

## Ion Pairing in Triphenylmethyl and Diphenylmethyl Carbanions from Spectrophotometric Studies

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**Summary** Triphenylmethyl and diphenylmethyl alkali metal salts in ethereal solvents exhibit visible absorption spectra which are dependent on the cation, solvent, and temperature, indicative of equilibrium formation of contact and solvent separated ion pair species and in overall agreement with results from  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectroscopic studies.

THE concept of ion pairing has been central to understanding of the reactivities of carbanions in different environments.<sup>1,2</sup> The observation of more than one type of ion pair for stable carbanions was first made by u.v.-visible spectroscopy with fluorenyl salts.<sup>3</sup> The well resolved spectra enabled direct observation of the bands due to the contact and the solvent separated ion pairs in these systems, which have thus been extensively investigated as a function of cation, solvent, and temperature.<sup>4</sup> However, with few exceptions such as the indenyl<sup>5</sup> and phenylallyl<sup>6</sup> carbanions, severe overlapping of the absorption bands of the two types of ion pairs has precluded the general application of u.v.-visible spectroscopy for ion pairing studies of a variety of carbanion systems.

The delocalized carbanions of the arylmethyl type have been important in evaluation of structure-reactivity relationships, including establishing of a  $pK_a$  scale for very weak carbon acids.<sup>2,7</sup>  $^1\text{H}$  and  $^{13}\text{C}$  N.m.r. studies of arylmethyl carbanions have been used to give detailed information on  $\pi$ -electron densities and hybridisation effects.<sup>8</sup> However, in the case of triphenylmethyl and diphenylmethyl carbanions the results of studies of chemical shift changes as a function of cation, solvent, and temperature have been interpreted on the basis of equilibria between contact and solvent separated ion pair species.<sup>9,10</sup>

The importance of using independent methods for investigating ion pairing has been pointed out.<sup>11</sup> We now

present direct evidence from u.v.-visible spectroscopy on ion pairing in these arylmethyl carbanions.<sup>12</sup> With the exception of a single study concerned with triphenylmethyl-lithium and caesium in cyclohexylamine,<sup>5a</sup> there has been no investigation by u.v.-visible spectroscopy of arylmethyl carbanions, and the role played by the cation, solvent, and temperature.

TABLE

Contact ( $\text{R}^-\text{M}^+$ ) and solvent separated ( $\text{R}^-||\text{M}^+$ ) ion pairs of triphenylmethyl and diphenylmethyl carbanions in ethereal solvents at room temperature: effect of solvent and counterion

R-M <sup>+</sup>	Solvent	$\lambda_{\text{max}}/\text{nm}$		Fraction R <sup>-</sup>   M <sup>+</sup> at 25 °C
		R <sup>-</sup> ,M <sup>+</sup>	R <sup>-</sup>   M <sup>+</sup>	
TPM-Li <sup>+</sup>	Et <sub>2</sub> O	446,390sh		0.1
	THF		500,435 sh	1.0
	DME		496,432 sh	1.0
TPM-K <sup>+</sup>	Et <sub>2</sub> O	476,414 sh		0.0
	THF		486,420 sh	0.6
	DME		494,430 sh	0.9
DPM-Li <sup>+</sup>	Et <sub>2</sub> O	407		0.0
	THF	418	448	0.4
	DME		448	0.8
DPM-K <sup>+</sup>	Et <sub>2</sub> O	432		0.0
	THF	440		0.0
	DME	441		0.0

Our results for the lithium and potassium salts of triphenylmethane (TPM) and diphenylmethane (DPM) (TPM-Li<sup>+</sup>, TPM-K<sup>+</sup>, DPM-Li<sup>+</sup>, and DPM-K<sup>+</sup>) in several ethereal solvents are given in the Table. In most cases the absorption spectra allow clear differentiation between the contact and solvent separated ion pair species, as based on the effect of solvent and counterion. Thus our assignment of species in the Table shows the following relationships.† (i) Solvent separated ion pairs exhibit bathochromic shifts with respect

† An alternative possible explanation of the results would invoke the formation of externally solvated contact ion pairs, in addition to the conventional contact ion pairs and the solvent separated ion pairs (ref. 6). This possibility will be discussed in the full paper.

to contact ion pairs. (ii) The tendency for solvent separated ion pair formation is greater for lithium than for potassium salts. (iii) For the solvent separated ion pairs the absorption spectra vary only slightly with the nature of the counterion and the solvent. (iv) For the contact ion pairs the absorption maxima show a bathochromic shift on changing the cation from  $\text{Li}^+$  to  $\text{K}^+$ .

We have also studied the temperature dependence of the contact  $\rightleftharpoons$  solvent separated ion pair equilibria in these systems. Reversible spectral changes were observed for the  $\text{TPM}^-\text{Li}^+-\text{Et}_2\text{O}$ ,  $\text{TPM}^-\text{K}^+$ -tetrahydrofuran (THF), and  $\text{DPM}^-\text{Li}^+-\text{THF}$  systems on lowering the temperature ( $25 \rightarrow -60^\circ\text{C}$ ), in accord with a shift in the equilibria from the contact to the solvent separated ion pair species. Correspondingly, increasing the temperature ( $0 \rightarrow 40^\circ\text{C}$ ) for  $\text{TPM}^-\text{Li}^+-\text{THF}$ ,  $\text{TPM}^-\text{K}^+$ -dimethoxyethane (DME),

and  $\text{DPM}^-\text{Li}^+-\text{DME}$  caused a partial shift in the equilibria from the solvent separated to the contact ion pairs.

Our results regarding contact and solvent separated ion pair formation as a function of solvent, cation and temperature, compare favourably with those from  $^1\text{H}$  n.m.r. studies<sup>9</sup> for  $\text{TPM}^-$ , and  $^{13}\text{C}$  n.m.r. studies<sup>10</sup> for  $\text{DPM}^-$ .<sup>‡</sup> We are extending the u.v.-visible studies to other anions in the arylmethane series for which n.m.r. data are currently not available. The results should aid the meaningful interpretation of the spectral characteristics of the series of arylmethyl carbanions and the correlation with calculable molecular parameters.<sup>13</sup>

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‡ The  $^1\text{H}$  n.m.r. studies (ref. 9) with  $\text{TPM}^-$  yielded the following results for the fraction of solvent separated ion pairs at room temperature in the ethereal solvents. For  $\text{TPM}^-\text{Li}^+$ ,  $\text{Et}_2\text{O}$ , 0; THF, 1.0; DME, 1.0; and for  $\text{TPM}^-\text{K}^+$ ,  $\text{Et}_2\text{O}$ , 0; THF, 0.3; DME, 0.7. Results of  $^{13}\text{C}$  n.m.r. studies (ref. 10) for  $\text{DPM}^-$  were reported for THF and DME. The values of the fraction of solvent separated ion pairs at room temperature are: for  $\text{DPM}^-\text{Li}^+$ , THF, 0.75; DME, 0.9; and for  $\text{DPM}^-\text{K}^+$ , THF, 0; DME, 0. These results are in substantial agreement with the present work.

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