

A Note on the Measurement of Charge Distribution in 4-Propenyl Phenolate Ions with ^{13}C NMR

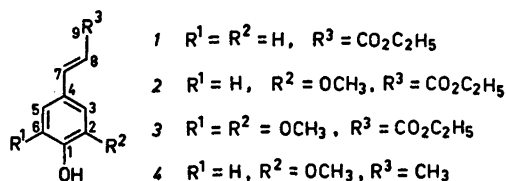
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In the course of investigations into the condensation reactions of lignins during alkaline pulping¹ it has become apparent that coniferyl alcohol is an important intermediate and that it reacts as an anion with quinone methides formed under the pulping conditions. Coniferyl alcohol forms an anion which has one nucleophilic position more than non-conjugated phenolate ions.

We have studied a series of 4-propenyl phenolate ions by ^{13}C NMR as an aid to the estimation of the nucleophilic reactivity of the carbon atoms in coniferyl alcohol under alkaline conditions. This reactivity is assumed to be proportional to the amount of negative charge on each carbon in the anion and this should be reflected in the chemical shifts of the corresponding ^{13}C NMR signals. In order to minimize the effects of solvation on the NMR shifts it is necessary to use aprotic solvents with relatively low solvating power. The availability of crown ether complexes makes possible the study of non-solvated ("naked") anion in such solvents.

We now report results from measurements of charge distributions in chloroform solution of the anions of 1–4 using ^{13}C NMR shifts of the crown ether complexes of their potassium salts.



Results and discussion. Phenols 1–4 formed solid potassium salts which were dissolved in chloroform-*d* with the aid of an equimolar amount of 18-crown-6. (Coniferyl alcohol did not form a stable potassium salt and had to be excluded from the study). The chemical shift assignments were made with the aid of off-resonance decoupled and non-decoupled spectra. The assignments for the phenols were checked by comparison with published data for similar compounds.²

The charge distributions in the anions were estimated by subtracting the shift value for each carbon in the phenol from the value for the corresponding carbon in the anion. Thus a negative shift difference ($\Delta\delta$) means that the carbon nucleus is more shielded in the anion than in the free phenol and hence may be assumed to carry a negative charge proportional to the numerical value of the shift difference. In unsaturated frameworks, delocalization of charge across the π -electron system produces shielding changes due to the dependence of the paramagnetic shielding term on the effective nuclear charge. The assumption is made here that the $\Delta\delta$ values reflect the effective nuclear charge. No attempt has been made to include the effects of other terms in the Karplus-Pople expression for the paramagnetic shielding term.³ The results are collected in Tables 1 and 2.

All the anions show a marked negative charge at carbons 4 and 8. Comparison of the shift data for the anions of 1–3 shows that methoxyl groups on the aromatic ring increase the amount of negative charge at carbons 4 and 8. The absence of negative charge at carbons 2 and 6 was unexpected. Semiempirical MO calculations (CNDO/2) of the charge distributions⁴ predict negative charges at carbons 2, 4, 6 and 8 (Table 2). A similar effect has been observed in ^1H NMR spectra of phenolate ions and has been attributed to a deshielding effect exerted by the metal cation.⁵ In chloroform solution the crown ether complex probably forms an ion pair with the phenolate oxygen and thus may influence the charge density on the nearest ring carbons.

Table 1. ^{13}C NMR chemical shifts (δ) obtained for compounds 1–3, their anion crown ether complexes (δ^-) and the shift differences ($\Delta\delta$).

Carbon	Compound 1			Compound 2			Compound 3		
	δ	δ^-	$\Delta\delta$	δ	δ^-	$\Delta\delta$	δ	δ^-	$\Delta\delta$
1	158.5	168.7	+10.2	147.9	165.8	+17.8	137.1	157.4	+20.3
2	116.0	119.5	+3.5	146.8	151.3	+4.5	147.2	151.0	+3.8
3	130.0	130.6	+0.6	109.4	109.6	+0.2	105.0	108.5	+3.5
4	126.6	117.6	-9.0	126.9	115.6	-11.3	125.9	112.2	-13.7
5	130.0	130.6	+0.6	122.9	126.8	+3.9	105.0	108.5	+3.5
6	116.0	119.5	+3.5	114.7	118.5	+3.8	147.2	151.0	+3.8
7	145.2	147.0	+1.8	144.7	147.3	+2.6	144.9	147.5	+2.6
8	114.9	107.1	-7.8	115.5	105.7	-9.8	115.9	105.3	-10.6
9	168.4	173.4	+5.0	167.3	168.8	+1.5	167.1	168.9	+1.8

Table 2. ^{13}C NMR chemical shifts (δ) for isoeugenol (4), its anion crown ether complex (δ^-) and the shift differences ($\Delta\delta$). The figures in the last column are the calculated (CNDO/2) π -electron charge and π -overlap density differences between the anion of 4 and the free phenol.

Carbon	δ	δ^-	$\Delta\delta$	Calc.
1	144.8	156.6	+ 11.8	+ 0.07
2	146.6	150.2	+ 3.6	- 0.01
3	107.9	112.8	+ 4.9	+ 0.09
4	130.6	120.3	- 10.3	- 0.12
5	119.3	122.4	+ 3.1	+ 0.03
6	114.4	117.7	+ 3.3	- 0.04
7	130.8	132.1	+ 1.3	+ 0.06
8	123.3	109.2	- 14.1	- 0.09
9	18.3	18.3	+ 0.0	+ 0.03

In a preliminary reactivity study the phenolate ions of 1-4 were allowed to react as crown ether complexes with methyl iodide in chloroform. In all cases the reaction was slow and the main product was the *O*-methylated product. This indicates that the $\text{S}_{\text{N}}2$ reactivity of these complexes is centered on the phenolate oxygen at room temperature.

Experimental. The NMR spectra were run on a JEOL JNM-PS-100 (10 mm sample tubes, 0.5 M solutions in CDCl_3) in the Fourier Transform Mode collecting 300-500 pulses of 8 μs duration at 2 s intervals.

The phenols 1-4 were synthesized as described in the literature.⁶⁻⁹

Preparation of potassium salts. The phenol (1 g) was dissolved in 75 ml of toluene. A solution of 0.83 g of potassium *t*-butoxide in 20 ml of *t*-butyl alcohol was added and the precipitate filtered off and dried in a desiccator.

Preparation of crown ether complexes. Equimolar amounts of phenoxide potassium salt and 18-crown-6 (the commercial product was purified as the crystalline acetonitrile complex) were mixed and the mixture dissolved in chloroform-d to give a 0.4-0.5 M solution.

Reactions with methyl iodide. The reactions were run in dried chloroform and the methyl iodide, which was used in excess, was freshly distilled over copper turnings.

The anion complex of 1 reacted almost to completion in 24 h. The main product was isolated on a silica gel column (acetone-light petroleum 1:9). The NMR spectrum showed that it was the *O*-methylated product. ^1H NMR (60 MHz, CDCl_3): δ 1.35 (3 H, t, J 7.2 Hz), 3.83 (3 H, s), 4.24 (2 H, q, J 7.2 Hz), 6.29 (1 H, d, J 15 Hz), 6.90 (2 H, d, J 8.4 Hz), 7.49 (2 H, d, J 8.4 Hz), 7.65 (1 H, d, J 15 Hz).

The anion complex of 2 reacted more slowly; after 6 days at room temperature about 50 %

of unreacted starting material remained in the solution. The main product was isolated on preparative TLC (acetone-light petroleum 3:7) ^1H NMR (60 MHz, CDCl_3): δ 1.35 (3 H, t, J 7.2 Hz), 3.89 (6 H, s, OCH_3), 4.24 (2 H, q, J 7.2 Hz), 6.27 (1 H, d, J 15 Hz), 6.8-7.2 (3 H, m), 7.61 (1 H, d, J 15 Hz).

The anion of 3 reacted with a rate similar to that of 2. The solution was worked up as for 2. ^1H NMR (60 MHz, CDCl_3): δ 1.37 (3 H, t, J 7.2 Hz), 3.90 (9 H, s, OCH_3), 4.30 (2 H, q, J 7.2 Hz), 6.37 (1 H, d, J 15 Hz), 6.79 (2 H, s), 7.66 (1 H, d, J 15 Hz).

In the reaction of the anion of 4 with methyl iodide 50 % starting material remained after 2 days. After work-up as for 2 the main component isolated was isoeugenol methyl ether. ^1H NMR (60 MHz, CDCl_3) δ 1.83 (3 H, d, J 4.8 Hz), 3.83 (3 H, s, OCH_3), 3.86 (3 H, s, OCH_3), 6.23 (1 H, dq, J 13.8 and 4.8 Hz), 6.37 (1 H, d, J 13.8 Hz), ~6.8 (3 H, m).

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