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INTRAMOLECULAR HYDROGEN BONDING
TO π -ELECTRONS IN SUBSTITUTED PHENOLS^(a)

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INTERMOLECULAR HYDROGEN BONDING
TO π -ELECTRONS IN SUBSTITUTED PHENOLS^(a)

W. E. Keder

Our recent work on the separation of the alkali metals by solvent extraction has involved the solvation of the extracted metal ions by substituted phenols. We have attempted to establish the identity of the extracted species and to discuss the nature of the bonding involved in these solvates.⁽¹⁾ The best of the phenolic solvating agents which have been studied contain either a phenyl or benzyl substituent ortho to the phenol group.

Infrared measurements on carbon tetrachloride solutions of these phenols show three independent OH - stretching frequencies. For the case of 4-sec-butyl-2(α -methylbenzyl)-phenol (BAMBP) these frequencies have been assigned by earlier workers to monomeric, dimeric, and polymeric phenols, in order of decreasing frequency.⁽²⁾ Our experience has convinced us that this assignment is not correct, and the present note concerns this point. In this work, we have measured the infrared spectra of solutions of several substituted phenols. The results demonstrate that the intermediate OH - stretching frequency in the BAMBP spectra is due not to intermolecular dimer formation, but to intramolecular hydrogen bonding to the π -electrons of the o - benzyl group.

Figure 1 shows the OH - stretching spectra of BAMBP and of 4-dodecylphenol (DDP) as a function of concentration in CCl_4 solution. In the higher concentration range the spectrum of DDP has two major peaks. Dilution behavior

indicates clearly that the sharp peak at 3608 cm^{-1} is due to the monomeric form. The broad peak at lower frequency is a combination of two peaks which have been assigned to dimeric (3470 cm^{-1}) and larger aggregates (3345 cm^{-1})(3). The spectrum of BAMBP, on the other hand, has a peak at an intermediate frequency, the origin of which is open to question. The width of this peak is much less than the peaks due to aggregated DDP and the dilution behavior suggests an intramolecular bond. The only reasonable bond of this type appears to be a hydrogen bond to the π -electrons of the benzyl ring.

Hydrogen bonding to π -electrons of solvents has been noted for some time,⁽⁴⁾ but systematic studies of this effect have begun to appear only very recently.⁽⁵⁾ Intramolecular bonds of this type have been noted in the past also, but do not seem to have received general attention.⁽⁶⁾

The near infrared spectra of CCl_4 solutions of o- and p-phenylphenols are shown in Figure 2. Intramolecular hydrogen bonding should be possible from a geometric standpoint in the ortho but not the para isomer. Formation of such a bond appears to be the only reasonable cause for differences between the absorption spectra of the two compounds. As the figure shows, the spectrum of the para compound is a single stretching frequency, while that of the ortho is a doublet with one peak at the same frequency and another 45 cm^{-1} lower. The latter spectrum is very similar to that of BAMBP at the same concentration, except that the peak height ratios are different indicating that the extent of intramolecular bonding is more nearly complete in the o-phenylphenol.

It may be noted that the solubility of o-phenylphenol is much greater in CCl_4 than that of the para isomer (0.016 molar). Presence of

intra-molecular bonding in solutions of the former compound requires less bonds to be broken upon dissolution of this compound and probably accounts for the solubility difference.

The occurrence of intramolecular hydrogen bonding in BAMBP can be further justified by comparison of frequency values and peak shapes with those of corresponding intermolecular bonding between aromatic solvents and phenols. Hydrogen bonding to π -electrons of solvents is known to result in OH - frequency shifts of about $50 - 75 \text{ cm}^{-1}$ and the resulting bands are much less broad than those due to aggregation through O-H....O bonds. As an example, the effect of the introduction of benzene into CCl_4 solutions upon the spectrum of DDP is shown in Figure 3. The spectrum of the solution containing 30 per cent benzene is similar to that of BAMBP- CCl_4 in every respect. The spectrum of BAMBP is changed similarly upon addition of benzene to CCl_4 solution with the 3560 cm^{-1} peak increasing and the higher frequency peak disappearing completely at 100 per cent benzene.

From the data in Figure 3 a stability constant of 0.16 was calculated for the reaction: $\text{DDP} + \text{benzene} \rightarrow \text{DDP} \cdot \text{benzene}$. This corresponds to a standard free energy change of $\Delta G^\circ = 1.0 \text{ kcal/mole}$. This is equal, within the experimental error, to the value of $+ 0.6 \text{ kcal/mole}$ obtained by Yoshida and Ōsawa for the reaction between simple phenol and benzene. Using the linear relationship between enthalpy of bond formation and OH-- stretching frequency found by Joesten and Drago⁽⁷⁾ a value of $\Delta H^\circ = - 1.40 \text{ kcal/mole}$ can be calculated for this reaction, which results in $\Delta S^\circ = -8 \text{ e.u.}$

The $\Delta v_{\text{O-H}}$, and therefore the enthalpy of hydrogen bonding, is nearly the same for all the molecules considered here. The extent of bonding between the

phenols and an equal concentration of benzene is low because of the large entropy decrease for the reaction. The ortho substituted phenols require a much smaller entropy decrease for intramolecular bonding and so the extent of bonding is great despite the low bond strength. It is of interest to note that the o - phenylphenol which has less internal rotational freedom than the o - benzyl molecule does show a greater extent of internal bonding.

Experimental - Spectra were measured at room temperature in CaF_2 cells with a Perkin-Elmer 521 spectrophotometer.

FIGURE LEGENDS

- Figure 1 Infrared spectra of p-dodecylphenol and of 4-sec-butyl-2-(α -methylbenzyl) phenol in CCl_4 . (molarity X cell thickness in mm. = 0.04.)
- Figure 2 Infrared spectra of CCl_4 solutions of o- and p-phenylphenols. (p-phenylphenols. (p-phenylphenol in saturated solution).
- Figure 3 Infrared spectra of 0.04 and 0.4 molar p-dodecylphenol in CCl_4 -benzene mixtures vs. solvent as reference.

Figure 1

Figure 2

Figure 3