Infrared Absorption Spectra of Trisubstituted Phenol Derivatives

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Infrared spectroscopy is being employed to an ever-increasing extent in organic chemistry for the recognition of structural units in unknown compounds, both in qualitative and quantitative analysis. In the interpretation of spectra, the analyst must rely upon accumulated data relating infrared absorption bands with structural units. As aromatic compounds give rise to a large number of very sharp characteristic bands, their identification by infrared methods is often straightforward.

Theoretical spectroscopists prefer to associate the absorption bands with general modes of molecular vibration. All vibration is regarded as motion along or across the bonds that join atoms to atoms. Stretching refers to motions along the bond and bending to those across the bond.

The present study consists of the spectra of twenty-four compounds, phenol and halogen substituted phenols. Several of the phenols were used as purchased; others were purified, and still others were synthesized, in the laboratory.

The spectra described in the following pages were obtained with a Perkin-Elmer 21B double beam spectrometer equipped with a rock-salt prism. The frequencies of the bands is given in reciprocal centimeters (cm^{-1}). The width of the bands was measured at one-half of the intensity (peak-height). Ofter the bands are characterized qualitatively as weak (w), medium (m), or strong (s); the strong bands are of same order of intensity as the strongest bands in the spectrum, the medium bands ⅓ to ⅔ as intense, the weak bands ¼ to ⅓ as intense. The percentage of light transmitted at the absorbancy maximum has been given, even though this quantity is not precisely reproducible.

The presence of an armatic-type structure is best recognized by the presence of the $=$C-H stretching vibration near 3030 cm^{-1}, and the C$=$C vibration in the 1600-1500 cm^{-1} region. In these regions, the absorption bands are least affected by the substitution pattern, although the C$=$C region can throw light on the nature of substitution and on the presence of conjugated double bonds. The $=$C-H stretching mode was readily identified in the spectra of all twenty-four phenols. It appears as a sharp, relatively weak band about 3030 cm^{-1}.

The change in certain regions which results from substitution is largely independent of the nature of the substituents; so it is possible to determine the degree and position of the substitution. This can be studied in the regions 2000-1660 cm^{-1}, 1250-1000 cm^{-1}, and 1000-650 cm^{-1}. The first of these regions is the most definite, and usually gives a clear indication of the type of substitution. Confirmation can be sought in the lowest region, 1000-650 cm^{-1}, and to a lesser extent at 1250-1000 cm^{-1}. The last region is complicated in some cases by the presence of groupings, absorptions, or overtone absorptions.

The substituted phenols have relatively weak absorptions in the region 2000-1650 cm^{-1} as compared to the other fundamentals. For studying this region a fairly thick cell (1.0 mm) with a 10 per cent solution of solid should be used. The solutions used were 1 M with a cell thickness of 0.05 mm and 0.1 M with a cell thickness of 0.5 mm.

A weak pattern sufficiently distinctive to permit recognition of characteristic types emerged. Monosubstituted phenols have a series of four bands gradually diminishing in intensity towards the long wave-length region. Di-, tri-, and tetrasubstituted materials show fewer bands.

The C=C stretching vibration, characteristic of aromatic compounds, associated with the three double bonds in the ring give two bands at 1600 cm^{-1} and 1500 cm^{-1}, resulting from a resonance splitting effect. In the mono-, di-, and trisubstituted phenols the bands are broad with peaks near the expected frequency range. The actual position of these bands was affected more by the arrangement of the substituent around the ring than by the nature of the substituted group. In 1, 2, 4, 5-tetrasubstituted phenols these bands were greatly reduced in intensity and in some cases failed to appear.

Monosubstituted aromatics normally have two easily recognized bands in the 770-730 cm^{-1} and 710-690 cm^{-1} regions, respectively. These bands are the strongest in this region of the spectrum. The absence of a band near 700 cm^{-1} is strong evidence for the absence of a monosubstituted product, but this does not hold when halogens are present giving bands in this region.

phenol	78%	750 cm^{-1}
	73%	680

Ortho-disubstituted aromatics absorb in approximately the same range of frequencies as the monosubstituted. The reduction from five to four free hydrogen atoms does not significantly affect the frequency. The general range found for four adjacent free hydrogen atoms is 770-735 cm^{-1}.

o-chlorophenol	82%	750 cm^{-1}
o-bromophenol	52%	750
o-iodophenol	84%	750

Three adjacent ring hydrogen atoms or 1,3-substitution may show a slightly higher range, 810-750 cm^{-1}, with a second band of medium intensity at 725-680 cm^{-1}.

m-chlorophenol	42%	840 cm^{-1}
m-bromophenol	42%	840

However, the above compounds also show a strong band at 860 cm^{-1} which may be considered due to one free adjacent hydrogen atom as it lies in the range of 900-860 cm^{-1}.

m-bromophenol	71%	860 cm^{-1}
m-chlorophenol	75%	890
	42%	860 triplet
	41%	840

With further reduction in number to two free adjacent hydrogen atoms in the ring, the absorption frequency of the out-of-plane C-H vibration shows a further shift to higher frequency and a strong band occurs in the range 860-800 cm^{-1}. These compounds are the 1,4-/and also the 1,2,4-substituted phenols.

p-chlorophenol	70%	825 cm^{-1}
p-bromophenol	70%	825
2,4-dibromophenol	72%	815
2,4-dichlorophenol	72%	815

One isolated ring hydrogen situated between two substituents or 1,2,3,5-substitution produces the expected high-frequency shift and the C-H absorption appears in the region 900-860 cm^{-1}. The reduction in the number of vibrating groups also reduces the intensity. As many as twelve spectra were measured, involving this type of substitution and all were found in agreement; only a representative few are given.

2,4,6-tribromophenol	38%	850 cm^{-1}
4-chloro-2,6-dibromophenol	64%	850
2,4,6-triiodophenol	75%	860
4-bromo-2,6-diiodophenol	61%	860

The following regions in the spectra of aromatics have been assigned; monosubstituted to 1075-1065 cm^{-1}, ortho-substituted to 1125-1085 cm^{-1}, meta-substituted to 1170-1140 cm^{-1}, and para-substituted to 1120-1090 cm^{-1} (Randall *et al.*, 1952)

o-chlorophenol	79%		1200 cm^{-1}		triplet
o-bromophenol	81%		1200		triplet
o-iodophenol	81%		1200		triplet
m-chlorophenol	63%	1255			triplet
m-bromophenol	69%	1255			doublet
p-chlorophenol	73%			1180	
p-bromophenol	79%			1175	
phenol	79%			1180	triplet

1,2-, 1,4-, 1,2,4-substituted phenols show weak absorption in the range 1225-1175 cm^{-1} and 1125-1090 cm^{-1}, together with two additional weak bands in range 1070-1000 cm^{-1}.

Mono-, and 1,3-substituted phenols absorb weakly between 1175-1125 cm^{-1} and between 1110-1070 cm^{-1}.

2,4-dichlorophenol	71%	1270	73%	1189	76%	1100 cm^{-1}
2,4-dibromophenol	77%	1265	78%	1175	57%	1070

The infrared absorption band arising from O-H valence vibration was one of the earliest known and most often studied in early papers. In more recent studies it has been found that infrared spectrographic studies afford a simple, convenient method of studying the phenomenon of hydrogen bonding, since when this occurs, the O-H bond-length is increased and absorption bands shifts to a lower frequency.

The hydroxyl group is very highly polar, and it is only in the vapour state and in dilute solutions in non-polar solvents that the absorption of free O-H vibration is observed. However, even in very dilute carbon disulphide solution, alcohols show some change in O-H frequency due to solvent association. Temperature changes will markedly influence the position of O-H absorption bands (Bellamy, 1954).

The absorption range for the O-H valence-stretching vibration for the free unbonded group is usually quoted to be 3700-3500 cm^{-1}. The upper limit at which absorption can occur is exhibited by water; the phenols and the alpha, beta-unsaturated alcohols are found at the bottom of this range. This is due to the influence of the aromatic ring, lowering the O-H frequency. The O-H absorption of phenol is most often placed at 3610 cm^{-1} (Bellamy, 1954).

phenol	56%	3610 cm^{-1}
m-chlorophenol	48%	3610
m-bromophenol	53%	3610
p-chlorophenol	32%	3610
p-bromophenol	53%	3610

With partly hinderd phenols the wave-length shifts from the free O-H position to a lower frequency as in the case of ortho-substituted phenols.

o-chlorophenol	51%	3570 cm^{-1}
o-bromophenol	50%	3535
o-iodophenol	50%	3415

also all tri-substituted (2,3,6-) phenols

Intermolecular hydrogen bonds in which no resonance structures are involved show broad bands in the range 3450-3200 cm^{-1}.

phenol	19%	3480 cm^{-1}	
m-chlorophenol	20%	3400	(all wide)
m-bromophenol	19%	3400	
p-bromophenol	12%	3470	
p-chlorophenol	11%	3470	

The wide bands in the range 3450-3200 cm^{-1} are absent in the spectra of ortho-substituted phenols and also in the trisubstituted (2,3,6-) phenols. The intramolecular hydrogen bond which is resonance-stabilized gives rise to a particularly strong band in the 3570-3450 cm^{-1} region, with a consequent large O-H frequency shift to a lower frequency. The shift was demonstrated an all ortho-substituted phenols.

Ortho-substituted phenols can have two configurations because the O-H lies in the plane of ring giving cis and trans-configurations. Thus the monosubstituted products give rise to two bands, the disubstituted products give rise to only one band. However, this phenomenon was not too well established in the spectra studied, as it shows best in the overtone region at 7050 cm^{-1} (Bellamy, 1954).

The only characteristic absorptions shown by halogen compounds in the rock-salt region are those arising from the C-X stretching mode. This single- band skeletal mode is subject to considerable frequency alteration as a result of interactions with neighboring groups. This is more true of the lighter F and Cl, the mass of which is not very different from the rest of the carbon skeleton. The C-Br band is more stable in its position.

The spectra of chlorinated compounds appear in a fairly broad range. The C-Cl stretching absorption in compounds with a single Cl should occur in the range 750-700 cm^{-1}. However, in chlorinated aromatics the interactions with $C=C$ raises the frequency as high as 845 cm^{-1}.

o-chlorophenol	82%	750 cm^{-1}	
m-chlorophenol	64%	670	
p-chlorophenol	53%	640	doublet
	31%	690	
2,4-dichlorophenol			

The more complex chlorinated compounds exhbit a reasonably strong band in the expected range but the correlation is of limited value in diagnostic work as the frequency range for this type of substitution is considerably wider. In most compounds in which a number of chlorine atoms are present the fundamental is very intense, also a medium-intensity band may be found at 1510-1470 cm^{-1}, which is possibly the first overtone.

2,4,6-trichlorophenol	75%	730 cm^{-1}	
	40%	705	
Possible overtone	9%	1575	
	7%	1450	
Pentachlorophenol	81%	765	doublet
	61%	700	
Possible overtone	14%	1420	triplet
	80%	1380	
	24%	1350	

It is found that in simple molecules the C-Br absorption occurs in the

600-500 cm^{-1} range, and the presence of more than one bromine may intensify the band or produce more than one band. However, some aromatic compounds have been found to produce two bands when only one bromine was present. When other halogens are present it is difficult to identify the bromine bands unless several bromine atoms are present; then this can be recognized by the intensity.

o-bromophenol	34%	655 cm^{-1}	
m-bromophenol	61%	675	
2,4-dibromophenol	59%	680	
2,4,6-tribromophenol	52%	675	doublet
	34%	660	

It is found in simple molecules that the C-I absorption occurs near 500 cm^{-1}.

o-iodophenol	32%	645 cm^{-1}	
2,4,6-triiodophenol	13%	635	
	24%	625	triplet
	26%	595	
4-bromo-2,6-diiodophenol	5%	750	
	70%	700	triplet
	5%	690	

An extensive examination of twelve trihalogenated phenols (2,4,6) was conducted. The over-all configuration of this ring substitution is tetra (1,2,4,6). The influence of this configuration on the C-H stretching frequency and other regions of the spectrum has been already mentioned.

It may be noted from the following data that greater hindrance of the O-H stretching frequency is found when the 2,6-positions are occupied by larger iodine atoms than when occupied by smaller chlorine atoms. No influence was apparent with the atom in the para position to the hydroxyl group.

2,4,6-trichlorophenol	54%	3530 cm^{-1}	75 width
2,4,6-tribromophenol	54%	3525	70
4-chloro-2,6-dibromophenol	54%	3525	70
2,4,6-triiodophenol	55%	3490	50
4-chloro-2,6-diiodopheno	53%	3495	50
4-bromo-2,6-diiodophenol	53%	3495	50

In the mixed halogenated compounds the trend was apparent but not as definite.

2-chloro-4,6-dibromophenol	55%	3550 cm^{-1}	75 width
2-bromo-4,6-dichlorophenol	51%	3530	70
2-chloro-4,6-diiodophenol	50%	3550	100
2,4-dichloro-6-iodophenol	52%	3520	80
2-bromo-4,6-diiodophenol	56%	3520	70
2,4-dibromo-6-diiodophenol	55%	3520	75

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