	23.5	2.04
4.00	5.25	2.98	35.9	27.4	1.83
4.40	5.59	3.12	38.5	28.9	1.59
2.32	3.72	2.23	66.2	40.2	1.31
3.37	5.73	3.41	102	53.7	1.56

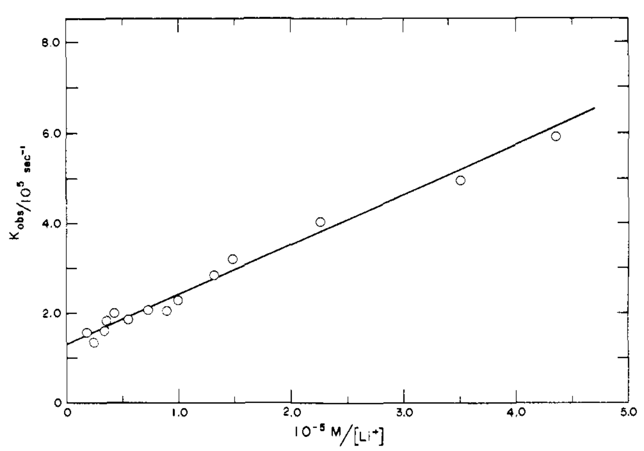

Figure 5. The observed rate constant, k_{obsd}, *vs.* reciprocal of the free lithium ion concentration.

It was established that under our experimental conditions the concentration of Li^+ ions is only slightly varied from its equilibrium value during the observed reaction and therefore it is permissible to assume $[Li^+] = [Li^+]_e$ = const for each run. (If necessary the appropriate corrections were introduced.) In order to increase the range of $[Li^+]_e$ in our experiments, lithium tetraphenyl boride was added to some reacting mixtures. The values of $[Li^+]_e$ in such experiments were calculated on the basis of the known[6] dissociation constant of Li^+,BPh_4^- (5.5×10^{-5} *M*).

The equilibrium concentrations of the reagents in each kinetic run are given in Table V.

It follows from the above discussion that ln $\{(a + bX)/X\}$ is a linear function of time, its slope being denoted by ak_{obsd}. This has been shown in each kinetic run and, for the sake of illustration, two such plots are shown in Figure 4. These lines refer to two experiments performed under the same conditions but monitored at different wavelengths, one at 495 nm, the other at 700 nm, and therefore they are superimposed each on the other (see Figure 4).

The proposed mechanism demands also a linear relation of k_{obsd} with $1/[Li^+]$, namely

$$k_{obsd} = k_{-1} + k_{-2}K_{D2}/[Li^+]$$

which, as shown by Figure 5, is confirmed by the experimental data. The slope of that line gives $k_{-2}K_{D2}$ and its intercept gives k_{-1}. Having K_1 and K_2, we may calculate also k_1 and k_2. Thus, the following kinetic constants were obtained: $k_1 = 1.1 \times 10^6$ $k_{-1} = 1.3 \times 10^5$, $k_2 = 1.8 \times 10^5$, and $k_{-2} = 2.4 \times 10^5$ M^{-1} sec^{-1}, all referred to 20°.

Comparison of the Lithium and Sodium System

The data given here, summarized in Table VI in conjunction with those reported previously,[1] demonstrate that $T\cdot^-,Li^+$ and $T\cdot^-,Na^+$ are alike in their structure. Both salts have virtually identical absorption spectra and their dissociation constants are similar, namely, in THF at 20° $K_{D1}(T\cdot^-,Li^+) = 54 \times 10^{-6}$ *M* while $K_{D1}(T\cdot^-,Na^+) = 100 \times 10^{-6}$ *M*. The corresponding heats of dissociation differ only slightly; *i.e.*, the ΔH_{D1}'s are −0.9 and −1.3 kcal/mol for the lithium and sodium salt, respectively, whereas the entropy change is the same for both, *i.e.*, 23 cal °K^{-1}. Hence, $T\cdot^-,Li^+$ and $T\cdot^-,Na^+$ form loose ion pairs in THF.

In contrast, the behavior of the lithium salts of T^{2-} considerably differs from that of the sodium salts. The spectrum of $T^{2-},2Li^+$, and presumably also of T^{2-},Li^+ (the shape of the spectrum of $T^{2-},2Li^+$ is not affected by dilution from 5×10^{-3} to 1×10^{-5} *M*, although the degree of dissociation of the dilithium salt into monolithium salt increases then from 3% to about 50%), has a strong absorp-

Table VI. Comparison of the Lithium and Sodium Systems (The Data Refer to 20°)

	Li^+	Na^+		Li^+	Na^+
10^6K_{D1}, *M*	54	100	10^6K_{D2}, *M*	4.6	0.83
ΔH_{D1}, kcal M^{-1}	−0.9	−1.3	ΔH_{D2}, kcal M^{-1}	−0.8	−7.2
ΔS_{D1}, cal °K^{-1}	−23	−23	ΔS_{D2}, cal °K^{-1}	−27	−53
K_1	8.7	400	K_2	0.74	3.3
ΔH_1, kcal M^{-1}	6.6	19	ΔH_2, kcal M^{-1}	6.7	13
ΔS_1, cal °K^{-1}	+27	+75	ΔS_2, cal °K^{-1}	+22	+45
$10^{-5}k_1$, M^{-1} sec^{-1}	11	<160	$10^{-5}k_2$, M^{-1} sec^{-1}	1.8	100
$10^{-5}k_{-1}$, M^{-1} sec^{-1}	1.3	<0.4	$10^{-5}k_{-2}$, M^{-1} sec^{-1}	2.4	30

tion band at 385 nm which does not appear in the spectrum of T^{2-},2Na^+; however, the absorption maximum at ~490 nm is common for both salts. Furthermore, the dissociation of the lithium salt is appreciably higher than that of T^{2-},2Na^+, *viz.*, $K_{D2}(T^{2-},2Li^+) = 4.6 \times 10^{-6}$ *M*, whereas $K_{D2}(T^{2-},2Na^+) = 0.83 \times 10^{-6}$ *M* only, both values referring to 20° in THF. Even more significant are the differences in ΔH_{D2}'s and ΔS_{D2}'s. At 20° ΔH_{D2} for T^{2-},2Na^+ is −7.2 kcal/mol and $\Delta S_{D2} = -52.6$ cal °K^{-1}, although both values absolutely decline at −70°. This clearly demonstrates that at 20° the dissociating Na^+ ion is tightly bound and poorly solvated in T^{2-},2Na^+. In contrast the dissociation of T^{2-},2Li^+ is only slightly exothermic, $\Delta H_{D2} = -0.8$ kcal/mol, and the loss of entropy is relatively small, $\Delta S_{D2} = -27$ cal °K^{-1}. It seems, therefore, that the dissociating Li^+ ion of T^{2-},2Li^+ is weakly bonded and well solvated in the T^{2-},2Li^+ aggregate, although the other Li^+ ion may be tightly associated with the dianion.

It is premature to discuss here the details of the structure of T^{2-},2Li^+ because this subject is still under investigation. However, we shall proceed with a tentative interpretation of our results by assuming that both Na^+ ions are tightly associated with T^{2-} in T^{2-},2Na^+, whereas only one Li^+ ion is strongly bonded and highly desolvated in T^{2-},2Li^+, the other being loosely attached and appreciably solvated. Of course, Li^+ and Na^+ ions are tightly associated with T^{2-} in the respective monoalkali salt.

The puzzling 385-nm band that appears in the spectrum of T^{2-},2Li^+, but not in the spectrum of T^{2-},2Na^+, is tentatively attributed to the charge-transfer transition to the desolvated, tightly bonded Li^+ ion. This suggestion is supported by two observations: (1) the 385-nm band still appears in the absorption of T^{2-},Li^+; (2) it vanishes when tetraglyme, added to the solution of T^{2-},2Li^+, converts the tightly bonded Li^+ into a loose, well solvated cation. Apparently the lower electron affinity of Na^+ prevents a similar charge transfer to be observed in the sodium salts.

The proposed model accounts for the features of the disproportionation. In the reaction

$$2T\cdot^-,\mathrm{Cat}^+ \rightleftharpoons T + T^{2-},2\mathrm{Cat}^+ \qquad K_1$$

the desolvation of *both* Na^+ makes ΔS_1 of the sodium system large (+75 cal °K^{-1}) and, by the same token, increases the endothermicity of this reaction, $\Delta H_1 = 19 \pm 2$ kcal/mol. However, in the lithium system only one Li^+ ion is desolvated, and thus the relevant ΔS_1 is only +27 cal °K^{-1} and $\Delta H_1 = 6.6$ kcal/mol. It is probable that the increased tightness of the cation deprives Na^+, but not Li^+, of its external solvation sheet, making $-\Delta S_1$ of the lithium system smaller than $-\frac{1}{2}\Delta S_1$ of the sodium system. Consequently, the disproportionation constant, K_1, of $T\cdot^-$,Li^+ (8.75) is much lower than that of $T\cdot^-$,Na^+ (400).

In the reaction

$$T\cdot^- + T\cdot^-,\mathrm{Cat}^+ \rightleftharpoons T + T^{2-},\mathrm{Cat}^+ \qquad K_2$$

the substitution of Li^+ for Na^+ leads to smaller effects because in either case the cation is converted from a loosely bonded form to a tightly associated one, although the loss of solvation shell is still greater for Na^+ than for Li^+ ion. In conformity with this view, the K_2's of both systems are more alike, namely, 0.74 and 3.3 for the lithium and sodium salts, respectively, and the same is reflected in the values of the corresponding ΔH_2's and ΔS_2's. For the lithium system ΔS_2 is smaller than ΔS_1 by 5 cal °K^{-1} only, whereas in the sodium system $\Delta S_2 - \Delta S_1 = 30$ cal °K^{-1}.

Finally, the kinetics of disproportionation has to be considered. The disproportionation is relatively slow because the structure of the hydrocarbon moiety is substantially altered as $T\cdot^-$ is converted into T^{2-} (see ref 1 and 2). The transition state of the reaction involving two ion pairs (reaction 1) is probably similar to the final state, and hence the desolvation of the cations adds to $\Delta S‡$. Therefore, one expects k_1 to be higher for the sodium salt (both cations partially desolvated) than for the lithium (only one cation being desolvated), and probably this is the case: $k_1 < 16 \times 10^6$ M^{-1} sec^{-1} for $T\cdot^-$,Na^+ and 1.1×10^6 M^{-1} sec^{-1} for the $T\cdot^-$,Li^+. The reverse reaction should be faster for T^{2-},2Li^+ than for T^{2-},2Na^+ because it involves the transfer of cation from the dianion to T and the Li^+ to be transferred is more labile than the corresponding Na^+ ion, hence, $k_{-1} = 13 \times 10^4$ M^{-1} sec^{-1} for Li^+ but $<4 \times 10^4$ M^{-1} sec^{-1} for Na^+.

The problem of cation transfer does not arise in reaction 2. The data indicate that the transition state of this reaction

$$T\cdot^- + T\cdot^-,\mathrm{Cat}^+ \rightleftharpoons T + T^{2-},\mathrm{Cat}^+ \qquad (2)$$

is different in the two systems. In the sodium system it resembles the final state, *i.e.*, the Na^+ ion is then desolvated to a great extent and therefore the relevant $\Delta S‡$ is large, but in the lithium system the transition state resembles the initial state, the Li^+ ion retaining much of its solvation shell. This difference may be associated with the higher electron affinity of Li^+ than of Na^+ and thus the former, but not the latter, may "conduct" the transferred electron even if solvated. In this respect the behavior of the system resembles the ability of the lithium salt to reveal a charge-transfer absorption band.

The proposed approach accounts then for the much higher value of k_2 for the reaction of the sodium salt ($k_2 = 100 \times 10^5$ M^{-1} sec^{-1}) than for the corresponding rate constant of the lithium salt ($k_2 = 1.8 \times 10^5$ M^{-1} sec^{-1}), since $\Delta S_2‡$ is much higher for the former than for the latter. The large degree of solvation needed in the reverse reaction 2, when the desolvated T^{2-},Li^+ attains the transition state on reacting with T, makes k_{-2} low for the lithium system ($k_{-2} = 2.4 \times 10^5$ M^{-1} sec^{-1}). This is not the case in the sodium system and therefore the respective k_{-2} is relatively large, *viz.*, 30×10^5 M^{-1} sec^{-1}.

It should be stressed that the reverse reactions 1 or 2 are relatively slow. The electron transfer from the sodium salt of tetracene dianion to tetracene was found to be nearly diffusion controlled,[7] the respective rate constant being 5×10^9 M^{-1} sec^{-1} in THF at 20°. Again, the need of reorganization of the hydrocarbon framework as T^{2-} is converted into $T\cdot^{-}$ is responsible for the slowness of those reactions.

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Preparation of an Alkyl Perbromate[1]

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Abstract: Silver perbromate was prepared by the reaction of dilute aqueous perbromic acid with silver oxide. Anhydrous silver perbromate suspended in carbon tetrachloride, cyclohexane, or 1,1,2-trichlorotrifluoroethane at −20° reacted with isopropyl bromide to give a 95% yield of isopropyl perbromate. At room temperature, isopropyl perbromate decomposed to give acetone in high yield.

Perbromic acid was prepared in 1968[2] after numerous unsuccessful synthesis attempts and theoretical rationalizations for its nonexistence were reported.[3] The chemistry of this interesting acid remains virtually unexplored, other than its oxidizing properties toward inorganic reagents[4] and the preparation of its alkali metal[4] and ammonium[5] salts. Reconciling the sluggish chemical oxidizing properties of perbromates, their electrode potential[6] (1.74 V compared to 1.23 V for perchlorate) and the difficulty of their preparation have been a subject of speculation.[3] The preparation of an ester of perbromic acid was of interest for the possibility that its properties might shed light on this problem, as well as from the standpoint of a new organic functional group.

One method that would appear attractive for the synthesis of alkyl perbromates is the reaction of dibromine heptoxide with alcohols, since the corresponding reaction of dichlorine heptoxide is a convenient source of alkyl perchlorates.[7] Dibromine heptoxide, however, has not been prepared, and attempts to dehydrate aqueous perbromic acid at room temperature resulted in autocatalytic decomposition after the dihydrate stage.[4] Another versatile route to alkyl perchlorates is the reaction of silver perchlorate with alkyl halides.[8,9] Application of this method to perbromates requires silver perbromate, which also has not been reported. Indeed, silver ion was reported to catalyze the decomposition of 6 *M* perbromic acid[4] at 100°.

Dilute aqueous perbromic acid is much more stable than the concentrated acid, and alkali salts of perbromic acid are relatively stable, both as solutions and as neat materials. The approach was therefore taken to prepare silver perbromate in dilute aqueous solution, followed by removal of water. A 0.5 *M* solution of perbromic acid was prepared by the procedure of Appelman, using elemental fluorine to oxidize bromate.[10] The perbromic acid was stirred at ambient temperature with the theoretical amount of silver oxide. The bulk of water was removed under vacuum, and the concentrate was dried by azeotroping with benzene. The product, which was soluble in benzene, was precipitated by the addition of hexane. The isolated yield was 88%.

$$Ag_2O + 2HBrO_4 \longrightarrow 2AgBrO_4 + H_2O$$

Silver perbromate was identified by analysis for silver, using sodium chloride. It reacted with saturated aqueous hydrobromic acid to give the theoretical amount of bromine, determined iodometrically, using the conditions reported for the analysis of perbromic acid.[10] The appearance and solubility properties of silver perbromate are similar to those of anhydrous silver perchlorate; it is a white hygroscopic solid, soluble in benzene and insoluble in saturated hydrocarbons. The material was unchanged in several months at ambient temperature.

Attempts were made to prepare alkyl perbromates by treating alkyl iodides with suspensions of silver perbromate in carbon tetrachloride at 0°. An immediate reaction took place, producing elemental iodine. No simple organic compounds were detected by nmr. When a solution of isopropyl perbromate in carbon tetrachloride, described below, was treated with ethyl iodide at −20°, iodine was also liberated rapidly. Thus, the oxidizing properties of alkyl perbromates are incompatible with their preparation from alkyl iodides and silver perbromate.

To avoid this oxidative side reaction, bromine was used as a leaving group. Simple primary alkyl bromides were not sufficiently reactive with silver perbromate to yield a product. Isopropyl bromide, however, was consumed completely within 15 min by an equivalent amount of silver perbromate suspended in carbon tetrachloride at −20°. The product, isopropyl perbromate, was formed in 95% yield, determined by nmr using a quantitative internal standard. The only other product detected was acetone (1%). In the same way solutions of isopropyl perbromate in cyclohexane and 1,1,2-trichlorotrifluoroethane were prepared.

$$(CH_3)_2CHBr + AgBrO_4 \longrightarrow (CH_3)_2CHOBrO_3 + AgBr$$

The structure assignment of isopropyl perbromate is based on its method of formation in high yield, its spectral properties and its decomposition product. The nmr spectrum of isopropyl perbromate in carbon tetrachloride consists of a septet at δ 5.17 for the methine and a doublet at δ 1.52 for the methyl. These chemical shift values indicate an isopropyl group with a strongly electron-withdrawing substituent. The values are very close to those of isopropyl perchlorate,[7] δ 5.10 for the methine and δ 1.58 for the methyl. The ir spectrum, detailed in the Experimental Section, also