Solution and solid state proton transfer from phenols to triphenylphosphine oxide studied by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy

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Several complexes between substituted phenols and triphenylphosphine oxide (TPPO) were examined both in solution and in the solid state by NMR spectroscopy. The degree of proton transfer from the phenol to TPPO in solution was studied by the ^{1}H chemical shift of the phenolic OH proton and by the ^{13}C chemical shifts of the phenol C–O (C1) and *para* (C4) carbons. As the pK_a of the acid decreases, the ^{1}H signal moves towards higher frequencies as a consequence of the deshielding produced by the proximity of the second oxygen. However, when the hydrogen is largely transferred to the oxide moiety, *e.g.* in the picric acid complex, the ^{1}H resonance shifts to lower frequencies again. In turn, the ^{13}C chemical shift of C1 is displaced to high frequencies, whereas C4 shifts in the reverse direction. The solid phase was studied through the changes in the ^{31}P shielding tensor of the TPPO residue and by the C1 and C4 ^{13}C chemical shifts of the phenols. The proton transfer process follows the same pattern observed in solution. The values of the principal components of the ^{31}P shielding tensor (σ_{ii}) move towards those corresponding to symmetric tetrahedral phosphorus environments as the pK_a of the phenol decreases.

Introduction

Many proton-transfer systems have been studied by means of both IR and NMR spectroscopy.[1–4] Substituted phenols have different pK_a values according to the electron-attracting properties of the substituents, and have provided the opportunity to study different degrees of proton transfer to a number of bases.[5–8] For large values of pK_a, the potential surface for the proton involved in the hydrogen bond is a single-minimum potential well, located at the phenol residue. As the pK_a of the phenol decreases, the potential surface becomes a double-minimum type. This is suggested by IR data, which show broad O–H stretching bands arising because of large proton polarisabilities.[1,9] With further decreases of pK_a, the potential surface turns into either a broad, flat single minimum where the hydrogen bond is practically symmetric or into a symmetric double-minimum well with a small internal energy barrier. With still smaller values of pK_a the proton potential surface transforms again into a double well, but in this case the minimum is located over the base residue. When the phenol substituents are strong electron attractors, the values of pK_a are still lower, leading to a complete transfer to the base residue, and consequently the proton potential surface has a single minimum with the well near the base moiety.[10] Previously, several systems composed of substituted phenols and trimethylamine oxide (TMAO) were studied by ^{1}H and ^{13}C NMR spectroscopy. Zundel and co-workers[10] have found that, in solution, these complexes present ^{1}H chemical shifts which vary from *ca.* 12 to 17.5 ppm as the pK_a of the substituted phenols decreases, reaching the maximum value for the 3,4-dinitrophenol–TMAO (3,4-DNP–TMAO) complex ($pK_{a_{3,4DNP}} = 5.42$).[10] For still lower pK_a values the ^{1}H chemical shift decreases again to a minimum, in this case for the picric acid–TMAO complex (13.75 ppm), because of a transfer of the proton to the TMAO moiety. These authors also studied the ^{13}C NMR signals in solution, calculating Δ_{1-4} according to eqn. (1). This Δ_{1-4} value has been used as an indicator of the

$$\Delta_{1-4} = [\delta_{C1} - \delta_{C4}]_{phenol-TMAO} - [\delta_{C1} - \delta_{C4}]_{phenol} \quad (1)$$

degree of proton transfer.[10–12] In the case of the phenol–TMAO complexes, Δ_{1-4} varies with the pK_a of the phenol, increasing its value as the pK_a decreases. These data, together with previous IR measurements, confirm that the proton potential profiles change as a function of the pK_a of the phenols.[10]

We have prepared adducts between substituted phenols and triphenylphosphine oxide (TPPO) in order to study them both in solution and in the solid state. We have probed the complexes by means of solution ^{1}H and ^{13}C and high-resolution solid-state ^{13}C NMR spectroscopy. Furthermore, the presence of a phosphorus atom near the oxygen site where the labile proton is transferred provides the opportunity to probe the transfer process through the sensitivity of solid-state ^{31}P NMR spectroscopy to slight changes in the electronic environment. It seemed interesting to verify whether the proton transfer process remains active in the solid state as well as in solution.

Experimental

All the phenols were commercially available, as was TPPO. The adducts were prepared by evaporation of chloroform solutions containing stoichiometric amounts of the phenol and TPPO. Picric acid–TPPO and 4-methoxyphenol–TPPO complexes could not be obtained as satisfactory powders either by evaporation of different solvent solutions or by grinding the solid phenol with solid TPPO because these procedures gave a paste.

Solutions of the adducts in [^{2}H]chloroform (except for the picric acid complex, for which acetonitrile was the solvent) were

Table 1 Solution-state phenolic ^1H and ^{13}C NMR data of substituted phenol–TPPO complexes and pK_a of phenols

Phenol	pK_a[28]	^1H δ(OH)	^{13}C δ(C1)	^{13}C δ(C4)	Δ_{1-4}[a]
Picric acid[b]	0.38	10.63	152.73	136.80	6.75
2,6-Dinitrophenol	3.71	11.38	149.05	118.67	5.28
2,4-Dinitrophenol	3.96	11.49	158.72	139.20	6.72
2,5-Dinitrophenol	5.22	11.02	151.21	115.18	5.63
4-Nitrophenol	7.15	10.91	164.05	139.85	4.31
4-Hydroxyacetophenone[c]	8.29	10.25	162.26	128.86	1.86
4-Chlorophenol	9.37	9.10	155.53	123.84	3.71
Phenol	9.89	8.63	157.12	118.67	4.25
4-Methoxyphenol	10.21	8.26	150.85	152.75	2.15

[a] These values were calculated using the experimental ^{13}C NMR data for chloroform solutions of the substituted phenols and of the complexes. Corrections were made for the 2-nitro and 2,6-dinitro substituted phenols according to the procedure described in reference 10 (see text). [b] Picric acid is 2,4,6-trinitrophenol. The spectrum was recorded in deuteriated acetonitrile. [c] Data for C1 and C4 are listed in the relevant columns for comparison with the other compounds, but formally the numbering in this system is different (the OH group being at position 4 rather than position 1).

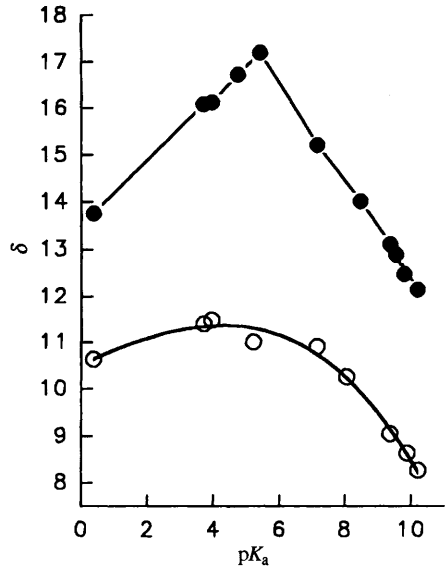

Fig. 1 Solution (OH) ^1H NMR data for substituted phenol–TPPO complexes as a function of pK_a for the phenols compared with those previously obtained for phenol–TMAO complexes according to reference 6; ○: complexes with TPPO as base residue; ● complexes with TMAO as base residue

prepared in order to record ^1H and ^{13}C NMR spectra on a Bruker AC 200 NMR spectrometer at ambient probe temperature (*ca.* 25 °C). The ^1H and ^{13}C nominal operating frequencies were 200.1 and 50.3 MHz respectively. For the latter, typical operating conditions were: 500 transients, recycle delay 3 s, pulse duration 3 μs, acquisition time 1.47 s. For the former, the spectrometer parameters were: 128 transients, recycle delay 1 s, pulse duration 2 μs (7.2 μs ≡ 90°). Tetramethylsilane (TMS) was used as an internal standard for the chemical shifts.

Solid-state ^{13}C and ^{31}P NMR spectra were recorded using a Chemagnetics CMX200H NMR spectrometer operating at 50.33 and 80.01 MHz respectively. The CPMAS technique was performed, with high-power proton decoupling. In some cases the powdered samples were mixed with flowers of sulfur to provide sufficient bulk to fill the 7.5 od MAS rotors. This procedure also rendered the samples which were pastes suitable for study. The TPPO complex of phenol contained less than equimolar phenol (because of its relative volatility), but this did not hinder the study, though it resulted in an extra band in the ^{31}P spectrum. Phosphorus-31 spectra were referenced against the signal for brushite (δ_{iso} = 1.2 with respect to 85% aqueous phosphoric acid). Spectral parameters were: spectral width, 25 kHz; 90° pulse duration, 5 μs; contact time, 5 ms; recycle delay, 10 s; acquisition time, 40.8 ms; number of transients, 64 or 256. For the ^{31}P spectra, the samples were spun at rates which varied from 1.2 to 3.2 kHz in order to obtain a suitable number of spinning sidebands. Principal components of the phosphorus shielding tensors were retrieved using the method developed by Fenzke *et al.*[13] All ^{13}C chemical shifts were referenced against the signal for TMS indirectly *via* the spectrum of adamantane (δ_{CH_2} = 38.4). Carbon-13 spectrometer operating conditions were: spectral width, 20 kHz; 90° pulse duration, 4 μs; contact time, 1–3 ms; recycle delay, 1–5 s; acquisition time, 51–102 ms; number of transients, 30 000. For 4-chlorophenol substantially longer recycle delays of *ca.* 60 s were necessary.

Results and discussion

Table 1 summarises the phenolic ^1H chemical shifts and the relevant ^{13}C NMR data [δ(C1) and δ(C4)] obtained in chloroform (and in one case acetonitrile) solution for the complexes studied, as well as the pK_a (for aqueous solutions at 25 °C) of each substituted phenol. Aqueous solutions could not be used for the NMR measurements because of rapid proton exchange. It can be seen that the chemical shift of the phenolic OH proton changes in the complexes as a result of the transfer to the TPPO moiety. The pattern followed by these adducts is similar to the one previously described by Zundel and co-workers for the substituted phenol–TMAO complexes.[10] Fig. 1 compares the present results with those obtained by Zundel *et al.* Two facts are noteworthy. First, the deshieldings found for the adducts with TPPO are smaller than those for the complexes with TMAO. Secondly, in the series of TPPO–phenol complexes the only one where the hydrogen seems to be significantly transferred to the base oxygen is picric acid–TPPO ($pK_{a_{picric\ acid}}$ = 0.38). This is suggested by the hydroxy ^1H chemical shift, which decreases from 11.49 ppm for 2,4-dinitrophenol–TPPO to 10.63 ppm for the picric acid–TPPO complex (see Table 1 and Fig. 1). These observations can be ascribed to the fact that TPPO is less basic than TMAO. Ref. 14 gives pK_a = −2.10 for TPPO, whereas TMAO has pK_a = 4.65.

The values of Δ_{1-4} for the adducts in solution were calculated according to eqn. (1),[11,12] and Table 1 shows how they vary as a function of pK_a. When the phenols have nitro substituents in the 2- or 6-positions, corrections of +5.1 ppm have been applied to the experimental values of Δ_{1-4} in order to take into account the fact that intramolecular hydrogen bonds are already present (between the hydroxy proton and an oxygen of a nitro group) in pure phenol solutions, which shift the ^{13}C signals.[10]

A consequence of the hydrogen transfer is that the ionised phenol carries a formal negative charge distributed over the aromatic ring. Thus, there is a contribution of a structure where this charge is supported by C4 and which has a higher C–O bond order. Accordingly, the ^{13}C NMR signals of C1 and C4 should be displaced to high and low frequency, respectively. Therefore, the Δ_{1-4} values increase as the hydrogen moves away from the phenol and should reach the largest value for the picric acid–TPPO complex. As seen in Table 1, there is a general tendency for Δ_{1-4} to increase as the pK_a decreases, and the picric acid–TPPO complex does indeed show the largest Δ_{1-4} among those studied, although this is considerably smaller than that observed in the series of phenol–TMAO complexes (*ca.* 27 ppm). However, there is considerable scatter in the data, and the apparent trend only occurs because the correction factor of 5.1 ppm to account for the intramolecular hydrogen bonding in some of the parent phenols is greater than the variations in Δ_{1-4}

Table 2 Relevant high-resolution solid-state ^{13}C NMR data for pure phenols and phenol–TPPO complexes

	Pure phenols		Phenol–TPPO complexes		
Compound	δ(C1)	δ(C4)	δ(C1)	δ(C4)	$\Delta_{1,4}$[a]
Picric acid[b]	155.0	137.3	152.4	135.5	4.3
2,6-Dinitrophenol	152.3	120.8	146.8	119.4	1.0
2,4-Dinitrophenol	159.1	140.2	159.0	137.8	7.4
2,5-Dinitrophenol	154.9	114.7	152.3	*ca.*114	*ca.*3
4-Nitrophenol	163.3	141.3	166.3	140.3	4.0
4-Hydroxyacetophenone[c]	162.9	128.8	164.2	128.3	1.8
4-Chlorophenol[d]	152.9	125.4	158.0	124.3	6.2
Phenol	154.6	121.3	158.6	119.5	5.8
4-Methoxyphenol	150.0	154.6	152.7	153.2	4.1

[a] Corrections were made for the 2-nitro and 2,6-dinitro substituted phenols according to the procedure described in ref. 10. [b] See footnote *b* of Table 1. [c] See footnote *c* of Table 1. [d] Average value of a doublet (splitting 8.4 ppm) caused by residual dipolar coupling[15,16] to the quadrupolar $^{35/37}Cl$ nuclei. A similar splitting is assumed for the complex, but the high frequency resonance is obscured by signals from TPPO.

without it. This is undoubtedly due to the less basic character of TPPO as compared with TMAO. However, it has already been indicated[10] that Δ_{1-4} is a less accurate parameter for the estimation of the degree of proton transfer than $\delta(^1H)$. Taking into account previous IR and NMR data, which showed the evolution of the ^1H potential surface with the strength of the acid, the picric acid–TPPO adduct should possess at least an unsymmetric double-minimum potential well, in which the lower minimum is localised at the TPPO moiety.[9,10]

Solid-state ^{13}C NMR data are summarised in Table 2 where the chemical shifts for the relevant carbon atoms [δ(C1) and δ(C4)] are shown. The data for Δ_{1-4}, with or without the correction for intramolecular hydrogen bonding in some of the present phenols, show no correlation at all with the pK_a of the phenols, though in all cases, with the correction, Δ_{1-4} is positive (suggestive of a moderate degree of proton transfer from the substituted phenols to the TPPO). The reported crystal structures[17] of 2,4-, 2,5- and 2,6-dinitrophenol, and of picric acid, reveal the presence of intramolecular hydrogen bonds, justifying the correction factor (though its magnitude may be disputed), but some correction may also be necessary for the other cases if the parent phenols have *inter*molecular hydrogen bonding in the crystalline state. Solution-to-solid shifts for the parent phenols and for the complexes for C1 and C4 individually range from −2.3 to +3.1 ppm. These modest changes doubtless reflect the influences of intramolecular packing and small geometry changes with phase (and solvent effects in solution). They clearly suffice to obscure any possible dependence of Δ_{1-4} on pK_a. It is noteworthy that the effects of phase on chemical shift are generally larger in magnitude for C1 than for C4.

Table 3 shows high-resolution solid-state ^{31}P NMR data. The isotropic ^{31}P chemical shifts δ_{iso} are listed for all the compounds studied. TPPO contains two different signals at 26.9 and at 28.6 ppm since the sample used (Aldrich) contains two crystalline polymorphs (monoclinic and orthorhombic) as described in ref. 18. It has been previously shown for TPPO–amide co-crystals that an approximately linear correlation exists between $\delta_{iso}(^{31}P)$ and the number of hydrogen bonds per TPPO molecule.[19] It was predicted that for singly hydrogen-bonded systems (for which no experimental data were observed), δ_{iso} should have a value in the range 31 to 34 ppm. In the presently studied complexes in the solid state (see Table 3), all the isotropic ^{31}P NMR shifts are deshielded with respect to solid TPPO. Moreover, these shifts lie in the range 29–37 ppm, depending on the pK_a of the substituted phenol. These values

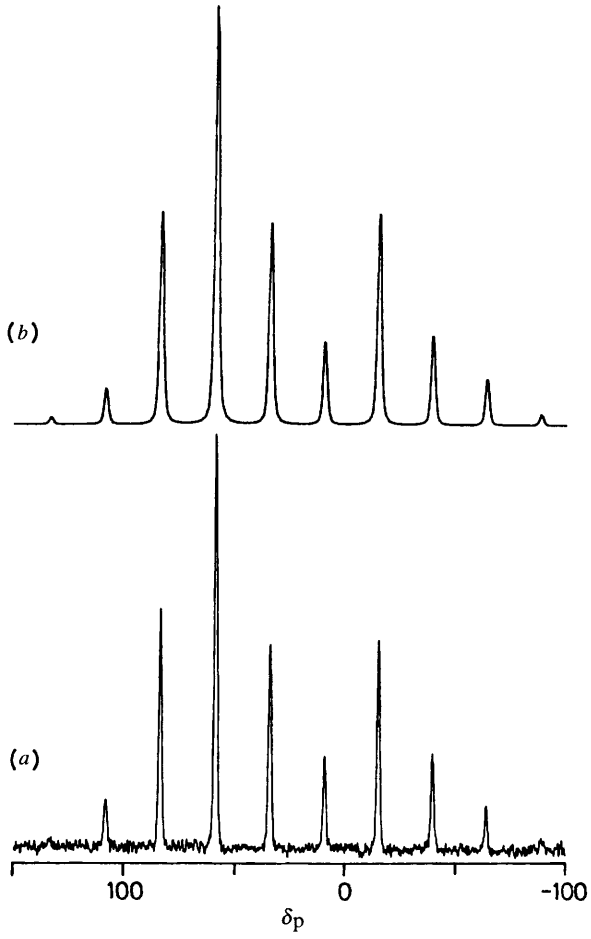

Fig. 2 Phosphorus-31 CPMAS spinning sideband manifold for 2,5-dinitrophenol–TPPO complex: (*a*) experimental, obtained with a 5 ms contact time, 10 s recycle delay, 256 transients and spin rate 2000 Hz; (*b*) simulated using the shielding tensor data given in Table 3

are in good agreement with the expectations for a single hydrogen bond between the hydroxylic phenolic proton and TPPO. The larger range of δ_{iso} values found for phenols (in comparison with amides) may be understood on the basis of the hydrogen bond strengths varying in a wide range because the pK_a of the phenols are spread between 0.38 and 10.21. This should lead to different degrees of proton transfer, whether the potential surface has a single-minimum potential well or a double-minimum one. The deshielding of the phosphorus nucleus in the complexes compared with free TPPO can be attributed to the contribution of Ph_3P^+–OH structures, in which the phosphorus carries a formal positive charge. It is thus understandable that the deshielding increases as the phenol becomes more acidic.

It is known that the variation of the shielding tensor components may be more sensitive to structural changes, as compared with the changes induced in the values of δ_{iso}.[20,21] Several studies have been published discussing the variation of the ^{31}P shielding tensor with changes in the electronic environment surrounding the phosphorus atom.[22,23] It has been demonstrated that the principal components of the ^{31}P shielding tensor are a function of the relative π bond order for the four bonds linking the phosphorus with the immediate neighbours.[24] This, in turn, may be dependent, as in dihydrogen phosphates, on the degree of proton transfer.[25] Fig. 2 illustrates the ^{31}P spinning sideband manifold for one of the complexes, together with the computer-simulated pattern. Table 3 collects the σ_{ii} values for the studied complexes, along with those of $\Delta\sigma$ and η. Although there is considerable scatter in the data, there is substantive evidence of a decrease in $\Delta\sigma$

Table 3 Relevant solid-state ^{31}P NMR data for substituted phenol–TPPO complexes and for triphenylphosphine oxide (TPPO)

Compound	δ_{iso}	$(\sigma_{11} - \sigma_{iso})^a$	$(\sigma_{22} - \sigma_{iso})^a$	$(\sigma_{33} - \sigma_{iso})^a$	$\Delta\sigma^b$	η^c
Picric acid[d]	34.3	−64	−40	105	157	0.23
2,6-Dinitrophenol	30.3	−58	−48	107	161	0.09
2,4-Dinitrophenol	36.6	−56	−44	99	149	0.12
2,5-Dinitrophenol	34.7	−61	−41	102	152	0.19
4-Nitrophenol	35.9	−59	−43	102	153	0.16
4-Hydroxyacetophenone[e]	29.7	−69	−47	115	173	0.19
4-Chlorophenol	28.8	−73	−53	125	188	0.16
Phenol	33.7	−58	−52	110	165	0.05
4-Methoxyphenol	32.5	−61	−51	112	168	0.09
TPPO[f] (orthorhombic)	28.8	−61	−54	116	174	0.06
TPPO[f] (monoclinic)	27.1	−63	−61	124	186	0.02

[a] Defined such that $|\sigma_{33} - \sigma_{iso}| \geq |\sigma_{11} - \sigma_{iso}| \geq |\sigma_{22} - \sigma_{iso}|$. The sign convention for all shielding data is, of course, opposite to that used for δ_{iso}. [b] $\Delta\sigma = \sigma_{33} - \frac{1}{2}(\sigma_{11} + \sigma_{22})$. [c] $\eta = 3(\sigma_{22} - \sigma_{11})/2\Delta\sigma$. [d] See footnote *b* of Table 1. [e] See footnote *c* of Table 1. [f] Signals from two polymorphs (see the text).

accompanying the formation of hydrogen-bonded complexes. Thus the four complexes involving phenols with $pK_a > 8$ have an average value of $\Delta\sigma$ 173 ppm whereas the five others have $\Delta\sigma$ (average) = 155 ppm. The average value of $\Delta\sigma$ for the two TPPO polymorphs is 180 ppm. Thus, a smaller anisotropy is a strong indicator that the ^{31}P environment is becoming more symmetric than in free TPPO, as a result of the contribution of a structure Ph_3P^+–OH having a smaller π P–O bond order relative to TPPO. In general, $\Delta\sigma$ decreases with decreasing pK_a, with noteworthy exceptions.

The 2,6-dinitrophenol and picric acid complexes appear to show a smaller degree of proton transfer than do those of other phenols substituted with nitro groups. This may arise from the steric effects exerted by two NO_2 substituents adjacent to the phenolic OH. If the nitro groups have a substantial hindrance to rotation in the solid, then the space available for the transfer of the proton to TPPO is also restricted. The larger distance between the acid and base residue may lead to a lower proton transfer process than expected, resulting in an apparent decrease in acidity. However, the likely errors of 5–10 ppm in $\Delta\sigma$ indicate that caution is needed in interpreting the results in detail. A similar comment applies to the data on the asymmetry, η, but these do show evidence of increasing as the pK_a of the relevant phenol decreases. We have carried out a series of simulations with various values of $\Delta\sigma$ and η for one of the complexes. These show that deviations from the iterated value of $\Delta\sigma$ by more than 8 ppm give substantial changes in the sideband pattern. We therefore believe the difference between the average values of $\Delta\sigma$ for the two groups of complexes discussed above is significant, and indicates a real effect caused by changes in the hydrogen-bond structures. However, the sideband patterns are less sensitive to the value of η, so differences in this parameter between the various complexes may not be significant. This conclusion is consistent with the known behaviour[26,27] of spinning sideband manifolds in cases of near-axial symmetry ($\eta < 2$).

The changes in δ_{iso}(see Table 3) with the pK_a of the phenol seem to parallel the results obtained from the values of $\Delta\sigma$. The nitro-substituted phenols, which possess the most effective electron-attractive powers, show larger deshielding of the phosphorus nucleus than the other phenols. As with $\Delta\sigma$, the 2,6-dinitrophenol complex (and to some extent the picric acid complex) has a deshielding of the ^{31}P which is smaller than the expectation based on pK_a. However, the range of observed changes in δ_{iso} (*ca.* 9 ppm) is naturally considerably smaller than the range of changes in $\Delta\sigma$ (*ca.* 40 ppm), demonstrating the higher sensitivity of the ^{31}P shielding tensor components towards structural and electronic changes in solid compounds, as compared with the isotropic counterparts.

Conclusions

Several adducts between substituted phenols and TPPO were studied by means of ^1H and ^{13}C NMR spectroscopy in solution and by high-resolution ^{13}C and ^{31}P NMR in the solid state. In solution, as the pK_a of the substituted phenol decreases the ^1H chemical shift of the phenolic hydrogen moves to higher frequencies, while the ^{13}C signals for C1 and C4 shift weakly to lower and higher frequencies, respectively. In the solid state, the effects on ^{13}C shifts are obscured by crystallographic influences, but the ^{31}P shielding anisotropy appears to decrease with the pK_a of the associated phenol. In summary, the sets of data for solution and solid state indicate that a proton transfer process takes place in both phases and that this process becomes more evident as the pK_a of the substituted phenol decreases.

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