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Carbanion Mechanisms. 9.[1]
Spectrophotometric Study of Triphenylmethyl Alkali Metal Salts. Contact and Solvent-Separated Ion Pairs in Ethereal Solvents

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Results of a spectrophotometric study of (triphenylmethyl)lithium (TPM^-Li^+) and (triphenylmethyl)potassium (TPM^-K^+) in dimethoxyethane (DME), tetrahydrofuran (THF), and diethyl ether are reported. The UV–vis spectral absorptions show characteristic dependence on the nature of the cation and the solvent, which can be interpreted on the basis of formation of contact and solvent-separated ion pair species. Addition of 18-crown-6 polyether causes a shift in the equilibria, from contact to crown ether complexed ion pair species having spectral characteristics closely similar to the solvent-separated ion pair. The temperature variation of the spectra for the TPM^-Li^+/Et_2O, TPM^-Li^+/THF, TPM^-K^+/THF, and TPM^-K^+/DME systems has allowed evaluation of the thermodynamic parameters for the contact $\rightleftarrows$ solvent-separated ion pair equilibria in these systems. The overall results compare satisfactorily with data obtained by means of a ^1H NMR study of triphenylmethyl alkali metal salts in ethereal solvents.

Ion pairing can play a profound role in the reactivities of carbanionic species. The importance of this concept was first highlighted about 1960, on the one hand in electrophilic substitution reactions at saturated carbon centers, where carbanions were invoked as transient intermediates,[2] and on the other hand in anionic polymerization of styryl alkali metal derivatives.[3] Spectroscopic investigation of ion pairing phenomena for stable carbanionic systems in inert solvents was first realized by UV–vis absorption spectroscopy[4] and subsequently by ^1H[5] and ^{13}C NMR[6] spectroscopy. As a result of these studies, the concepts of contact (tight) and solvent-separated (loose) ion pairs, as opposed to completely dissociated ionic species, have become fully established in carbanion chemistry, as they are in carbonium ion chemistry.[7,8]

Most of the existing spectrophotometric work on carbanionic species has been performed with fluorenyl derivatives[9,10] since the spectral absorptions of contact and solvent-separated ion pairs appear to be the most sharply resolved in these systems. The spectrophotometric method has been found to be less applicable in other carbanion systems due to severe overlapping of the absorption maxima which renders quantitative interpretation very difficult. Nevertheless, some limited spectrophotometric studies have been reported with carbanions of the arylmethyl type, namely, 1,1-diphenyl-*n*-hexyllithium[11] and the triphenylmethane/lithium and cesium cyclohexylamide systems,[12] while more extensive spectrophotometric studies have been made of 1,3-diphenylallyl type anions.[13]

We have been studying carbanions in the arylmethane series,[14] their formation in the tetrahydrofuran/potassium hydride/crown ether system and their reaction with molecular hydrogen, ammonia, and methylamine, in relation to the hydride acidities.[15] Our spectrophotometric studies have yielded information on ion pairing phenomena in these systems,[14e] and we report in this paper pertinent results for (triphenylmethyl)lithium and -potassium in ethereal solvents. Our findings regarding contact and solvent-separated ion pairs in these systems are complementary to those by Jackman and co-workers[5d] using ^1H NMR spectroscopy, allowing comparison between these methods.

Results and Discussion

(Triphenylmethyl)lithium (TPM^-Li^+). The spectra of TPM^-Li^+ in Et_2O, THF, and DME at room temperature are shown in Figure 1. In Et_2O the absorption maximum occurs at 446 nm with a shoulder at 390 nm, while in THF and DME the spectra exhibit λ_{max} 500 and 435 sh nm and λ_{max} 496 and 432 sh nm, respectively (Table I). The large change in λ_{max} on going from Et_2O to THF or DME is indicative of a change in the type of ion pair present. Results in the literature on related systems[9,10,13] indicate that the absorption maximum of a given type of ion pair, contact or solvent-separated, is generally only slightly dependent on the solvent medium over wide ranges of solvent type and polarity (vide infra). Additionally, for various carbanion systems, such as the fluorenyl alkali metal salts (F^-M^+) and the 1,3-diphenylallyl alkali metal salts in different solvents, the absorption maxima for the solvent-separated ion pairs occur at longer wavelength than for the contact ion pairs. Hence, it becomes reasonable to conclude that TPM^-Li^+ exists in Et_2O predominantly as the contact ion pair (TPM^-, Li^+) and in THF and DME predominantly as the solvent-separated ion pair ($TPM^- \| Li^+$).

The cation complexing properties of macrocyclic polyethers[16] render these agents particularly attractive in influencing the reactivities of carbanionic systems in general and the nature of ion pairing in particular. It was found in the

Table I. Contact (R^-,M^+), Solvent-Separated ($R^-\|M^+$), and 18-Crown-6 Ether Complexed (R^-,X,M^+) Ion Pairs of Triphenylmethyl Carbanions in Ethereal Solvents at Room Temperature: Effect of Solvent and Counterion

R^-M^+	registry no.	solvent	λ_{max}, nm (ϵ)[a] R^-,M^+	λ_{max}, nm (ϵ)[a] $R^-\|M^+$	fraction of $R^-\|M^+$ at 25 °C	R^-,X,M^+ λ_{max}, nm	R^-,X,M^+ registry no.
TPM^-Li^+	733-90-4	Et_2O	446, 390 sh (21 900)		0.15	494, 430 sh	68129-69-1
		THF		500, 435 sh (28 300)	0.95	500, 435 sh	
		DME		496, 432 sh (30 000)	1.00	496, 432 sh	
TPM^-K^+	1528-27-4	Et_2O	476, 414 sh (24 800)		0.00	492, 430 sh	68138-96-5
		THF		486, 420 sh (21 300)	0.65	495, 430 sh	
		DME		494, 430 sh (30 000)	0.85	494, 430 sh	

[a] Extinction coefficient at absorption maximum (L mol^{-1} cm^{-1}); ϵ (sh) is approximately half the absorption maximum value.

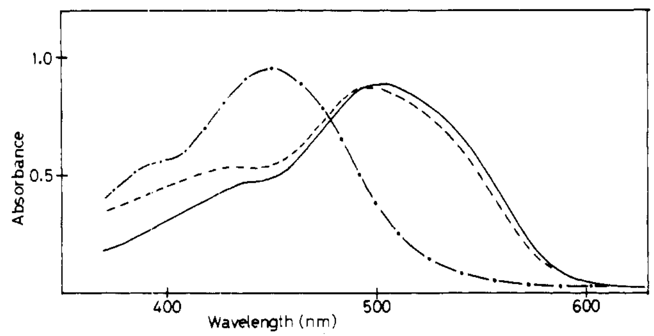

Figure 1. Visible absorption spectra of (triphenylmethyl)lithium in ether (- · -), tetrahydrofuran (—), and dimethoxyethane (- - -) at room temperature.

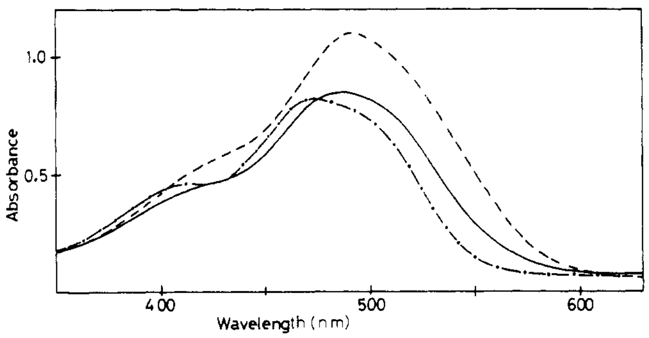

Figure 2. Visible absorption spectra of (triphenylmethyl)potassium in ether (- · -), tetrahydrofuran (—), and dimethoxyethane (- - -) at room temperature.

present system that 18-crown-6 polyether had no effect on the absorption of (triphenylmethyl)lithium in THF and DME but a large effect in the case of Et_2O as solvent. In the latter case, a shift in absorption occurred from λ_{max} 446 and 390 sh nm to λ_{max} 494 and 430 sh nm (Table I). It is noteworthy that the latter characteristics correspond almost exactly to the spectrum of the solvent-separated ion pair $TPM^-\|Li^+$ observed in THF or DME in the absence of crown ether. It had been found[4f] that addition of 18-crown-6 ether to fluorenylsodium in THF, existing as the contact ion pair, caused a spectral change corresponding to formation of the solvent-separated ion pair. However, the present case appears to be the first example where 18-crown-6 ether has this effect on a contact ion pair with lithium as the counterion. Complexation by ethers can occur externally to a contact ion pair,[9] but if this had occurred in the present system then one would not have expected as large a change in λ_{max} on addition of crown ether; hence, this possibility is discounted in the present case.

The temperature dependence of the contact ⇄ solvent-separated ion pair equilibrium constituted important evidence in the original work on fluorenyl alkali metal salts.[4b] Such equilibria have been found to be exothermic, due to the gain in solvation energy in formation of the solvent-separated ion pair. Concomitantly, the immobilization of solvent molecules round the cation leads to a negative entropy for the process. For example,[4b] for the equilibrium $F^-,Na^+ \rightleftarrows F^-\|Na^+$ in THF, $\Delta H = -7.6$ kcal/mol and $\Delta S = -33$ eu, so that lowering of the temperature strongly favors the solvent-separated species.

In the present work it was found that the solutions of TPM^-Li^+ in THF and DME were unaffected when the temperature was lowered from 25 to −50 °C, but the Et_2O solution on cooling showed a bathochromic shift from λ_{max} 446 and 390 sh nm to λ_{max} 494 and 430 sh nm. The lack of a noticeable effect for DME and THF is consistent with our previous conclusion that at ambient temperature TPM^-Li^+ exists in these media predominantly as the solvent-separated ion pair. Conversely, the low-temperature spectrum of TPM^-Li^+ in Et_2O corresponds to formation of the solvent-separated ion pair, as a result of the shift in the equilibrium (eq 1) from the contact to the solvent-separated ion pair; as required, the spectral changes for this system were reversible with change in temperature.

$$R^-,M^+ + nS \rightleftarrows R^-\|M^+ \qquad (1)$$

Since increase in temperature should favor formation of contact ion pairs, we examined the effect of raising the temperature for the TPM^-Li^+/THF and TPM^-Li^+/DME systems. The latter system showed no change in the absorption spectrum when the temperature was raised from 0 to 50 °C, beyond which decomposition of the carbanion became important. The former system showed a small change, corresponding to formation of ~10% of the contact ion pair species over this temperature range. The tendency for contact ion pair formation in THF, as compared with the lack thereof in DME, is in the expected order of the cationic solvating powers of these media.

In their studies of TPM^-Li^+ by ^1H NMR, Jackman and co-workers[5d] concluded that at room temperature in DME and THF only solvent-separated ion pairs were present, while in Et_2O only the contact ion pairs were present, in agreement in the main with the present work. The Et_2O solution on cooling to −25 °C showed ~5% of the solvent-separated ion pair. However, the THF solution showed no evidence of contact ion pair formation on raising the temperature to 47 °C, which contrasts with the present work.

(Triphenylmethyl)potassium (TPM^-K^+). The spectra of TPM^-K^+ in Et_2O, THF, and DME at room temperature are shown in Figure 2, with the absorption maxima occurring at 476 (414 sh), 486 (420 sh), and 494 (430 sh) nm, respectively (Table I). As we have seen, a bathochromic shift on solvent change is indicative of the formation of solvent-separated ion pairs, which suggests that at room temperature in DME we have predominantly solvent-separated ion pairs and in ether contact ion pairs, while in THF both species appear to coexist at equilibrium in comparable amounts. This is in accord with the order of coordinating abilities of the three solvents toward the metal cation. The assignment of the DME spectrum es-

Table II. Thermodynamic Parameters for Contact ⇌ Solvated Ion Pair Equilibria of (Triphenylmethyl)lithium and (Triphenylmethyl)potassium in Ethereal Solvents

R^-M^+	solvent	temp range, °C	K^a	ΔH,[b] kcal/mol	ΔS,[b] eu
TPM^-Li^+	Et_2O	−54–+10	0.1	−11.9	−46
TPM^-Li^+	THF	+2–+45	39	−9.2	−24
TPM^-K^+	THF	−53–+23	2.0	−6.7	−21
TPM^-K^+	DME	+1–+34	5.7	−11.8	−36

[a] $K = [R^-\|M^+]/[R^-,M^+]$ at 25 °C. [b] Uncertainty in ΔH and ΔS is ±10–±20%.

sentially to the solvent-separated species is corroborated by the observation that the TPM^-K^+ spectrum in DME is quite similar to that of TPM^-Li^+ in DME. The latter has been concluded to correspond to the separated ion pair, and the effect of cation change on the absorption of the solvent-separated ion pair is expected to be very small.[9,10,13] For the contact ion pairs, however, the effect of change in the counterion is predicted to be large, and in fact the ethereal spectra of the triphenylmethyl alkali metal salts exhibit a sizable bathochromic shift (from λ_{max} 446 to 476 nm) on changing the cation from Li^+ to K^+.

The results of addition of 18-crown-6 ether to the TPM^-K^+ solutions in the ethereal solvents are shown in Table I. It is seen that crown ether has no effect on the DME spectrum, which is in agreement with our previous conclusion that TPM^-K^+ is present in DME predominantly as the solvent-separated ion pairs, and that these and the crown ether complexed ion pairs have the same absorption spectra. For THF and Et_2O, addition of crown ether causes significant spectral shifts, such that the final spectra exhibit absorption maxima which are virtually identical with the solvent-separated species. It is seen, however, that a small hypsochromic shift occurs in the crown ether complexed ion pair as well as in the solvent-separated ion pair on changing the cation from Li^+ to K^+. The extent of this shift (2–5 nm) is very much smaller than the bathochromic shift occurring in the contact ion pairs on increasing the cationic radius but is found consistently for all the solvents.

The effect of temperature on the spectra of TPM^-K^+ in the ethereal solvents has provided further information on the nature of the ion pairing equilibria. The spectrum of TPM^-K^+ in DME was practically unaffected on lowering the temperature from 25 to −50 °C, which is in accord with the earlier conclusion that TPM^-K^+ in DME exists predominantly as the solvent-separated ion pairs at room temperature. Similarly, the spectrum in Et_2O was unaffected for the 25 to −50 °C range, further indicating that in this case only contact ion pairs were present over this temperature range. However, cooling of the THF solution was accompanied by a shift in absorption from λ_{max} 486 and 420 sh nm to λ_{max} 494 and 430 sh nm, corresponding to a shift in equilibrium toward the solvent-separated species; this spectral change was found to be reversible as required.

In order to investigate the possibility of significant displacement of the equilibrium from solvent-separated to contact ion pairs in the TPM^-K^+/DME system, the spectrum of this solution was examined at temperatures above ambient. On raising the temperature from 0 to 35 °C, a change in the spectrum took place indicative of ~15% contact ion pair formation. This spectral change was found to be reversible up to 35 °C, but above this temperature decomposition set in.

In their studies of TPM^-K^+ by ^1H NMR, Jackman and co-workers[5d] found that at room temperature in Et_2O only contact ion pair species were present, while in THF ~30% and in DME ~70% solvent-separated ion pair species were obtained. These results are in qualitative agreement with our own findings.

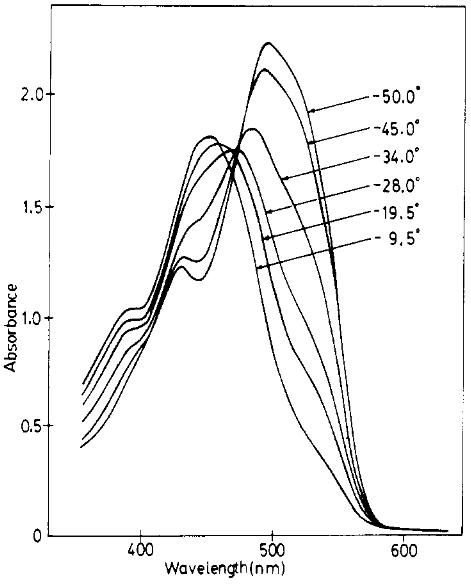

Figure 3. Temperature dependence of absorption spectra of (triphenylmethyl)lithium (7.51 × 10^{-5} M) in ether.

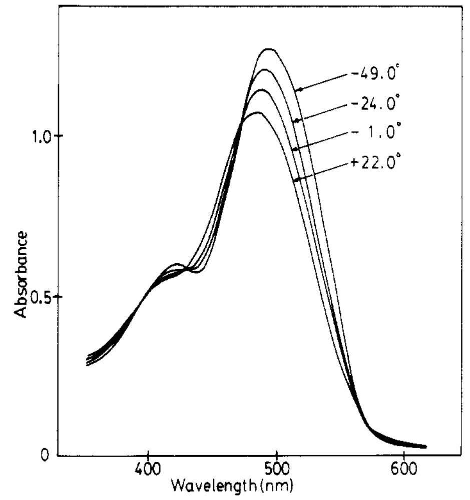

Figure 4. Temperature dependence of absorption spectra of (triphenylmethyl)potassium (5.23 × 10^{-5} M) in tetrahydrofuran.

Thermodynamic Parameters. The spectrophotometric studies of the equilibrium between contact and solvent-separated ion pair species at different temperatures have allowed evaluation of the ΔH and ΔS parameters for the process in eq 1 for the following systems: TPM^-Li^+/Et_2O, TPM^-Li^+/THF, TPM^-K^+/THF, and TPM^-K^+/DME. The temperature range employed was either ~25 to −50 °C (when the room temperature spectrum indicated that predominantly contact ion pairs were present, i.e., TPM^-Li^+/Et_2O and TPM^-K^+/THF) or ~0 to +40 °C (when predominantly solvent-separated ion pairs were found to be present at room temperature, i.e., TPM^-Li^+/THF and TPM^-K^+/DME). In the latter cases, the upper temperature used was limited by the advent of decomposition of the carbanions through attack on the ethereal solvents, at which point the spectral changes ceased to be reversible. The derived results, which supplement those by Jackman and co-workers,[5d] are given in Table II. In Figures 3 and 4 are presented examples of absorption spectra as a function of temperature for the TPM^-Li^+/Et_2O and TPM^-K^+/THF systems.

Conclusions

The results of this work point to the following conclusions concerning the state of the TPM$^-$Li$^+$ and TPM$^-$K$^+$ species in the ethereal solvents under the various conditions.

(1) TPM$^-$Li$^+$ is present predominantly as the contact ion pair in Et$_2$O and as the solvent-separated ion pair in THF and DME at room temperature. The state of ion pairing of TPM$^-$K$^+$ is analogous in Et$_2$O and DME, but in THF both contact and solvent-separated ion pairs coexist at equilibrium in comparable amounts.

(2) For the contact ion pair species, there is a bathochromic shift (30 nm) on changing the cation from Li$^+$ to K$^+$. The solvent-separated (or the crown ether complexed) ion pairs exhibit a small hypsochromic shift (2–6 nm) on changing from Li$^+$ to K$^+$ and also over the solvent range THF → DME → Et$_2$O. The solvent-separated ion pairs exhibit significant bathochromic shift (50 nm for TPM$^-$Li$^+$, 20 nm for TPM$^-$K$^+$) relative to the contact ion pairs.

(3) 18-Crown-6 ether converts the contact ion pair species to the crown ether complexed species, the latter having absorption maxima closely similar to the solvent-separated ion pair. This macrocyclic ether is effective for TPM$^-$Li$^+$ as well as for TPM$^-$K$^+$.

(4) The present conclusions based on the spectrophotometric studies of ion pairing are in overall agreement with results obtained from ^{1}H NMR studies[5d] of the effect of these solvents on contact/solvent-separated ion pair equilibria of triphenylmethyl alkali metal salts.

Experimental Section

Triphenylmethane (Aldrich) was recrystallized from ethanol, mp 93.5–94.0 °C. 18-Crown-6 ether (Aldrich) was dried in vacuo before use. *n*-Butyllithium was obtained (Ventron-Alfa) as a solution (1.8 M) in hexane. The solvents THF, DME, and Et$_2$O were distilled from lithium aluminum hydride under nitrogen and stored over *n*-butyllithium.

The reaction vessel used for preparation of the carbanion solutions, with the sealed-on 1-mm cuvette, has been described previously.[14b] For the preparation of TPM$^-$ Li$^+$ in a given solvent, TPM (1–2 mg) was introduced into the reaction vessel in a small glass ampule under nitrogen, followed by the solvent (~20 mL) which was transferred under vacuum and finally by the butyllithium solution (~0.5 mL) which was added by syringe under nitrogen. The extent of reaction was monitored spectrophotometrically by placing the reaction vessel into the modified cell compartment of a Unicam SP800 instrument. In THF solvent at room temperature conversion to TPM$^-$Li$^+$ was quantitative within 15 min of mixing, but in DME and Et$_2$O the extent of conversion after 20 h was only 7 and 16%, respectively. Solutions of TPM$^-$Li$^+$ in DME and Et$_2$O were prepared from the THF solution by removing this solvent under vacuum and introducing the DME or Et$_2$O under vacuum from a reservoir into the reaction vessel. The preparation of TPM$^-$K$^+$ in THF has been described previously.[14d] Solutions of TPM$^-$K$^+$ in DME and Et$_2$O were obtained by a similar procedure. The extinction coefficients in Table I were determined from two separate experiments using different concentrations of TPM.

The spectra given in Figures 1 and 2 were obtained by the above procedure. For TPM$^-$Li$^+$ (Figure 1), the concentrations were as follows: Et$_2$O, 4.65×10^{-4} M; THF, 2.96×10^{-4} M; DME, 2.79×10^{-4} M. For TPM$^-$K$^-$ (Figure 2), the concentrations were as follows: Et$_2$O, 3.14×10^{-4} M; THF, 3.25×10^{-4} M; DME, 3.51×10^{-4} M. The concentrations are calculated from the weights of TPM and solvent employed. The spectra were taken in a 1-mm cuvette.

In the experiments for the study of the effect of 18-crown-6 ether, the latter was introduced in excess into the reaction vessel, under nitrogen, by means of a glass vial. The crown ether complexed carbanions showed less stability than the uncomplexed species. The extent of decomposition was greatest in the case of TPM$^-$,X,K$^+$.

The low-temperature study of the ion pair equilibria was performed on a Beckman Mark IV spectrophotometer using a Beckman variable temperature cell accessory fitted with a thermocouple and measuring the temperature to ±0.2 °C. The solutions were prepared in the reaction vessel now having a 10-mm cuvette attached which was then sealed off under vacuum.

The ratio [separated]/[contact] was calculated from the absorbance changes at the wavelength (λ^s) corresponding to λ_{max} of the solvent-separated ion pairs. The absorbances were first corrected for solvent density changes. Then, at any given temperature $[S]/[C] = (A - A_C)/(A_s - A)$, where A is the corrected absorbance value while A_s and A_c are, respectively, the absorbances characteristic of 100% solvent-separated and contact ion pairs at λ^s. A_s was available experimentally since at the lowest temperatures complete conversion to the solvent-separated species occurred in all of the cases studied. For TPM$^-$K$^+$/THF and TPM$^-$K$^+$/DME the value of A_c used was derived by extrapolation from the TPM$^-$K$^+$/Et$_2$O spectrum since in Et$_2$O only the contact ion pair was present. For TPM$^-$Li$^+$/Et$_2$O and TPM$^-$Li$^+$/THF A_c was taken from the highest temperature spectrum recorded for TPM$^-$Li$^+$/Et$_2$O, although this could introduce a small error. However, it appeared from results of repeated experiments that the overall procedure is subject to other larger errors, and the ΔH and ΔS data given in Table II are believed to have uncertainty limits ranging from ±10 to ±20%.

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Registry No.—Triphenylmethane, 519-73-3.

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