

THE NMR SPECTRA OF MODEL STYRYL-ALKALI METAL COMPOUNDS

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(Received June 9th, 1971)

SUMMARY

The active chain end in the anionic polymerization of styrene in benzene and THF solution has been studied by preparing model compounds and one unit "living" polymer chains and measuring their NMR spectra. From the spectra it appears that half or more of the charge of an electron resides in the aromatic ring, and this increases on changing from benzene to THF, on changing from Li^+ to K^+ as counterion, and with increasing alkyl substitution on the ring. It also appears that there is hindrance to rotation of the phenyl ring in the carbanion, this appears to increase as the charge on the ring increases, and the whole benzylic anion system appears planar.

INTRODUCTION

The NMR chemical shifts of aromatic protons in benzyl lithium have been reported to be markedly different in tetrahydrofuran (THF) solution and benzene solution¹. From these shifts it has been inferred that the charge residing in the phenyl ring of this compound in benzene solution is markedly lower than in the more polar THF. Differences were also noted in the UV spectra of this compound in the two solvents. These results, supported by α -¹³C and ⁷Li chemical shifts, could be interpreted by a much more covalent form of the C-Li bond in the hydrocarbon solvent. If this were so, by extrapolation to anionic polymerization systems, it might lend credence to the suggestion, sometimes put forward, that in hydrocarbon solvents the propagation reaction could proceed by a covalent insertion reaction, as opposed to the generally held view that it is an ion pair reaction.

To ascertain the effect of solvent on the charge distribution in living polymerization systems of styrene, low molecular weight models of the "living" polymers were prepared in benzene and in THF solution, and their proton resonance spectra measured.

EXPERIMENTAL

The deuterated solvents and tert-butyl chloride-*d*₉ were bought from Merck, Sharp and Dohme Ltd. The benzene-*d*₆ was dried over calcium hydride and then butyllithium. The THF-*d*₈ was freed of moisture and aldehyde contaminants by

shaking with potassium metal. All manipulations were performed in vacuum systems, the final preparations in all glass sealed apparatuses.

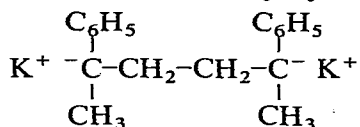
tert-Butyllithium-*d*₉ was prepared from the chloride in hexane in a vacuum system by stirring with Li metal dispersion (2% Na) which had been washed with butyllithium solution. The *tert*-butyllithium-*d*₉ after filtration and freeing from solvent was vacuum sublimed, and distributed as a benzene solution into a number of vessels fitted with breakseals.

Benzyllithium in benzene solution was prepared from dibenzylmercury and lithium emulsion and filtered into the NMR tube¹. The 1/1 addition product of *tert*-butyllithium and styrene was formed by adding an equimolar amount of styrene in an 8% solution of THF in benzene to the alkyllithium. After filling and sealing off one NMR tube, the solvent could then be changed to THF-*d*₈ by removing the solvent in vacuum, and adding further THF-*d*₈.

The 1/1 addition product did not form in benzene solution because the rate of addition of styrene to the already formed product is too rapid, and polymer formed instead, leaving unreacted *tert*-butyllithium. To overcome this, 2-butyllithium was used because its rate of reaction is higher with styrene. Nevertheless, still half the butyllithium remained when the starting proportions were equimolar, and gas chromatography showed that on the average a two unit chain was formed. The spectrum of the phenyl ring adjacent to the charge was well defined, but the high field region of the spectrum was very complex and not assigned as only undeuterated 2-butyllithium was available, and the end group absorptions obscured those of the non-aromatic protons.

The reaction of *tert*-butyllithium with α -methylstyrene was carried out in benzene. In this case the major product is the 1/1 adduct, but it is not very soluble in this solvent and mostly precipitated. The filtrate contained a sufficient concentration of the product to obtain a satisfactory spectrum using the Fourier transform technique and summing. The residue was dissolved in THF-*d*₈, in which the product is soluble, to give the normal concentration, about half molar.

To form the α -methylstyrene dimer potassium compound²:



the monomer was shaken with a potassium film in THF-*d*₈ at room temperature for two days, and then filtered into the NMR tube. Cumylpotassium* was similarly prepared from cumyl methyl ether in THF-*d*₈ solution. Potassium methoxide precipitated and was filtered off. The complexity of the spectrum at high field suggested that side reactions were occurring, but at low field the aromatic protons of the ring adjacent to the C-K bond were well defined as expected. Gas chromatography of the hydrolysed product showed the presence of a dimer. It is suggested that some isomerization to an isopropyl substituted phenylpotassium occurs, which then attacks as yet unreacted cumyl methyl ether to give the dimer and potassium methoxide. This product dimethyl(isopropylphenyl)phenylmethane would be consistent with the extraneous peaks in both the hydrolysed and unhydrolysed reaction mixture. Three isomers are possible according to the position of the isopropyl substituent, and in fact all the

* Cumyl = (α,α' -dimethylbenzyl).

lines are closely doubled. The dimers presence would not be expected to modify the NMR spectrum as no association is expected in THF.

All spectra were measured at 100 MHz on a Varian spectrometer.

RESULTS AND DISCUSSION

The presence of the negative charge in the benzylic anion caused the aromatic protons to be displaced upfield, and separated in a characteristic pattern³, Fig. 1. The *para* proton is a triplet, the *ortho* protons doublets, both split by the adjacent *meta* protons which give in turn a multiplet. All, under favourable circumstances, show extra fine structure from longer range coupling. The splitting of the absorption of the α and β proton into a triplet and a doublet respectively in the styryl compounds, Fig. 2, identified them in the solvents containing THF, and this was confirmed by an experiment using β -styrene- d_2 .

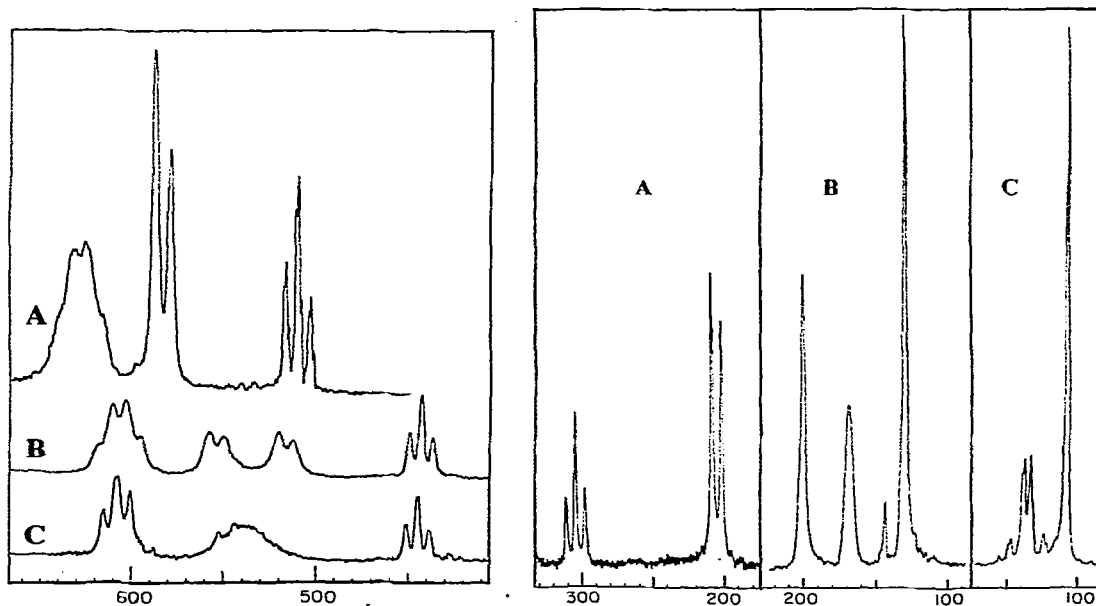


Fig. 1. Low field portion of NMR spectra: (A), styryllithium in THF- d_8 at 25°. (B), α -Methylstyryllithium in THF- d_8 at 25°; and (C), at 60°.

Lowest field bands assigned to the *meta* protons, highest field bands to the *para* protons, the central bands to the *ortho* protons.

Fig. 2. High field portion of NMR spectra: (A), styryllithium in benzene + 8% THF- d_8 , low field band assigned to α -proton, high field to β -protons. (B), Dimer α -methylstyrene potassium in THF- d_8 , low field band β protons, high field the methyl group, central peaks due to residual protons on THF- d_8 and an impurity. (C), 2,5-Dideuterio-2,5-diphenylhexane, low field band the methylene protons, high field peak the methyl groups.

The chemical shifts of the aromatic protons of all these compounds are listed in Table 1, together with the aliphatic proton shifts where they were identifiable. From the shift of the corresponding protons relative to benzene it is possible to estimate the

charge on the carbons of the phenyl ring by the method suggested by Fraenkel *et al.*⁴. There are only protons on five of the carbons so it is not possible to find the true charge on the ring, but in Table 2 are given the charges and the total for the carbons 2–6, using as constant $1e = 10.7 \text{ ppm}^5$ shift upfield.

TABLE 1

PROTON CHEMICAL SHIFTS OF SUBSTITUTED BENZYL COMPOUNDS

Compound	Solvent	δ^a					J^b		
		<i>o</i>	<i>m</i>	<i>p</i>	α	β	CH ₃	<i>o, m</i>	<i>p, m</i>
1 Benzyllithium	Benzene	6.41	6.77	6.58	0.88			8	7
2 Benzyllithium ³	THF	6.09	6.30	5.50	1.62			8	6.2
3 Styryllithium	Benzene	5.98	6.53	5.52				8	7
4 Styryllithium	Benzene + 8% THF	6.00	6.62	5.32	3.02	2.06		8.5	6.5
5 Styryllithium	THF	5.87	6.32	5.12	2.36	1.85		8.5	6.5
6 (α -Methylstyryl)lithium	Benzene	5.67	6.23	4.66		1.60	1.20		
		5.29							
7 (α -Methylstyryl)lithium	THF	5.57	6.10	4.46		1.88	1.51	8	6.5
		5.19							
8 Cumylpotassium	THF	5.15	6.08	4.41			1.48	8	6.5
9 Dimer- α -methylstyrene potassium	THF	5.43	5.98	4.24		2.00	1.30	8	6.5
		4.85							

^a Ppm downfield from TMS. ^b In Hz.

TABLE 2

CHARGE ON AROMATIC CARBON ATOMS^a

System ^b	<i>o</i>	<i>m</i>	<i>p</i>	Total
1	0.07	0.04	0.06	0.29
2	0.10	0.08	0.16	0.53
3	0.11	0.06	0.16	0.51
4	0.11	0.05	0.18	0.50
5	0.12	0.08	0.19	0.61
6	0.16 ^c	0.09	0.24	0.74
7	0.17 ^c	0.10	0.26	0.80
8	0.19	0.10	0.26	0.85
9	0.19 ^c	0.11	0.28	0.89

^a $1e = 10.7 \text{ ppm}$ shift upfield. ^b Systems as in Table 1. ^c Average values.

From Table 2 it is seen that there is a fall of measured charge on the ring from near $0.6e$ to $0.3e$ with benzyllithium in changing from THF to C_6D_6 solvent. Waack *et al.*¹ suggested a change of $0.6e - 0.2e$. As no details of the spectrum of the phenyl ring were given an exact comparison is difficult, but the charge reduction is much the same. In C_6D_6 solution, however, the δ value measured here for the methylene protons indicates a 0.74 ppm upfield shift from that in THF solution. Waack *et al.* report a resonance for these protons 0.58 ppm downfield in C_6D_6 compared with

THF¹, or at a position of 0.21 ppm upfield of toluene⁶, which is close to that of the α protons of dibenzylmercury in C₆D₆. If the shift in position of the peak is indicative of the charge on the α carbon¹, as these authors suggest, the upfield shift would indicate more of the charge must reside there. If this is so, the assumption by Waack *et al.*¹ is no longer valid, that in benzene solution the α -methylene charge is reduced to 0.1 or 0.2 e , in proportion to the charge on the ring. It would appear in fact, that the loss in charge on the ring is compensated by an increase in charge on the methylene carbon, and the total charge on the benzyl moiety would not change very much. In this case the benzyl-lithium could still be thought of as largely ionic, as in THF solution, the redistribution of charge being a consequence of the dimeric form of the benzyl-lithium in benzene solution, as opposed to THF where it is monomeric. But such arguments based on the shifts of the methylene protons are uncertain as many other factors could affect them. For example in the dimer if it had a head to tail structure in benzene solution, the methylene protons and also the Li and the α -C could be opposite the face of the other phenyl ring, and thus exposed to its diamagnetic field. Upfield shifts of all their resonances could then be expected, relative to the spectra in THF, as indeed was found¹. In benzene solution, the *o*-proton shift is at higher field than the *p*-proton, in contrast to their relative positions in all the other spectra. Perhaps again local disturbances due to the dimeric nature of the compound in benzene are the cause, although the styryl and α -methylstyryl compounds which are also dimeric in this solvent do not show this effect.

The UV spectrum of benzyl-lithium in benzene was measured and it was confirmed that the absorption maximum is at 292 nm¹, compared with 330 nm in THF. Styryl and α -methylstyryl compounds show much smaller changes in absorption maximum between benzene and THF or with different alkali metal counterions. The behaviour of benzyl-lithium in benzene is obviously anomalous, although whether this is due to the aggregation into a tighter dimer because of its compactness, or caused by a change in the bond nature is uncertain.

In a parallel fashion styryl-lithium in all the three solvents shows a considerable total charge on the phenyl ring, although the shifts of the phenyl protons vary. This charge is close to that of benzyl-lithium itself in THF when the solvent has a low ϵ , but is rather higher in pure THF. The presence of excess 2-butyllithium in benzene solution could modify the spectrum through its cross association, whereby some of the effects described for benzyl-lithium would be removed. However, the extent of cross association is probably not extensive as it has been found that a severalfold excess is necessary to break down the dimer.

Cumylpotassium in THF, appears to have over 0.8 e charge on the ring, perhaps because of a greater electron transfer from potassium to carbon, but perhaps also caused by the two methyl groups tending to donate electrons to the α -carbon forcing more charge into the ring. The potassium dimer of α -methylstyrene also shows this large ring charge. When the counterion is changed to lithium in the α -methylstyryl-lithium model the charge drops by about 0.1 e , but is still greater than for the unsubstituted polystyryl-lithium. At room temperature in THF both the lithium and potassium compounds are mostly in the form of intimate ion pairs⁷, the closer approach possible for the Li⁺ ion may favour more localization of the charge on the α -C atom.

In both the potassium dimer of α -methylstyrene and in the α -methylstyryl-

lithium model compound in benzene and THF solution, the two *ortho* protons are magnetically nonequivalent having markedly different chemical shifts at room temperature, appearing as two doublets with fine structure. The *meta* protons also are non-equivalent, but considerable overlap of the multiplets occurs. Evidently the rate of rotation of the phenyl ring is slow on the NMR time scale. Raising the temperature to 85° did not alter the potassium compound's NMR spectrum, but at 60° the two *ortho* peaks merged into a broad band in the spectrum of the α -methylstyryllithium compound in THF, demonstrating the onset of more rapid rotation of the ring. It is possible that it is the methyl group that causes this restriction of rotation, but it would seem more likely that it is due to extensive sp^2 hybridisation in the α -carbon, introducing a large degree of double bond character in the bond joining it to the phenyl ring. The whole benzylic system would be planar and the two edges of the phenyl ring in magnetically different environments^{8,9}.

Additional evidence for the planarity of this system is found in the narrowness of the CH_2 resonance in the potassium dimer compound, Fig. 2, suggesting that the two protons are magnetically equivalent. This would be the case if the anions were planar and the α -carbon largely sp^2 hybridised. The product of reacting the potassium dimer with water has a normal sp^3 hybridised α -carbon atom, and protons of the methylene group could be expected to have magnetically dissimilar environments. The compound has two isomers and, when isolated, the higher melting isomer shows the expected multiplet in the NMR spectrum for the methylene protons, as is also reported for the low melting isomer¹⁰. On deuteration of the α position by reacting the potassium dimer with deuterium oxide, the β multiplet simplified, Fig. 2, but does not become the singlet expected should the protons be coincidentally magnetically equivalent. Hence the singlet for the β protons of the potassium dimer is also unlikely to be caused by their being coincidentally magnetically equivalent next to an sp^3 hybridised α -carbon, but is a result of the symmetry of the molecule with an sp^2 hybridised α -carbon.

The styryllithium compound does not exhibit this phenomenon at room temperature, and has only a single doublet for the *o*-protons indicating freer rotation of the ring. On lowering the temperature, however, marked changes in the spectrum of the styryllithium occur in THF which indicate that at -20° rotation is slow for this system also. But in this case the chemical shifts of the two *ortho* protons are almost identical, and the *meta* protons show the greater but still small effect. From models the presence of an extra methyl group in the α position imposes considerably more restriction to rotation. The order of increasing hindrance to phenyl rotation in THF is styryllithium < α -methylstyryllithium < α -methylstyrylpotassium dimer. This follows the order of increasing ring charge. It is possible that the presence of the α -methyl group has some effect in hindering rotation, but that it is not the sole effect is shown by examination of models. These indicate that the α -methylstyryl dimer di-anion should be less hindered than is the simple tert-butyl- α -methylstyryl adduct anion. The effect of counterion position cannot, of course, be estimated, but the results are consistent with the supposition that double-bond character in the ring to α -carbon bond mainly determines hindrance to rotation.

In summary, the ring charge appears to be increased by side-chain alkyl substitution, probably because of the decreased charge stability at the α -position caused by the electron-donating group. The nature of the cation also has an effect, the

smaller Li^+ ion tending to localize charge on the α -carbon by its closer approach. It would be possible¹ to suggest that the charge at the α -position is, in this case, decreased by cation-anion interaction, but the presence of at least one half an electronic charge on the ring in all cases except benzyl lithium in benzene, would suggest that appreciable charge should still reside at this position. The effect of solvent is not large, but it should be remembered that in benzene the dimeric form could result in some perturbations of chemical shift which would produce errors in charge assignments. The close agreement between systems 3 and 4 suggest this effect may not be large for the styryl compound, for the presence of 8% THF in benzene is amply sufficient to dissociate the dimeric form.

All the styryl and α -methylstyryl compounds give evidence of being largely ionic in character in both polar and non-polar solvents, although some differences in charge delocalization occur. This suggests that polymerization mechanisms involving this type of species should be considered as of the same type under all conditions *i.e.* ionic either ion pair or free ion. The small changes in the microstructures of the polymers found in these systems¹¹ are probably the result of the small variations in the ion pair structures. Only benzyl lithium shows rather large differences in NMR and optical spectra between benzene and THF solutions. The reason for this behaviour is not clear as it is not obvious why it should differ from the alkyl substituted species. There is a possibility that a more closely interacting dimer is formed in hydrocarbon solvents in the absence of alkyl substituents and that perturbations of both chemical shift and energy levels in the anion can occur.

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