FUEL AND OIL EVALUATION METHODS

ABSORPTION SPECTRA OF COMMERCIAL ALKYL PHENOLS IN IN THE RANGE 1670-2000 cm^{-1}

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To determine the structures of commercial alkyl phenols (which are intermediates in the synthesis of many additives) we can use not only the 700-1000 cm^{-1} range of extra-planar deformation vibrations of the C—H bonds, but also the 1670-2000 cm^{-1} range, in which we observe overtones and combination tones of these vibrations [1].

According to [2], in this range each type of substitution of the benzene ring has a characteristic spectrum which is not influenced by the nature of the substituents. In this connection, greater importance attaches to the number and relative intensities of the bands than to their exact positions.

The authors have studied alkyl phenols obtained by alkylating phenol with α-octene (b.p. 78°C at 7 mm), α-nonene (b.p. 144-144.5°C at 745 mm), α-cetene (b.p. 142°C at 10 mm), diisobutylene (b.p. ~ 101°C), trimers of propylene* (132-138°C fraction), α-olefins† (120-140 and 240-320°C fractions), and also by alkylating cresols and xylenols‡ with α-octene, n-octanol, and trimers of propylene (130-140°C fraction).

C_8-C_{18} alkyl radicals were found in the following positions: 2-; 4-; 2,4-; 3,4-; 2,6-; 2,4,6-; 3,4,5-; 2,4,5-; 2,3,4- (Tables 1 and 2).

The spectra of these alkyl phenols did not display marked deviations from Joung's law and the number of bands and their relative intensities corresponded to those established by Joung for each type of benzene-ring substitution.

It was found that a knowledge of the exact positions of the bands enables us to make a more detailed study of alkyl phenols, particularly as regards determination of substitution in alkyl phenols with the same type of benzene-ring substitution, the number of large alkyl radicals and their position relative to the hydroxyl group in 2,4-dialkyl phenols.

Figure 1 shows the spectra of the alkyl phenols in the 1670-2000 cm^{-1} range, recorded in a UR-10 spectrophotometer under the following conditions: slit program 4, scanning rate 50 cm^{-1}/min, per recording time 32 sec, movement of paper 32 mm/100 cm^{-1}; we used a 0.612 mm cell with compensation of background absorption by a mesh (50% of the absorption is removed). The solid alkyl phenols were dissolved in carbon tetrachloride (10 wt. %) and photographed in a 1.00 mm cell with compensation of solvent absorption.

o-Alkyl phenols with C_8-C_{18} alkyl radicals have very characteristic and constant spectra. The strong bands have frequencies ~1700, 1782, 1897, and 1930 cm^{-1} (Fig. 1, I).

The spectra of p-alkyl phenols with C_8-C_{18} alkyl radicals (Fig. 1, II) have two strong bands at 1757 and 1880 cm^{-1}. The ratio of the optical densities of these bands is ~2.8.**

According to Montigny and Bichet [4], 2,4-dialkyl phenols Fig. 1, III) do not obey Joung's law. However, this inference applies only to alkyl phenols with two large alkyl radicals. 2,4-Alkyl phenols with one large radical obey the general law.

The spectra of 2,4-alkyl phenols have two strong and two weak bands, observed at 1750-1770 and 1860 to 1880 cm^{-1} and 1810-1830 and 1910-1920 cm^{-1}, respectively.

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† Obtained by N. A. Dmitrieva and V N Vasil'eva (VNII NP).

‡ Synthesized by O. N. Tsvetkov (NGI); the method of preparation was discussed in [3].

** The optical densities were calculated from the base line. The alkyl phenols were photographed in a cell with x = 0.155 mm, with an NaCl window for compensation.

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TABLE 1. Absorption Bands in the 1670-2000 cm^{-1} Range of Alkyl Phenols of the 2-, 4-, 2,4-, and 3,4- Substitution Types

Position of alkyl radicals			Alkylating agent	Frequencies in the 1670-2000 cm^{-1} range						
2-	3-	4-								
sec-C_8	—	—	α-Octene	$\underline{1680}$	(1710)	$\underline{1780}$	1816	1866	$\underline{1897}$	$\underline{1934}$
sec-C_9	—	—	α-Nonene	(1680)	$\underline{1705}$	$\underline{1782}$	1816	1866	$\underline{1897}$	$\underline{1935}$
sec-C_{16}	—	—	x-Cetene	1680	$\underline{1705}$	$\underline{1782}$	1817	1866	$\underline{1896}$	$\underline{1934}$
iso-C_9	—	—	Trimer of propylene, 132-138°C fraction	$\underline{1682}$	(1700)	$\underline{1780}$	1811	1868	$\underline{1897}$	1930
			Total	1680	$\underline{1705}$	$\underline{1782}$	1816	1866	$\underline{1897}$	1934
C_{14}–C_{18}	—	—	α-Olefins, 240-320°C fraction (catalyst, benzene, sulfonic (acid)	$\underline{1684}$	(1712)	$\underline{1782}$	1818	1869	$\underline{1900}$	1935
C_{14}–C_{18}	—	—	The same (KU-2 catalyst)	$\underline{1682}$	(1710)	1778	1813	1865	$\underline{1896}$	1929
—	—	tert-C_8	Diisobutylene	—	—	$\underline{1753}$	—	—	$\underline{1866}$	—
—	—	iso-C_9	Trimer of propylene, 132-138°C fraction	—	—	$\underline{1759}$	—	—	$\underline{1883}$	—
			Total	—	—	$\underline{1757}$	—	—	$\underline{1880}$	—
—	—	C_8	α-Olefins, 120-140°C fraction	—	—	$\underline{1758}$	—	—	$\underline{1884}$	—
—	—	C_{14}–C_{18}	α-Olefins, 240-320°C fraction (catalyst, benzene sulfonic acid)	—	—	$\underline{1756}$	—	—	$\underline{1880}$	—
—	—	C_{14}–C_{18}	The same (KU-2 catalyst)	—	—	$\underline{1757}$	—	—	$\underline{1877}$	—
CH_3	—	sec-C_8	α-Octene	—	—	$\underline{1755}$	1818	—	$\underline{1881}$	1913
CH_3	—	sec-C_8	n-Octanol	—	—	$\underline{1756}$	1813	—	$\underline{1870}$	1915
CH_3	—	iso-C_9	Trimer of propylene, 130-140°C fraction	—	—	$\underline{1756}$	1819	—	$\underline{1875}$	1920
sec-C_8	—	CH_3	α-Octene	—	—	$\underline{1754}$	1814	—	$\underline{1867}$	1920
iso-C_9	—	CH_3	Trimer of propylene, 130-140°C fraction	—	—	$\underline{1755}$	1811	—	$\underline{1863}$	(1915)
sec-C_8	—	sec-C_8	α-Octene	—	—	~ $\underline{1765}$	1825	—	~$\underline{1875}$	1910
			Total	—	—	$\underline{1755}$	1818	—	$\underline{1869}$	1915
—	CH_3	sec-C_8	α-Octene		1710	1740	—	—	$\underline{1875}$	—
—	CH_3	sec-C_8	n-Octanol	—	1714	1740	1810	—	$\underline{1877}$	—
—	CH_3	iso-C_9	Trimer of propylene, 130-140°C fraction	—	1700	1740	1792	—	$\underline{1882}$	—
			Total	—	1707	1740	1800	—	$\underline{1880}$	—

Note: The figures in brackets indicate bends in the main band; the frequencies of the strongest bands are underlined.

TABLE 2. Absorption Bands in the 1670-2000 cm^{-1} Range of Alkyl Phenols of the 2,6-, 2,3,4-, 2,4,5-, 2,4,6-, and 3,4,5- Substitution Types

Position of the alkyl radicals					Alkyl agent	Frequencies in the 1670-2000 cm^{-1} range						
2-	3-	4-	5-	6-								
sec-C_8	–	–	–	sec-C_8	α-Olefins, 240-320°C fraction (catalyst, benzene sulfonic acid)	1644	1693	–	–	1794	1851	1907
C_{14}–C_{18}	–	–	–	C_{14}–C_{18}		1654	1698	–	1767	1796	1856	1915
C_{14}–C_{18}	–	–	–	C_{14}–C_{18}	The same (KU-2 catalyst)	1646	1698	–	1770	1796	1856	1915
CH_3	CH_3	sec-C_8	–	–	α-Octene	–	–	1714	1732	–	1865	–
CH_3	CH_3	sec-C_8	–	–	n-Octanol	–	–	1710	1730	–	1865	–
					Mean	–	–	1712	1731	–	1865	–
CH_3	–	sec-C_8	CH_3	–	α-Octene	–	–	1710	1765	–	1870	1923
CH_3	–	sec-C_8	CH_3	–	n-Octanol	–	–	1710	1760	–	1870	1920
sec-C_8	–	CH_3	CH_3	–	α-Octene	–	–	1710	1760	–	1875	1930
sec-C_8	–	CH_3	CH_3	–	n-Octanol	–	–	1710	1757	–	1880	1927
					Mean	–	–	1710	1760	–	1875	1925
sec-C_8	–	CH_3	–	CH_3	α-Octene	–	–	–	1743	–	–	1910-1920
sec-C_8	–	CH_3	–	CH_3	n-Octanol	–	–	–	1743	–	–	1910
CH_3	–	sec-C_8	–	CH_3	α-Octene	–	–	–	1742	–	–	1913
					Mean	–	–	–	1742	–	–	1910
–	CH_3	sec-C_8	CH_3	–	α-Octene	–	~1700	–	–	–	1888	–
–	CH_3	sec-C_8	CH_3	–	n-Octanol	–	~1700	–	–	–	1885	–
					Mean	–	~1700	–	–	–	1886	–

Note: The frequencies of the strongest bands are underlined.

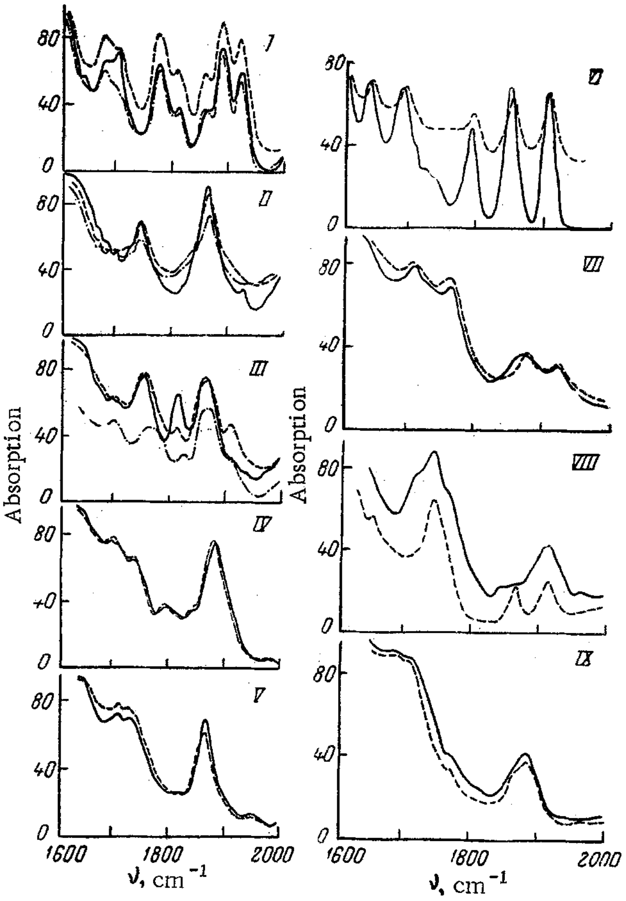

Fig. 1. Spectra of alkyl phenols in the range 1670-2000 cm^{-1}. The alkyl radicals are in the following positions: 2-; (I)—2-sec-cetyl; – – –)2-sec-octyl; –·–)C_{14}–C_{18}; 4-; (II). C_{14}–C_{18}; – – –)4-iso-nonyl; – · –) 4-tert-octyl; 2,4-; (III) —·—)2-sec-octyl-4-methyl; – – –)2-methyl-4-sec-octyl; –· –)2,4-di-sec-octyl; 3,4-; (IV) ——)3-methyl-4-sec-octyl; ——)3-methyl-4-iso-nonyl; 2,3,4- (V) ——)2,3-dimethyl-4-sec-octyl (alkylating agent—octene); – – –)2,3-dimethyl-4-sec-octyl (alkylating agent n-octanol; 2,6-; (VI) ——)2,6-di-sec-octyl; – – –)C_{14}–C_{18}; 2,4,5-; (VII) ——)2,5-dimethyl-4-sec-octyl; – – –)2-sec-octyl-4,5-dimethyl; 2,4,6-; (VIII) ——)2-sec-octyl-4,6-dimethyl; – – –)2,6-dimethyl-4-sec-octyl; 3,4,5-; (IX) —)3,5-dimethyl-4-sec-octyl (alkylating agent n-octanol); – – –)3,5-dimethyl-4-sec-octyl (alkylating agent α-octene).

In the case of 2,4-alkyl phenols the 1755 cm^{-1} band has a constant position and its intensity is close to that of the 1860-1880 cm^{-1} band. The ratio of the optical densities of these bands is 1-1.5. In di-sec-octylphenol this band is displaced to ~1770 cm^{-1} and becomes much weaker than the 1860-1880 cm^{-1} band; the ratio of the optical densities increases to 2.0.

The displacement of the 1810-1830 and 1860-1880 cm^{-1} bands varies with the type of radical adjoining the hydroxyl group. If a methyl group is present in the ortho position, the bands have frequencies ~1817 and 1873 cm^{-1}. If the methyl group is in the para-position, the bands are displaced to ~1812 and ~1865 cm^{-1}. If large alkyl radicals are present in the 2,4-position, the bands appear at 1825 and 1870-1880 cm^{-1}.

The intensity of the 1810-1830 cm^{-1} band varies from medium in alkyl phenols with large alkyl radicals in the ortho position to weak in those with large alkyl radicals in the para-position.

In the case of 3,4-dialkyl phenols (Fig. 1, IV) which, like 2,4-dialkyl phenols, belong to the same type of 1,2,4-substitution of the benzene ring, the spectra are different to those of 2,4-alkyl phenols: we observe one intense band at 1880 cm^{-1} and the remaining bands at 1707, 1740, and 1800 cm^{-1} are weak.

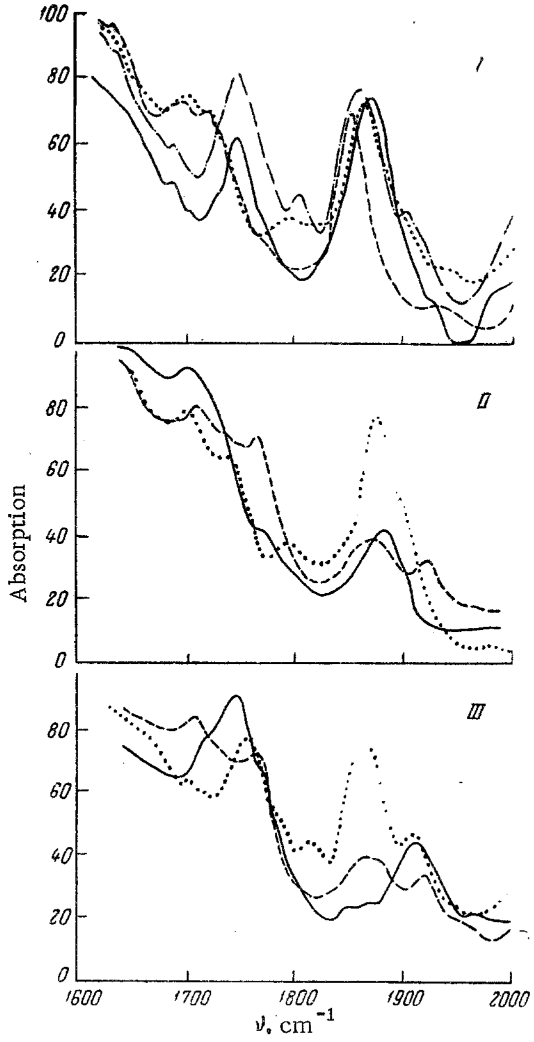

Fig. 2. Relation between particular absorption bands of alkyl phenols in the range 1670-2000 cm^{-1} and the following vibrations: I) two neighboring unsubstituted C—H bonds; substitution type: ——)4-; – · –)2,4-; . . . .)3,4-; – – –)2,3,4-; II) an isolated C—H bond adjoining the hydroxyl group; substitution type: ——)3,4,5-; – – –)2,4,5-; . . . .)3,4-; III) an isolated C—H bond at a considerable distance from the hydroxyl group; substitution type: ——)2,4,6-; – – –)2,4,5-; . . . .)2,4-.

The spectra of 2,4,6- (Fig. 1, VIII) and 3,4,5-trialkyl phenols (Fig. 1, IX), which belong to the 1,2,3,5-type of benzene ring substitution, also differ from one another as regards intensity and position of the bands. The spectra of 2,4,6-alkyl phenols have bands at 1742 and 1910 cm^{-1}, and those of 3,4,5-alkyl phenols at ~1700 and 1886 cm^{-1}.

It is evident that this regularity in the spectral difference of alkyl phenols of different structure, belonging to the same type of benzene ring substitution, will be observed for all pairs of alkyl phenols and will help us to determine the structures of alkyl phenols.

The spectrum of 2,3,4-trialkyl phenol (Fig. 1, V) is like that of 3,4-dialkyl phenol. However, the strong isolated band is displaced to 1865 cm^{-1} and is narrower because the absorption due (as explained below) to vibration of the isolated C—H bond, adjoining the hydroxyl group, disappears. The two other weak bands have frequencies 1712 and 1731 cm^{-1}.

The spectra of 2,6-dialkyl phenols (Fig. 1, VI) have five strong bands (1644, 1696, 1795, 1853, and 1907 cm^{-1}), of which the positions and relative intensities do not change as we go from alkyl phenols with C_8 radicals to those with C_{18} radicals.

The spectra of 2,4,5-trialkyl phenols (Fig. 1, VII) have four bands of different intensities with mean frequencies 1710, 1760, 1875, and 1925 cm^{-1}.

From a study of the spectra of 27 specimens of alkyl phenols with different types of substitution, we established a relation between particular bands in the 1670-2000 cm^{-1} range and the vibrations of the two neighboring unsubstituted C—H bonds and the C—H bonds at a considerable distance from the hydroxyl group or adjoining it.

Alkyl phenols with two neighboring unsubstituted hydrogen atoms, i.e., those with 4-, 2,4-, 3,4-, and 2,3,4-substitution, have strong absorption bands at 1860-1885 cm^{-1}. It is difficult to assess the type of substitution from the frequency of this band, but it can be determined fairly simply with the aid of the other part of the spectrum in the 1670-2000 cm^{-1} range (Fig. 2, I).

Alkyl phenols with an unsubstituted isolated C—H bond adjoining the hydroxyl group (3,4-, 3,4,5-, and 2,4,5-substitution) are characterized by absorption in the range 1700-1710 cm^{-1} and a band of medium intensity at about 1883 cm^{-1} (Fig. 2, II).

Alkyl phenols with an unsubstituted isolated C—H bond at a considerable distance from the hydroxyl group (2,4-, 2,4,6-, and 2,4,5-substitution) absorb at ~1750 and 1915 cm^{-1}; the bands are of high and medium to weak intensity, respectively (Fig. 2, III).

It should be noted that in the spectrum of 4-alkyl phenol the intensity of the band corresponding to vibrations of the two neighboring unsubstituted C—H bonds is greater than the intensities of the analogous bands in the spectra of 2,4-, 3,4-, and 2,3,4- alkyl phenols (Fig. 2, I) because the contribution to the vibration is made by two pairs of unsubstituted neighboring C—H groups.

A similar picture is observed for the 1886 and 1910 cm^{-1} bands (Fig. 2, II and III), corresponding to vibrations of isolated C—H bonds adjoining the hydroxyl group or at a considerable distance from it. It is evident that if two C—H groups of identical position participate in the vibration, the bands due to these vibrations are stronger.

This investigation has revealed a number of regularities in the spectra of alkyl phenols in the 1670-2000 cm^{-1} range; these can help us to determine the structures not only of individual hydrocarbons, but also of particular commercial fractions used for the synthesis of various additives.

SUMMARY

1. The authors have shown that we can determine the position of a substituent in alkyl phenols with the same type of benzene ring substitution, the number of large alkyl radicals, and their position relative to the hydroxyl group in 2,4-dialkyl phenols.

2. A relation has been established between particular absorption bands and vibrations of the C—H bonds.

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