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SPECTRA AND STRUCTURE OF SCREENED PHENOLS,THEIR RADICALS AND IONS

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ABSTRACT

The vibrational spectra of screened phenols, stable phenoxyl radicals and ions obtained by addition (loss) of the proton to the phenol molecule, and one-electron reduction (oxidation) of the phenoxyl radical, were studied and interpreted. The proton phototransfer between phenol molecules of the same type in frozen aliphatic hydrocarbon solutions was revealed by luminescence.

RESULTS AND DISSCASION

Changes in the electronic structure of phenols during their conversion to free radicals and ions, as well as the possibility of photoprotolytic reactions were established by IR, Raman, UV-Vis, PMR spectroscopies, luminescent and excited luminescent techniques.

The vibrational spectra of screened phenols (I-IV), phenoxyl radicals (V-VII) and the like quinoid molecules (VIII,IX) are examined and interpreted (see the Figure). Their interpretation was possible by comparing with those of the related molecules and isotope-substituted analogs, as well as, by calculating the frequencies and the modes of vibrations.

The comparison of the spectra for V-VII with those of sterically hindered I-IV indicates that they are essentially different mainly in the high-frequency region where the CC ring and CO group stretching vibrations occur (see Table 1). The spectra of V-VII are shown to resemble markedly those of VIII-IX.

The identity of the spectra for X in KBr, methyl and ethyl alcohols, DMPA and the absence of the counter ion effect indicate that the solid salt has an ionic structure and solvated or free ions are present in solution. The comparison and analysis of the IR spectra for X,II and VI suggest the charge delocalization in the ion along two rings as a result of the disappearance of bands at 1615 and 1158 cm^{-1} assigned to the C=O and C-O (III) stret-

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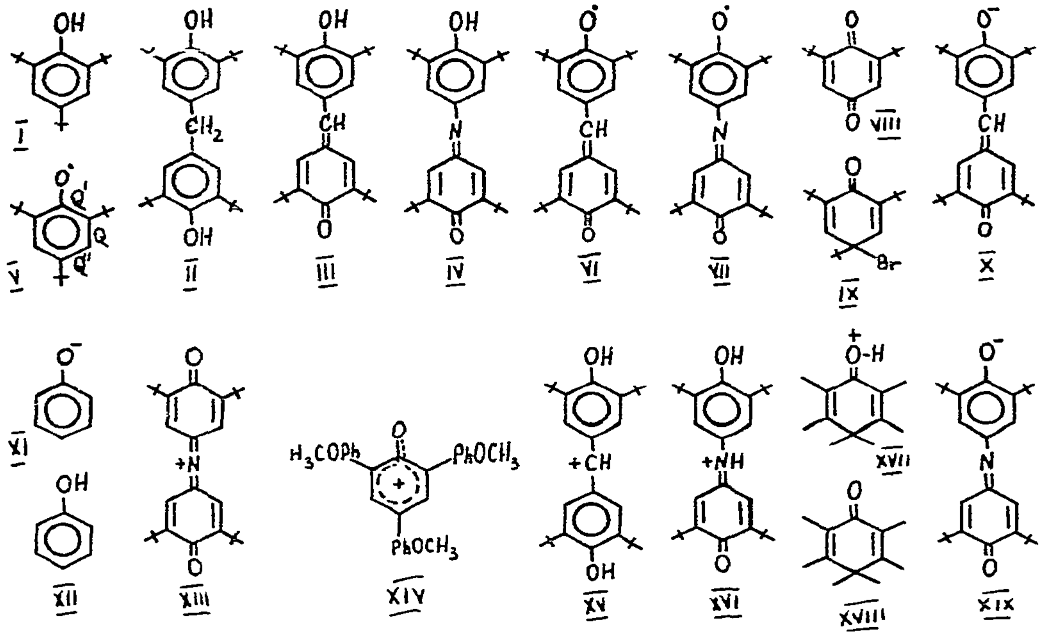

Figure. The compounds studied.

TABLE 1

The CO and CC ring vibrations of frequencies (cm^{-1}) for phenols, phenoxyl radicals and quinoid molecules.

C_{2v}	I		V		IX	
	IR, ν	Assignment	IR, ν	Assignment	IR, ν	Assignment
A_1	1156	q(C-O),q(C-C)	1573	q(C-Ȯ),Q(CC)	1636	q(C=O)
B_1	1436	Q(CC),β(COH)	1506	Q(CC),Q"(CC)	1658	Q(C=C),β(CCH)

C_2	II		VI			VIII		
	IR, ν	Assignment	IR, ν	R, ν	Assignment	IR, ν	R, ν	Assignment
B A	1153	q(C-O),q(C-C)	1583	1601	q(C-O),q(CC) q(C-O),β(CCC)	1656	1670	q(C=O)
A B	1432	Q(CC),β(CCH)	1523		Q'(CC),Q(C=C) Q(C=C),Q"(CC)	1596	1609	Q(C=C)

ching vibrations and the occurence of a band at 1195 cm^{-1} corresponding to the C-O vibration of X. A small increase in the $C-O^-$ vibrational frequency and the force constant, K_{C-O}, of X in comparison with those of III (see Table 2) suggest that a negative charge of X should be localized largely on two oxygen atoms stipulating the similarity of the spectra of X and II.

TABLE 2

Frequencies (cm^{-1}) and force constants (mdyn/Å) of the C-O stretching vibrations in phenols, radicals and ions.

Compound	XII	XI	XVII	V	XVIII
ν_{C-O}	1256(ref.1)	1281(ref.1)	1510(ref.2)	1573	1635(ref.2)
Compound	III	X	XV	VI	
ν_{C-O}	1158	1195(ref.3)	1203(ref.4)	1583	
$\nu_{C=O}$	1615				
K_{C-O}	4.49	4.72	4.90	8.90	
$K_{C=O}$	9.55				
Compound	IV	XVI	VII	XIII	
ν_{C-O}	1156	1203(ref.4)	1586	1625(ref.4)	
$\nu_{C=O}$	1642	1660(ref.4)			

An intensive band at 1625 cm^{-1} is assigned to the C=O vibrations of XIII because judging by the quantum-chemical calculations it should occur between ν_{C-O} of VII (1586 cm^{-1}) and $\nu_{C=O}$ of IV (1642 cm^{-1}). Such an assignment agrees with ν_{C-O} (1613 cm^{-1}) for XIV (ref.5) and a band at 1865 cm^{-1} for XIII which is interpreted as an antisymmetric stretching vibration of the $C=\overset{+}{N}=C$ system.

XV was found to be formed in the interaction of III with acids. The resemblance of its IR spectrum with those of X allowed us to assign these molecules to the same symmetry point group, C_2. It implies that XV has two equivalent rings and two OH groups. It is confirmed by its PMR spectra consisting of four signals with the following chemical shifts (ppm): 1.42(36H,tert-butyl);6.64(2H, hydroxyl); 7.22(4H,ring protons); 7.89(1H,bridge CH). The observed signals are shifted to lower fields as compared to the corresponding signals of III: 1,25;1.36;1.42(tert-butyl); 5.38(hydroxyl); 4.87(bridge proton,CH). It indicates to a positive charge on the product molecule. As the highest shift is observed for the bridge proton ($\Delta\delta$=3.02) the positive charge is largely localized on the CH bridge group C atom. A signal for the protons of tert-butyl groups and a signal for the ring metaprotons indicate that the rings are equvalent.

In the IR spectra for XV the band of the OH group is observed at 3570 cm^{-1}. An intensive band at 1203 cm^{-1} is assigned to the C-O vibration. In IR spectra of XVI obtained by protonation via a N atom of IV one can observe the bands corresponding to the vibrations of phenyl and quinonimine rings. The O-H stretching vibrations (3615 cm^{-1}) for XVI are shifted to lower frequencies as against those of IV (3627 cm^{-1}). A broad band at 3515 cm^{-1} is attributed to the N-H vibration. Shifts of ν_{O-H} and ν_{N-H} to the lower frequencies as compared to those of the neutral molecules show that the N-H bond is stronger than the O-H bond. The observed shifts in frequencies and variations in the force constants indicate to the changes in the structure of the compounds considered. The contribution of quinoid structures is decreased by addition of the proton to the phenol C=O group and an electron to the radical, and it is increased by the electron extraction and addition of the proton to the bridge nitrogen (see Table 2).

Luminescense of the frozen III and IV solutions in a 1:1 n-pentane-isooctane mixture has induced proton phototransfer.

$$III + III \xrightarrow[77K]{h\nu} X + XV; \quad IV + IV \xrightarrow[77K]{h\nu} XVI + XIX;$$

The products obtained were identified by the resemblance of the excited luminescence spectra with the electronic absorption spectra.

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