Optical Studies of Triphenylene Anion

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Abstract: The optical absorption spectra have been measured of alkali metal reduced solutions of triphenylene in 2-methyltetrahydrofuran from −155 to +75°. Several ion pairs have been observed. A linear correlation between frequency of absorption and reciprocal of cation radius has been demonstrated for both solvated and contact ion pairs. The low-temperature spectra show a clear equilibrium between two types of ion pairs at high radical concentrations. Its thermodynamic parameters have been measured for sodium, potassium, and rubidium triphenylene solutions. At low-radical concentration dissociation occurs into free ions. The dissociation enthalpy and entropy have been determined. The high-temperature spectra show a gradual increase in frequency as the temperature is increased. This shift has been interpreted as due to an equilibrium between solvated and contact ion pairs. For potassium, rubidium, and cesium triphenylene solutions the thermodynamic constants characterizing the latter equilibrium have been calculated.

In recent years interest in ion pairing has produced several outstanding studies using electron spin resonance[1] (esr) and optical spectroscopy.[2] In these studies it was demonstrated that both temperature and cation changes introduced large effects on both types of spectra. These effects were rationalized in terms of several types of ion pairs.

In this paper we will discuss the ion pairs derived from triphenylene (Tp). The mononegative ion of Tp is orbitally degenerate in its ground state. Anions with degenerate ground states are of special interest because small changes in their surroundings can cause relatively large perturbation in their energy levels. Both counterions and solvent molecules can cause these changes. van Willigen, van Broekhoven, and de Boer[3] (hereafter referred to as I) studied the various species of Tp anion in solution by means of esr. However, with esr information obtained is in certain aspects limited, because one is confined to studying low concentrations of radicals over a limited temperature range. In this paper we would like to show that with optical spectroscopy more detailed information is obtained about the Tp species in solution. The combined results of both studies provide a complete picture of the various ion-pair equilibria.

The optical absorption spectra of Tp anions dissolved in 2-methyltetrahydrofuran (MTHF), with Na, K, and Rb as counterion, pointed to the existence of at least three different species. With Cs as counterion only two species were found and with Li only one. We propose that the concentrations of these species are interrelated by several equilibria and that at least four different species are needed to explain all the effects observed with variations in temperature and concentration. The temperature-dependent changes in the optical spectra were used to calculate the thermodynamic quantities in these equilibria. All equilibria showed a marked dependence on the counterion.

Experimental Section

Commercially available Tp (mp 199°) was recrystallized from cyclohexane and sometimes sublimed before use. The solvent MTHF was stored over Na–K alloy and distilled into the glass apparatus just prior to use. The alkali metals (except Li) were sublimed at least twice to obtain a good mirror. Fresh pieces of Li were washed with ether and used as such. The preparation of alkali metal reduced solutions followed the usual procedures described elsewhere (see I). The entire glass apparatus was rinsed with a solution of Tp anion after which this solution was discarded and a fresh one was made for the optical absorption measurements.

The optical spectra were measured with a Cary 14 spectrophotometer equipped with a variable-temperature dewar. A Cryoson temperature controller monitored the flow of cold nitrogen into the dewar and heated it when necessary. The temperature in the dewar was measured by a copper–constantin thermocouple. The temperature was stable at the lower temperatures (below −50°) within 1° (±0.5°) but at higher temperatures the stability was somewhat less (±1°). Partially reduced solutions of Tp were used, to avoid the formation of the dinegative ion.

For spectra where isosbestic points were observed (see Results), the concentrations of the species present were calculated using optical densities measured at the characteristic frequencies of each species (see Table I). The extinction coefficients were calculated based on $\epsilon_{750\ \mathrm{nm}} = 5550$ measured for Tp monoanion in tetrahydrofuran at 25°.[4] The temperature-dependent change in the extinction coefficients for the range where isosbestic points were observed was no more than 15% and had negligible effect on the calculation of the equilibrium constant K_1, because K_1 is equal to the ratio of two concentrations, which are calculated from the equally temperature affected extinction coefficients.

Furthermore the occurrence of isosbestic points (see Figures 1 and 2) and the fact that superposition spectra could be simulated perfectly from the spectra of the two components demonstrate the correctness of our approach.

Results

The optical spectra of Tp anion dissolved in MTHF were measured from −155 to +75°. From the measurements the following observations can be made.

Li Reduced Solutions. No shifts in the spectra were found over the whole temperature range for Tp anion concentrations from 1×10^{-4} to 8×10^{-4} *M*.

Na Reduced Solutions. Between −110 and −70° the spectra changed quite dramatically. The spectrum observed at −110° was replaced at higher temperatures by a similar spectrum shifted to higher frequencies. Several spectra measured between −120 and −70° for a 6×10^{-4} *M* Tp anion solution are shown in Figure 1. The presence of several isosbestic points indicates that one species is converting into another. If the concentration of Tp anion is below *ca.* 5×10^{-4} *M*, the same pattern of spectra is observed but at a particu-

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[1] See, for example, N.Hirota in "Radical Ions," E. T. Kaiser and L. Kevin, Ed., Wiley-Interscience, New York, N. Y., 1968, Chapter 2.

[2] R. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307, 318 (1966), and subsequent papers in the series.

[3] H. van Willigen, J. A. M. van Broekhoven, and E. de Boer, *Mol. Phys.*, **12**, 533 (1967).

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

Table I. $\gamma_{\max}$ Measured at Various Temperatures for the Three Main Absorption Bands in the Optical Spectra of Triphenylene Monoanion in MTHF with Different Counterions (Frequencies in 1000 cm^{-1})

Counter-ion	T, °C	Type 1			T, °C	Type 2			T, °C	Type 3		
		Band 1	Band 2	Band 3		Band 1	Band 2	Band 3		Band 1	Band 2	Band 3
Li	−108	13.12	14.56	18.35								
Na	−110	13.12	14.58	18.35	−70	13.66	15.04	19.31	+20	13.77	15.15	19.53
K	−142	13.14	14.60	18.35	−88	13.48	14.88	19.01	+72	13.78	15.02	19.42
Rb	−155	(13.25)[a]	(14.71)[a]		−130	13.44	14.84	18.94	+23	13.62	14.99	19.31
Cs					−145	13.39	14.82	18.83	+33	13.58	14.93	19.08

[a] Lowest values measured, probably not indicative for the type 1 spectra.

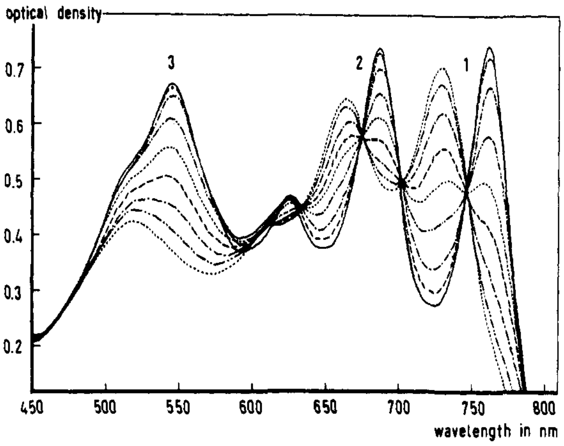

Figure 1. Several spectra measured for a 6×10^{-4} M NaTp solution at −130 (——), −121 (- - -), −112 (-·-), −102 (-··-), −96 (---), −89 (- - -), −81 (-·-), −74 (-··-), and −66° (---). The three prominent bands starting at the highest wavelength are designated 1, 2, and 3.

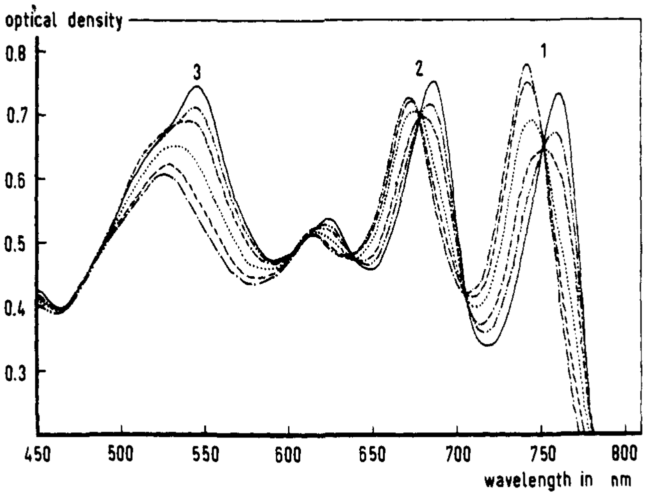

Figure 2. Several spectra measured for a 5×10^{-4} M KTp solution at −139 (——), −133 (-··-), −127 (-·-), −121 (···), −112 (- - -), and −105° (-·-).

lar temperature the shape of the spectrum depends on the total radical concentration.

The latter phenomenon was not observed when the concentration of radical anion was much higher. Between −70 and +30° the spectra continue to shift to higher frequencies but the change is much slower and neither concentration effect nor isosbestic points were observed. Further, the absorption peaks broaden and the extinction coefficients appear to decrease. Several concentrations of Tp anion were investigated ranging from 2×10^{-5} to 1×10^{-2} M.

K Reduced Solutions. The same pattern outlined for NaTp solutions was found for KTp solutions except that the temperatures at which these effects were observed were lower. Thus, between −139 and −90° the spectra change drastically, with the spectrum at −139° replaced at higher temperatures by a similar one shifted to higher frequencies. Several spectra observed between −139 and −90° are shown in Figure 2. Various isosbestic points are clearly present. Further, the same concentration effect was observed as for NaTp solutions when the concentration was below *ca.* 4×10^{-4} M. Above −90° the spectra continue to shift to higher frequencies, but above +60° no further shift was seen. Several concentrations of Tp anion were investigated ranging from 2×10^{-4} to 1×10^{-2} M.

Rb Reduced Solutions. The same pattern occurs for RbTp solutions as was found for solutions of NaTp and KTp, but at still lower temperatures. Between −155 and −130° the spectrum changes rapidly and isosbestic points are present; above −130° the shift in frequency is slow. No concentration effects were observed in the anion concentration range from 1×10^{-4} to 5×10^{-4} M.

Cs Reduced Solutions. Between −150 and +30° the spectrum slowly shifts to higher frequencies. In contrast to the previously discussed studies of NaTp, KTp, and RbTp solutions, no temperature range was found where rapid changes in the optical spectra occurred.

From the outline of the temperature-dependent changes in the optical spectra of the alkali metal reduced solutions of Tp it is clear that three different types of spectra need to be examined: those spectra observed at the lowest temperatures measured (type 1), the spectra that replace these type 1 spectra upon raising the temperature (type 2), and the spectra observed at the highest temperatures (type 3). The numbering of the three types of spectra is the same as the numbering used for the three different esr spectra observed for NaTp solutions and which have been previously reported in I. The positions of the three prominent absorption maxima of these types of spectra are listed in Table I. When the frequencies of the absorption maxima of type 2 and type 3 spectra are plotted *vs.* the inverse of the cation radius, linear plots are obtained. In Figure 3 such a plot is given for the second absorption band. As expected, these correlation plots predict frequencies for infinite cation radius which appear to be nearly identical with the frequencies measured for LiTp solutions and for NaTp and KTp solutions at low temperatures (type 1).

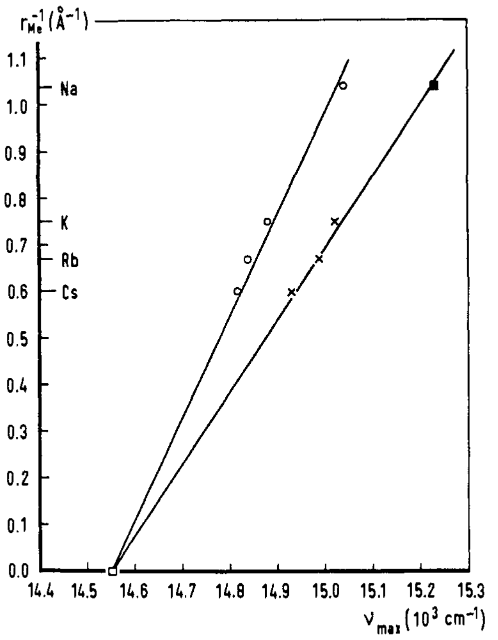

Figure 3. A plot of the absorption maximum frequency of band 2 *vs.* the reciprocal of the alkali metal cation radius for type 2 (○) and type 3 (×) spectra for alkali metal reduced solutions of Tp: ☐ refers to the absorption maximum frequency of band 2 for infinite cation radius (type 1 spectra); ☒ calculated point for the absorption maximum frequency of NaTp (see text).

Discussion

Type 1 and Type 2 Spectra. As established previously,[5] the formation of "free" ions is favored by small cation radius, low temperatures, and low concentrations. These conditions are probably best fulfilled for Li reduced solutions of Tp where only one species is observed. Since in Na and K reduced solutions of Tp at sufficiently low temperatures spectra are measured which are identical with the spectra found in solutions of LiTp (see Table I, column 1), these too should be ascribed to the "free" ion. Thus the observed spectral changes could be attributed to the following equilibrium

$$\mathrm{Tp^-//Me^+ \rightleftarrows Tp^- + Me^+}$$

where $\mathrm{Tp^-//Me^+}$ is a solvent-separated ion pair and $\mathrm{Tp^-}$ the free ion. This equilibrium will be concentration dependent. As noted earlier, concentration dependence was observed for NaTp and KTp solutions with concentrations below *ca.* 5×10^{-4} *M* but not at radical concentrations much larger. To explain the concentration independency at high radical concentration, we propose that more than one equilibrium is involved. If the existence of a second solvent-separated ion pair is assumed, denoted by $\mathrm{Tp^-/S/Me^+}$, then the following set of equilibria can be written.

$$\mathrm{Tp^-//Me^+} \underset{K_1}{\rightleftarrows} \mathrm{Tp^-/S/Me^+} \underset{K_{diss}}{\rightleftarrows} \mathrm{Tp^- + Me^+}$$

Clearly only the dissociation is concentration dependent and can be neglected at high radical concentrations. The measured optical superposition spectra in this concentration range can then be explained by means of equilibrium 1, which can be considered as a solvent isomerization reaction. Calculating the ratio of the ion-pair concentrations from the spectra, we can determine K_1 as a function of the temperature. The results of this analysis for NaTp, KTp, and RbTp can be found in Figure 4, where ln K_1 has been plotted *vs.* the absolute value of the temperature. The thermodynamic values obtained from these plots are summarized in Table II, column 3. Both ΔH and ΔS appear to become less negative when the radius of the cations increases. The larger the cation radius, the less entropy and enthalphy are involved in the transformation of the ion pairs.

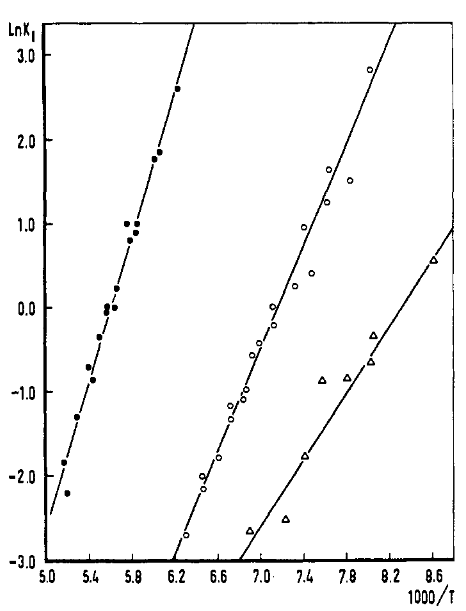

Figure 4. Plot of ln K_1 *vs.* the reciprocal of the absolute temperature for NaTp (●), KTp (○), and RbTp (△).

Table II. Thermodynamic Parameters for the Equilibria Involving Triphenylene Anion and Its Ion Pairs with Alkali Ions in MTHF

	$\mathrm{Tp^- \cdot Me^+ \rightleftarrows Tp^-//Me^+}$		$\mathrm{Tp^-//Me^+ \rightleftarrows Tp^-/S/Me^+}$	
Counterion	ΔH_2, kcal mol^{-1}	ΔS_2, eu	ΔH_1, kcal mol^{-1}	ΔS_1, eu
Na	$-5^a \pm 1$	$-19^a \pm 4$	-8.8 ± 0.5	-49 ± 3
K	-4.8 ± 1	-18 ± 3	-6.1 ± 0.3	-44 ± 3
Rb	-3.2 ± 1	-13 ± 3	-4.0 ± 0.5	-33 ± 5
Cs	-3.0 ± 1	-12 ± 4		

[a] Taken from ref 3 (see text).

There is much evidence that the species giving rise to spectrum of type 2 is a solvent-separated ion pair, which we formulated as $\mathrm{Tp^-//Me^+}$. First, in the optical absorption spectra a shift in the absorption maxima to higher frequencies is observed when the temperature is increased. This can be explained by a mutual interaction between the two partners in the ion pair. The existence of an ion pair is substantiated by the observed dependence of the absorption maxima on the cation radius (Figure 3). Second, the esr experiments on NaTp in MTHF show that between −120 and −70° superposition spectra are measured of esr spectra 1 and 2 (see I). Figure 5a shows such a spectrum at −87°; the computer simulation for which the input data are

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[5] N. M. Atherton and S. I. Weissman, *J. Amer. Chem. Soc.*, **83**, 1330 (1961); K. H. Buchow, J. Dieleman, and G. J. Hoytink, *J. Chem. Phys.*, **42**, 1993 (1965).

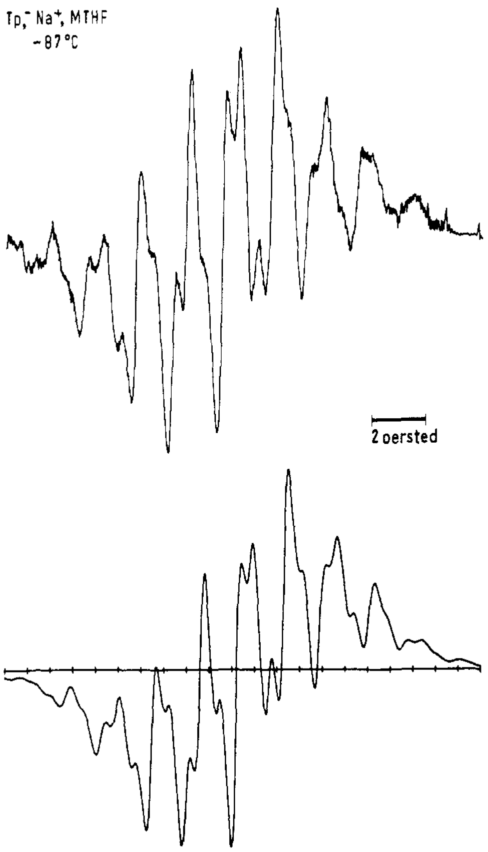

Figure 5. (a, upper) Superposition esr spectrum of NaTp in MTHF at −87°. (b, lower) Computer simulation (see text).

Table III. Input Data for the Computer Simulation Shown in Figure 5b

	Spectrum 1 Tp^- or $Tp^-/S/Me^+$	Spectrum 2 $Tp^-//Me^+$
Splitting constants	1.10 Oe	1.28 Oe
	1.61 Oe	1.57 Oe
Derivative line width	0.50 Oe	0.50 Oe
Weight	80%	20%
g value	$2.002839 \pm 7 \times 10^{-6}$	$2.00273 \pm 1 \times 10^{-5}$

given in Table III is shown in Figure 5b. The lower *g* value of spectrum 2 points to an ion pair, since generally spin–orbit interaction between the unpaired electron and the alkali nucleus decreases the *g* value.[6] The asymmetrical shape of the spectrum is due to the difference in *g* values, which corresponds to 0.16 Oe. The esr spectrum 2 does not contain an alkali hyperfine splitting; therefore, we attributed this spectrum and the optical spectrum of type 2 to a solvent-separated ion pair and not to a solvated contact ion pair, which may be denoted as $Tp^- \cdot Me^+,S$. Other investigators[7] have found evidence for the presence of this species. In our case it can be discarded, since such a species should have in its esr spectrum an alkali hyperfine splitting. The same reasoning was followed by Höfelmann, *et al.*,[8] in studying the ion pairs of the negative ion of naphthalene. Esr studies by these authors revealed two different ion pairs, one with a large alkali hyperfine splitting constant denoted as a contact ion pair and one with a small alkali hyperfine splitting constant (decreasing to zero at lower temperatures) denoted by them as a solvent-separated ion pair. The latter ion pair corresponds to our species $Tp^-//Me^+$, the former to the species $Tp^- \cdot Me^+$ (*vide infra*, type 3 spectra).

Figures 1 and 2 illustrated that the species giving rise to spectrum of type 2 is converted upon lowering of the temperature into another species giving rise to spectrum of type 1. We attribute the latter spectrum to a free ion (Tp^-) and/or a second solvent-separated ion pair, symbolized by $Tp^-/S/Me^+$. With the symbol S we try to indicate that so many solvent molecules are situated between the anion and the cation that the anion is only weakly perturbed by the cation. The perturbation of the cation must be so small that the optical spectra of species Tp^- and $Tp^-/S/Me^+$ are indistinquishable in shape. This implies that also the esr spectra of Tp^- and $Tp^-/S/Me^+$ will be identical (see I, esr spectrum of type 1).

It may be remarked that Höfelmann, *et al.*,[8] also found evidence for the presence of two solvent-separated ion pairs in the system Na–naphthalene–tetraglyme. These two species showed quite different electron-exchange rates with neutral naphthalene. This was attributed to a difference in solvation spheres around the cations. The differences in the physical properties of the two solvent-separated ion pairs proposed by us must also arise from a difference in solvation spheres around the cations. The close similarity between the properties of Tp^- and $Tp^-/S/Me^+$ suggests that the cation in $Tp^-/S/Me^+$ is symmetrically encircled by solvent molecules. The solvation of the species $Tp^-//Me^+$ is less and probably more on the outside, resulting in a smaller cation–anion distance and to changes in the optical spectrum and in the esr spectrum (proton splitting constants become different; see I, spectra 1 and 2). Hence, the conversion of $Tp^-//Me^+$ into $Tp^-/S/Me^+$ should be exothermic and accompanied by a loss of entropy.

It is now possible to analyze the measurements carried out at low radical concentrations, where the dissociation plays a role. For the analysis we made the reasonable assumption that both Tp^- and $Tp^-/S/Me^+$ have the same extinction coefficients. This assumption is supported by the coincidence of the spectra for NaTp and KTp solution at low temperatures with that of the LiTp solution. Moreover, changing the concentration of Tp from 4×10^{-4} to 1×10^{-4} *M* and thus changing the ratio of free ions to solvent-separated ion pair by a factor of more than 2 did not alter the calculated total extinction coefficient for the species giving rise to type 1 spectra.

Using this assumption, all concentrations required to calculate K_{diss} can be determined. The concentration of $Tp^-//Me^+$ is measured directly from the optical densities of its absorption maxima. Using values of K_1 measured at higher concentrations (see Figure 4), the concentration of $Tp^-/S/Me^+$ can be deduced. The total concentrations of $Tp^-/S/Me^+$ and Tp^- can be calculated from the optical densities of the absorption spectra. Then the concentration of free Tp ions can be

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(6) J. L. Sommerdijk and E. de Boer in "Ions and Ion Pairs in Organic Reactions," Vol. I, M. Szwarc, Ed., Wiley-Interscience, New York, N. Y., 1972, Chapter 8.

(7) R. V. Slates and M. Szwarc, *J. Amer. Chem. Soc.*, **89**, 6043 (1967); I. L. Chan, K. H. Wong, and J. Smid, *ibid.*, **92**, 1955 (1970); J. W. Burley and R. N. Young, *J. Chem. Soc. B*, 1018 (1971).

(8) K. Höfelmann, J. Jagur-Grodzinski, and M. Szwarc, *J. Amer. Chem. Soc.*, **91**, 4645 (1969).

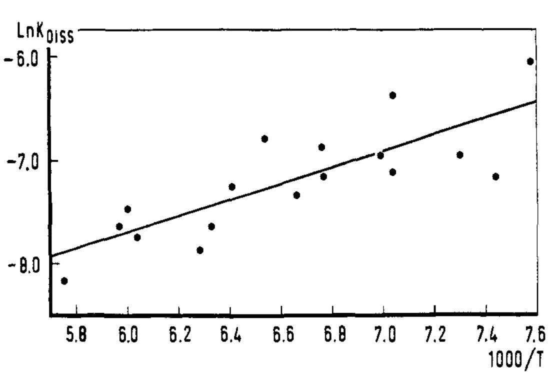

Figure 6. Plot of ln K_{diss} *vs.* the reciprocal of the absolute temperature for KTp.

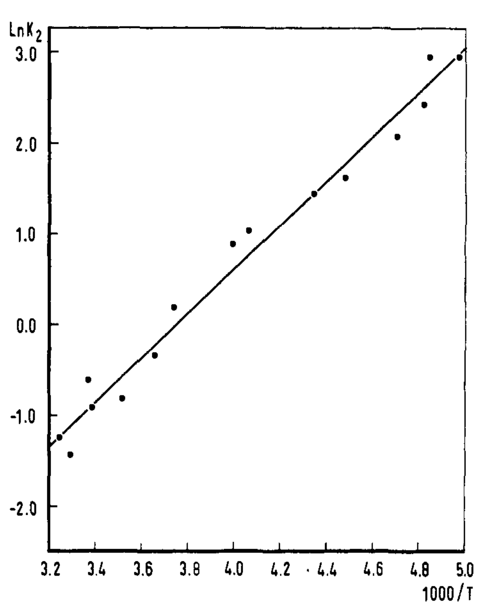

Figure 7. Plots of ln K_2 *vs.* the reciprocal of the absolute temperature for KTp.

arrived at by substracting [$Tp^-/S/Me^+$] from the total concentration of $Tp^-/S/Me^+$ and Tp^-.

A plot of ln K_{diss} *vs.* the reciprocal of the absolute temperature for KTp is shown in Figure 6. From the position of the various points it is clear that ΔH_{diss} is almost zero. A zero ΔH_{diss} was also found for NaTp by van Broekhoven.[9] It is interesting to remark that the conductance studies of Chang, Slates, and Szwarc[10] on NaTp in tetrahydrofuran also indicated a zero enthalphy difference for the ion-pair dissociation at low temperature. Our measurements seem to confirm this. If the measured points are linearly correlated by a least-squares fit, it is found that $\Delta H_{\mathrm{diss}} = -2 \pm 1$ kcal mol^{-1} and $\Delta S = -25 \pm 5$ eu. The small ΔH means that the electronic energy levels of Tp anion are only weakly perturbed by the counterion in the solvent-separated ion pair; the large ΔS reflects the difference in solvation spheres around the free ion and its association form.

Type 3 Spectra. As has been stated before, the frequencies of the three absorption maxima of spectra of type 3 increase slowly as the temperature is raised. Limiting values were obtained for KTp, RbTp, and CsTp solution but not for a solution of NaTp. For the latter solution the limiting value is expected at a temperature higher than +60°, the temperature where the absorption frequency maxima are reached for the KTp solution. Measurements above +60° are hampered by the low boiling point of MTHF. In Table I the limiting frequency values are listed, together with the value observed for NaTp at +20°. As has been demonstrated before these limiting frequencies depend linearly on the cation radius (see Figure 3).

The gradual shift in the absorption maxima on increasing the temperature can be described in terms of a static ion pair,[10,11] which changes its structure gradually with temperature (static model). An alternative way of explaining the experimental results has been introduced by Hirota and Kreilick.[12] These authors assumed that two distinct ion pairs exist in the solution, interconverting rapidly into each other (dynamic model). Especially when line width alternation effects are observed on the alkali hyperfine lines in the esr spectra, this dynamic model accounts for the experimental facts in a natural way. Line width alternation effects on Na hyperfine lines have indeed been observed for NaTp in diethyl ether (see I) but not for NaTp in MTHF. However, the dynamic model proved to be applicable also to the latter case. It was shown in I that the experimental spectra measured for NaTp in MTHF at temperatures higher than −70° could be interpreted with the help of the following equilibrium

$$\mathrm{Tp^-\cdot Me^+} \underset{K_2}{\rightleftarrows} \mathrm{Tp^-//Me^+}$$

where $Tp^-\cdot Me^+$ represents a contact ion pair showing an alkali hyperfine splitting in its esr spectrum. The observed esr spectra were weighted averages of the esr spectra of these two ion pairs.

The optical spectra of NaTp in diethyl ether and MTHF are identical. In view of the esr results obtained in these two solvents one might also endeavour to interpret the reversible changes in the optical absorption spectra observed at higher temperatures in terms of two distinct ion pairs. In contrast to the averaged spectra observed with esr the optical spectra should correspond to superposition spectra due to the quite different time scale of the optical technique. Since the difference between the optical spectra of type 2 and 3 is small (see Table I), no isosbestic points are observed in the relevant temperature range but only a shift of the absorption bands. In the cases where limiting frequency values were reached, *i.e.*, for solutions of KTp, RbTp, and CsTp, we have calculated from the positions of the absorption maxima the ratio of contact to solvent-separated ion pairs for various temperatures, analogous to the analysis of the esr spectra of type 3 observed for NaTp in MTHF. As an example, in Figure 7 a plot of ln K_2 *vs.* the reciprocal of the absolute temperature is shown for KTp. The thermodynamic constants calculated from these linear plots are listed in Table II. The values for NaTp included in Table II are taken from I and are derived from esr spectra of type 3. The thermodynamic parameters thus determined appear to be reasonable and are comparable with those obtained by Hirota and Kreilick[12] for sodium anthracene ion

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[9] J. A. M. van Broekhoven, Thesis, University of Nijmegen, The Netherlands, 1970.

[10] P. Chang, R. V. Slates, and M. Szwarc, *J. Phys. Chem.*, 70, 3180 (1966).

[11] E. Grunwald, *Anal. Chem.*, **26**, 1696 (1954).

[12] N. Hirota and R. Kreilick, *J. Amer. Chem. Soc.*, **88**, 614 (1966).

pairs in MTHF. As was observed for the previously discussed equilibria, both ΔH and ΔS become less negative as the cation radius increases. It is also gratifying that the results for NaTp and KTp, arrived at *via* different techniques, are so similar.

Finally, using the equilibrium constant K_2 at +20° given in I, we have calculated the limiting frequency maximum for NaTp in MTHF. Figure 3 shows that this calculated frequency maximum satisfies rather well the linear relation of frequency *vs.* the cation radius, indicating the overall consistency of our treatment.

Conclusion

From examination of the absorption spectra of alkali metal reduced solutions of Tp at various temperatures, we have been able to demonstrate the existence of four different species, the free ion and three ion pairs. Further we have measured the equilibria that connect one with the other. For two species the dependence of both the absorption spectra and the equilibria on the cation radius was clearly shown. From the temperature dependence of the equilibria we have calculated the thermodynamic constants for these processes. The values show that all solvation processes studied are accompanied by both a loss of enthalphy and entropy, the effect being strongest for the smallest cation.

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Yields of Chemically Produced Excited States

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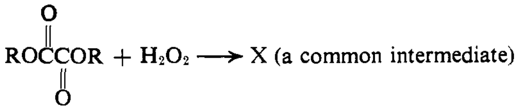
Abstract: The chemiluminescence quantum yields of ten substituted 2,3-dihydrophthalazine-1,4-diones and the fluorescence quantum yields of the corresponding phthalic acids were measured. From these data, the yields of excited state formation were calculated. The results show that the excited state yield is dependent on the substituents, and they indicate that an important factor in this dependence may be the energy of the excited state formed.

Chemically produced excited electronic states are involved in chemiluminescence[2] and bioluminescence,[3] and they have been used as sources of energy for "photochemical reactions."[4] The efficiency of production of these excited states is usually low, the overall efficiency of light production of most chemiluminescent reactions being less than 1%.[2a] A few reactions are notably more efficient. Fused ring hydrazides are up to 7% efficient in DMSO,[5] the oxalate–H_2O_2–fluorescer system can be up to 23% efficient,[6] and the bioluminescence of *Cypridina*[7] and firefly[8] luciferins are 28 ± 15 and 88 ± 25% efficient, respectively. In some cases the yield of excited states has been determined; the cleavage of dioxetanes leads to the production of excited states with 4,[4b] 15,[9] or 20–100%[10] efficiency, depending on the system, and benzoperylenedicarboxylic hydrazide is about 50% efficient in the production of excited states.[5]

In situations where energy transfer is occurring to a common emitter, the efficiency of excited state production can be obtained readily as a function of some substituent, such as R, from measurement of the total light emitted (eq 1 and 2),[6] provided that conditions are such that the energy transfer step is of unit efficiency.



$$\mathrm{RO}\overset{\overset{\displaystyle O}{\|}}{C}\underset{\underset{\displaystyle O}{\|}}{C}\mathrm{OR} + H_2O_2 \longrightarrow X \text{ (a common intermediate)} \qquad (1)$$

$$X + A \longrightarrow A^* \longrightarrow h\nu \qquad (2)$$

Many chemiluminescent reactions lead, however, to an excited state product which is also the light emitter (eq 3). Thus, the efficiency of fluorescence of C must

$$B \longrightarrow C^* \longrightarrow C + h\nu \qquad (3)$$

be factored out to determine the effect of substituents on the efficiency of excited state production from B. We now report on one of the first of such studies;[2c] we have examined the effect of substituents on the efficiency of chemiluminescence of the cyclic hydrazides.

The oxidation of cyclic hydrazides (**1**) in basic media leads to the formation of the corresponding carboxyl-

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