Free-Radical Anions and Dianions of Tetraphenylethylene

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Abstract: Conductance studies demonstrated that the dianions of tetraphenylethylene, T^{2-}, are not paired with counterions in hexamethylphosphoramide (HMPA). The lack of pairing permitted us to determine the relative electron affinity of tetraphenylethylene, T, using spectrophotometric and potentiometric methods. Thus, the electron affinity of T in HMPA is by 0.50 V higher than that of biphenyl. The disproportionation constant of the radical ions, $T\cdot^-$, in HMPA is $K_3 = 2 \times 10^{-4}$, $2T\cdot^- \rightleftarrows T + T^{2-}$ (K_3), while the disproportionation of ion pairs in THF, *i.e.*, $2T\cdot^-,Na^+ \rightleftarrows T + T^{2-},2Na^+$, corresponds to $K_1 = 400$ and that of $T\cdot^- + T\cdot^-,Na^+ \rightleftarrows T + T^{2-},Na^+$ in THF is $K_2 = 3.3$, all at 25°. The significance of these data is discussed. The esr spectrum of the unpaired $T\cdot^-$ radical ions consists of at least 61 evenly spaced lines. It was shown that such spectrum is consistent with the following hyperfine splitting constants: $a_m = 0.38$ G, $a_o = 1.5$ G, and $a_p = 2.3$ G, these results being confirmed by computer simulation of the experimental spectrum. The electron-transfer processes $T\cdot^- + T \rightleftarrows T + T\cdot^-$, k_1, and $T\cdot^- + T^{2-} \rightleftarrows T^{2-} + T\cdot^-$, k_2, were investigated. The overlap of the closely spaced lines prevents accurate determination of k_1 and k_2, but it was shown that both are of about $10^7\ M^{-1}\ \mathrm{sec}^{-1}$.

The radical anions, $T\cdot^-$, and dianions, T^{2-}, of tetraphenylethylene, T, are formed when one or two electrons, respectively, are donated to this hydrocarbon. In the past these species were generated in ethereal solutions[1-3] where at least a partial pairing of anions with counterions takes place. The pairing is particularly pronounced for the dianions and, consequently, only $T^{2-},2Na^+$ and T^{2-},Na^+ were present in those solutions, the concentration of the free T^{2-} dianions being negligible. Our present studies showed that virtually all $T^{2-},2Na^+$ are dissociated into $T^{2-} + 2Na^+$ in hexamethylphosphoramide (HMPA), and, therefore, properties of the free T^{2-} dianions could be investigated in this solvent.

The extensive dissociation of $T^{2-},2Na^+$ in HMPA permitted us to determine the disproportionation constant, K_3, of the equilibrium shown in eq 3. K_3 was found

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

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

$$2T\cdot^- \rightleftarrows T + T^{2-} \qquad (3)$$

to be much smaller than K_1 or K_2. The latter refer to the previously investigated[3] equilibria 1 and 2 maintained in tetrahydrofuran. The minuteness of K_3 makes it possible to prepare solutions of $T\cdot^-$ in HMPA[4] practically free of T or T^{2-}. This greatly simplifies studies of the free $T\cdot^-$ radical anions.

Conductance Studies in Hexamethylphosphoramide (HMPA)

Most of the alkali salts of organic anions are extensively dissociated in HMPA, the pairing being negligible at concentrations lower than $10^{-2}\ M$. For such solutions the equivalent conductance, Λ, is nearly linear with the square root of salt concentration; this behavior has been observed for the salts of tetraphenylboride, anthracenide, and tetraphenylethylene dianions. The slopes of the relevant lines have values which approximate those predicted by the Onsager limiting law. This is illustrated in Figure 1. The extrapolation led to the limiting conductances, Λ_0, listed in Table I.

Table I. Limiting Conductance Λ_0 of Alkali Salts in Hexamethylphosphoramide at 25°[a]

	Li^+	Na^+	$(Isoamyl)_3BuN^+$
Tetraphenylboride	10.7	11.5	12.1
Anthracenides	16.4	17.2	...
Tetraphenylethylene dianion	...	25.3	...

[a] All the data in $cm^2\ ohm^{-1}\ equiv^{-1}$.

Fuoss has shown[5] that cations and anions derived from $(isoamyl)_3BuN^+,BPh_4^-$ equally contribute to the conductance of this salt. On this basis the $\lambda_0^-(BPh_4^-)$ in HMPA was calculated as 6.0. Having this value, we computed the λ_0^+ and λ_0^- of other ions using the data given in Table I. The pertinent results are collected in Table II. No rigid solvation shells are formed around $(isoamyl)_3BuN^+$ cations or around BPh_4^- or anthracenide$\cdot^-$ anions. This is demonstrated by the validity of Walden rule (see Table II).

Assuming that the dissociation of $T^{2-},2Na^+$ yields $T^{2-} + 2Na^+$, we calculate $\lambda_0^-(T^{2-})$ as 14.5. The size of this ion is likely to be comparable to that of BPh_4^- or $T\cdot^-$ and, therefore, its λ_0^- should be about twice as high as the respective λ_0^- of the latter two ions. This is the case: $\frac{1}{2}\lambda_0^-(T^{2-}) = 7.2$ while $\lambda_0^-(BPh_4^-) = 6.0$, and $\lambda_0^-(T\cdot^-)$ was calculated to be 7.1 by applying Walden rule to the data reported in ref 3. On the other hand, an unreasonably large value of 20 would be derived for $\lambda_0^-(T^{2-},Na^+)$ if our data characterize a solution in which the dissociation of $T^{2-},2Na^+$ is limited to the first step only.

The above calculation provides the strongest evidence

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[1] (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).

[2] (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).

[3] R. C. Roberts and M. Szwarc, *ibid.*, **87**, 5542 (1965).

[4] A. Cserhegyi, J. Chaudhuri, E. Franta, J. Jagur-Grodzinski, and M. Szwarc, *ibid.*, **89**, 7129 (1967).

[5] M. A. Coplan and R. M. Fuoss, *J. Phys. Chem.*, **68**, 1177 (1964).

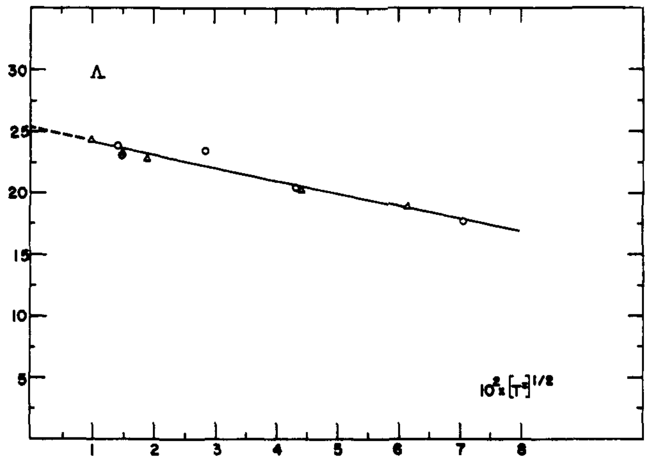

Figure 1. Equivalent conductance Λ in cm^2 ohm^{-1} equiv^{-1} as a function of the square root of the concentration of tetraphenyldisodium: solvent hexamethylphosphoramide, temperature 25°, concentration range 1×10^{-4}–5×10^{-3} *M*; – – –, calculated limiting slope (see R. M. Fuoss and D. Edelson, *J. Am. Chem. Soc.*, **73**, 269 (1951); **75**, 2914 (1953)).

Table II. Ionic Limiting Conductances and Walden Products in Hexamethylphosphoramide (HMPA) and in Tetrahydrofuran (THF) at 25° [a]

Cation	λ_0^+ in HMPA	$\eta\lambda_0^+$ in HMPA	$\eta\lambda_0^+$ in THF
$(\text{Isoamyl})_3\text{BuN}^+$	6.0	18.7	18.9
Li^+	4.6	14.4	22.8
Na^+	5.4	16.9	20.8
Anion	λ_0^- **in HMPA**	$\eta\lambda_0^-$ **in HMPA**	$\eta\lambda_0^-$ **in THF**
B(Ph)_4^-	6.0	18.7	18.9
Anthracene$^-$	11.8	36.5	35.4
T^{2-}	14.5	45.0	...

[a] The viscosities are given in centipoises, λ's in cm^2 ohm^{-1} equiv^{-1}.

Table III. Product of the Equivalent Conductance, Λ, of $\text{T}^{2-},2\text{Na}^+$ and Solvent's Viscosity, η, at Different Temperatures[c]

Temp, °C	15	25	35	45	55	70
ηΛ, ohm^{-1} *M*$^{-1}$, cm^3 g sec^{-1}	0.59	0.58	0.58	0.57	0.57	0.56

[a] $[\text{T}^{2-},2\text{Na}^+] = 5 \times 10^{-3}$ *M*.

for the virtually quantitative dissociation of $\text{T}^{2-},2\text{Na}^+$ into $\text{T}^{2-} + 2\text{Na}^+$. The findings shown in Table III support this conclusion. The product ηΛ is virtually constant in the temperature range 15–70°, η denoting the viscosity of HMPA and Λ the equivalent conductance of a 5×10^{-3} *M* solution of $\text{T}^{2-},2\text{Na}^+$. For a partially dissociated salt the product ηΛ is constant only if $\Delta H_{\text{diss}} = 0$. This is unlikely and, therefore, we again conclude that in a 5×10^{-3} *M* HMPA solution the dissociation of $\text{T}^{2-},2\text{Na}^+$ is virtually quantitative, and yields T^{2-} and 2Na^+.

Electron Affinity of Tetraphenylethylene and the Disproportionation of Its Radical Anions

Table IV. Equilibrium $\pi\cdot^- + \text{T} \rightleftarrows \text{T}\cdot^- + \pi$ in Hexamethylphosphoramide at 25°

$[\text{T}]_0$, 10^3 *M*	$[\text{T}\cdot^-]_0$ (effective), 10^3 *M*	$[\pi]_0$, 10^3 *M*	$[\pi\cdot^-]_0$, 10^3 *M*	$[\text{T}\cdot^-]_e$, 10^3 *M*	$[\pi\cdot^-]_e$, 10^3 *M*	$K_{\text{T},\pi}$
0.6	5.1	2.7	0.0	3.8	1.15	2.7
0.6	5.1	5.4	0.0	2.9	1.6	2.5
0.11	0.39	0.24	0.0	0.29	0.08	2.8
0.11	0.39	0.50	0.0	02.4	0.12	2.9
3.1	0.0	6.1	0.73	0.42	0.32	3.0
6.3	0.0	6.1	0.73	0.54	0.22	2.8
					Average	2.8

Relative electron affinity of tetraphenylethylene was determined by two techniques: spectrophotometric and potentiometric.[6] The difference of electron affinities of tetraphenylethylene and pyrene was evaluated by determining spectrophotometrically the equilibrium constant of the electron-transfer reaction

$$\pi\cdot^- + \text{T} \rightleftarrows \text{T}\cdot^- + \pi$$

Here π denotes pyrene and $\pi\cdot^-$ its radical anion. The potentiometric titration of tetraphenylethylene with sodium biphenyl in HMPA gave the difference of electron affinities of T and biphenyl. Because both studies were performed in HMPA, the investigated processes involved the free ions and not the ion pairs.

Pyrene was chosen for the spectrophotometric studies because the spectra of $\text{T}\cdot^-$ and $\pi\cdot^-$ do not overlap unduly, and because electron affinities of T and π were expected to be comparable. The following absorption bands were used in the investigation (see ref 3 and 6).

λ	498 mμ	660 mμ
$\pi\cdot^-$	$\varepsilon\ 4.95 \times 10^4$ (max)	$\varepsilon\ 0.11 \times 10^4$
$\text{T}\cdot^-$	$\varepsilon\ 0.94 \times 10^4$	$\varepsilon\ 1.13 \times 10^4$ (max)

The details of the experimental technique were described elsewhere.[6,7] The results are summarized in Table IV. The average value of $K_{\text{T},\pi} = 2.8 \pm 0.2$; *i.e.*, the electron affinity of tetraphenylethylene in hexamethylphosphoramide is by 0.03 V higher than that of pyrene.

The investigated mixtures of $\text{T}\cdot^- + \text{T}$ contained a small amount of T^{2-} (~1%) as was evident from the spectrophotometric data. Consequently, the effective $[\text{T}\cdot^-]_0$, listed in the second column of Table IV, was calculated as $[\text{T}\cdot^-]_0 + 2[\text{T}^{2-}]_0$. The amount of T^{2-} present in equilibrated $\text{T} + \text{T}\cdot^-$ mixture is compatible with a value of about 8×10^{-4} for the equilibrium constant K_3 of the disproportionation. This value represents only the order of magnitude for K_3 because the concentration of T^{2-} could not be determined accurately. A more reliable value for K_3 was obtained from potentiometric studies.

The potentiometric titrations were performed in an apparatus originally developed by Hoijtink and modified in our laboratory.[6] The titrating solution of 10^{-2} *M* sodium biphenyl in HMPA contained about five times excess of the parent hydrocarbon. The titration curve is shown in Figure 2; the points marked on the curve give the uncorrected $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$. The difference $\Delta\varepsilon_{1,\text{T}}^0$ of the standard redox potentials of tetraphenylethylene

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(6) J. Jagur-Grodzinski, M. Feld, S. L. Yang, and M. Szwarc, *J. Phys. Chem.*, **69**, 628 (1965).

(7) J. Chaudhuri, S. Kume, J. Jagur-Grodzinski, and M. Szwarc, *J. Am. Chem. Soc.*, **90**, 6421 (1968).

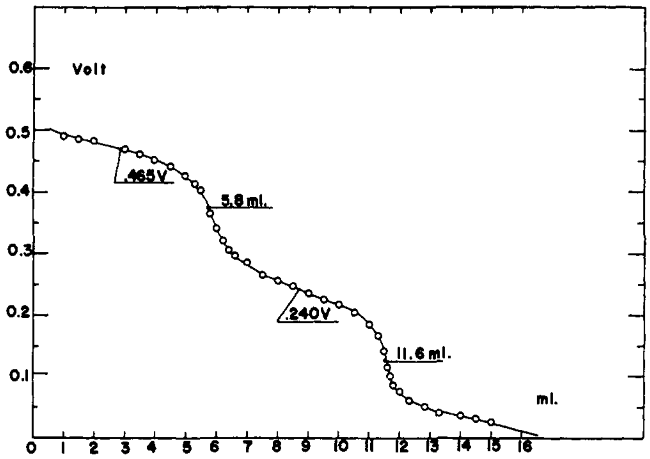

Figure 2. Potentiometric titration of tetraphenylethylene with 10^{-2} M sodium biphenyl: solvent hexamethylphosphoramide, temperature 25°.

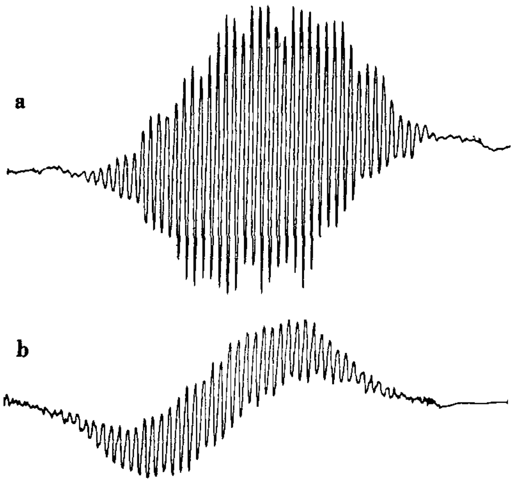

Figure 3. Radical anion of tetraphenylethylene in HMPA at 35°: first-derivative esr spectrum, scan time 10 min, range 50 G: (a) $[T^{2-}] \sim 0$, (b) $[T^{2-}] = 5 \times 10^{-2}$ M.

and biphenyl is therefore 0.50 V. The titration of pyrene[8] led to $\Delta\varepsilon_{1,\pi}{}^0 = 0.48$ V; *i.e.*, the difference of electron affinities of T and π in HMPA is 0.02 V in agreement with the spectrophotometric findings.

The second potential $\Delta\varepsilon_2$ refers to the process $T\cdot^- + e \rightleftarrows T^{2-}$, and therefore the equilibrium constant, K_3, of the disproportionation in HMPA

$$2T\cdot^- \rightleftarrows T + T^{2-}$$

is given by $-0.06 \log K_3 = \Delta\varepsilon_1 - \Delta\varepsilon_2$, *i.e.*, $K_3 = 2 \times 10^{-4}$.

The disproportionation constants were previously determined in tetrahydrofuran, namely, K_1, referring to the process $2T\cdot^-,Na^+ \rightleftarrows T + T^{2-},2Na^+$, and K_2, describing the reaction $T\cdot^- + T\cdot^-,Na^+ \rightleftarrows T + T^{2-},Na^+$. It was shown[3] that due to the bulkiness of $T\cdot^-$, the $T\cdot^-,Na^+$ forms a solvent-separated ion pair, whereas the $T^{2-},2Na^+$ aggregate forms a poorly solvated quadrupole. Hence, the disproportionation of $2T\cdot^-,Na^+$ into $T + T^{2-},2Na^+$ is driven by a substantial gain in the entropy of the system resulting from the release of the ether molecules tightly bounded around the Na^+ ions in the $T\cdot^-,Na^+$ solvent-separated ion pairs as well as from the decreased order in the solvent caused by the replacement of strongly polar $T\cdot^-,Na^+$ ion pairs by quadrupoles of $T^{2-},2Na^+$. The gain in entropy more than balances the loss of solvation energy and, therefore, this process is favored, in spite of its endothermicity, as indicated by the large value of $K_1 = 400$. Similar gain in entropy, although smaller, is responsible for the favorable disproportionation of $T\cdot^- + T\cdot^-,Na^+$; $K_2 = 3.3$ only albeit ΔH_2 is smaller than ΔH_1. No entropy gain is available for the disproportionation of the free $T\cdot^-$ radical ions in the gas phase, while crowding of two electrons on one molecule makes the process endothermic. Although a small entropy gain may be expected for the disproportionation of free $T\cdot^-$ ions in HMPA, the endothermicity of the reaction accounts probably for the low value of 2×10^{-4} for K_3 in this solvent. The magnitude of ΔH_3 is not known. Assuming $\Delta S_3 \approx 0$, we calculate $\Delta H_3 \sim 5$ kcal/mole.

Comparison of the titration curve of tetraphenylethylene in HMPA with that obtained previously[6] in tetrahydrofuran is interesting. When the titration is carried out in the ether, the potential remains approximately constant until nearly 2 equiv of sodium biphenyl is added, and then rapidly decreases (see Figure 2 of ref 6). The removal of $T\cdot^-$ radical ions, which disproportionate in tetrahydrofuran, accounts for the shape of this titration curve. Such a complication is avoided in HMPA.

The Esr Studies of $T\cdot^-$ Radical Ions

The esr studies of $T\cdot^-$ radical ions are greatly facilitated if one avoids their pairing with counterions and ascertains the absence of T or T^{2-} in their solutions. These conditions may be fulfilled when the radical ions are prepared in HMPA. The presence of T or T^{2-} broadens the esr lines, and this distorts the spectrum. Such an effect is clearly seen in Figure 3.

Examination of the spectra obtained by other workers[1,9] as well as those recorded in this laboratory showed the presence of equally spaced lines only, their spacing being determined in our spectra as 0.38 G. A more complex spectrum was published by Warhurst, *et al.*,[10] who claims a better resolution; their line width was 60 mG as compared with 130 mG found for the wing of our spectra.

It seems that the hyperfine splitting constants (hpsc) of *para*, *ortho*, and *meta* protons are multiple integers of 0.38 G; however, as shown by Warhurst's spectrum, the coincidence is not perfect. The largest number of lines was found in our studies; 57 lines were definitely observed, and probably 4 more lines were recorded, although their relative intensities could not be reliably determined because of the low signal-to-noise ratio.

Denote by 0 the center line and by positive and negative integers the subsequent lines of the low- and high-field wings, respectively. It was established that (a) the number of lines is greater than 57 and probably greater than 61; (b) all the lines from 0 to ±29 (and probably to ±30) are spaced by 0.38 G; (c) within the

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[8] J. Chaudhuri, J. Jagur-Grodzinski, and M. Szwarc, *J. Am. Chem. Soc.*, in press.

[9] J. F. Garst and R. S. Cole, *ibid.*, **84**, 4352 (1962).

[10] J. C. Chippendale, P. S. Gill, and E. Warhurst, *Trans. Faraday Soc.*, **63**, 1088 (1967).

Table V. Relative Intensities of the 28 Lines of the Low-Field Half of the First Derivative Esr Spectrum of T$\cdot^-$

Line no.	Expt1[a]	6:4:1 65 lines[b]	Line no.	Exptl	6:4:1 65 lines[b]
27	1.0[c]	1.0[c]	13	127	115
26	1.8	2.1	12	139	135
25	2.5	4.0	11	145	165
24	5.5	5.6	10	171	190
23	8.0	7.1	9	204	203
22	12	11	8	224	218
21	17	17	7	*202*	244
20	21	25	6	225	274
19	33	32	5	242	302
18	50	38	4	248	306
17	58	49	3	*236*	*304*
16	68	64	2	*234*	309
15	85	84	1	240	336
14	110	107	0	257	350

[a] Determined at 25° in HMPA from a blown-up spectrum with 1 G = 15 in. [b] Computer simulation. [c] Intensity of line no. 27 was used as reference.

Table VI. Proton Splitting Constants of T$\cdot^-$ in Gauss

	Present work[a]	Garst, *et al.*[9]	Warhurst, *et al.*[10] [b]	Calculated[10] McLachlen	Calculated[10] Hückel
a_m	0.38 ± 0.02	0.83	0.45	0.46	0.04
a_o	1.52 ± 0.04	1.7 or 2.1	...	1.45	1.10
a_p	2.28 ± 0.04	2.1 or 2.5	2.12	1.68	1.26

[a] In hexamethylphosphoramide at 25°. [b] In dimethoxyethane, K^+ counterion.

series 27 to 0 the heights of the spikes (measured from their minimum to maximum) form a monotonic series, the lines 2 and 3 and probably 7 and 8 being the only exceptions (the lines 28, 29, and 30 are definitely weaker than the 27 one); (d) the ratio of heights (and of areas) of the center line and of the 27 line is about 250:1. The intensity of the latter is reliable within 25%. Hence, the ratio of the respective absorptions must be even greater because the overlap reduces the ratio of the heights.

Definite assignment of the *para*, *ortho*, and *meta* splitting constants would be possible had the intensities of the very last lines of the *complete* esr spectrum been reliably determined. This was unfeasible, and therefore an alternative method was chosen to solve the problem. It was assumed that the ratio of hfsc of *para*:*ortho*:*meta* protons is given by the integer multiples of 0.38 G. It was established, however, that small deviations from the integers do not affect our basic conclusions. Using the observations a and d as the criteria, we demonstrated that the integers cannot be greater than 7 and those for *para* and *ortho* protons cannot be simultaneously smaller than 4. Criteria b and c allowed us to rule out most of the assignments that were still consistent with conditions a and d. Thus, the plausible assignments are 7:3:1, 6:4:1, 5:4:3, and 5:4:1. Computer simulations based on Lorentzian lines having three different line widths (100, 130, and 150 mG) were then performed, the best results being obtained with the assignment 6:4:1 as shown in Table V. The reliability of this conclusion was tested by repeating the computer calculations with hfsc which slightly deviated from the integer multiples of 0.38 G (deviations which are larger than 0.04 G lead to more complex structures of the spectrum, even for the line width 130 mG, this being contrary to the observations).

In conclusion, it seems that the hfsc for the free T$\cdot^-$ radical ion in HMPA are 2.28 G for *para*, 1.52 G for *ortho*, and 0.38 G for *meta*. These values are compared in Table VI with those proposed by other workers and with those calculated on the basis of Hückel and of McLachlan approaches.

On addition of T or T^{2-} to the investigated solution, the esr spectrum of T$\cdot^-$ collapses (compare Figures 3a and 3b). The distortion is caused by the electron-transfer processes, *viz.*

$$T + T\cdot^- \rightleftarrows T\cdot^- + T \qquad k_1$$

$$T^{2-} + T\cdot^- \rightleftarrows T\cdot^- + T^{2-} \qquad k_2$$

Because of the overlap in the original spectrum, the broadening of the lines is manifested by the decrease of their intensities. Accurate calculation of k_1 and k_2 is therefore somewhat ambiguous. Approximate treatment of the data indicates that both rate constants are of the order of $10^7\ M^{-1}\ \text{sec}^{-1}$.

Finally, the unusual broadness of the lines of the pure T$\cdot^-$ radical ions (~130 mG) calls for comments. The effect cannot be due to the hindered rotation of the radical ion caused by the high viscosity of HMPA because the esr lines of many radical anions (planar aromatics or their nitrogen derivatives) in HMPA were found to be sharp.[7] Perhaps the high viscosity of HMPA hinders the flapping motion of the phenyl groups in the T$\cdot^-$.

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