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Influence of Steric Factors on the Structure and Physicochemical Properties of Monohydric Phenols

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The specificity of a series of chemical properties of sterically hindered phenols depends greatly on their structure. In the series of 2,6-di-t-alkylphenols in which conjugation of the aromatic ring and hydroxyl group is retained (insignificant departure from coplanarity) the C-O-H bond system is subjected to some deformation due to the bulky o-alkyl groups (a steric effect), which is reflected in the energy of homolytic breaking of the O-H bond and the physicochemical parameters of these phenols. The unusual nature of the spectral characteristics (ultraviolet, infrared, and NMR) of sterically hindered phenols is due to the steric effect of the ortho-substituent. For the same reason these compounds do not form self-associates; the hydrogen bond is somewhat stretched and weaker. Steric effects also play a decisive part in the reduction of acidity of sterically hindered phenols, preventing the solvation of the anion formed. For all the examples considered data are given on the effect of a para-substituent on the physicochemical parameters of the phenols. 98 references.

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I. INTRODUCTION

Sterically hindered phenols have found wide application as additives to prevent the oxidation of fats, oils, fuels, and various polymeric materials. The ability of sterically hindered phenols to retard (inhibit) radical-chain processes of oxidation of organic substances led to a very intense study of various practical and theoretical aspects of the chemistry of these compounds. The large number of studies in this field show distinctly that in many instances sterically hindered phenols show specific properties due to peculiarities in their structure. The physicochemical properties of sterically hindered phenols are largely responsible for their behaviour as oxidation inhibitors. In this connection the effect of the steric factor on the change in one or another property of phenolic compounds has frequently been investigated and a large body of experimental results on this problem has now accumulated, allowing certain generalisations to be made. In both the Russian and foreign literature there have been reviews dealing solely with the oxidation of sterically hindered phenols[1,2], their participiation in inhibited oxidation[3-6] and the properties of the phenoxyl radicals formed from them[7-10].

2,6-Dialkyl substituted phenols and their numerous derivatives are usually associated with the idea of sterically hindered (screened) phenols in the Soviet and foreign literature. Even in the first stages (1945-1950) of the intensive study of the 2,6-dialkylphenols it was observed that their properties depend on the effective volumes of the alkyl substituents. In this connection it was proposed[11,12] to classify such phenols in a separate group, termed sterically hindered phenols. To this period belong also the first attempts to evaluate the steric influence exerted by alkyl groups on the properties of the phenols. Thus Coggenshall[13,14], who used ultraviolet and infrared spectroscopy to study the ability of phenols to form hydrogen bonds (self-association), divided the phenols into three groups: non-screened, semiscreened, and screened. Naturally, the most pronounced steric influence is shown by phenols containing tertiary alkyl groups in the ortho-positions, and therefore specific properties of sterically hindered phenols were studied mainly for examples of compounds of this type.

II. STRUCTURE AND ENERGY OF THE O-H BOND OF STERICALLY HINDERED PHENOLS

The problem of the structure of sterically hindered phenols mainly reduces to a consideration of the relative arrangement in space of the aromatic ring, and the hydroxyl and alkyl groups. It is well known[15], that many physical and chemical properties of ordinary phenols are determined by the electron-withdrawing properties of the aromatic ring. Hence their enhanced acidity (in comparison with aliphatic alcohols), corresponding position of the signal of the hydroxyl proton in the NMR spectra, tendency to participate in radical processes, peculiarities of the mechanism of electrophilic substitution, etc. Evidently, the most characteristic properties of a phenol correspond to a structure in which the hydroxyl group (the C-O bond) is coplanar with the aromatic ring. The departure of the hydroxyl group from the plane of the ring will decrease the conjugation of the lone pair of electrons of the oxygen atom with the π-electrons of the aromatic ring, and consequently the properties of the phenol will approximate on the one hand to the properties of benzene, and on the other to the properties of aliphatic alcohols. Such a departure of the hydroxyl group most probably occurs in sterically hindered phenols containing t-alkyl groups, since it should be facilitated by the effect of bulky alkyl groups in the ortho-positions relative to the phenolic hydroxyl. Even a simple comparison of the effective radii of the hydroxyl and t-butyl groups shows the possibility of the destruction of the coplanarity of the hydroxyl group and aromatic ring in compounds of the series of sterically hindered phenols. Many investigators working in this field were primarily interested in this very question. And since a breakdown in the

conjugation of the *p*-electrons of the oxygen atom with the aromatic system in sterically hindered phenols should lead to a marked change in the physicochemical properties of the phenol, that possibility and the nature of the departure of the hydroxyl group from the plane of the ring were usually investigated with the aid of various physical methods[16-27]. The first studies in this field were made by Ingold, using infrared spectroscopy[22-25]. He showed[22] that the increase in the hydroxyl group frequency in the infrared spectra observalbe in 2,6-di-t-butyl-4-substituted phenols in comparison with the corresponding 4-substituted phenols is too great to be the result of only electronic effects of the t-butyl groups. Evidently, in this instance the steric effect of the alkyl groups is considerable. However, the changes in the frequencies of the O–H bond vibrations in a series of 4-substituted phenols and in a series of 4-substituted 2,6-di-t-butylphenols with change in substituent obey the same law. Fig. 1 shows the variation of ν_{OH} with σ_p for 4-substituted phenols and their sterically hindered analogues. The parallelism of the straight lines on the graph shows that both groups of phenols have similar spatial structure.

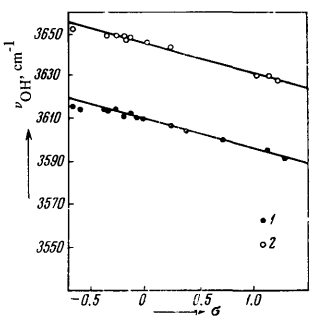


Figure 1. Variation of ν_{OH} with σ_p of para-substituents in the series of 4-X-phenol (*1*) and 4-X-2,6-di-t-butylphenol (*2*).

A similar conclusion can also be reached on the basis of the following discussion. The displacement of the hydroxyl group from the plane of the ring should sharply reduce its resonance interaction with strongly accepting substituents in the para-position, that is, σ_p, for example, for the nitro-group should have a value intermediate between the maximal (1.27, characteristic for *p*-nitrophenol) and the minimal (0.78, characteristic for other nitroderivatives of benzene in which direct conjugation of the substituents is absent). However, the best correlation in the series of sterically hindered phenols in coordinates ν_{OH} against σ_p is observed on using the maximal values of σ_p. The picture is analogous when maximal values of σ_p for the formyl and nitrile groups are used.

The coplanarity of the aromatic ring and hydroxyl group is also shown by the following calculation, given by Ingold[22,25]. It is known that the fundamental frequency of the carbonyl group in various substituted benzaldehydes is linearly dependent on σ_p for the *p*-substituent. If the hydroxyl group is coplanar with the aromatic ring for 2,6-di-t-butyl-4-formylphenol, then:

$$\sigma_{eth} = \sigma_p^{OH} + 2\sigma_m\text{-t-butyl} = -0.36 + 2\cdot(-0.12) = -0.60.$$

When there is a linear relation between ν_{CHO} and σ_p, the shift in frequencies on going from 4-formylphenol to 2,6-di-t-butyl-4-formylphenol should be in the ratio 0.36 : 0.60 (3 : 5), which agrees with the experimental results.

On the basis of the above facts it could have been suggested that in 2,6-di-t-butylphenols the hydroxyl group lies in the plane of the aromatic ring or close to this position. However, it must be borne in mind that the infrared spectroscopic results do not permit the electronic influence of the substituents on the nature of the absorption by the hydroxyl group to be evaluated with sufficient accuracy, and consequently the above discussion is approximate, since at small angles of departure from coplanarity the resonance energy and electron density hardly change because these quantities are approximately proportional to the square of the cosine of the dihedral angle[28].

The electronic spectra can be a more sensitive characteristic of the electronic interaction of the hydroxyl group and the aromatic ring. Ultraviolet spectroscopy is interesting because the position of the absorption bands of the benzenoid system is determined mainly by the resonance effect of the substituent and therefore is more sensitive to a change in coplanarity than ν_{OH} in the infrared region.

For example, having obtained a series of resonance parameters for para-substituents ($\sigma_{R'} = \sigma_p - \frac{2}{3}\sigma_m$), Cohen and Jones[18] showed that in a plot of $\sigma_{R'}$ against $\Delta\bar{\nu}$ there is satisfactory correlation for any substituents. It is characteristic that the straight lines for 4-X-phenols and 4-X-2,6-di-t-butylphenols are only approximately parallel. The presence of two t-butyl groups increases the value of ρ both for phenols and for the phenolate ions by 11%. This shows the insignificant departure of the C–O bond from the plane of the aromatic ring.

Finally, data on the molecular polarisability of phenols have been used to find the coplanarity of the hydroxyl group and the aromatic ring[21]. Unlike dipole moments, which depend weakly on the volume of the replacing groups[19], the molar polarisability of the compounds allows the spatial position of the individual fragments of the molecule to be calculated rather precisely. A comparison of the observed Kerr constants with the values calculated theoretically for various conformations of 2,4,6-tri-t-butylphenol showed that here the hydroxyl group is displaced ~ 14° out of the plane of the aromatic ring.

It is noteworthy that the observed departure from coplanarity is increased significantly when the hydroxyl group in 2,6-di-t-butylphenyl is replaced by methoxyl. In this instance, as spectroscopic investigations have shown[26,29,30] the angle made by the C–O bond at the ring plane approaches 90°.

The departure (although insignificant) of the hydroxyl group from coplanarity in 2,6-di-t-butylphenol is due to the interaction of the electron clouds of the hydroxyl and t-butyl groups. As an investigation of molecular models showed[31], the overlap of the effective radii of the phenol hydrogen and each of the equivalent hydrogen atoms of the neighbouring t-butyl groups found in the most convenient conformation is approximately 0.25 Å. This suggests that the total bond strain energy is within the range 0.1–0.2 kcal mole^{-1}, appreciably less than the energy of conjugation which is gained by the hydroxyl group being in the plane of the ring (~ 7.0 kcal mole^{-1}).

The steric hindrances created by the t-butyl groups also prevents the normal rotation of the hydroxyl group around the C–O bond, increasing the rotational barrier. This barrier calculated on the basis of dielectric measurements is 2.2–2.8 kcal mole^{-1} for 2,4,6-tri-t-butylphenol[32,33]. It is interesting to note that this value is

lower than for the unsubstituted phenol (4.4 kcal mole^{-1}). The high value of the rotational barrier in unsubstituted phenol is due to its self-association, whereas in 2,6-di-t-butylphenol this is completely absent and consequently, the presence in it of a rotational barrier is due solely to the existence of steric hindrances created by the bulky *o*-alkyl groups.

Hence, the general features of the structure of the sterically hindered phenols are that when the conjugation of the aromatic ring with the hydroxyl group is retained (insignificant departure from coplanarity) the system of C–O–H bonds is subjected to certain deformations, in addition to which there is a rather high rotation barrier (restricted rotation) of the hydroxyl group around the C–O bond. All this leads to the specificity of certain physicochemical properties in a series of sterically hindered phenols.

The strains which arise in a system of C–O–H bonds of a phenol on the introduction in the ortho-position of t-butyl groups should evidently cause some change in the bond energy in this system, particularly the dissociation energy of the O–H bond. However, the direct determination of the dissociation energy of the O–H bond is extemely difficult and has been done only in the simplest instances.

To the first approximation the dissociation energy of the O–H bond in phenol ($D_{O...H}$) is proportional to the energy of the highest filled molecular orbital (E_{hfmo}),[34-36] and in this connection quantum-mechanical investigations of the activity of the phenolic compounds in oxidations yield a satisfactory correlation between the inhibiting activity of phenols and E_{hfmo}.[37] An extremely successful version of the estimation of the strength of the O–H bond is a combination of Fiesser's experimental method[38] used for the determination of the redox potential of unstable systems (E_C) and quantum-mechanical calculations of the dissociation energy of the O–H bond ($D_{O...H}$).[34] By combining these methods the dissociation energies of the O–H bond were calculated for a series of the simplest phenols, particularly unsubstituted phenol $D_{O...H}$ = 84 kcal mole^{-1}.

In the series of sterically hindered phenols the strength of the O–H bond was calculated on the basis of results obtained in investigating the equilibrium reactions of substituted 2,6-t-butylphenols with one of the nitrogenous radicals (2,2,6,6-tetramethyl-4-ketopiperidyl-1-oxyl) with the aid of the EPR method[39]. It has been shown that the strength of the O–H bond of certain sterically hindered phenols varies within the limits 76 ± 3 kcal mole^{-1}.

As the data show, the introduction of two t-butyl substituents into the ortho-positions to the hydroxyl group causes some weakening of the O–H bond, which agrees with results on the structure of sterically hindered phenols.

III. SPECTROSCOPIC CHARACTERISTICS OF STERICALLY HINDERED PHENOLS

1. Electronic Spectra

The first spectroscopic investigations of sterically hindered phenols were in 1948, when Coggenshall[14], on the basis of shifts in the absorption maxima of these phenols in the range 265–275 mμm, produced on replacing octane by alcohol as solvent, attempted to estimate the steric effect of *o*-alkyl substituents. However, the more detailed ultraviolet characteristics and their change with the structure of the phenol and medium were investigated much later[18,40-43].

Like their unscreened analogues, sterically hindered phenols exhibit two characteristic absorption bands in the ultraviolet range: 210–220 mμm (the B-band with high absorptivity) and 260–280 mμm (the C-band with low absorptivity). Table 1 gives the ultraviolet spectra of ortho-substituted phenols with gradual increase in the volume of the ortho-alkyl substituents. As Table 1 shows, the change in the size of the alkyl groups does not affect the characteristics of the ultraviolet spectra strongly, but the following two facts must be considered. The first is the low sensitivity of the position of the B-band to increase in the volume of the ortho-substituent. Dearden[40] considers that this anomaly is explained by the considerable contribution to the ground state of the phenol of the bipolar structure of the type:

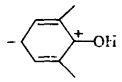


Table 1. The ultraviolet spectra of *o*-alkylphenols[40].

Compound	Cyclohexane				Ethanol			
	B-band		C-band		B-band		C-band	
	λ_{max}, mμm	E_{max}	λ_{max}, mμm	E_{max}	λ_{max}, mμm	E_{max}	λ_{max}, mμm	E_{max}
Phenol	210	6000	269	2200	218	6000	271	1900
o-Cresol	213	7000	270	1850	213	7100	272	2050
o-Isopropylphenol	211	7500	270	2100	215	6200	271	2250
o-t-Butylphenol	213	5900	268	2050	216	5100	271	2300
2,6-Dimethylphenol	211	7900	275	1600	214	8500	271	1550
2,6-Di-isopropylphenol	211	9200	275	1950	214	8000	270	1850
2,6-Di-t-butylphenol	211	7500	275	1800	212	7600	268	1550

The second fact is the shift of the B-band to longer wavelengths on going from a non-polar solvent to a polar one. It is suggested[14,40] that this effect is connected with steric hindrances which arise during the formation of associates with the solvent. The most pronounced change in form and position of the maxima in the spectrum are observed on increasing the pH of the medium. Thus, when an alcoholic solution of phenols is made alkaline there is a displacement of both bands to longer wavelengths and simultaneously there is an increase in the absorptivity. These facts are evidently due to an increase in the fraction of quinonoidal structure in the ground state of the ionised form of the phenol, which in the reactivity scheme leads to an increase in the ambidentate properties of the phenoxide anion.

The introduction of various substituents into the para-position of sterically hindered phenols also has a considerable effect on the parameters of the ultraviolet spectra. As might be expected, the presence of electron-withdrawing substituents brings about a shift of B- and C-bands to longer wavelengths, the shift increasing with the electronegativity of the substituent (Table 2). Since the parameters of the ultraviolet spectrum are extremely sensitive to changes in the effects of conjugation of the hydroxyl group with the para-substituents[44,45], they should be correlated with the constants of the para-substituent. Such a relation is observed sufficiently well in using σ_R' constants[18], which reflect the resonance constituent in the

total value of σ_p^- on allowing for the regular change in the inductive effect with distance, that is,

$$\sigma_{R'} = \sigma_p^- - {}^2/_3\sigma_m.$$

Table 2. Ultraviolet spectra of 4-X-2,6-di-t-butylphenols in 50% ethanol[43].

X	Neutral media				Alkaline media			
	B-band		C-band		B-band		C-band	
	λ_{max}, mμm	E_{max}	λ_{max}, mμm	E_{max}	λ_{max}, mμm	E_{max}	λ_{max}, mμm	E_{max}
H	214	6250	271	1600	244	11000	295	3630
CH_3	222	6900	278	1800	250	10600	303	3780
$C(CH_3)_3$	223	9500	272	1700	251	10200	300	3450
OCH_3	229	8200	285	3400	—	—	—	—
$(CH_3)_3N^+$	224	6350	270	1025	261	8800	298	4200
Br	226	11500	280	1275	257	16000	305	3580
SO_3^-	233	12300	272	1150	270	18400	300	3000
COO^-	250	13700	—	—	302	20400	—	—
COOH	260	13300	—	—	—	—	—	—
$CONH_2$	258	12000	—	—	321	22200	—	—
$COOC_2H_5$	261	14800	—	—	324	29600	—	—
CN	252	16900	—	—	307	31200	—	—
$COCH_3$	284	13300	—	—	363	32500	—	—
CHO	293	15000	—	—	370	38400	—	—
NO_2	325	10000	—	—	450	30500	—	—
NO	305	13250	—	—	382	18500	—	—

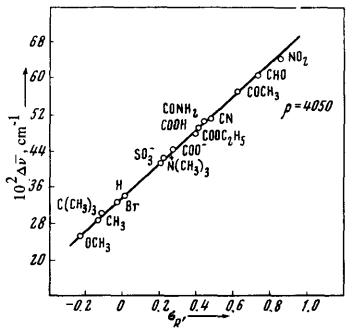


Figure 2. Correlation of $\Delta\bar{\nu}$ and $\sigma_{R'}$ in the 4-X-2,6-di-t-butylphenol series.

This correlation is made in the coordinates $\Delta\bar{\nu}$ against $\sigma_{R'}$ (Fig. 2). The shift in frequencies is calculated from the equation

$$\Delta\bar{\nu} = \bar{\nu}_a - \bar{\nu}_b,$$

where $\bar{\nu}_a$ is the frequency of the B-band of 4-X-2,6-di-t-butylphenol, and $\bar{\nu}_b$ that of the band for the corresponding substituted benzene. Table 2 gives the results for the ultraviolet spectra of 4-X-2,6-di-t-butylphenols in neutral and alkaline solutions. The shift in the bands observable on going from a neutral medium to an alkaline one increases with the electronegativity of the substituent and also depends linearly on $\sigma_{R'}$. The marked shift of the B-band in an alkaline medium in comparison with a neutral one with strongly electron-withdrawing substituents (CHO, CN, COOR, $COCH_3$, NO, and NO_2) is due to the considerable contribution of the quinonoid structure to the ground state of the ionised form[18,46].

2. Infrared Spectroscopy of 2,4-Dialkylphenols

The infrared spectra of sterically hindered phenols has been investigated in considerable detail[13,18,20,22-26,47-59]. The studies made in this field deal mainly with two problems: finding the spatial structure of the phenols of this series and their ability to form a hydrogen bond.

Table 3. Frequencies (ν_{OH}, cm^{-1}) of the hydroxyl group in the alkylphenol series (CCl_4).

Alkylphenol	ν_{OH}	Reference
Phenol	3612	16, 23, 25, 50, 51, 61, 62
2,6-Dimethylphenol	3622	20, 61, 62
2,6-Diethylphenol	3623	20, 53
2,6-Di-isopropylphenol	3623	20, 50, 53, 61, 62
2,6-Di-t-butylphenol	3651	20, 23, 25, 50, 51, 53, 61, 62
2,6-Di-t-pentylphenol	3646	59
p-Cresol	3617	51
2,4,6-Trimethylphenol	3626	51
2,6-Di-isopropyl-4-methylphenol	3628	23, 25, 51
2,6-Di-t-butyl-4-methylphenol	3650	16, 20, 23, 25, 51, 53, 54
4-Methyl-2,6-di-t-pentylphenol	3642.5	23, 25
4-Methyl-2,6-bis(triethylmethyl)phenol	3635	23, 25

In examing the infrared spectra of sterically hindered phenols the most noteworthy effect is that the band of the hydroxyl group is a narrow signal strongly displaced to shorter wavelengths in comparison with unsubstituted phenol (in KBr and CCl_4). The observed increase in the frequency of the hydroxyl group is evidently due to the interaction of the electron clouds of the hydroxyl and *o*-t-butyl groups[22,25]. Such an explanation was given in the interpretation of the results of an investigation of the chemical shifts in the PMR signal from the hydrogen atom of the hydroxyl group for a series of di-*o*-alkylphenols[60]. Table 3 gives results on the change in frequency of the hydroxyl group with the effective volume of the ortho-substituent for certain di-*o*-alkylphenols. It can be seen that the frequency of the hydroxyl group reaches maximal value when t-butyl groups are present.

Table 4. Frequencies (ν_{OH}, cm^{-1}) of the hydroxyl group in a series of 4-X-2,6-di-t-butylphenols in CCl_4.[18,22]

X	ν_{OH}	σ_p	X	ν_{OH}	σ_p
NO_2	3626.5	1.24	Cl	3643.5	0.23
CHO	3630.0	1.04	H	3647.0	0.00
CN	3632.5	0.88	OCH_3	3649.0	−0.13
$COCH_3$	3633.0	0.84	CH_3	3649.0	−0.15
COOH	3634.0	0.77	$C(CH_3)_3$	3649.0	−0.14
$COOC_2H_5$	3636.5	0.64	OH	3649.0	−0.37
Br	3643.0	0.25	NH_2	3650.5	−0.66

An increase in the lengths of the alkyl chains at the tertiary carbon atom in the ortho-substituents leads to a decrease in the frequency, which is evidently due to a decrease in the steric hindrances resulting from the breakdown of spherical symmetry of the substituents as a whole owing to the large number of possible conformations.

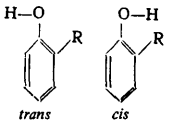
The results of an investigation of the variation of the frequency of the hydroxyl group with the electronegativity of the para-substituent in the 4-X-2,6-di-t-butylphenols is given in Table 4, from which clearly the frequency of the

hydroxyl group decreases as the electronegativity of the para-substituent, which affects the polarisation of the O–H bond, is increased. There is good correlation of the data in Table 4 with one another (Fig. 1).

It is noteworthy that the hydroxyl group band for sterically hindred phenols in CCl_4, which is a narrow isolated signal, does not change when the solution is diluted. This is possible only if self-association is absent[47,51,53,57]. A rise in temperature decreases the intensity of the absorption band of the hydroxyl group of sterically hindered phenols[55,56].

There is another interesting, but not completely strict, correlation based on the infrared spectra of sterically hindered phenols, which can yield additional information about the structure of this series of compounds. This is the correlation of the difference in free energy (ΔG) between the *cis*- and *trans*-isomers of mono-*o*-t-alkylphenols with $\Delta\nu_M$ and the change in the band intensity (ΔA) for 2,6-di-t-alkylphenols[24,25].

Careful study of the infrared spectra of *o*-alkylphenols in the range of absorption of the hydroxyl group led to the observation of a group of bands consisting of a band of high intensity with approximately the same frequency as for the unsubstituted phenol, and an incompletely resolved band with intensity and position close to the band of 2,6-di-t-alkylphenols[16,23,24]. The more intense band at the lower frequency was assigned to the so-called *trans*-isomer of the *o*-t-alkylphenol, and the second band to the *cis*-isomer:



The properties of these isomers are different. When the polarity of the medium is varied, the *trans*-isomer behaves like phenol (ν_{OH} decreases as the polarity is raised) but the *cis*-isomer exhibits all the spectroscopic properties of 2,6-di-t-alkylphenols. It is characteristic that for *o*-t-alkylphenols the *trans*-form is more stable than the *cis* form. This again shows the existence of a steric repulsion between the hydroxyl group and the alkyl residues. As Ingold has shown[24,25], the ratio of the intensities of the bands of the isomers can be used to calculate the difference in free energy (ΔG) between these isomers. When from these results ν_{OH} and ΔA are plotted against ΔG for the corresponding 2,6-dialkyl phenols, curves with a maximum or minimum are obtained, showing a sharp difference between the 2,6-dialkylphenols. However, it is noteworthy that the increase in ΔG with the effective volume of the *o*-alkyl substituents is slower than expected. This is evidently because of the decrease in energy as the angle C–H–O is increased.

3. Nuclear Magnetic Resonance Spectra

With the development of the NMR method a more detailed study of the electronic interaction in sterically hindered phenols arising as a result of the steric effect of the alkyl groups became possible. Measurement of the chemical shift of the hydroxyl group proton signal for a series of mono- and di-*o*-alkylphenols showed that as the volume of the substituent is increased there is a successive displacement of the signal to weaker fields, owing to the decrease in the magnetic screening of the hydroxyl group. This behaviour could be due solely to the steric influence of the *o*-alkyl groups, since the other possible factors affecting the position of the signal (appreciable departure from coplanarity, influence of the inductive effect, dipole moment, and magnetic anisotropy) should here result in a displacement to stronger fields. Table 5 shows the values of the chemical signals (τ_{OH} and $\Delta\tau_{OH}$) of the hydroxyl group proton in *o*-alkylated phenols. Clearly, from these results[31,60] the magnetic screening of the hydroxyl group proton decreases in the following order of substituents:

$$H > CH_3 > CH(CH_3)_2 > C(CH_3)_3 .$$

In addition, there is a decrease in screening on going from monoalkylphenols to dialkylphenols.

Table 5. Chemical shifts of the signal of the proton of the hydroxyl group in *o*-alkylphenols[31].

Compound	τ_{OH}	$\Delta\tau_{OH}$	ν_{OH}
Phenol	5.77	—	3612
o-Cresol	5.62	—0.15	3615
o-Isopropylphenol	5.54	—0.23	3614.5
o-t-Butylphenol	5.36	—0.41	3607; 3647
2,6-Dimethylphenol	5.56	—0.21	3622
2,6-Di-isopropylphenol	5.48	—0.29	3623
2,6-Di-t-butylphenol	5.13	—0.64	3648

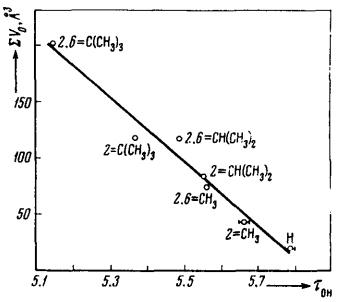


Figure 3. Correlation of the chemical shift of the hydroxyl-group proton and the total volume of the *o*-alkyl substituents in a series of alkylphenols.

It is characteristic that the values of ν_{OH}, also given in Table 5, follow the same relation but in the reverse order. Evidently the reason for this change in the two parameters is the same. In the examples considered the mutual repulsion of the electron clouds of the hydroxyl-group hydrogen and *o*-alkyl substituents leads to a decrease in the electron density at the hydroxyl proton, and consequently to a decrease in its diamagnetic screening. Furthermore, in this there is a definite decrease in the symmetry of the cloud of *S*-electrons of the hydroxyl-group hydrogen, which should lead to an increase in the paramagnetic contribution in the screening and a shift of the signal to weaker fields. The facts examined are illustrated well by the linear dependence of the chemical shift of the hydroxyl proton on the total volume of the *o*-alkyl substituent (Fig. 3). The screening of the hydroxyl proton is also altered by the introduction of a para-substituent into the 2,6-dialkylphenol[19,60]. With increase in the electronegativity of the para-substituent there is a shift of the signal from the hydroxyl-group proton to weaker fields and

this shift is correlated with the $\sigma\tilde{p}$-values of the substituents. This once again agrees with Ingold's results[22,23,25] on the investigation of the vibrations of the O–H bond in a series of 2,6-di-t-butylphenols. Direct confirmation of the correctness of the conclusions drawn is given by the linear dependence of τOH on νOH.

The above results suggest that the para-substituent brings about a redistribution of the electron density not only in the benzene ring but also at the oxygen atom of the hydroxyl group. In this connection, there is also a linear relation between the chemical shift of the signal of the hydroxyl proton and the charge on the oxygen atom (q_0).[31]

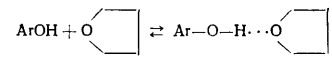
IV. THE HYDROGEN BOND OF 2,6-DIALKYLPHENOLS

Usually, hydroxyaromatic compounds are capable of forming a hydrogen bond and for many of them the formation of self-associates is also characteristic. It is noteworthy that all the spectroscopic methods considered above allow us to estimate in some measure the ability of alkylphenols to form associates with the solvent or self-associates. And since the hydrogen bond is especially sensitive to steric hindrances, the observable spectroscopic effects are often criteria of the steric hindrances created by the *o*-alkyl substituents. Most of the information on the influence of steric factors on the formation and strength of the hydrogen bond in a series of sterically-hindered phenols has been given by use of infrared[13,47–51,53,57,63,64] and NMR[31,65–69] spectroscopy.

It is known that many *o*-alkylphenols form self-associates in inert solvents at appreciable concentrations, whereas at a sufficiently great dilution they exist as monomers. In this connection, during the dilution of the solution with an inert solvent (for example, CCl_4) there is a displacement, the stronger the tendency of the phenol to form a hydrogen bond and consequently the hydroxyl group is less sterically screened. This change in the frequency of the hydroxyl group during the dilution of the solutions ($\Delta\lambda = \lambda^{OH}_{conc} - \lambda^{OH}_{dil}$) was also suggested by Coggenshall[13] for use in evaluating the steric effect of alkyl substituents in the formation of a hydrogen bond in the alkylphenol series. By using this parameter, which characterises the strength of the hydrogen bond, he divided the phenols into three groups: $\Delta\lambda > 0.15$ mμm, unscreened phenols; 0.04 mμm $< \Delta\lambda <$ 0.15 mμm, semiscreened phenols; $\Delta\lambda <$ 0.04 mμm, screened phenols. However, later[47] an empirical index of the hydrogen bond was introduced, which correlated with the screening effect of the alkyl substituents, and it was shown[51] that 2,6-di-t-butyl-4-methylphenol generally does not form self-associates.

More rigorous results can be obtained by investigating the association of 2,6-dialkylphenols with various substituents. Thus Bellamy[57] found that the relative strength of the hydrogen bond formed between solvents and di-*o*-alkylphenols is independent of the effective volume of the ortho-substituent. An exception is 2,6-di-t-butylphenol for which the steric hindrance is so great that during the formation of its associates with the solvent the volume of the solvent molecules (acceptor) starts to play a decisive role. Careful analysis of the frequencies[63] of the hydroxyl group of 2,6-di-t-butyl-4-methylphenol showed that the associates of this phenol with the solvent can exist in two forms: in the first the hydroxyl-group proton lies in the plane of the ring (or close to it), and in the second it is perpendicular to the plane. In the second form resonance stabilisation of the hydrogen bond is assumed to be absent but there is also a decrease in the steric hindrances of solvation.

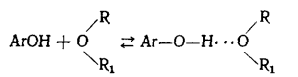
The existence of two forms of associates is confirmed by the results of Borod'ko's work[65], who observed, in an investigation of complex formation between 2,6-di-t-butylphenol and tetrahydrofuran, two bands from an associated hydroxyl group (3560–3390 cm^{-1}). On the basis of the thermodynamic parameters of the equilibrium:



he calculated the length of the hydrogen bond for each form: 2.85 and 3.05 Å. It is noteworthy that the length of the hydrogen bond for the unsubstituted phenol is ~ 2.7 Å. There is also a noticeable difference in the energy of the hydrogen bond. Thus for the unsubstituted phenol it is 6 kcal $mole^{-1}$, but for 2,6-di-t-butylphenol it is only 2 kcal $mole^{-1}$.

Spectroscopic results[63] have also been used to calculate the fraction of non-bonded hydroxyl groups of sterically hindered phenols in various solvents. However, the correlation between the basicity of the solvent and the fraction of non-bonded hydroxyl groups could not be deduced. Evidently, the reason for this lies in the geometry of the solvent molecules.

The change in the frequency of the hydroxyl group during association and the equilibrium constants of the reaction



have been used for a quantitative estimation of the steric factor in the series of sterically hindered phenols[53].

Table 6. Equilibrium constants and shift of the frequencies of the hydroxyl group in the formation of associates of alkylphenols with ethers[51].

Phenol	Ethers											
	di-t-butyl		di-iso-propyl		tetra-hydrofuran		di-n-butyl		diethyl		$[(CH_3)_2Si]_2O$	
	K_{equil}	Δν	K_{equil}	Δν	K_{equil}	Δν	K_{equil}	Δν	K_{equil}	Δν	K_{equil}	Δν
Phenol	3.90	325	7.20	308	10.4	301	4.90	292	6.00	288	0.40	168
o-Cresol	1.70	309	3.20	301	5.5	294	2.60	288	3.40	283	0.00	159
o-Isopropylphenol	2.00	300	3.90	300	6.7	296	3.00	289	3.90	285	0.06	163
o-t-Butylphenol	2.30	280	4.10	291	5.7	284	2.90	280	3.70	278	0.00	169
2,6-Dimethylphenol	0.22	205	0.62	234	2.0	229	0.63	228	0.67	220	0.03	—
2,6-Di-isopropyl-phenol	0.19	197	0.48	215	1.7	201	0.23	201	0.51	191	0.06	—
2,6-Di-t-butylphenol	0.00	—	0.00	—	0.0	—	0.00	—	0.00	—	0.00	—

It was assumed here that the equilibrium constants are a measure of the overall effect and the frequency shift reflects the change in the strength of the hydrogen bond since it is determined by the changes in the force constant of the O–H bond. Table 6 gives the results obtained in this work.

As Table 6 shows, the value of $\Delta\nu$ changes symbathically with the basicity of the ether and increase in the steric effect of the alkyl substituents. An exception is 2,6-di-t-butylphenol, for which the steric hindrances during solvation are too great. On the other hand, the equilibrium constants for the association are not correlated

with the basicity of the ether but are arranged in the order of an increase in the steric effects of the ethers. The small difference in the value of $\Delta\nu$ shows that the contributions of the hydrogen bond to the free energy of the system are approximately the same and the significant differences in the equilibrium constants are evidently due to the entropy factor, which is especially sensitive to steric effects. Similar results were obtained by Singh and Rao[50]. They noted that despite the decrease in the equilibrium constant for the association as the volume of the substituent is increased there is an increase in the enthalpy of the reaction. The decrease in $\Delta\nu$ accompanying the increase in the enthalpy of the reaction is evidently the result of an increase in the activation energy during the change of a proton into a hydrogen bond. If the conclusions drawn are correct then a direct relation between $\Delta\nu$ and the change in free energy of the system (ΔF_0) is to be expected. Actually, such a correlation between $\Delta\nu$ and ΔF_0 was observed. Subsequently Singh and Rao investigated the structure of the associate formed. They obtained equilibrium constants in the association of 4-X-2,6-di-t-butylphenols with tetrahydrofuran and the absence of a correlation of these constants with σ_p for the X substituent.

The observed behaviour is explained by certain breakdowns in coplanarity of the hydroxyl group, which leads to a non-planar hydrogen complex. The latter brings about a hindrance to the transfer of electronic effects of the para-substituent to the reaction centre and consequently to the destruction of the linearity between σ_p and Kequil. It should be noted that the relief of steric hindrances created by alkyl groups leads to a linear relation between these quantities, which occurs with an unsubstituted phenol[70].

The NMR method played a great part in the investigation of the hydrogen bond of sterically hindered phenols. The main parameter in studying a hydrogen bond by this method is the chemical shift of the proton participating in the formation of the hydrogen bond and also the dependence of this quantity on the concentration of the test substance in various solvents. The change in the position of the signal is due to the fact that with dilution or rise in temperature there is breaking of hydrogen bonds and the signal is shifted to higher fields. The existence of a hydrogen bond, on the other hand, shifts the signal to weaker fields, that is, there is a decrease in the magnetic screening of the proton. Theoretical analysis[71] of the causes of the change in the magnetic screening of the proton showed that the principal ones are the change in polarity of the O–H bond (displacement of the centre of gravity of the electron cloud to the side of oxygen) and the formation of a donor–acceptor bond ArO–H...X (shift of the lone pair of electrons of atom X to the side of the hydrogen atom).

In investigating the hydrogen bond arising in the self-association of alkylphenols and the nature of the complexes formed there have been several studies[31,67,68,72] of the concentration dependence of the parameters of the PMR spectra. In these studies it was found that the position of the signals for the protons of the alkyl groups and benzene ring are almost independent of the concentration of the substance whereas the signal from the proton of the hydroxyl group is usually shifted to higher fields on dilution. Consequently, the change in position of the signal of the hydroxyl proton is the result of the formation of self-associates. With increase in the volume of the alkyl substituents the chemical shift corresponding to the undiluted solution increases; the difference in the chemical shifts also changes on going from a dilute solution to a concentrated one. Both these facts are due to the increase in the length of the hydrogen bond during self-association owing to the increase in the volume of the substituents, that is, with decrease in the possibility of self-association. Table 7 gives the parameters of the self-association process:

$$n \cdot \mathrm{ArOH}_{\text{monomer}} \rightleftarrows n\text{—ArOH}$$

showing the effect of the volumes of the *o*-alkyl substituents. Evidently the equilibrium constants (K_n) and chemical shift (δ_n) in the associated state gradually drop as the steric hindrances increase. The nature of the associate also changes. 2,6-Di-t-butylphenol does not give self-associates ($n = 1$), 2,6-dimethylphenol and 2,6-di-isopropylphenol form cyclic tetrameric associates ($n = 4$), and in the self-association of unsubstituted phenol a cyclic trimer is formed ($n = 3$).

Table 7. Comparison of the self-association parameters with the effective volume of the ortho-substituents[31].

Compound	Total volume, A^3	δ_n	K_n	n
Phenol	14.4	—3.11	4.78	3
2,6-Dimethylphenol	67.0	—0.82	$5.7\cdot10^{-2}$	4
2,6-Di-isopropylphenol	131.0	—0.44	$1.25\cdot10^{-2}$	4
2,6-Di-t-butylphenol	226.2	0.00	0.00	1

Interesting results were obtained in investigating the associates of phenols with proton-withdrawing solvents[31,72]. The ease of formation of such associates and their stability are determined not only by steric hindrances in the phenol molecule, but also by the volume and proton-acceptor properties of the solvent molecule. These investigations were made with the following solvents: acetone[31], diethylether[31], triethylamine[31], dioxan[72], and ethanol[72]. With decrease in the concentration of phenols in ether, acetone, ethanol, and dioxan the chemical shift of the signal of the hydroxyl proton decreases. This shows that associates with these solvents are more stable that self-associates. When solutions of dialkylphenols in triethylamine are diluted the concentration dependence observed has a characteristic minimum. This anomaly can evidently be explained by the existence of two processes:

$$\mathrm{ArOH} + \mathrm{N(C_2H_5)_3} \rightleftarrows \mathrm{ArOH\cdots N(C_2H_5)_3};\quad \mathrm{ArOH} + \mathrm{N(C_2H_5)_3} \rightleftarrows \mathrm{ArO^{\ominus}} + \mathrm{\overset{+}{H}N(C_2H_5)_3}.$$

The concentration dependences of phenols in proton-withdrawing solvents usually reflect the competition of two processes: the dissociation of the self-associates and complex formation with the solvent. With 2,6-di-isopropyl-, 6-t-butyl-2-methyl-, and 2,6-di-t-butyl-phenols the first process can be neglected, which allows the equilibrium constant of the reaction

$$\mathrm{ArOH} + \mathrm{X} \rightleftarrows \mathrm{ArOH\cdots X},$$

to be estimated.

The results in Table 8 show that with increase in the steric factor in the phenol the stability of the complexes decreases. An increase in the volumes of the solvent molecules also affects their stability in the same direction.

Investigation of the association of 4-X-2,6-di-t-butylphenols with t-butyl alcohol showed that the nature of a para-substituent in the nucleus of the phenol has an effect on the nature of the association[69]. Unlike the results of Singh and Rao[50], obtained by infrared spectroscopy, the

value of the chemical shift (τ_{OH}) of the phenol in the presence of t-butyl alcohol is correlated with the σ constants of substituent X (see Fig. 4, straight line *3*). The parallelism of straight lines *2* (in the absence of an alcohol) and *3* (in the presence of an alcohol) shows that the hydroxyl group of the 4-substituted 2,6-di-t-butylphenol in a complex with t-butyl alcohol is subjected to the same effect of the para-substituent as it is for a phenol unsubstituted in the ortho-positions.

Table 8. Equilibrium constants for the complex formation by alkylphenols [31,72].

Compound	Solvent and K_{equil}		
	ether	acetone	dioxan
2,6-Di-isopropylphenol	—	—	7.1
6-t-Butyl-2-methylphenol	3.0	4.2	5.6
2,6-Di-t-butylphenol	0.6	1.9	0.7

It is interesting to note the effect of substituent X in the phenol nucleus on τ_{OH} for t-butyl alcohol (see Fig. 4, straight line *1*). It can be seen that the increase in the degree of association of the phenol with the alcohol brings about the destruction of the alcohol–alcohol associates (shift of the signal of the proton of the hydroxyl group of the alcohol to a stronger field). The shift increases with increase in the electronegativity of the substituent. The latter is evidently due to the polarisation of the O–H bond of the phenol, which brings about an increase in the acidity of the phenol, that is, its proton-donating properties.

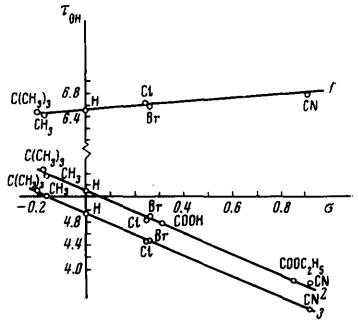


Figure 4. Correlation of τ_{OH} for 4-X-2,6-di-t-butylphenols (*2*, in the presence of t-butyl alcohol; *3*, in its absence) and τ_{OH} of t-butyl alcohol (*1*) with the σ^--factors of the para-substituent.

Bearing in mind the symbathic nature of the strength and bond order, an increase in the order ($P_{O...O}$) and polarisability ($\pi_{O...O}$) of the hydrogen bond with increase in the electronegativity of the para-substituent in the series of phenols must be expected. Such relations are actually observed [69]. They confirm the conclusion that the hydrogen bond in the associate is influenced by the nature of the para-substituent.

Generalising the above results, the following conclusions can be drawn: (*a*) all the 2,6-dialkylphenols are capable of forming hydrogen bonds; (*b*) the increase in the volume of the ortho-substituent reduces the capability of phenols for self-association; (*c*) 2,6-di-t-butylphenols do not give self-associates but can form a hydrogen bond with proton-withdrawing solvents, the nature of which depends on the nature of the substituent in the para-position of the phenol and the geometry of the solvent molecule.

V. ACIDITY OF STERICALLY HINDERED PHENOLS

The increased acidity of phenols in comparison with aliphatic alcohols is a characteristic feature of hydroxy-aromatic compounds. This is due to the electron-withdrawing properties of the aromatic ring. Naturally, the change in the conjugation of the π-electrons of the nucleus with the p-electrons of the oxygen atom of the hydroxyl group should be reflected in the ease of heterolytic splitting of the O–H bond.

The introduction into the ortho-position to the hydroxyl group of alkyl substituents usually brings about a marked drop in the acidity of the phenol [73–85]. The reasons for the drop in acidity can be as follows: a positive inductive effect of the alkyl substituents, leading to electronic saturation of the O–H bond (however, as Table 9 shows, its contribution is small), the breakdown of the coplanarity of the aromatic ring and hydroxyl group, which decreases the effect of the electron-withdrawing properties of the ring, and finally the steric hindrances of the solvation of the anion formed.

Table 9. Dissociation constants of alkylphenols [43,73,82].

Compound	pK, 25°	pK, 25°
	water	methanol
Phenol	10.02	14.20
o-Cresol	10.33	14.80
o-Propylphenol	10.55	15.07
o-t-Butylphenol	11.35	16.25
2,6-Dimethylphenol	10.63	15.27
2,6-Di-isopropylphenol	11.08	15.11
2,6-Di-t-butylphenol	11.70	17.08
p-Cresol	10.27	14.55
2,4,6-Tri-t-butylphenol	12.19	—
2,6-t-Butyl-4-methylphenol	12.23	17.51

It has already been shown above that the introduction of even two t-butyl groups into ortho-positions displaces the OH group from the plane of the aromatic ring by $\geqslant 14°$, which is almost without effect on the conjugation of the p-electrons of the oxygen atom with the aromatic ring. This shows that the contribution of this effect to the decrease in acidity of the derivatives of 2,6-di-t-butylphenols is very small. Therefore the main reason for the drop in acidity is the steric hindrances of the solvation which is clear from Table 9, which gives the dissociation constants of the phenols in water and methanol for the three groups of compounds. It is suggested [42,43,80,81,86,87] that voluminous alkyl groups hinder the solvation of the anion formed as a result of dissociation and decrease its stability. Furthermore, the alkyl groups in the phenol molecule decrease the effective dielectric constant around the hydroxyl group, which increases the electrostatic energy of the anion and

leads to a decrease in the dissociation constant. This conclusion is confirmed also by an investigation of the electrical conductivity of solutions of alkylphenols [88], which drops sharply with increase in the volume of the *o*-alkyl substituents.

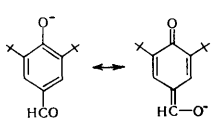
In considering the effect of the nature of the para-substituent on the acidity of the phenol it must be borne in mind that for some para-substituted phenols there is the possibility of tautomeric conversions (for example, quinoxime ⇌ nitrosophenol). This leads to rather complex dependences, especially for sterically hindered phenols, which generally tend to be converted into compounds with quinolide or quinonoid system of bonds. Problems of the tautomerism of phenols have been discussed in detail in a review [85].

From the example of unsubstituted phenol [43,89] and 2,6-dichlorophenol [74,90], it was repeatedly noted that the introduction of electron-withdrawing substituents into the para-position markedly increases the acidity of the phenol and it increases with the electronegativity of the substituent. A similar picture is observed for sterically hindered phenols [42,46,79,84,91,92]. Table 10 gives results on acidities for two series of 4-substituted phenols, which are correlated well with the σ_p constants of the para-substituents.

Table 10. Dissociation constants of 4-X-phenols at 25°C (water). [43]

X	pK_a unsubstituted phenol	pK_a 2,6-di-t-butyl phenol	σ_p	X	pK_a unsubstituted phenol	pK_a 2,6-di-t-butyl phenol	σ_p
CH_3	10.26	12.23	−0.15	$COOC_2H_5$	8.50	9.50	0.64
$C(CH_3)_3$	10.23	12.19	−0.14	$(CH_3)_3N^+$	8.21	9.84	0.77
OCH_3	10.21	12.15	−0.13	$COCH_3$	8.05	8.68	0.84
H	9.99	11.70	0.00	CN	7.97	8.70	0.88
COO^-	9.39	10.80	0.24	CHO	7.60	8.05	1.04
Br	9.36	10.83	0.25	NO_2	7.15	6.65	1.24
SO_3^-	9.03	10.40	0.40	NO	6.36	8.18	1.60
$CONH_2$	8.56	9.53	0.61				

It should be noted that for some 4-X-2,6-di-t-butylphenols with strongly electron-withdrawing substituents, (for example, CHO) the changes in pK_a on going from the corresponding 4-X-phenol is not so great and can be satisfactorily explained by the inductive effect of the *o*-t-butyl groups without allowance for their steric factor. Values of pK_a for a series of sterically hindered phenols in various solvents were found experimentally and calculated with allowance only for electronic effects of the two t-butyl groups; these values of pK_a agreed satisfactorily for 2,6-di-t-butyl-4-formylphenol. When X is an alkyl residue, there is no such agreement, that is, in addition to the inductive effect of the para-substituent there is also the steric effect of the *o*-t-butyl groups. The observed anomaly can be explained by assuming delocalisation of the negative charge in the phenoxide ion with participation of the para-substituent.



If the requirements for solvation of both oxygen atoms in the anion formed are the same, then the total solvation of the 4-formylphenoxide and 2,6-di-t-butyl-4-formylphenoxide anions should be approximately the same. This suggests that although the steric effect of t-butyl groups greatly reduces the solvation of the phenol oxygen, it simultaneously facilitates the redistribution of the electron density at the oxygen atom of the formyl group and increases its degree of solvation, that is, the total change in the solvation of the anions as a whole is probably extremely small.

Hence the steric hindrances created by bulky alkyl groups show the twofold action on the ionisation of sterically hindered phenols. On the one hand, the strain in the O−H bond produced in the screening of the hydroxyl group facilitates the heterolytic breaking of the O−H bond, and on the other hand the phenoxide anion formed loses its stability due to the hindered solvation. The introduction of a para-substituent changes the value of some effect and leads to a marked change in the acidity of sterically hindered phenols.

VI. DIPOLE MOMENTS AND SORPTION PROPERTIES OF STERICALLY HINDERED PHENOLS

The steric effect of *o*-alkyl substituents is also decisive for certain other physicochemical parameters of sterically hindered phenols. First of all there are the dipole moments and the related sorption properties of phenols. These aspects have been discussed in a series of studies, in which the importance of steric hindrances is stressed to some extent. Thus, it was noted [19,93,94] that the introduction of t-butyl groups brings about a change in conjugation. This is expressed in an increase in the moment of the C−O bond from 0.66 D in phenol to 1.53 D in 2,4,6-tri-t-butylphenol. However, it must be remembered that the dipole moment is less sensitive to different steric effects than the physicochemical characteristics discussed above.

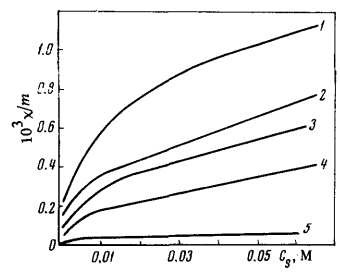


Figure 5. Freundlich isotherms in the adsorption of alkylphenols from cyclohexane on carbon: *1*) H; *2*) CH_3; *3*) *p*-t-C_4H_9 phenol; *4*) $CH(CH_3)_2$; *5*) $C(CH_3)_3$.

The more pronounced dependences on the values for the *o*-alkyl substituents were obtained in investigating the sorption properties of phenols [95-98]. The study of the sorption on carbon [97] and aluminium oxide [96] shows a decrease in the degree of sorption with increase in the volume of the *o*-alkyl substituents. Fig. 5 shows the Freundlich isotherms for several di-*o*-alkylphenols, where X is the amount of working adsorbent, *m* the total amount of adsorbent, and *C* the equilibrium concentration of adsorbent.

Fig. 5 shows there is a sharp difference in the sorption properties of phenols. Similar results were obtained in studying the chromatographic behaviour of phenols[95] (Table 11).

Table 11. Sorption of alkylphenols on silicic acid[95].

Alkyl	R_f		
	o-alkyl-phenol	*p*-alkyl-phenol	2,6-dialkyl-phenol
H	0.26	0.26	0.26
CH_3	0.37	0.28	0.55
C_2H_5	0.43	0.30	—
$CH(CH_3)_2$	0.52	0.30	0.95
$C(CH_3)_3$	0.74	0.31	1.00

Table 11 gives the R_f values obtained in the adsorption of phenols on silicic acid. A comparison of the change in frequency of the adsorption of the hydroxyl group of the phenol in the infrared range with the K_a values, where $K_a = 1/(R_f - 1)$, depending on the value of the *o*-alkyl substituents, obeys a first-order equation[98]. Evidently, the observed increase in the value of R_f with increase in the volume of the *o*-alkyl substituents also shows the decisive role of the steric screening of the hydroxyl group.

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The above features of the structure and certain physicochemical properties of sterically hindered phenols greatly determine the behaviour of compounds of similar type in various chemical changes. Thus a very characteristic property of these phenols is the ease with which they lose the hydrogen atom of the hydroxyl group as a proton or radical in ionic or radical processes. At the same time the considerable steric hindrances ensure that this oxygen is a not very accessible reaction centre of the molecule. These very properties agree well with the structure of sterically hindered phenols and are responsible for many interesting features of their behaviour: the inhibition of radical reactions, the formation of stable phenoxide radicals, the change into cyclohexadienones and methylenequinones, etc.

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