# Anionic Polymerization of Polar Monomers. I. Ultraviolet–Visible Spectroscopic and Conductometric Studies of Ion Pairs of Alkali Salts of Vinyl 2-, 3-, and 4-Pyridine-Type Carbanions and Their Crown Ether Complexes in Aprotic Media

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Abstract: The 2-, 3-, and 4-pyridyl isomers of 1-phenyl-1-pyridylethene have been prepared. The carbanions formed by addition of the 1,1,4,4-tetraphenylbutane dianion salts of Li, Na, and Cs and their crown ether complexes to the 1-phenyl-1-pyridylethenes have been studied by uv–visible spectrometry and conductimetry in a variety of low dielectric constant solvents. Both types of measurements indicate the ion pairs of the Li, Na, and Cs carbanion salts of the 2 and 4 isomers in THP, THF, and DME to be tight, while the structure of ion pairs of the 3 isomer in these solvents depends in a predictable way on the cation–solvent combination similar to the dianion of 1,1,4,4-tetraphenylbutane. The apparent tightness of the ion pairs of the 2 and 4 isomers has been interpreted in terms of a strong coulombic attraction between the electron-rich region around the N atoms and the cation in accordance with the expected resonance structures of these two carbanions. The alternate explanation of the tightness of 2-pyridyl carbanions of this type in terms of intramolecular solvation by nitrogen lone-pair electrons is discussed and is found to be inconsistent with the observed spectral and conductometric results. The high π-electron density on nitrogen in the 2- and 4-pyridyl carbanions demands double-bond character of the methylene to ring carbon bond which suggests the existence of rotamers in case of the 2-pyridyl carbanion. Independent NMR evidence for the existence of these rotamers is discussed. Possible consequences for anionic polymerization of 2-vinyl pyridine-type monomers are suggested.

The structure of ion pairs of delocalized carbanions, especially of the fluorenyl,[1] benzyl,[2] and allyl[3] type, and of aromatic radical ions[4] has been extensively studied in recent years by a variety of spectroscopic, conductometric, and kinetic techniques.[5]
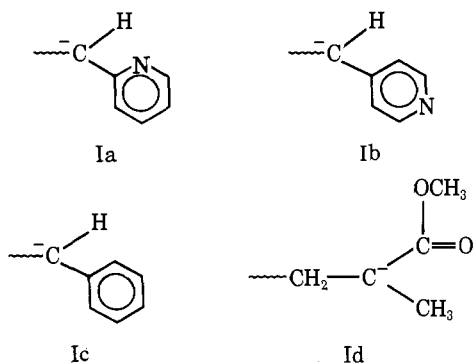

However, the structures of ion pairs of a variety of other carbanion salts, notably those of the vinyl pyridine type (Ia and Ib) and those obtained by addition of anions to acrylates (Id), have largely not been studied by direct (i.e., uv–visible) spectroscopic methods, mainly because many of the simple derivatives of I do not possess spectra that are useful in terms of interpretation of ion-pair structure. The information to date on the structure of ion pairs of Ia has mainly come from conductometric work.[6,7] Indirect information on ion pairs of Id has been obtained by conductometry[8a] and by NMR investigations on the stereochemistry of anionic polymerization of partially deuterated acrylates.[8b] This latter work strongly suggests a correlation between ion-pair structure and the stereochemistry of the propagation process. It was, for instance, reported that addition of minute quantities of strongly cation complexing solvents such as THF to the "living polymer" system in toluene decidedly affects the tacticity of the resulting polymer.

It seemed accordingly of interest to investigate in (further) detail the structure of ion pairs of systems such as Ia

and Ib in a variety of aprotic solvents if possible by direct, i.e., uv–visible spectroscopic and conductometric methods.

In the present work, we wish to report the results of such studies on Li, Na, and Cs salts of carbanions II, III, and IV obtained by addition of carbanion V to the 2-, 3-, and 4-pyridyl isomers of 1-phenyl-1-pyridylethene in solvents such as tetrahydrofuran (THF), tetrahydropyran (THP), dimethoxyethane (DME), dioxane, toluene, etc., in and without the presence of crown ethers (CE). All three isomers were investigated, because it appeared of interest to see whether the extent of delocalization of charge into the pyridine ring, which should be influenced by the nitrogen position, is a significant factor in the ion-pair structure. Also, a comparison of the three carbanions should shed further light on the question of intramolecular complexation of cation by the nitrogen lone-pair electrons as had previously been proposed.[6]
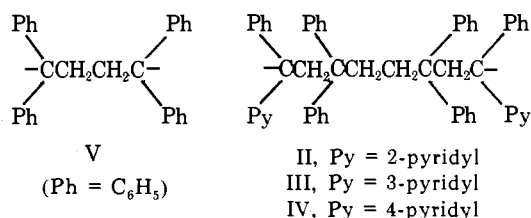
Experimental Section

Preparation of 1-Phenyl-1-(2-pyridyl)ethene (2-PPE). Following the procedure of Gilman and Spatz[9] a solution of 25.2 g of 2-bromopyridine in ether was added over a 3-min period to an equivalent amount of butyllithium in ether at −18°. To this (red) solution of 2-pyridyllithium was added over a period of 10 min a slight excess (5%) of acetophenone in ether. The solution was kept at −18° throughout. After hydrolysis with an ice-cold solution of ammonium chloride, the ether layer was extracted with 10% HCl. Neutralization of the acid extract gave a dark oil which was dissolved in ether and dried over Na₂SO₄. Vacuum distillation at 130–135° (≈0.7 mmHg) gave 18 g (62% yield) of colorless 1-phenyl-1-(2-pyridyl)ethanol which solidified in the freezer, mp 38–40° (lit.[10,11] 32, 53–54°). The alcohol (14 g) was dehydrated in 35 ml of 85% (v/v) sulfuric acid at 95° for 15 min. The mixture was
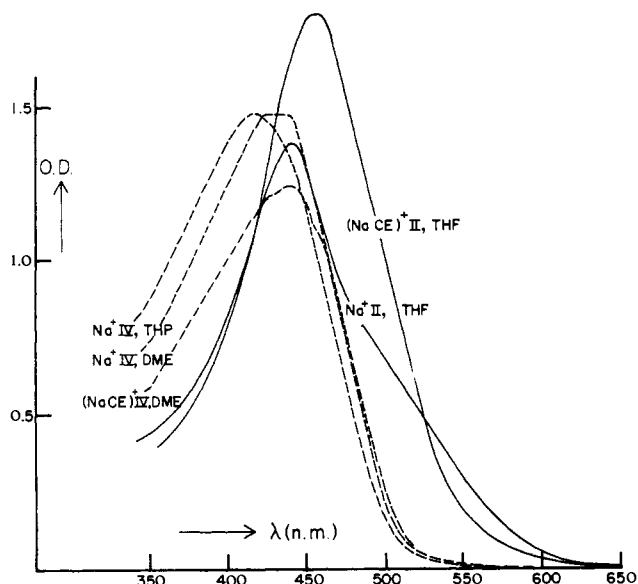
Figure 1. Absorption spectra of the sodium salts of II and IV and their crown etherates in THP, THF, and DME at 25°. (CE is dicyclohexyl-18-crown-6.)

Table I. Absorption Maxima (nm) of Alkali Salts of Addition Products of Carbanions to 1,1-Diphenylethene and 1-Phenyl-1-pyridylethene in a Number of Aprotic Low Dielectric Constant Solvents[g]

Salt	λ_{max}, nm						
	Tol-uene	Diox-ane	THP	THF	DME	TG[a]	DCE[b]
V[i] Li$^+$	450	446	462	496	494	495	
V 2Li$^+$	434	452	450	485	495	495	
V 2Na$^+$	h	462	468	470			501[c]
V 2Cs$^+$	h	h	476	478			
III[i] Li$^+$				440	439		
II 2Li$^+$	435	443	443	443	443	443[d]	
II 2Na$^+$	431	443	444	444	444	444[d]	458[c]
II 2Cs$^+$	h	436	435	441	442		
IV[i] Li$^+$	403	405	434	436	435	435	
IV 2Li$^+$	388	398	416	420	419	420	
IV 2Na$^+$	389	403	419	440[e]	440[e]	440[e,f]	442[c]
IV 2Cs$^+$	h	408	410	409	428		
III 2Li$^+$			484	483		481	
III 2Na$^+$			475	475			484[c]
III 2Cs$^+$		476					

[a]TG is tetraglyme $(CH_3-O[CH_2CH_2-O]_4-CH_3)$. [b]DCE is dicyclohexyl-18-crown-6. [c]One equivalent was added in THF; further additions did not alter the spectrum. [d]Tetraglyme concentration about 0.1 M. [e]Flat maximum 425–440 nm. [f]Tetraglyme concentration about 1 M. [g]Carbanion concentrations 10^{-3} to $10^{-4} M$. [h]Solubility too low ($<10^{-5} M$). [i]One-ended Li salt.

poured into water, excess of aqueous ammonia was added, and the organic base was extracted with chloroform. After washing with water and drying (Na_2SO_4), this extract was evaporated, and the residue was vacuum distilled to give 5.8 g (35% yield) of 1-phenyl-1-(2-pyridyl)ethene, bp 108° ($\simeq$5 mmHg) [lit.[12] 120–122° (0.8 mm)]. The product was purified by recrystallizing the HCl salt from an acetone chloroform mixture, mp 189–190° (lit.[12] 186–187°). The HCl salt was then neutralized with NaOH and extracted with benzene. The benzene extract was dried (Na_2SO_4) and vacuum distilled giving a slightly yellow viscous oil, 3.2 g. The product was confirmed by uv, nmr, and mass spectrometry.

1-Phenyl-1-(4-pyridyl)ethene (4-PPE) was prepared in a similar fashion from 4-bromopyridine. Temperature was kept at −70° during reaction with butyllithium and subsequently with acetophenone. The reaction mixture was hydrolyzed with water during which process the alcohol precipitated (yield 56%). It was recrystallized from benzene, mp 145–146° (lit.[11,13,14] 140–142, 144.2–144.7, 146–147°). The alcohol (12.5 g) was dehydrated using the procedure described above. The crude product was vacuum distilled giving 9.1 g of a yellowish oil. Repeated vacuum distillation at 92–93° (0.3 mmHg) [lit.[14] 113–114° (1 mm)] gave a colorless oil. The product was confirmed by NMR and mass spectrometry.

1-Phenyl-1-(3-pyridyl)ethene (3-PPE) was prepared similarly to the 2-pyridyl analog. The temperature during the reaction with butyllithium and acetophenone was kept at −40° to −50°. The reaction mixture was hydrolyzed with NH_4Cl solution and extracted with 10% HCl. Neutralization gave a dark reddish oil that was dried over $MgSO_4$ (yield 66%). Twenty-six grams of the crude product was dehydrated without further purification by heating it for 5 min at 97° in 20 ml of 81% H_2SO_4. After cooling, the mixture was poured in an ice–water mixture and extracted with chloroform. The solution was dried over $MgSO_4$ and evaporated. Vacuum distillation of the resulting viscous oil yielded 10 g of a colorless oil, bp 140° (0.75 mmHg). The structure of the product was confirmed by NMR.

Preparation of Carbanion Salts. The alkali metal salts to be studied were prepared by adding THP solutions of metal salts of 1,1,4,4-tetraphenylbutane dianion (V) to a slight excess of the phenylpyridylethene compounds in THP. The reactions were quantitative and instantaneous for 2- and 4-PPE and took somewhat longer for the 3-PPE ($\simeq$10 min). The addition of $(Cs^+)_2V$ to this compound could not be monitored with certainty, possibly because of the similarity of the spectra of $(Cs^+)_2V$ and the Cs salt of the addition product.

Both NMR and mass spectral evidence confirm the product of these reactions as the head-to-tail addition product of $^-DD^-M_2^+$ and two phenylpyridylethene molecules. The NMR spectrum ($CDCl_3$) of the protonated Na salt IV product shows aromatic ab-

sorptions at 8.24–8.30 and 6.55–7.29 ppm and the expected triplet, doublet, and singlet at 3.28, 2.70, and 1.47 ppm, respectively. The mass spectrum shows the expected series of peaks due to the parent ion at m/e 724, 725, 726, and 727. Due to instrumental limitations, a high-resolution mass could not be obtained for the parent ion; however, exact masses could be obtained for the major ions $HC(Py)(Ph)CH_2C(Ph)_2(CH_2)_2C(Ph)_2^+$ (calcd for $C_{41}H_{36}N$, 542.2803, observed 542.2831) and $HC(Py)(Ph)CH_2C(Ph)_2^+$ (calcd for $C_{26}H_{22}N$, 348.1751, observed 348.1779).

The one-ended Na salt was made by addition of 4-PPE to 1,1-diphenylethyl carbanion. This carbanion in turn was prepared by reacting 1,1-diphenylethane and an equivalent of two-ended "living" polystyryl$^-$ Na$^+$ salt in THF. The one-ended Li salt, 1,1-diphenylhexyllithium, was prepared by reaction of equimolar quantities of n-butyllithium and 1,1-diphenylethylene.

Solutions in other solvents were prepared by evaporating the THP on the vacuum line, distilling in a small quantity of the desired solvent followed by evaporation, and redistilling in of the desired volume of solvent. The spectra obtained in this way were identical with spectra of solutions directly prepared in the desired solvent in the case of THF and DME. Assuming an extinction coefficient of 26000 for $^-DD^-M_2^+$,[15] the extinction coefficients of the 2-, 3-, and 4-pyridyl$^-$ M$^+$ salts were found to be 15900, 27500, and 15400, respectively.

On addition of $^-DD^-M_2^+$ to 2-, 3-, and 4-PPE, no polymerization is expected. This was confirmed by inspection of the NMR spectra of systems where large excess of 4-PPE was added to $^-DD^-M_2^+$. Only PPE monomer was detected in the NMR spectrum.

Measurements. All experiments were carried out under high vacuum in a glass apparatus equipped with quartz optical cells and conductometric cells. These methods and purification of solvents have been previously described.[5] Conductances were measured on a "General Radio" automatic capacitance bridge assembly (1680-A at a frequency of 1 kHz). The uv–visible spectra were measured on a Beckman Acta V spectrophotometer.

Results

Spectral Studies. Visible and near-uv spectra of the Li, Na, and Cs salts of carbanions II, III, IV, and V were obtained in several solvents (Figure 1 and Table I). The salts II, III, and IV were obtained by reacting equimolar quantities of the 1,1,4,4-tetraphenylbutane dianion metal salt (V) or butyllithium with the corresponding 1-pyridyl-1-phenylethene (see Experimental Section).

The spectral results at once indicate that the spectral shifts in the pyridyl carbanions II and IV are dissimilar to those observed with V. In the latter case, the spectra have been satisfactorily explained by assuming equilibrium between tight and loose ion pairs.[1] For instance, Li ion pairs of V in THF are predominantly loose (496 nm) while, in THP, the salt exists essentially as tight ion pairs (462 nm). The Cs and Na salts of V in THF are tight, while the Na salt is apparently converted to loose ion pairs in dimethoxyethane (DME). In the carbanion salts of II and IV, however, no substantial shifts are apparent for either Li or Na salt in going from ethereal solvents of lower cation solvating power such as THP to more powerful solvents such as THF and DME as was observed with the $^-DD^-$ derivatives. An exception is the Na salt of IV in THP (see below).

Moreover, addition of tetraglyme ([TG] $\simeq 1 \times 10^{-1}$) to a THF solution of the Li and Na salts of II and IV does not affect the spectra. However, addition of 1 equiv of dicyclohexyl-18-crown-6 (DCE) or dibenzo-18-crown-6 (BCE)[15] to the Na salt of II in THF or THP resulted in a 14-nm red shift. Further addition of crown ether did not affect the spectrum.

Addition of DCE or BCE to the Na salt of IV in THF, however, changes the spectrum only very little. The broad band (427-440 nm) is slightly red shifted (442 nm), and the broad maximum narrows (Figure 1). Further addition of crown ether again has no effect on the spectrum.

Inspection of Table I indicates substantial blue shifts for the Li, Na, and Cs salts of II and IV in going from THF to dioxane to toluene. It is interesting that, for the Li and Na salts of II, there is no significant shift until toluene, while the Cs salt blue-shifts from THF (441 nm) to THP and dioxane (435 nm). Similarly for the salts of IV, λ_{max} is essentially unchanged until dioxane for the Li salt, until THP for the Na salt, and until THF for the Cs salt.

From inspection of Table I, it is obvious that the spectral behavior of carbanion salts II and IV is very different from that of their hydrocarbon analogs. No obvious trends in λ_{max} with cation solvating power, the dielectric constant of the solvent, or the cationic radius are discernible. Since no common ion effect on the spectra of II or IV was observed in the 10^{-3} to 10^{-5} M range, it is clear that we are not dealing with free ions but with ion pairs and/or their aggregates.

Though aggregation cannot be ruled out, especially in dioxane and toluene, no dilution effect on the spectra was observed down to $\sim 10^{-6}$ M.

Table I indicates different maxima for one- and two-ended Li salts of II and especially of IV (435 and 420 nm, respectively). To test for intramolecular interactions between the two ends of the bola form electrolyte IV, the two-ended Li salt of IV was carefully titrated with a dilute THF solution of menthol until approximately 80% conversion. The resulting spectrum was indistinguishable from the spectrum of the two-ended salt. Barring extensive disproportionation into the dicarbanionic salt and the diprotonated product, this result indicates an absence of ionic interactions between the two ends. This result is also confirmed by conductance measurements (see below).

The spectra of the carbanion III are consistent with a description that is similar to that of the 1,1,4,4-tetraphenylbutane dianion (V). The ion pairs, however, seem to be somewhat "looser". For instance, the Li III salt in THP and THF is essentially separated, while $Li^{+-}DD^-Li^+$ in THP is predominantly tight (Table I). The Na salt is tight in both THP and THF but, on addition of crown ether (1 equiv), the spectrum is converted to that resembling the loose ion pairs of the Li salt in THP and THF. The Cs salt is presumably largely of the tight ion-pair variety and is very slightly
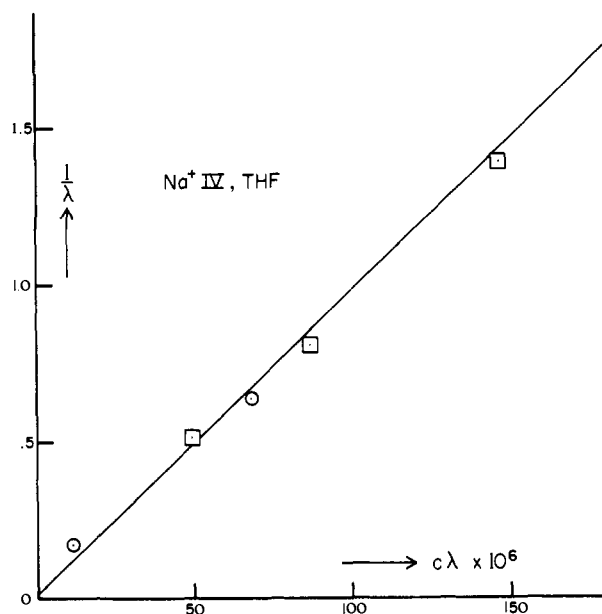
Figure 2. Conductance ($1/\lambda$ vs. $c\lambda$) plot of the sodium salt of IV in THF at 25°. (⊙ and □ refer to different runs.)

red shifted with respect to the "tight" ion pair of the Na salt in THF. It is, however, uncertain whether, in this case, complete reaction and conversion to III has been achieved (Experimental Section).

Conductance Studies. Electric conductance was measured for the four carbanion salts as a function of counterion size and, in case of carbanion IV, of temperature as well. Four to eight concentrations were measured in the range 1×10^{-3} to 5×10^{-6} M by dilution in vacuo as previously described.[1b,5] The data were plotted according to the equation

$$\frac{1}{\lambda} = \frac{1}{\lambda_0} + \frac{c\lambda}{K_d\lambda_0^2}$$

(λ and λ_0 are equivalent conductance and equivalent conductance at zero concentration, respectively, K_d is dissociation constant, and c is concentration in moles/liter.)

The usual corrections[16] are not applied because of the considerable uncertainty in the value of the $1/\lambda$ vs. $c\lambda$ slope in many cases that makes this correction unnecessary (see below).

The λ_0^+ values for Li^+, Na^+, and Cs^+ ions in THF at 25° are taken as 36.6, 48.2, and 68.4, respectively.[5] The λ_0^- values of II or IV and V are calculated as 28.2 and 35.2, respectively, using $\lambda_0^- \simeq M^{-1/2}$[17] and λ_0^-(fluorenyl) = 51.8. Reproducibility was found to be satisfactory in all cases (Figure 2). The slopes of log λ vs. log c plots are close to -0.5 in most cases.[18] Exceptions are the Li and Na salts of IV in THF where slopes were found to be -0.36 and -0.39, respectively. For the Na salt, the slope increases to -0.45 in the 10^{-4} to 10^{-5} M range.[19] Similar findings are reported by Sigwalt.[6]

This lower value of the slope is possibly caused by an unexpectedly high value of λ at higher concentrations. This is also indicated by the strongly curved $1/\lambda$ vs. $c\lambda$ plots. This is probably due to the formation of ionic aggregates at higher concentrations (see Discussion). The expected error in the value of the dissociation constants is quite large ($\sim 50\%$) for the systems V Li^+, II $(NaCE)^+$, IV Li^+, and IV $(NaCE)^+$, caused in part by the error in the $1/\lambda$ vs. $c\lambda$ slope due to a strong curvature over much of the concentration region. This latter phenomenon has also been observed in conductance studies on vinyl pyridine carbanions[6,7] and is probably at least partially due to triple ions (see Discus-

Table II. Dissociation Constants of Alkali Salts of Carbanions II, IV, and V in Tetrahydrofuran at 25°[a]

	$K_d \times 10^8, M$[b]
V 2Li[+b]	≅400
V 2Na[+]	83
V 2Cs[+]	2.6
II 2Li[+]	28
II 2Na[+]	37
II 2Cs[+]	8.7
II 2(NaCE)[+b]	≅400
IV 2Li[+b]	≅0.6
IV 2Na[+]	1.9
IV 2(NaCE)[+b]	≅30
IV Na[+c]	2.3

[a]Concentration range 10^{-3} to 10^{-5} M. Dissociation constants ±30%. [b]K_d values ±50%. [c]One-ended salt.

Table III. Enthalpy and Entropy of Dissociation of Na and Li Salts of Carbanion IV in Tetrahydrofuran over the Temperature Range 25 to −25 and −35 to −75°, Respectively[a]

	IV 2Li[+]	IV 2Na[+]
$\Delta H_d°$ (25 to −25°)	1.2 kcal	≅0 kcal
$\Delta S_d°$ (25 to −25°)	−30.5 eu	−36.8 eu
$\Delta H_d°$ (−35 to −75°)	0.07 kcal	−0.86 kcal
$\Delta S_d°$ (−35 to −75°)	−36 eu	−39.9 eu

[a]Enthalpy and entropy values ±0.5 kcal and ±5 eu, respectively.

sion). The conductance data are shown in Table II. It is apparent that the Li and Na salts of II and IV are less dissociated than their hydrocarbon analogs. The difference between the Li salt of V and those of II and IV is especially obvious since the former salt is known to exist as loose ion pairs in THF[1a] and is accordingly more dissociated. On the other hand, the Cs salts of II and V have similar dissociation constants.

To verify the absence of intramolecular ion-pair interactions in these systems, the dissociation constant of the one-ended analog of the system IV, Na^{+}, in THF, was measured and found to be the same as that of the two-ended system within experimental error (Table II). This is also indicated by the uv–visible spectrum of the partially protonated salt that is identical with that of the two-ended system (see Results).

Addition of 1 equiv of DCE to the Na salts of II and IV causes appreciable increases in conductance indicating complexation of crown ether with Na ion. Further addition of crown ether does not influence the conductance of the solution measurably.

No extensive conductance measurements were carried out on alkali salts of III. However, it was observed that conductances of a THF solution of the Na salt of III were the same or slightly higher than the Na salts of V. This confirms the spectral results of alkali salts of III that show that ion pairing of III and V is similar (see Discussion).

Because of the apparent differences between ion-pair structure of carbanions III and V on the one hand and carbanions II and IV on the other, it was decided to further investigate the structure of one of the tight ion pairs of II or IV by conductance vs. temperature studies. Carbanion IV was selected because of its greater apparent tightness. The Li and Na salts of this carbanion were studied from −75 to +25°. The temperature dependence of λ_0^- and λ_0^+ has been determined in this temperature range.[5] Because of the strong curvature in the $1/\lambda$ vs. $c\lambda$ plot at all temperatures, it is clear that the accuracy of the K values is not great, as previously pointed out. The plots in all cases, however, were drawn through the same set of points so that any systematic error in the K values should be significantly less in determination of thermodynamic quantities.[20]

Inspection of Table III shows that the enthalpies of the Li and Na salts of IV are higher than the corresponding styryl[21] or fluorenyl[1b] carbanion salts. For instance, in the 25 to −25° range, the ΔH of Li and Na salts of IV in THF is +1.2 and 0 kcal, respectively. At lower temperature, the ΔH decreases slightly in both cases.

Discussion

$^-DD^-M_2{}^+$ adds readily to the 2- and 4-pyridyl isomers of 1-phenyl-1-pyridylethene and probably also to 1-phenyl-

1-(3-pyridyl)ethene. This result is unexpected since $^-DD^-M_2{}^+$ does not add to 1,1-diphenylethene.[5] Similarly addition of 4-PPE to carbanion IV does not result in polymerization (see Experimental Section). Since the steric repulsion experienced by pyridine is probably not much different from that of the phenyl group, it appears that the increased stability of carbanions II and IV, due to greater delocalization of charge into the pyridine moiety, is the driving force for the addition process.

As pointed out above, the spectral results on the salts of II and IV show cation and solvent effects that are different from those observed with delocalized hydrocarbon carbanions such as fluorenyl[−] or $^-DD^-$ (V). However, on addition of DCE to the Na salts of II and IV, red shifts of 3 and 14 nm, respectively, are observed. In the case of II, this shift is probably best explained by formation of a crown ether-separated ion pair[21] also observed on crown ether addition to the Na salt of V (Table I). This implies that, for all other alkali salts of II, we are dealing with tight ion pairs.

This is especially remarkable for the Li and Na salts of II in DME and THF tetraglyme mixtures since, in the case of their hydrocarbon analog salts, these systems exist as separated ion pairs (Table I). Apparently the anion competes very effectively for the cation with the solvent. The ion pairs are thus very tight compared with the corresponding salts of $^-DD^-$ (V) (see below).

On the basis of the very small red shift observed on adding DCE to the Na salt of IV (Figure 1), it appears that complexation takes place, but that cation coordination is external:

$$IV^- M^+ + DCE \rightleftharpoons IV^- M^+, DCE$$
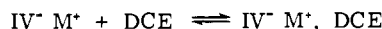
This type of complex has been found on adding crown ethers to fluorenyl salts in THP and THF.[22] Moreover, this type of complex is also indicated on the basis of conductance measurements (see below). It appears then that the Na and Na, DCE salts of IV are present as tight ion pairs also. The fact that even the crown complex is tight suggests that the IV anion is very effective in competing with solvent or complexing molecule for the cation. This suggests that the Li and Cs salts are also tight, and this is confirmed by the conductance measurements (see below).

Inspection of Table I indicates substantial blue shifts in going from THF or DME to dioxane and toluene. These observations may suggest specific solvation effects since correlation with any reasonable measure of polarity is inconsistent. Since presumably the ion pairs of II and IV are "tight" in all solvents, the blue shifts may indicate peripheral desolvation in which the cation is deprived of its peripherally held solvent molecules:

$$C^-M^+ \overset{X}{\underset{X}{\diagup\diagdown}} \rightleftharpoons C^-M^+ + \rightleftharpoons C^-M^+$$

Whether such peripheral desolvation involves one or more distinct steps is not clear. Aggregation of ion pairs is another possible factor in the observed shifts. It was, however, found that, at least in THP, THF, and DME, the spectra

are essentially concentration independent in the 10^{-3} to 10^{-6} M range. It is, however, likely that other factors are also involved in determining spectral shifts in some of the carbanions studied.

For instance, in comparing one-ended with two-ended Li salts, Table I shows that, for salt IV, the one-ended salt has generally longer wavelength absorption maxima. Two explanations are possible to account for this behavior. First, it could be caused by interaction of the two ends of the bola form electrolyte to give an intramolecular ion pair dimer or similar ion cluster. Secondly, the effect could be due to the many steric interactions in this molecule containing eight bulky phenyl and pyridyl groups. These interactions could distort the π system inhibiting conjugation and causing a blue shift.[23] The menthol titration experiment (see Results) indicates no intramolecular association. This conclusion is supported by conductometric measurements (Table II) showing that dissociation constants of the one- and two-ended Na salts of IV are the same within experimental error. This confirms that intramolecular association to dimers or triple anions is nonexistent. This conclusion is also supported by inspection of models that show that approach of the two carbanionic ends is extremely hindered by the eight phenyl and pyridyl groups in the molecule. As a result the molecule is probably fairly rigid. In addition the results indicate that the contribution of one carbanionic end to the electrostatic potential of the other is negligible. Inspection of Table II further indicates that the K_d values of the Li and Na salts of II and especially of IV are low compared with those of V. This agrees with the low K_d value found for the Na salts of vinyl pyridine carbanions in THF[6,7] and seems to suggest that these salts exist as tight ion pairs, the ion pairs of IV being tighter than those of II. The similar K_d values of Li^+V^- and $Na^+,CE\ II^-$ suggests also that $Na^+,CE\ II^-$ exists as crown ether-separated ion pairs. However, the much lower K_d value of the $Na^+,CE\ IV^-$ salt indicates that, in this case, no crown ether-separated ion pairs exist since crown ether-separated ion pairs of II and IV should have nearly the same dissociation constants. It is therefore likely that the Na^+,CE salt of IV is peripherally complexed by crown ether as was also suggested by the spectroscopic results.

A second possibility is that the increased dissociation constant of IV is caused by extensive coordination of free Na^+ ion by crown ether:

$$C^-Na^+ \overset{K_1}{\rightleftharpoons} C^- + Na^+$$
$$+ DCE$$
$$\Big\updownarrow K_2$$
$$[Na, DCE]^+$$

If we define an apparent dissociation constant K where $K = ([Na^+] + [Na,DCE^+])[C^-]/[C^-M^+]$, it follows that $K = K_1(1 + K_2[DCE])$ and, since K_2 is very large,[21] K equals $K_1K_2[DCE]$. One expects, therefore, the conductance to continue to increase with increasing DCE concentration, and this is not in accordance with our observations (see above). It appears, therefore, that peripheral complexation takes place:[22,24]

$$C^-M^+ + DCE \overset{K_3}{\rightleftharpoons} C^-M^+DCE \quad (K_3 \gg 1)$$

The tightness of the Li and Na salts of IV is possibly caused by a stronger cation–anion electrostatic interaction compared with the hydrocarbon analog V. In such a case, one expects a more positive enthalpy of dissociation. This is borne out by the results in Table III. For instance in the 25 to $-25°$ range, the ΔH_d of Na IV in THF is about 0 kcal/

mol. In the same temperature range, the ΔH_d of fluorenyl sodium in THF is about -8.0 kcal and, from spectroscopic data, the ΔH_d of Na V in THF is expected to be similar. The interaction between metal ion and carbanion is apparently strong enough to decrease the heat of dissociation by about 8 kcal/mol. A comparison between the ΔH_d values of the Li salts gives a difference on the same order of magnitude.

As pointed out above in many of the systems, curved $1/\lambda$ vs. $c\lambda$ plots were observed making an accurate evaluation of K_d impossible. This phenomenon may be due to triple ions or higher aggregates. Triple ions have recently been detected in similar systems.[25] A c vs. $c\lambda^2$ plot,[26] however, did not yield a straight line suggesting that perhaps higher ionic aggregates are present. It should, however, be stressed that our conclusions regarding the tightness of the II and IV salts will not be affected since the presence of additional charged species would raise the apparent K_d.

Both spectral and conductometric results indicate then that the Li and Na salts of II and especially of IV are tight in such solvents as THF, DME with or without the presence of tetraglyme. The greater apparent tightness of the salts of IV compared with those of II was initially surprising in view of earlier conductance studies[6] in which the low apparent dissociation constant of the carbanion Ia was explained by coordination of metal ion by the nitrogen lone pair:

Ia

Consequently on dissociation, the (negative) entropy of dissociation would be more negative for this salt compared with that for the hydrocarbon analog. However, this model would predict a looser ion-pair structure for the 4-pyridyl analog where such an intramolecular solvation of metal ion is not possible, and this is at variance with our results.

It appears, therefore, that the apparent tightness of II and IV as compared with that of III and V is caused by high π-electron density on nitrogen consistent with resonance structures such as:

In this description, the cation is to a very large extent coordinated to the N atom by virtue of its high π-electron density. It follows that ion pairing in III, where π-electron density of nitrogen is not expected to be large, will be comparable to that in V, and this is borne out by the spectral and conductometric measurements. The above anion then has considerable nitranion character. Recently a similar carbazole nitranion K salt has been studied by conductometry[27] and was found to be also much less dissociated compared with the corresponding fluorenyl salt.

The sizable effect of the N atom in delocalizing charge in these systems is demonstrated by recent work concerned with the measurement of the acidity of 2- and 4-methylpyridine in KNH_2–liquid NH_3 solutions by NMR.[28] It was found that the pK_a of the α hydrogen of 4-methylpyridine was about 28, approximately seven to eight powers of ten lower than that of toluene. The α hydrogen acidity of 2-

methylpyridine was found to be somewhat higher ($28 >$ p$K_a < 32$). The double-bond character of the methylene to ring carbon bond in the 2-methylpyridine carbanion was demonstrated by observation of a clear AB pair of doublets of the methylene group at $-40°$ that did not collapse on warming to room temperature. Similar NMR observations had previously been made for the lithium salt in THF.[29] These observations seem to support our interpretation regarding the unusual tightness of ion pairs of the Li^+ and Na^+ salts of II and IV. High electron density on nitrogen compared with that on methylene carbon is also indicated by a CNDO calculation[30] on the unpaired 4-methylpyridyl carbanion. Calculated electron density on nitrogen was comparable with that on the methylene carbon. It is furthermore possible that high electrostatic field-strength ions such as Li^+ and Na^+ may accentuate charge density on nitrogen. This is also consistent with the large differences in dissociation constant between the lithium salts of V and those of II and IV, while the dissociation constants of the Cs salts of II and V are comparable. A cation-dependent charge distribution in the α-naphthyl methyl carbanion has recently been described.[31]

If the above interpretations are correct, the polymerization of vinyl pyridine-type monomers may be more complicated than previously realized. If the interconversion between rotamers A and B is slow compared with the rate of propagation, chemically distinguishable forms of the carbanion may be contributing to the polymerization:
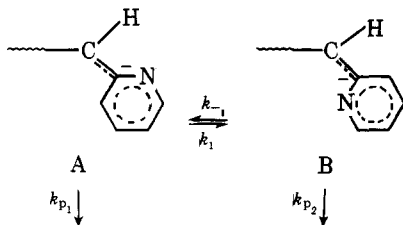
each with its characteristic rate and mode of propagation. This problem is presently under investigation.

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(18) -0.53, -0.45, and -0.45 for the Li, Na, and Cs salts of II, respectively.
(19) For the Li salt of IV in THF, the slope decreases drastically in the 10^{-5} to 10^{-6} M range. This is reflected in the $1/\lambda$ vs. $c\lambda$ plot. The extrapolated intercept corresponds to an unreasonably low λ_0 value of about 3. The K_d therefore has been calculated from measurements in the 10^{-5} to 10^{-6} M range and represents only an order of magnitude.
(20) K_d equals $1/s\lambda_0^2$ where s is the slope of the $1/\lambda$ vs. $c\lambda$ plot. Assuming that Walden's rule $\lambda_0\eta = c$ (c = constant, η = solvent viscosity) holds, it follows that $\log K_d = -\log s -2(\log c - \log \eta)$. Differentiating with respect to $1/T$ gives

$$-\frac{\Delta H}{R} = \frac{-d \ln s}{d(1/T)} + 2\frac{d \log \eta}{d(1/T)}$$

It follows that errors in ΔH are essentially only due to errors in the quantity $(d \ln s)/d(1/T)$.
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(24) Taking the process

$$C^-Na^+ + DCE \xrightleftharpoons{k_3} C^-Na^+, DCE$$

into account, the apparent dissociation constant becomes

$$K = \frac{K_1(1 + K_2[DCE])}{1 + K_3[DCE]} \simeq \frac{K_1K_2[DCE]}{1 + K_3[DCE]}$$

Since K does not continue to change with [DCE] after an equimolar quantity has been added, K_3[DCE] must be very large reducing K to K_1K_2/K_3.
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(30) This calculation was kindly carried out by Mr. W. Moreshead.
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