

mole. Consequently, about 0.37 mmole of the alkaloids, some of it leurosine, was still on the resin. Since the resin capacity was about 0.78 mequiv., it was concluded that these dimeric vinca alkaloids occupy two resin sites per mole. It is also apparent that pyridine is not capable of replacing these alkaloids on the resin, and that the leurosine appearing in fractions 1 through 8 is merely a breakthrough. Since the pK_a values of these alkaloids were reported⁴ as 5.4–5.5 for the first ionization, we have to conclude that the selectivity of the resin toward these alkaloids is larger than expected from base strength. The increased selectivity may be a consequence of the divalent nature of the molecule. When elution was continued with a dilute solution of *n*-butylamine, the balance of the alkaloids was liberated. The individual fractions were assayed by thin layer chromatography, through courtesy of Eli Lilly and Co. Fractions 12 and 13 were pure leurosine, fraction 15 was pure vincalkeboblantine (confirmed also by infrared spectroscopy), and fraction 14 was an about equal mixture of the two. Fraction 16 contained vincalkeboblantine with about 15% impurities and fraction 17 contained only a combination of minor impurities. Since these alkaloids are extremely similar in many of their physical and chemical characteristics, notably in their pK_a values, this sharp separation is quite unexpected. A possible reason for this strong difference in selectivity may be a difference in the relative steric position of the two valence sites in the two alkaloids.

Conclusions

The results in this paper have shown that once an ion exchanger is modified to permit its swelling in nonpolar solvents, its behavior in polar and nonpolar solvents becomes rather similar. The exchanging species need not be ionic in solution, just capable of forming a salt

(4) G. H. Svoboda, T. S. Johnson, M. Gorman, and N. Neuss, *J. Pharm. Sci.*, **51**, 707 (1962).

with the ionic group of the resin. If the exchanger possesses a swollen, open structure, the solvent effects on exchange rates and selectivities become minor.

The postulated mechanism of nonaqueous ion exchange, namely that of an association–dissociation equilibrium whose constant is dependent on the base strength of the exchanging species, is supported by the results with diphenylamine. The prediction of selectivity coefficients from the ratio of base dissociation constants in water involves further assumptions and can be expected to have only limited validity. These predictions were right, qualitatively, with bases of widely varying strengths, and also for the reserpine alkaloids. The vinca alkaloids showed pronounced selectivity with no difference in base strength, pointing out the importance of some secondary contribution, perhaps owing to their divalent nature. In the case of pyridine and aniline the strong secondary binding of aniline rendered the prediction wrong, even qualitatively. Based on base dissociation constants in water, a K_a^p value of about 4.5 was expected, but one in the neighborhood of 0.5 was obtained. Also, the derivation based on base strengths alone fails to explain the variation of the selectivity coefficient with the equivalent ionic fraction, which in the case of pyridine and aniline was considerable.

Results in this paper showed that our oleophilic resins were capable of rapid removal of basic substances from organic solvents, and that they were also suitable for the separation of certain bases in organic solvents by column chromatography. The strength of the eluting agent could be varied by using eluting bases of different pK_a values at different concentrations.

Acknowledgment. This work was supported by a grant from the National Institutes of Health. We wish to express our gratitude to Dr. Paul R. Ulshafer of CIBA Pharmaceutical Co. and to Dr. Albert J. Barnes of Eli Lilly and Co. for their help in obtaining and analyzing the alkaloid samples.

The Chemistry of the Radical Anion of Tetraphenylethylene

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Contribution from the Chemistry Department, The New York State College of Forestry at Syracuse University, Syracuse, New York. Received August 3, 1965

The reaction of the disodium salt of tetraphenylethylene, $T^{2-}, 2Na^+$, with its parent hydrocarbon, T , has been investigated spectrophotometrically and conductometrically in tetrahydrofuran in the temperature range $+20$ to -70° . The conductance studies showed that at 20° the dissociation constant $K_{D,2}$ ($T^{2-}, 2Na^+ \rightleftharpoons T^{\cdot-}, Na^+ + Na^+$) is about $1/100$ times that of the corresponding dissociation constant $K_{D,1}$ of the related radical ion, $T^{\cdot-}, Na^+$. The exothermicity of dissociation $-\Delta H_{D,2}$ decreases from 7.2 at 20° to 0.9 kcal./mole at -70° , whereas $-\Delta H_{D,1}$ is substantially lower and changes in this range only slightly, viz. from 1.3 to 0.7 kcal./mole. This, as well as other evidence, indicates that $T^{2-}, 2Na^+$ forms a contact ion pair, whereas $T^{\cdot-}, Na^+$ forms a solvent

separated pair. The equilibrium constants K_1 ($2T^{\cdot-}, Na^+ \rightleftharpoons T^{2-}, 2Na^+ + T$) and K_2 ($T^{\cdot-}, Na^+ + T^{\cdot-} \rightleftharpoons T^{2-}, Na^+ + T$) were determined over a wide temperature range, providing data for the respective ΔH_1 , ΔH_2 and ΔS_1 , ΔS_2 . The results are interpreted in terms of the different stereochemical structures of $T^{2-}, 2Na^+$ and $T^{\cdot-}, Na^+$.

The addition of alkali metals to tetraphenylethylene, T , was first studied by Schlenk¹ in 1914. The product was identified as a dianion



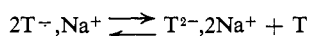
(1) W. Schlenk, J. Appenrodt, A. Michael, and A. Thal, *Ber.*, **47**, 473 (1914).

Table I. Extinction Coefficients ($\epsilon \times 10^{-4}$) of $T^{2-}, 2Na^+$ and $T^{\cdot-}, Na^+$ in THF at 20°

Investigators	$T^{2-}, 2Na^+$		370 $m\mu$ max.	$T^{\cdot-}, Na^+$	
	485 $m\mu$ max.	660 $m\mu$		485 $m\mu$ max.	660 $m\mu$ max.
This work	3.7 ± 0.1	0.22	(?)	0.85 ± 0.04	1.13 ± 0.05
Garst ^{3a}	3.4	...	~ 2.0	0.75	1.0
Evans ⁴	1.8^a (?)	$\sim 0.$	3.1^a (for Li^+)
	2.7 (for Li^+)				

^a The absorption maxima reported by Evans differ from those reported by Garst and by us. λ_{max} of T^{2-} is given at 466 $m\mu$ and that of $T^{\cdot-}$ at 675 $m\mu$. The results of Evans for $T^{\cdot-}$ (ϵ 3.1) is given for Li^+ counterion, ours and those of Garst refer to Na^+ . Perhaps this may account for some shift in λ_{max} , but not, in our opinion, for the large differences in extinction coefficients. Remark: The 10% difference between ours and Garst's extinction coefficients causes only a trivial change in K_{ap} , e.g., calculation by Dr. Garst led to a factor of 1.085.

and no radical ions, $T^{\cdot-}, Na^+$ ($Ph_2C=CPh_2^{\cdot-}, Na^+$), were detected even in the presence of an excess of the hydrocarbon. The early application of e.s.r. confirmed Schlenk's conclusion. No signals were recorded when the reaction was carried out in dioxane² or diethyl ether,^{3a} although the radical ion had been predicted to be more stable than the dianion.^{3b} Subsequent investigations in tetrahydrofuran and dimethoxyethane revealed the presence of a radical ion,^{4,5} its e.s.r. spectrum being reported by Evans, *et al.*,^{4a} early in 1962. Since then the disproportionation reaction



has been extensively studied by Evans,⁴ Garst,^{3a,5} and their co-workers. Solvation and aggregation of the ionic species was shown to be important in determining the position of the equilibrium. The reaction is endothermic, the proportion of radical ions increasing at lower temperatures.

To provide further information about the nature of this system, we investigated the conductance of these species in tetrahydrofuran. Our findings, combined with our spectrophotometric studies, are reported here.

Experimental Section

Tetraphenylethylene was repeatedly crystallized from toluene and then sublimed on a high-vacuum line into sealed ampoules. Its purity was verified by v.p.c. using a hydrogen flame ionization detector.

Tetrahydrofuran (THF) was refluxed over potassium and then fractionated on a 1-m. column. The distilled solvent, to which sodium benzophenone was added to scavenge traces of moisture, oxygen, etc., was stored in a flask attached to the high-vacuum line.

All experiments were carried out on the high-vacuum line, using break-seals and constrictions wherever possible. The spectra were measured on a Cary Model 14 recording spectrophotometer using quartz optical cells having path lengths of 0.01, 0.2, 1.0, 5.0, and 10 cm. Solutions of tetraphenylethylene absorb at λ_{max} 308 $m\mu$ (ϵ 1.46×10^4). Their reaction with a sodium mirror is completed within a few hours, as shown by the

(2) D. W. Ovenall and D. H. Whiffen, Special Publication No. 12, The Chemical Society, London, 1958, p. 139.

(3) (a) J. F. Garst and R. S. Cole, *J. Am. Chem. Soc.*, **84**, 4352 (1962); (b) N. S. Hush and J. Blackledge, *J. Chem. Phys.*, **23**, 514 (1955).

(4) (a) A. G. Evans, J. C. Evans, E. D. Owen, and B. J. Tabner, *Proc. Chem. Soc.*, 226 (1962); (b) J. E. Bennett, A. G. Evans, J. C. Evans, E. D. Owen, and B. J. Tabner, *J. Chem. Soc.*, 3954 (1963); (c) A. G. Evans and B. J. Tabner, *ibid.*, 4613 (1963).

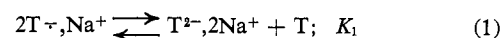
(5) (a) J. F. Garst, E. R. Zabolotny, and R. S. Cole, *J. Am. Chem. Soc.*, **86**, 2257 (1964); (b) J. F. Garst and E. R. Zabolotny, *ibid.*, **87**, 495 (1965).

methyl iodide titration.⁶ The resulting THF solution of $T^{2-}, 2Na^+$ has a broad absorption band in the visible, λ_{max} $485 \pm 5 m\mu$ (ϵ $3.7 \pm 0.1 \times 10^4$) (based on the results of titration), which shifts to longer wave lengths at lower temperatures, e.g., at -78° λ_{max} 510 $m\mu$. The extinction coefficient remains unchanged (the volume contraction of the solution being accounted for).

The hydrocarbon was dried rigorously by adding dropwise T^{2-} solution to a THF solution of sublimed tetraphenylethylene until a slight permanent coloration was observed. The THF was then distilled off and the tetraphenylethylene sealed in the ampoule. The excess of the added T^{2-} was small, less than 0.1% of the T^{2-} used in any experiment.

The Spectrum of the Radical Ion, $T^{\cdot-}, Na^+$. The intensity of the original peak of the dianion (λ_{max} 485 $m\mu$) decreases on the addition of dry tetraphenylethylene while two new peaks appear at 660 and 370 $m\mu$. The latter were observed by the previous investigators^{3a,4,5} and attributed to the radical ion $T^{\cdot-}, Na^+$. In a $10^{-3} M$ solution of $T^{2-}, 2Na^+$, containing a 20-fold excess of T, the absorption at 660 $m\mu$ increases and that at 485 $m\mu$ decreases as the temperature is lowered. Below -50° the spectrum remains constant and still exhibits the three absorption maxima at 370, 485, and 660 $m\mu$. We concluded, therefore, as did Garst,^{5b} that $T^{\cdot-}, Na^+$, like $T^{2-}, 2Na^+$, has an absorption maximum at 485 $m\mu$, although the respective extinction coefficient is lower than that of the dianion. Moreover, since no change of spectrum is observed between -50 and -78° , the conversion of $T^{2-}, 2Na^+$ into $2T^{\cdot-}, Na^+$ seems to be virtually quantitative below -50° . On this basis the extinction coefficients, listed in Table I, were calculated.

Spectrophotometric Investigation of the Disproportionation. If the disproportionation is governed only by eq. 1, the relative concentrations of all the reagents



should not change on dilution, and $K_{ap} = [T^{2-}, 2Na^+]_t [T] / [T^{\cdot-}, Na^+]_t^2$ should be constant. The subscript t indicates that the concentrations refer to the total amounts of the dianions, or radical ions, whether ionized or paired with Na^+ .

To avoid any destruction of the sensitive organometallic compounds on dilution, the following technique was used. The investigated solution was kept in a flask to which another flask and three optical cells (optical path length 0.2 with a 0.19-cm. spacer, 1, and 10 cm.)

(6) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 608, 612 (1965).

Table II. Effect of Dilution on K_{ap} ^a

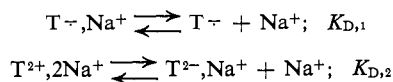
Series	$[T^{2-}] \times 10^4, M$	$[T^-] \times 10^4, M$	$[T] \times 10^4, M$	K_{ap}	$\frac{[T]}{[T^{2-}] + 1/2[T^-]}$
At 20°					
A	36.7	11.2	859	241	20.2
A	2.89	1.58	71	82	19.2
A	1.50	0.98	38	60	19.0
A	0.49	0.46	15.3	35	21.2
B	11.8	3.13	138	167	10.3
B	2.9	1.16	37.3	79	10.6
B	0.75	0.47	9.9	33	10.0
B	0.16	0.21	2.6	9.4	10.0
B	0.048	0.098	0.925	4.7	9.6
B	0.016	0.055	0.42	2.2	9.8
C	1.84	1.15	58.5	81	24.4
C	0.76	0.63	23.9	46	22.4
C	0.28	0.32	10.4	28	23.6
C	0.31 (?)	0.33 (?)	8.9 (?)	26 (?)	19.0
C	0.098 (?)	0.176 (?)	2.35 (?)	7.4 (?)	12.5
C	0.050 (?)	0.124 (?)	1.5 (?)	4.9 (?)	13.4
At 0°					
C	29.9	27.6	980	39	22.2
..	28.0	28.9	873	29	..
D	2.6	4.0	96.7	16	21.0
D	1.3	2.34	47.8	11	19.5
D	0.51	1.23	22.8	7.7	20.5
D	0.18	0.62	9.2	4.4	18.8
At -20°					
..	10.6	68.6	869	1.96	..
..	0.95	8.3	110	1.52	..
..	0.56	5.5	70.3	1.28	..
..	0.064	1.44	20.4	0.63	..

^a The concentrations given in this table were calculated by computer from the following equations: o.d. (660) = $(0.22[T^{2-}] + 1.13[T^-]) \times 10^4$ for 1-cm. path; o.d. (485) = $(3.7[T^{2-}] + 0.85[T^-]) \times 10^4$ for 1-cm. path. Concentration of T is given by the o.d. at 308 μ . At this wave length the corrections for T^{2-} and T^- were $\sim 5\%$ since the hydrocarbon was in at least 10-fold excess and ϵ (308) of T^{2-} was found to be 0.66×10^4 only. The original concentration of the hydrocarbon was determined from its weight, the volume of the solution, and the amount consumed in the reaction ($= 0.5[T^-]$)

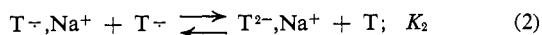
were attached (see, e.g., Figure 8 in ref. 6). The spectrum was first measured in the narrowest optical cell. About three-fourths of the solution was then transferred to the empty flask and the solvent returned to the first by chilling its contents. Thus, the dilution was accomplished by removal of the solute and not by addition of the solvent. The spectrum of the diluted solution was determined and the procedure repeated again. Thus K_{ap} was found for successive dilutions. Any delay was avoided when working with the more dilute solutions since spontaneous destruction of the organometallic compounds becomes relatively more pronounced at low concentrations.

The results obtained at +20, 0, and -20° are given in Table II. Since K_{ap} is not constant, eq. 1 is not sufficient to describe the reaction. This has been recently concluded by Garst.^{5b}

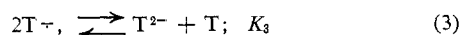
Ion pairs dissociate in tetrahydrofuran and therefore two additional equilibria should be considered.



Hence, disproportionation 2 must also be included in the process



whereas disproportionation 3



may be neglected, since the concentration of T^{2-} is

expected to be exceedingly low. $K_{D,1}$ and $K_{D,2}$ were determined by investigating the conductance of $T^{2-}, 2Na^+$ solution and of its mixture with tetraphenylethylene.

Studies of Conductance. An apparatus described in ref. 6 (see Figure 8) was used in studies of the conductance of $T^{2-}, 2Na^+$. The measurements were made in the range +20 to -70° at concentrations varying from 10^{-3} to 10^{-6} M. The conductance cell was kept in a constant temperature bath (a dewar flask) filled with isooctane and cooled with solid carbon dioxide to about -80°. The temperature was measured by a calibrated thermocouple having one junction in a cell pocket in the vicinity of the electrodes and the other in ice-water. After reaching thermal equilibrium (10-15 min.) the resistance of the cell was measured (see ref. 7 for details of technique). The temperature was then raised by about 10° using a heating coil and the conductance determined again after the new thermal equilibrium had been established. This procedure was continued until room temperature was reached. The solution was then diluted by removal of solute⁶ and the conductance determined again for the whole temperature range. The concentration was determined spectrophotometrically at 20° and corrected for the volume contraction at lower temperatures. Thus, a series of smoothed curves was obtained, each giving the conductance at constant concentration as a function of temperature, and these served to construct the curves re-

(7) C. Carvajal, J. K. Tölle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, 87, 5548 (1965).

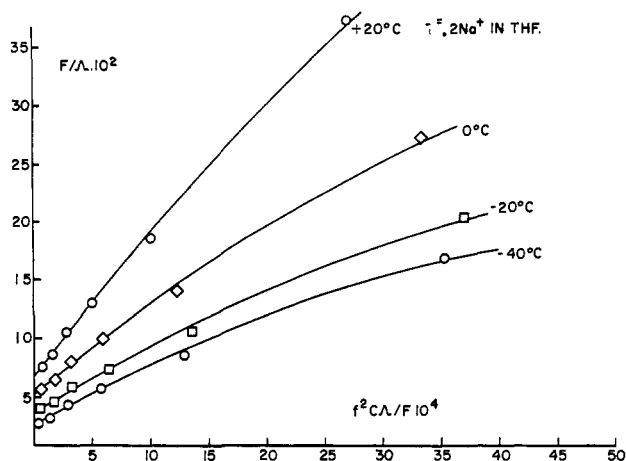


Figure 1. Fuoss plot for $T^{2-}, 2Na^+$ in THF

lating the specific conductance at constant temperatures with the concentration. The usual procedure⁸ gives then Λ_0 values and K_D , as exemplified⁸ by Figure 1. All the results are given in Table III. The constancy of the ratio $\Lambda_0(T^{2-}, 2Na^+)/\Lambda_0(Na^+, BPh_4^-)$ for all the investigated temperatures manifests the reliability of the data. Its value is 1.2 with a maximum deviation of ± 0.05 . The Walden product (third column of Table III) decreases slightly at lower temperatures, a general phenomenon discussed elsewhere.⁷ The plot of $\log K_{D,2}$ vs. $1/T$ is shown in Figure 2.

Table III. Conductance Data in THF

Temp., °C.	Λ_0	$\eta\Lambda_0 \times 10^2$	Slope = $1/\Lambda_0^2 K_D$	$K_D \times 10^6, M$
$T^{2-}, 2Na^+$				
20	100	48.5	120	0.83
10	90	49.0	100	1.23
0	77	47.2	82	2.1
-10	68	46.8	70	3.15
-20	59	46.8	64	4.5
-30	50	45.5	56	7.15
-40	42	45.0	60	8.7
-50	36	45.0	66	11.8
-60	27	42.0	99	13.9
-70	22	42.5	150	13.8
$T^{\cdot-}, Na^+$				
20	86	42	1.29	100
10	71	39	1.69	115
0	61	37.5	2.52	105
-10	53.5	37.0	3.45	100
-20	46	36.5	4.15	115
-30	40	36.5	5.6	112
-40	34	36.3	7.1	122
-50	27.5	34.7	9.1	144
-60	22	34.2	12.1	169
-70	17.5	33.9	18.0	179

Since one cannot prepare a pure solution of the radical ion, we investigated the conductance of a $10^{-3} M$ solution of $T^{2-}, 2Na^+$ containing a tenfold excess of the hydrocarbon. Spectrophotometric studies showed that the conversion of T^{2-} to $T^{\cdot-}$ exceeded 95%

(8) F. Accascina and R. M. Fuoss "Electrolytic Conductance," John Wiley and Sons, Inc., New York, N. Y., 1959.

(9) The following data are necessary for the calculation of Fuoss' lines: density of THF at 25° = 0.880 g./ml.; $d \ln V/dT = 0.001085$; dielectric constant $\epsilon = -1.495 + 2659/T$; viscosity η , $\log \eta = -3.655 + 393/T$. These relations are taken from ref. 7.

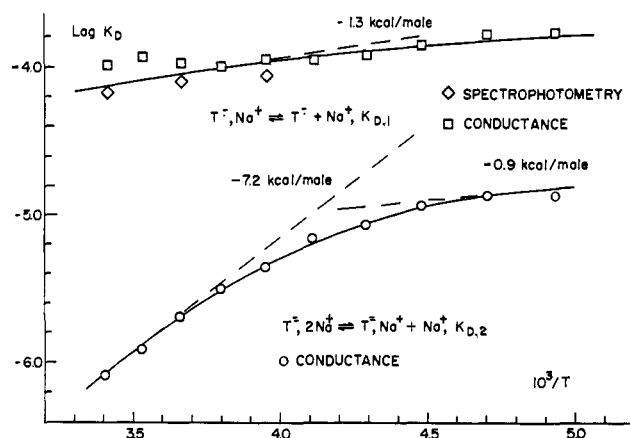


Figure 2. Log of dissociation constants for $T^{\cdot-}, Na^+$ and $T^{2-}, 2Na^+$ in THF as functions of $1/T$.

below -30° , and hence the data obtained below this temperature were treated conventionally. At 20° the calculations were based on concentrations of $T^{\cdot-}$ determined spectrophotometrically; however, direct determinations were unfeasible at 10, 0, -10 , and -20° as the optical cells needed for the dilute solutions were too large to fit into the low-temperature dewar. It was assumed that the change in the apparent equilibrium constant with temperature is the same for the dilute solutions as for a more concentrated solution (see Table IV), and this allowed us to calculate $[T^{\cdot-}]$ from the equilibrium constants. The Λ_0 's and $K_{D,1}$ for $T^{\cdot-}, Na^+$ dissociation are also given in Table III and in Figure 2. *A posteriori* calculation proved that the contribution of $T^{2-}, 2Na^+$ to the conductance amounted to only 5% at the highest temperature and concentration and it decreases with dilution.

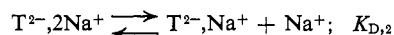
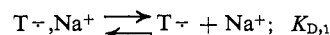
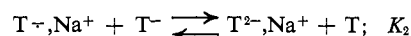
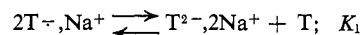
Table IV. Effect of Temperature on K_{ap} ^a

Temp., °C.	30	20	-2	-23	-37
K_{ap}	1080	241	29.3	1.96	0.352

^a At 20° , $[T^{2-}] = 3.67 \times 10^{-3} M$, $[T^{\cdot-}] = 1.15 \times 10^{-3} M$, $[T] = 8.64 \times 10^{-2} M$. Calculations are based on the extinction coefficients given in Table I. The same solution was used at all the temperatures.

Discussion

The experimental results reported above, like those of Garst,^{5b} confirm the existence of the following equilibria



which are interrelated by the proportionality $K_1/K_2 = K_{D,1}/K_{D,2}$. The apparent equilibrium constant, K_{ap} , is defined as

$$K_{ap} = \frac{\{[T^{2-}, 2Na^+] + [T^{2-}, Na^+]\}[T]}{\{[T^{\cdot-}, Na^+] + [T^{\cdot-}]\}^2}$$

It is assumed that the spectrophotometric measurements give the respective sums $\{[T^{2-}, 2Na^+] + [T^{2-}, Na^+]\}$

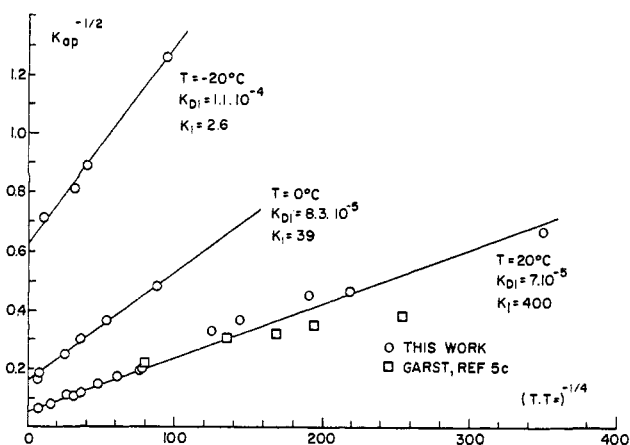


Figure 3. Plot of $1/K_{ap}^{1/2}$ vs. $([T][T^{2-}])^{-1/4}$.

and $\{[T^{\cdot-},Na^+] + [T^{\cdot-}]\}$; *i.e.*, that the extinction coefficients of $T^{2-},2Na^+$ and T^{2-},Na^+ are identical as are those of $T^{\cdot-},Na^+$ and $T^{\cdot-}$. Although technical reasons prevented us from testing this assumption, there is circumstantial evidence for its validity. Hence

$$K_{ap} = K_1(1 + K_{D,2}/[Na^+])/(1 + K_{D,1}/[Na^+])^2$$

The conductance data show that in not too dilute solution and above -30° $K_{D,2} \ll [Na^+]$ and thence, in agreement with Garst^{5b}

$$1/K_{ap}^{1/2} = 1/K_1^{1/2} + (K_{D,1}^{1/2}/K_1^{1/4})([T][T^{2-}_{total}])^{-1/4}$$

Figure 3 shows $1/K_{ap}^{1/2}$ plotted vs. $([T][T^{2-}])^{-1/4}$ for 20, 0, and -20° . The intercepts give the respective K_1 , *viz.*, 400, 39, and 2.6, and the slopes the corresponding $K_{D,1}$, namely, 7×10^{-5} , 8.3×10^{-5} , and $11 \times 10^{-5} M$, respectively. The latter are shown in Figure 2 together with the data derived from the conductance studies. The agreement between both sets of data is fair, particularly if one considers the uncertainties encountered in the conductance studies at higher temperatures.

The disproportionation constants K_1 and K_2 are given in Table V. An additional value of K_1 was calculated for -37° using the respective K_{ap} given in Table IV in conjunction with $K_{D,1}$. The corresponding K_2 values were calculated from K_1 by using the proportionality $K_1/K_2 = K_{D,1}/K_{D,2}$. The plots of $\log K_1$ and $\log K_2$ vs. $1/T$ are shown in Figure 4.

Table V. Calculated Values of K_1 and K_2 ^a

Temp., °C.	K_1	K_2
20	400	3.3
0	39	0.72
-20	2.6	0.10
-37	0.44	0.038

^a At 20° $\Delta H_1 = 19 \pm 2$, $\Delta H_2 = 13 \pm 2$ kcal./mole; $\Delta S_1 = 75$, $\Delta S_2 = 45$ e.u.

Superficially, our results for K_1 differ considerably from those of Garst. Figure 5 of his paper^{5b} shows, however, that our K_{ap} values differ insignificantly from his (see Figure 3). The difference in K_1 arises from the extrapolation; *e.g.*, at 20° our $K_1 = 400$ while Garst's is 32 at 21° . However, if the first four points shown

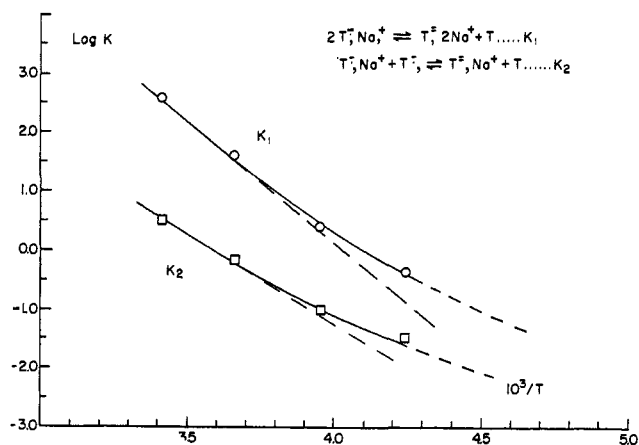


Figure 4. Log of the equilibrium constants for the disproportionation of $2T^{\cdot-},Na^+$ and $T^{\cdot-},Na^+ + T^{\cdot-}$ as functions of $1/T$.

in his Figure 5 are used for extrapolation, $K_1 \sim 100$. For other temperatures, the extrapolation of data shown in Figure 5 or ref. 5b becomes difficult owing to the experimental scatter. We overcame this difficulty by working with higher concentrations of the reagents.¹⁰

The Nature of $T^{\cdot-},Na^+$ and $T^{2-},2Na^+$ Ion Pairs. Inspection of Figure 2 reveals two striking differences in the behavior of $T^{\cdot-},Na^+$ and $T^{2-},2Na^+$: (1) The former ion pair dissociates 10–100 times more than the latter. (2) The heat of dissociation of $T^{\cdot-},Na^+$ is about 1.3 kcal./mole at 20° , decreasing perhaps to 0.7 at -70° , whereas that of $T^{2-},2Na^+$ is 7.2 kcal./mole at room temperature, decreasing to ~ 0.9 kcal./mole at the lowest temperature.

Consider the process of association of a sodium ion with a negative hydrocarbon ion. In THF the Na^+ ion is solvated and let Δr denote the increase in the radius caused by the solvation shell. Following Fuoss and Sadek¹¹ we represent the electrostatic free energy of formation of a contact ion pair by

$$\Delta F_{elec} = Ne^2/(r + \Delta r)\epsilon + Ne^2\{1/r\epsilon_{eff} - 1/(r + \Delta r)\epsilon_{eff}\}$$

The second term provides the driving force for the desolvation of the cation. If the cation can approach close to the anion, r is small. The free energy gain is then sufficient to overcome that lost on desolvation and a stable contact ion pair is formed. However, if a close approach is impossible, r is large and the free energy gain may not be sufficient to permit the desolvation. A solvated ion pair is then more stable.

Examination of models demonstrates that the phenyl groups in tetraphenylethylene are twisted out of the plane of the $C=C$ bond (see ref. 12). The same geometry is expected for the $T^{\cdot-}$ radical ion which still possesses a rigid $C=C$ bond. The Na^+ counterion cannot, therefore, approach closely the negative charge, *i.e.*, r is large and the resulting associate forms a solvent-separated ion pair.

The double bond character is destroyed in the T^{2-} ion. This allows rotation about the central $C-C$ bond and permits coplanar configurations of the $Ph-C-Ph$ groups in two mutually perpendicular planes.^{3,5a,13}

(10) See Appendix for the possible effect of triple ion formation ($T^{2-},3Na^+$) upon the K_{ap} values at high concentrations of $T^{2-},2Na^+$.

(11) R. M. Fuoss and H. Sadek, *J. Am. Chem. Soc.*, **76**, 5905 (1954).

(12) G. Favini and M. Simonetta, *Theoret. Chim. Acta*, **1**, 294 (1963).

Table VI. Comparison of $K_{D,1}(T^{\cdot-}Na^+)$ with $K_D(Na^+BPh_4^-)$

Temp., °C.	25	20	10	0	-10	-20	-30	-40	-50	-60	-70
$K_{D,1} \times 10^6$...	10.0	11.5	10.5	10.0	11.5	11.2	12.2	14.4	16.9	17.9
$10^6 \times K_D(Na^+, BPh_4^-)^a$	8.82	...	10.7	12.0	12.9	14.0	14.1	14.2	15.1	16.5	15.3 (?)

^a These data are taken from ref. 7.

The counterions may then approach closely the respective C^- centers making r small. Therefore, $T^{2-}, 2Na^+$ forms a contact ion pair.

The large dissociation constant and the low heat of dissociation of $T^{\cdot-}, Na^+$ confirm its structure of a solvent-separated ion pair. Since the solvated Na^+ ion and the propeller-shaped $T^{\cdot-}$ radical anion are large, the Fuoss treatment¹⁴ applies, *viz.*

$K_{D,1} = \{3000/4\pi(r + \Delta r)^3 N\} \exp[-e^2/(r + \Delta r)\epsilon kT]$ and the Denison and Ramsey¹⁵ treatment gives ΔH , *i.e.*

$$\Delta H = \{e^2/(r + \Delta r)\epsilon\} \{1 + \partial \ln \epsilon / \partial \ln T\}$$

$\partial \ln \epsilon / \partial \ln T = -1.2$ at $300^\circ K$.⁷; therefore the latter equation gives $r + \Delta r = 7 \text{ \AA}$. Hence, the Fuoss equation gives $K_{D,1} = 2.2 \times 10^{-5} M$, in fair agreement with the observed value of 7×10^{-5} .

$T^{2-}, 2Na^+$ forms a contact ion pair and the Na^+ ion becomes solvated on dissociation. This accounts for the high observed heat of dissociation. Contact ion pairs may be transformed into solvent-separated ion pairs at lower temperatures.¹⁶ This seems to be the case with $T^{2-}, 2Na^+$. Its heat of dissociation decreases at lower temperatures, and, as has been pointed out earlier, the λ_{max} shifts from 485 to 510 $m\mu$. Such a bathochromic shift has been observed for sodium fluorenyl and attributed to the transformation of the contact ion pair into the solvent-separated pair.¹⁶ The stabilization of the ground state by the counterion is decreased when the latter is solvated.

Finally, the similarity of behavior between $T^{\cdot-}, Na^+$ and Na^+, BPh_4^- should be stressed. Both anions have similar shape and size. It is not surprising therefore to find nearly identical values for their dissociation constants over the whole range of temperature (see Table VI). Since $T^{\cdot-}, Na^+$ seems to form a solvent-separated pair, the same is expected for Na^+, BPh_4^- in THF.

The $T^{2-}, 2Na^+$ ion pair may resemble in regard to its dissociation the dianion of 1,1-diphenylethylene dimer. Indeed, at 25° the dissociation constant of the latter was found to be $\sim 1 \times 10^{-6} M$ (unpublished data from this laboratory) whereas $K_{D,2} = 0.8 \times 10^{-6} M$ at 20° .

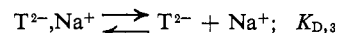
Thermodynamics of the Disproportionation. The Na^+ ion in the $T^{\cdot-}, Na^+$ ion pair seems to be coordinated with probably four molecules of THF, whereas in the $T^{2-}, 2Na^+$ contact ion pair these ions are not solvated. Therefore, disproportionation 1 resembles the association of ions where solvated species are transformed into nonsolvated ones. Desolvation of ions increases the entropy of the system and makes the association endothermic, in spite of the gain in electrostatic energy of the pair. The same argument applies to the disproportionation, and this explains the results, $\Delta H_1 = 19$ kcal./mole and $\Delta S_1 = 75$ e.u. At lower temperatures $T^{2-}, 2Na^+$ becomes solvated, as indicated by the bathochromic shift in its spectrum. Consequently ΔH_1 and ΔS_1 decrease accordingly (see Figure 4).

Disproportionation 2 transforms only one fully solvated Na^+ ion into a nonsolvated one; therefore the respective ΔH_2 and ΔS_2 should be correspondingly lower, as shown in Table V. The same conclusion follows from the consideration of the dissociation processes, $T^{\cdot-}, Na^+ \rightleftharpoons T^{\cdot-} + Na^+$ (D,1), and $T^{2-}, 2Na^+ \rightleftharpoons T^{2-}, Na^+ + Na^+$ (D,2), since $\Delta H_1 - \Delta H_2 = \Delta H_{D,1} - \Delta H_{D,2}$ and $\Delta S_1 - \Delta S_2 = \Delta S_{D,1} - \Delta S_{D,2}$. Similar ideas have been outlined recently by Shatenstein.¹⁷

The equilibrium constant K_3 of the disproportionation (3) could be calculated from the relation

$$K_3/K_2 = K_{D,3}/K_{D,2}$$

where $K_{D,3}$ is the dissociation constant



Unfortunately, there is no reliable way of estimating the value of $K_{D,3}$; it is much smaller than $K_{D,2}$ and therefore $K_3 \ll K_2$.

Appendix

It has been suggested by a referee that the formation of triple ions (charged associates of the neutral $T^{2-}, 2Na^+$ or $T^{\cdot-}, Na^+$ with free ions) could distort the observed K_{ap} and lead to an apparent discrepancy between Garst's and our K_1 . The triple ions become significant at higher concentrations of T^{2-}_{total} and it has been argued that their presence could increase the observed K_{ap} , making the values larger than anticipated. To test this hypothesis the experiments listed in Table VII were performed. K_{ap} was determined in the presence and in the absence of Na^+, BPh_4^- at various dilutions of the reagents. The technique described in the paper was used. Moreover, the results of the experiments performed in the presence of the boride permit us to calculate K_1 directly, *viz.*

Table VII.^a

Series	Concn., $10^3 M$				K_{ap}	K_1^b
	$[T^{2-}]$	$[T^{\cdot-}]$	$[T]$	$[Na^+ BPh_4^-]$		
1	3.67	1.12	85.9	0.0	241	...
1	3.33	1.29	96.3	46.2	193	~ 200
1	0.28	0.87	6.8	3.3	250	360
2	4.31	1.17	80.8	0.0	252	...
2	0.25	0.11	5.16	0.0	105	...
2	0.042	0.037	1.07	0.0	33	...
2	4.10	1.34	80.8	35.7	185	196
2	0.28	0.78	5.46	2.41	253	385
2	0.073	0.024	1.44	0.65	176	365

^a Temperature, 20° . ^b Calculated from $[Na^+]$.

(13) Discussion remarks by M. J. S. Dewar and P. Gray in The Chemical Society Symposium, Special Publication No. 12, The Chemical Society, 1958, pp. 164-166.

(14) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

(15) J. T. Denison and J. B. Ramsey, *ibid.*, **77**, 2615 (1955).

(16) T. E. Hogen-Esch and J. Smid, *ibid.*, **87**, 669 (1965).

(17) A. I. Shatenstein, E. S. Petrov, and M. I. Belusova, "Organic Reactivity," Vol. 1, Tartu State University, Estonia, U.S.S.R., 1964, p. 191; also the paper presented at the IUPAC Meeting on Macromolecules, Prague, Czechoslovakia, Oct. 1965.

$$K_1 = K_{ap}(1 + K_{D,1}/[Na^+])^2 \quad (\text{see text})$$

where

$$[Na^+] = \{K_{D,Na^+,BPh_4^-} \cdot [Na^+,BPh_4^-]\}^{1/2}$$

Inspection of the data given in Table VII reveals:

(1) K_{ap} values observed in the experiments performed in the absence of sodium boride fit the line shown in Figure 3.

(2) The addition of $Na^+BPh_4^-$ increases K_{ap} if $[Na^+,BPh_4^-] < 10^{-2} M$. This is to be expected since an increase in $[Na^+]$ depresses the concentration of T^- and T^{2-},Na^+ ions. In fact, the K_1 values calculated from the equation involving $[Na^+]$ are consistent with those obtained by the linear extrapolation shown in Figure 3, *viz.*, $K_1 = 400$.

(3) For a high concentration of $Na^+,BPh_4^- (>10^2 M)$, *i.e.*, for a relatively high concentration of Na^+ and BPh_4^- ions, K_{ap} decreases. Under these conditions, one expects a substantial proportion of triple ions, *i.e.*, $(T^{2-},2Na^+)Na^+$, $(T^{2-},2Na^+)BPh_4^-$, $(T^-,Na^+)Na^+$, and $(T^-,Na^+)BPh_4^-$. The binding of Na^+ or BPh_4^- by

T^-,Na^+ arises from a dipole-charge interaction, that of $T^{2-},2Na^+$ with the free ions has to be attributed to a quadrupole-charge interaction. The former is stronger than the latter, and therefore the formation of triple ions removes from the system a greater fraction of T^-,Na^+ than of $T^{2-},2Na^+$. This decreases the K_{ap} in accordance with our observations.

Let us summarize our findings. The formation of triple ions distorts the value of K_{ap} at rather high concentration of the free ions. It seems that this effect is negligible in the absence of Na^+,BPh_4^- , even in the experiments which were performed at the highest concentration of $T^{2-},2Na^+$. However, had this effect been important it would decrease the K_{ap} . Therefore, any corrections which would account for the triple ion formation could only amplify the discrepancy between Garst's and our K_1 .

Acknowledgment. We wish to thank Dr. Garst for his constructive comments. This work was supported by the National Science Foundation and by the U. S. Army Research Office, Durham.

Studies of Solvation Phenomena of Ions and Ion Pairs in Dimethoxyethane and Tetrahydrofuran

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Density, viscosity, and dielectric constant of dimethoxyethane (DME) and tetrahydrofuran (THF) were investigated in the temperature range $+25$ to -70° and found to be remarkably similar for both solvents. Conductance of tetraphenylboride salts of Na^+ , Cs^+ , and $Bu(AM)_3N^+$ were investigated in both media, down to $5 \times 10^{-6} M$ concentration and over the whole temperature range of $+25$ to -70° . The respective λ_0^+ , K_{dis} , and $-\Delta H_{dis}$ showed that $Bu(AM)_3N^+,BPh_4^-$ forms contact ion pairs in both solvents and dissociates into free $Bu(AM)_3N^+$ and BPh_4^- ions not coordinated with solvent. The simple "sphere in continuum" model accounts for the quantitative behavior of this salt in DME and THF. However, to account for the behavior of Na^+,BPh_4^- , it is necessary to assume that in both media the salt forms mainly solvent-separated pairs which dissociate into solvent-coordinated Na^+ ions. While the behavior of $Bu(AM)_3N^+,BPh_4^-$ or Na^+,BPh_4^- is similar in THF and DME, that of Cs^+,BPh_4^- is different in DME from that in THF. It was shown that the medium-size, free Cs^+ ion is coordinated with DME but not with THF, whereas the Cs^+,BPh_4^- forms mainly contact ion pairs in both solvents. Therefore, the "sphere in continuum" model reasonably accounts for the dissociation of Cs^+,BPh_4^- in THF but not in DME. At ambient temperatures the dissociation constant of Cs^+,BPh_4^- is ~ 20 times greater in DME than in THF. Lowering the temperature leads to conversion of contact ion pairs to solvent-separated pairs as shown by the substantial decrease in $-\Delta H_{dis}$.

In reactions involving ions or ion pairs, the role played by solvent cannot be overestimated. Even a small modification of its structure may cause a large change in the rate and in the pattern of an investigated process. Propagation of anionic polymerization may serve as an example. The reaction involves free ions, *e.g.*, $\sim\text{styrene}^-$, and ion pairs such as $\sim\text{styrene}^-,Na^+$. The latter grow rapidly in tetrahydrofuran,¹ the respective $k_{p\pm}$ being 80 l./mole sec., but slowly in dioxane,² $k_{p\pm} = 3-5$ l./mole sec. Moreover, in THF the $\sim\text{styrene}^-,Li^+$ ion pair is the most reactive and the $\sim\text{styrene}^-,Cs^+$ the least. In dioxane the pattern is reversed, $\sim\text{styrene}^-,Cs^+$ being the most reactive and $\sim\text{styrene}^-,Li^+$ the most inert ion pair.

It seems that a thorough characterization of solvents is required before quantitative understanding of their role can be contemplated. Therefore, we started a comprehensive program of characterization of ethereal solvents, and in this communication our findings for tetrahydrofuran (THF) and dimethoxyethane (DME) are reported. The physical properties of these solvents, *i.e.*, density (d), dielectric constant (ϵ), and viscosity (η) were determined for a temperature range of -70 up to $+25^\circ$. In addition, the conductance of Na^+ , Cs^+ , and $(i-Am)_3BuN^+$ ($i-Am = \text{isoamyl}$) salts of BPh_4^- was investigated in the same temperature range.

(1) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965).

(2) D. N. Bhattacharyya, J. Smid, and M. Szwarc, *ibid.*, **69**, 624 (1965).