

EFFECT OF ION PAIR STRUCTURE ON THE EQUILIBRIUM
ADDITION OF CARBANIONS TO SUBSTITUTED VINYL PYRIDINES

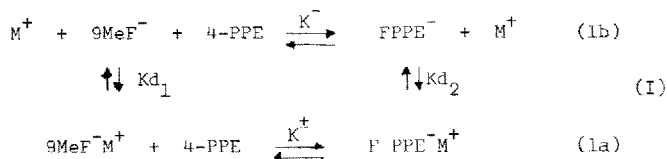
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The effect of ion pairing on the equilibrium of radical anion electron transfer¹

and disproportionation reactions² and of proton transfer³ has been the focus of a few recent studies. We now wish to report the first such study dealing with the equilibrium addition of carbanions to carbon-carbon double bonds indicating that ion pairing effects are potentially enormous when the newly generated carbanion differs considerably from the reacting carbanion in charge distribution.

The reaction studied was the addition of 9-methyl fluorenyl carbanion alkali salts to 1-phenyl-1-(4-pyridyl)ethene.⁴ The olefin was chosen since anionic homopolymerization does not occur⁴ and because the carbanion salts of the reacting carbanion^{5, 6} and of the reaction product⁴ have been characterized in terms of ion pairing. The reaction was carried out in vacuo in tetrahydropyran (THP) and THF in and without the presence of tetraglyme and dibenzo-18-crown-6 using Li⁺, Na⁺ and Cs⁺ as counterions.



The addition product $FPPE^-M^+$ was characterized by its UV/Visible spectrum that was identical to that of previously characterized addition products of 4-PPE and substituted diphenyl methyl carbanion salts.⁴ The absorption maxima of $9MeF^-$ and $FPPE^-$ are well separated at 370-390 nm and 420-440 nm respectively depending on cation and are easily resolvable since the spectra of the individual salts are well known. Extinction coefficients were taken from the literature.^{4, 6}

Reactions were all completed within a few seconds. Over a period of a few hours, in some cases, a slow increase in the 420-240 nm band was observed as well as a simultaneous decrease

of the 9-MeF⁻ band with occurrence of an isosbestic point. This may indicate a reaction between 9MeF⁻ and unconverted 4-PPE through addition of carbanion at the 2-position of the pyridine ring. Similar reactions leading to species absorbing between 400 and 500 nm have been described in the anionic homopolymerization of 4-vinyl pyridine.⁷ However, if temperatures in between measurements were kept low (<0°C) the side reactions did not seriously interfere. Series of measurements could be made in one apparatus by successive dilution in vacuo. The method is illustrated in fig. 1 in which the ratio $\frac{[FPPE^-]}{[9MeF^-]}$ is plotted

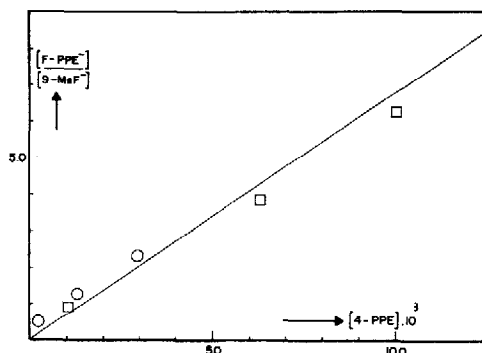


Figure 1

against [4-PPE] for the Li/THF system. The equilibrium constant K given by the slope equals 680 M^{-1} . In most other cases a smaller number of separate measurements were carried out largely because measurable $[FPPE^-]/[9MeF^-]$ ratios require a high [4-PPE] concentration thus precluding successive in vacuo dilution.

The results are shown in Table I and show dramatic effects of cation and solvent on the addition equilibrium. In tetrahydropyran for instance, K_{Li} exceeds K_{Cs} by a factor of about 1.6×10^5 . On the other hand K_{Li} is reduced from THP to THF by a factor of 20 and from THP to THP/tetraglyme (TG) by a factor of about 150. Generally K decreases with increasing cationic radius and with increasing cation solvation. Since the degree of dissociation of the ion pairs (equation I) into free ions is unimportant because of the relatively high concentrations of carbanion (10^{-4} - 10^{-2} M) the apparent equilibrium constant K should be close to K^\ddagger if no other processes such as ion pair aggregation and triple ion formation are important.

Table I. Equilibrium Constants for the Equilibrium:

$$9\text{-MeF}^- \text{M}^+ + 4\text{PPE} \xrightleftharpoons{K} \text{FPPE}^- \text{M}^+ \text{ at } 25^\circ\text{C.}$$

Cation	Solvent	Crown ether/Glyme ^a	K(M ⁻¹)
Li	THF		14,200
Li	THF	TC ^(b)	97
Li	THF		680
Na	THF		3.20
Na	THF	CE ^(c)	0.39
Na	THF		2.95
Cs	THF		0.09
Cs	THF	CE ^(d)	0.04
Cs	THF		0.05

(a) Dibenzo-18-crown-6 and Tetraglyme respectively.

(b) [TG]/[C⁻] ≈ 100. (c) [CE]/[C⁻] = 1.48. (d) [CE]/[C⁻] = 4.73

Inspection of equilibria (I) indicates that $K^{\pm} = K_{d1}/K_{d2} \cdot K^-$ so that, at least qualitatively, the change in $K^{\pm} (=K)$ with cation should parallel the change in K_{d1}/K_{d2} . The dissociation constants in THF of the Li, Na, (Na, CE) and Cs salts of a similar carbanion adduct of 4-PPE have been measured and the K_{d1} values of the 9MeF⁻ salts may reasonably be approximated from the reported values of the 9-propyl fluorenyl⁶ and fluorenyl^{5b, 8} salts. These results are shown in Table II and bear out at least qualitatively the expected correlation of K and K_{d1}/K_{d2} values.

Table II. Dissociation Constants of 4-PPE⁻M⁺ and Fluorenyl Salts in THF at 25°C.

	K(M ⁻¹)	K _{d1}	K _{d2}	K _{d1} /K _{d2}
Li ⁺	680	390 ^(a)	0.6 ^{(d)(f)}	650
Na ⁺	2.95	96 ^(b)	2.0 ^(d)	48.0
(Na, CE) ⁺	0.39	370 ^{(c)(g)}	30 ^(d)	12.3
Cs ⁺	0.05	1.6 ^(b)	19 ^(e)	0.08

(a) Ref. 5b. (b) Ref. 6. (c) Ref. 8. (d) Ref. 4. (e) Ref. 9.
(f) Order of magnitude only. (g) Extrapolated to 25°C.

The results indicate that the dramatic increase with decreasing cationic radius can, at least partially, be described in terms of ion pair dissociation. Thus the right shift of the equilibrium with small cations such as Li⁺ may be attributed to the stability of the of the very tight FPPE⁻M⁺ ion pairs. The results in THF cannot be related to dissociative equilibria since the relevant K_{d2} values are not known. However, as in THF, an important

part of the driving force for the forward reaction must be the decrease in free energy on formation of the FPPE^-M^+ pairs.

The effect of cation solvation is a left displacement of the addition equilibrium (see above). Clearly in a more strongly solvating medium the free energy of the system on the left side of the equation is relatively decreased due to cation solvation. This is reasonable since cation coordination in $4\text{-PPE}^-\text{M}^+$ salts appears to be less extensive than in fluorenyl salts and their derivatives. For instance even the Li salt of 4-PPE^- is a contact ion pair at 25°C in dimethoxyethane⁴ while fluorenyl lithium in this solvent exists as solvent-separated ion pairs.

In conclusion it was shown that in addition equilibria in which a carbanion is generated that is very different from the reacting carbanion, the ion pair effects can be very large and may be at least partially described in terms of dissociation and solvation equilibria of the participating species.

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