

OPTICAL AND VOLTAMMETRIC STUDIES ON TETRAPHENYLETHYLENE SALTS

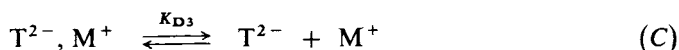
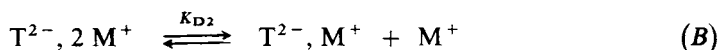
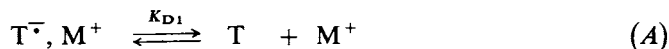
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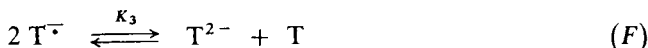
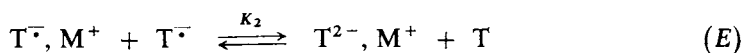
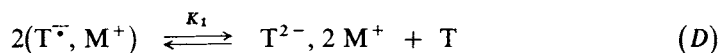
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Optical spectra of tetraphenylethylene salts with lithium, sodium, potassium, rubidium, and tetrabutylammonium as counter ions, were recorded in tetrahydrofuran. Also the optical spectrum of sodium salt of tetraphenylethylene was recorded at very high dilution. On computer resolution of the optical spectra it was found that the observed bands were composed of three peaks, located around 385, 490, and 585 nm. Depending upon the counter ions and the environments these occur in different height ratios. These findings pointed to ion pairs formation and helped in elucidating their structure. The cyclic voltammetric studies on tetraphenylethylene helped in the evaluation of dissociation constant of T^{2-} , M^+ and the disproportionation constant $2 T^- \rightleftharpoons T^{2-} + T$. The former was found to be $1.2 \cdot 10^{-5} \text{ mol l}^{-1}$, the latter 0.42 in dimethylformamide.

There has been a great deal of interest in the salts of tetraphenylethylene vis-a-vis ion pairing and electron transfer processes¹⁻⁵. Optical, NMR, conductometric, and even polarographic⁶ (though not cyclic voltammetric) studies have been carried out and some interesting information regarding the structure, disproportionation, dissociation, and (counter ion) exchange equilibria have been obtained. Attempt has also been made to explore the possibility of two-electron transfers between the salt and the parent compound⁵. Here we present a preliminary report on the optical and cyclic voltammetric studies of this compound. Analysis of the optical spectra throws new light on the structure of the salt and at the same time, the cyclic voltammetric studies give information regarding the hitherto unknown dissociation constants, K_{D3} , and disproportionation constants, K_3 , of the processes.



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EXPERIMENTAL

Chemicals. The solvent tetrahydrofuran was purified by first stirring it with LiAlH_4 and then distilling under vacuum over sodium-perylene or sodium-anthracene and kept over it on the vacuum line. Tetraphenylethylene was vacuum sublimed. Dimethylformamide and benzene were spectrograde, while tetrabutylammonium perchlorate was "suitable for polarographic grade".

Equipment. For voltammetric studies, PAR 174A Polarographic Analyser was used in conjunction with an X-Y recorder. A hanging mercury drop was used as working electrode, while a saturated calomel electrode was used as reference. A 2.5 cm platinum wire was used as the counter-electrode. Optical spectra were recorded on a Hitachi UV-VIS spectrophotometer (Model S220).

Preparation of the salt. Lithium, sodium, and potassium salt of tetraphenylethylene were prepared as described before¹⁻³. Rubidium salt was prepared by exchanging lithium cation for rubidium cation using rubidium tetraphenylboron or adding rubidium tetraphenylboron in large excess to a solution of $\text{T}^{2-}, 2\text{Na}^+$. The tetrabutylammonium salt was similarly prepared by exchanging the lithium cation for tetrabutylammonium using large excess of tetrabutylammonium perchlorate.

RESULTS AND DISCUSSION

Optical Studies

The disodium and dilithium salts of tetraphenylethylene, $\text{T}^{2-}, 2\text{M}^+$ ($\text{M} = \text{Na}, \text{Li}$), in tetrahydrofuran (THF), show absorption maxima at 485 nm ($\epsilon = 3.7 \cdot 10^4 \text{ l mol}^{-1} \cdot \text{cm}^{-1}$) ($\text{T}^{2-}, 2\text{Na}^+$), 395 nm ($\epsilon = 2.6 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$), and 385 nm ($\epsilon = 3.0 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$) (for $\text{T}^{2-}, 2\text{Li}^+$). Attempts were made to interpret these two bands¹⁻⁴. A look at the $\text{T}^{2-}, \text{Na}^+$ optical spectrum showed a shoulder around 385 nm, which prompted us to record the optical spectrum of potassium, rubidium, and tetrabutylammonium salts in THF and also to study the optical spectrum of the sodium salt at high dilution. Also, it was thought necessary to resolve the optical spectra of all these salts by a computer. The spectra of $\text{T}^{2-}, 2\text{M}^+$ ($\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{TBA}^+$) with the computer resolution are given in the Figs 1-6). The counter ion effects on the observed λ_{max} , the half width, and the ratio of the heights of peaks are collected in Table I.

On computer resolution, most surprisingly, we found that actually the observed bands are composed of three peaks with different heights. These component absorp-

tion peaks are located around 385 nm, 490 nm, and 585 nm, i.e. the position of the center peak is the average of the left and right peaks. With lithium the 385 nm and 490 nm peaks are pronounced. Otherwise, it is the 490 nm peak which is predominant. These component peaks can be interpreted as follows.

The 490 nm peak belongs to the free dianion¹⁻⁵, T²⁻, which is very close to C_{2v} structure: The two phenyl rings in a plane, the other two perpendicular to the plane containing the ethylenic carbon atoms and the other two phenyl rings. This structure is distorted to quite an extent when a lithium cation comes close to T²⁻ to form

TABLE I

Counter ion effect of the observed λ_{\max} , the half width β , and the ratio γ of the *O.D.* (375 nm) to *O.D.* λ_{\max} . T²⁻, 2 M⁺ in THF, conc. 10⁻²–10⁻⁴ mol l⁻¹, $\alpha(C/L)$, $\alpha(C/R)$ — ratio of the heights of the center (C), left (L), right (R) computer resolved peaks; β' — half width of the computer resolved peaks

Quantity	Li ⁺	Na ⁺	K ⁺	Rb ⁺	TBA ⁺
$\alpha(C/L)$	0.95	3.9 (3.3 ^a)	5.1	5.2	5.3
$\alpha(C/R)$	3.27	4.8 (5.5 ^a)	5.8	11.4	25.0
γ	0.88	2.7	3.0	3.8	4.5
β , nm	—	162	159	144	140
λ_{\max} , nm	385, 495	485	492	505	510
β' , nm	(48) (120)	(125)	(125)	(120)	(120)

^a Concentration 1 . 10⁻⁶ mol l⁻¹.

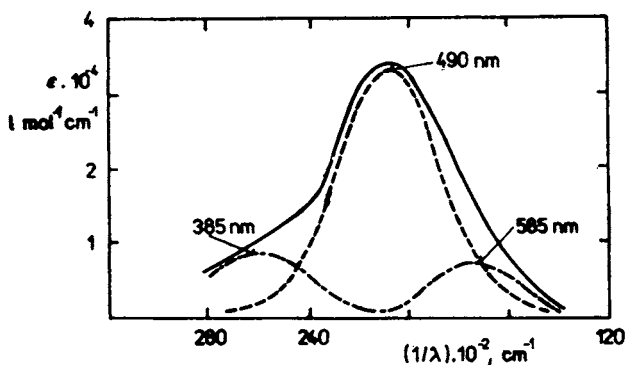


FIG. 1

Optical spectrum of T²⁻, 2 Na⁺ (10⁻²–10⁻⁴ mol l⁻¹ in THF (solid line); computer resolution (broken line)

T^{2-} , Li^+ , the structure becoming skewed with the lithium cation sticking to one pair of the "chromophores" very strongly and interacting very little with the other pair, hence a very strong absorption at 385 nm and a weak absorption at 585 nm. The sodium ion being of a "moderate" size, does not perturb much the T^{2-} free dianion structure and it is also located in such a way that it interacts, though moderately, with both the pair of the chromophores, hence the (resolved) peaks at 385 and 585 nm. The Rb^+ and TBA^+ being too big to interact with both the pairs of chromophores, interact moderately with one pair (note the ratio of the heights of the peaks at 385 and 490 nm, which is much smaller than the corresponding ratio for T^{2-} , Na^+). Also note the small height of the 585 nm band).

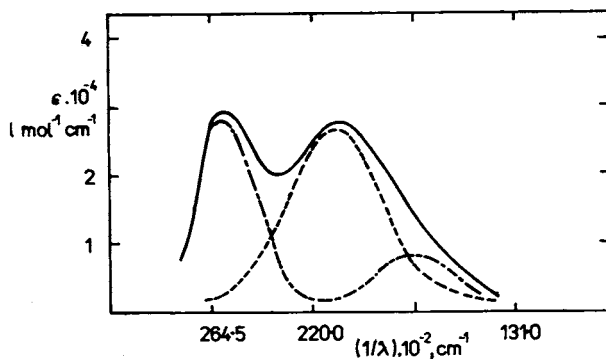


FIG. 2
Optical spectrum of T^{2-} , 2 Li^+ (10^{-2} — 10^{-4} mol l^{-1}) in THF

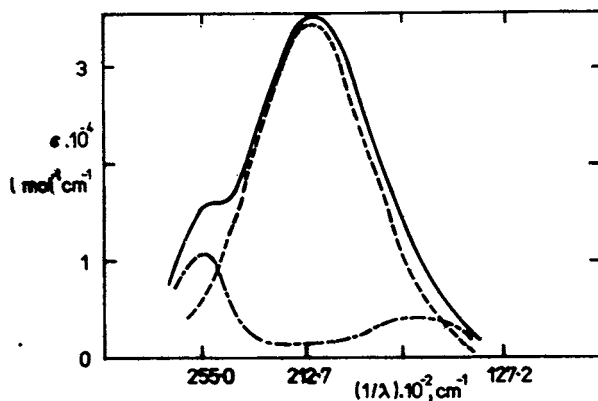


FIG. 3
Optical spectrum of T^{2-} , Na^+ at high dilution (10^{-6} mol l^{-1}) in THF

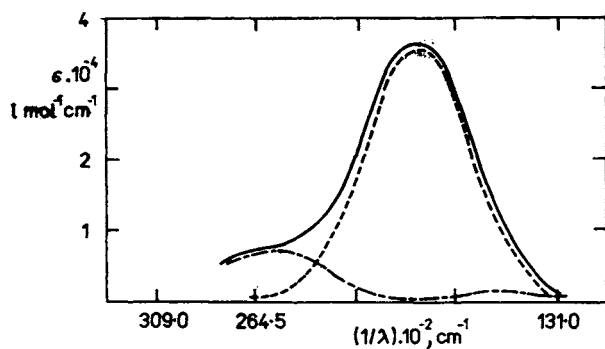


FIG. 4

Optical spectrum of T^{2-} , $2 K^+$ (10^{-2} – 10^{-4} mol l^{-1}) in THF

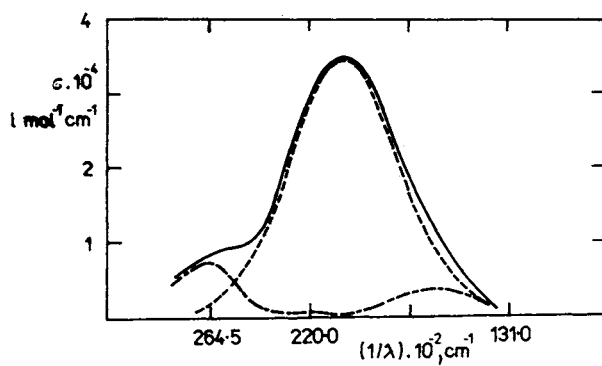


FIG. 5

Optical spectrum of T^{2-} , $2 Rb^+$ (10^{-2} – 10^{-4} mol l^{-1}) in THF

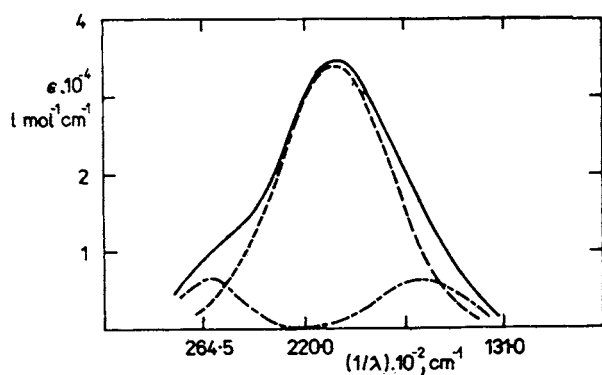


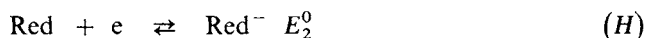
FIG. 6

Optical spectrum of T^{2-} , $2 TBA^+$ (10^{-2} – 10^{-4} mol l^{-1}) in THF

Another interesting information comes from the optical spectra of T^{2-} , $2 Na^+$ at high dilution ($10^{-6} \text{ mol l}^{-1}$). One can clearly see the well resolved peak at 385 nm, and the ratio of the heights of these peak is also different from T^{2-} , $2 Na^+$ at higher concentration ($10^{-2} - 10^{-4} \text{ mol l}^{-1}$, Figs 1, 3).

Cyclic Voltammetric Studies

A redox system giving reversible redox processes:



will give two reversible cyclic voltammograms from which the disproportionation constant, K , for the reaction



can be obtained from the relationship $\log K = \Delta E_{1/2}/0.060$.

TABLE II

Disproportionation constant K_3 (Eq. (F)) and calculated values of K_{D3} . K_3 is the average value calculated from line shape analysis (ref.¹³), from high scan rate and $(E_p)_c - (E_p)_a$ (ref.⁸), and from $E_p - E_{p/2}$ (ref.⁹); Z is the value of the solvent mixture; ϵ^0 is the dielectric constant of the solvent mixture

Mole fraction	K_3	Z	ϵ^0	$K_{D3} \cdot 10^{5a}$
DMF-benzene				
1.0	0.42 (± 0.16)	68.4	36.7	1.2
0.8	0.34 (± 0.14)	65.4	28.5	1.0
0.6	0.26 (± 0.12)	62.2	22.2	0.8
0.4	0.22 (± 0.11)	59.5	14.3	0.7
0.3	0.16 (± 0.10)	56.6	12.2	0.5
0.0	0.07 ^b	54.0	2.2	0.2
Dioxane-water ^c				
0.4 (75% diox)	0.21	78	47.9	0.6
0.8 (95% diox)	0.14	63.5	17	0.4

^a For T^{2-} , Na^+ , values of K_2 and K_{D1} are 3.3 and $10 \cdot 10^{-5} \text{ mol l}^{-1}$, respectively; ^b extrapolated value; ^c taken from Hojtink (ref.⁶).

Theories are available⁷⁻¹¹ to obtain $\Delta E_{1/2}$ and hence K from the observed cyclic voltammogram, even if it is a composite of two. The cyclic voltammograms of tetraphenylethylene were recorded in dimethylformamide (DMF) and DMF-benzene mixture, with tetrabutylammonium perchlorate as supporting electrolyte. Tetra-butylammonium ion does not form an ion pair in this solvent. Thus $\Delta E_{1/2}$ would give the desired K , i.e., K_3 of the process given in Eq. (F). This disproportionation constant (not available from earlier work) thus calculated is given in Table II.

Szwarc and Robert¹ showed that K_3 should be much smaller than K_2 (Eq. (E)) for sodium salt of tetraphenylethylene which is equal to 3.3. Our data confirm this observation (Table II). The decrease in K_3 with the dielectric constant (DMF-benzene mixture with increasing benzene content) is explained on the basis of decrease in the free energy of the solvation process¹² (since $\Delta G_d = A - \Delta S$, where ΔG_d is free energy of disproportionation, $A = \text{constant}$, and ΔS is free energy of solvation) based on the Born model.

It can be shown that $K_3/K_2 = K_{D3}/K_{D1}$. K_2 and K_{D1} values are available in the literature¹ (but note the typographical error in the expression for K_3 on p. 5547 of ref.¹), K_{D3} (the second ionization constant of the tetraphenylethylene salts) can be calculated, since K_3 values are now available (Table II). Values of K_{D3} for T^{2-} , Na^+ were calculated and are also given in Table II.

Thus, information about the tetraphenylethylene salt at room temperature has been obtained. Extension of the study to lower temperatures and other solvent systems will be a subject of another communication.

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