stirring the yellow solid was filtered and recrystallized from benzene to give an 80% yield of product, m.p. 160° (with decomposition).

*Anal.* Calcd. for $C_{18}H_{15}BiS$: S, 6.78. Found: S, 6.79.

**Triphenylmercaptobismuth.**—Refluxing a mixture of 4.4 g. (0.01 mole) of triphenylbismuth, 5.5 g. (0.05 mole) of thiophenol and 25 ml. of xylene for 15 hours gave a quantitative yield of the product, needles, m.p. 90–91°, after recrystallization from absolute alcohol.

*Anal.* Calcd. for $C_{18}H_{15}BiS_3$: S, 17.93. Found: S, 17.20.

Identity was further established by a mixed m.p. with the product obtained by the reaction of anhydrous bismuth chloride and thiophenol.[4]

**Tri-*o*-carbomethoxyphenylmercaptobismuth.**—This compound was obtained in 78% yield as described above in the preparation of triphenylmercaptobismuth. The product had a m.p. of 141–143°, after recrystallization from petroleum ether.

*Anal.* Calcd. for $C_{24}H_{21}BiO_6S_3$: S, 13.52. Found: S, 13.14, 13.21.

**Phenylbismuth Thiosalicylate.**—A mixture of 4.4 g. (0.01 mole) triphenylbismuth and 1.4 g. (0.01 mole) thiosalicylic acid was heated in a graphite-bath at 150° for one hour. The fused solid was powdered, and triturated successively with hot benzene, chloroform and ether. The product was insoluble in all the solvents tested and could not be recrystallized. It did not melt up to 250°.

*Anal.* Calcd. for $C_{13}H_9BiO_2S$: Bi, 47.73. Found: Bi, 47.55.

**α-Naphthyldiphenylmercaptobismuth.**—Diphenyl-α-naphthylbismuth, 2.45 g. (0.005 mole), 0.55 g. (0.005 mole) of thiophenol and 25 ml. of chloroform were refluxed three hours, cooled, the precipitated solid filtered and recrystallized from chloroform to give 0.35 g. of α-naphthyldiphenylmercaptobismuth, which did not melt up to 240°.

*Anal.* Calcd. for $C_{22}H_{17}BiS_2$: S, 11.98. Found: S, 11.55.

The recovery of unreacted diphenyl-α-naphthylbismuth was 0.7 g.

When a mixture of 2.95 g. (0.005 mole) of tri-α-naphthylbismuth and 0.55 g. (0.005 mole) of thiophenol in 25 ml. of xylene was refluxed two hours and cooled there was recovered 2.81 g. of unreacted bismuth compound, m.p. and mixed m.p. with an authentic specimen, 229°. A qualitative test for sulfur in the recovered material was negative.

**Phenylbismuth Dicinnamate.**—When a mixture of 4.4 g. (0.01 mole) of triphenylbismuth and 1.4 g. of cinnamic acid were heated in a graphite-bath at 150°, a vigorous reaction set in and benzene refluxed. The heating was continued for 1.5 hours. The cooled mass was pulverized and triturated thoroughly with ether. The residual white powder, 1.1 g. (20% yield) which did not melt up to 230°, was insoluble in all solvents and could not be recrystallized.

*Anal.* Calcd. for $C_{24}H_{19}BiO_4$: Bi, 36.29. Found: Bi, 36.72.

The recovery of triphenylbismuth was 2.7 g. (61%).

**Phenylbismuth Dibenzoate.**—This compound was prepared in 44% yield by heating molecular equivalents of benzoic acid and triphenylbismuth for two hours on the steam-bath. The crude product was purified as above for the dicinnamate, m.p. 215–216°.

*Anal.* Calcd. for $C_{20}H_{15}BiO_4$: Bi, 39.59. Found: Bi, 40.48, 40.58.

**Cleavage of Triphenylbismuth with Thioglycolic Acid.**—The reaction was carried out between 4.4 g. of triphenylbismuth and 0.92 g. of thioglycolic acid in 25 ml. of benzene. The yellow solid was triturated with solvents as above and the product was obtained as a yellow powder.

*Anal.* Calcd. for $C_8H_7O_2SBi$: S, 8.51. Calcd. for $C_6H_9O_6S_3Bi$: S, 19.92. Found: S, 16.97.

AMES, IOWA RECEIVED NOVEMBER 1, 1950

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CONTRIBUTION OF THE RESEARCH AND DEVELOPMENT BRANCH, OFFICE OF SYNTHETIC LIQUID FUELS, BUREAU OF MINES]

# Infrared Spectra of Phenols

BY R. A. FRIEDEL

Infrared spectra are presented for 22 phenols, principally the simple alkyl derivatives. The well known steric hindrance effect of ortho-substituents on the OH band is demonstrated. On the basis of the OH bands at concentrations of 4.70 mole per cent. in $CS_2$, the phenols are divided into four main classes: (1) no ortho-substituents, (2) one methyl group in the ortho position, (3) larger than methyl group in the ortho position, and (4) two methyl groups in both ortho positions. These classes differ as to band position or absorption intensity or both; intensities within a class are constant to within ±3% absorption.

The infrared spectra of various alkylphenols have been published by Whiffen and Thompson,[1] Kletz and Price,[2] Richards and Thompson,[3] and Friedel, Pierce and McGovern.[4] The present paper records the spectra of 14 alkylphenols with methyl or ethyl substituents, and 8 phenols which have larger substituents or poly-ring systems. These spectra cover the range from 7.5 to 15 microns, and from 2.5 to 3.5 microns, where investigation of intermolecular association involving the OH group can be made (Figs. 1 and 2). A method of quantitative analysis for phenol and the $C_7$ and $C_8$ alkylphenols (Fig. 1) was reported previously.[4]

Intermolecular association in phenols, and the effect of steric hindrance thereon, have been discussed by various authors. Coggeshall[5] demonstrated the strong hindrance to association of large alkyl groups, ortho to the OH, by showing the variation in spectral shifts between dilute solutions and the solid states. Richards and Thompson[3] demonstrated the same effect and gave examples showing the hindering effect of methyl groups in positions ortho to the OH. Sears and Kitchen[6] in a recent paper have achieved finer distinction between various steric hindrance effects by comparison of phenols in solution, liquid and solid states. They arrived at an empirical "hydrogen bonding index," which correlates gradual spectral shifts with methyl and larger groups in one and in both positions ortho to the OH.

## Experimental

The Perkin–Elmer Model B spectrometer was used in this work. Measurements were made in carbon disulfide solutions, concentrations of which are indicated on the spectra. Transmittance or

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(2) T. A. Kletz and W. C. Price, *ibid.*, 644 (1947).

(3) R. E. Richards and H. W. Thompson, *ibid.*, 1260 (1947).

(4) R. A. Friedel, L. Pierce and J. J. McGovern, *Anal. Chem.*, **22**, 418 (1950).

(5) N. D. Coggeshall, THIS JOURNAL, **69**, 1620 (1947).

(6) W. C. Sears and L. J. Kitchen, *ibid.*, **71**, 4110 (1949).

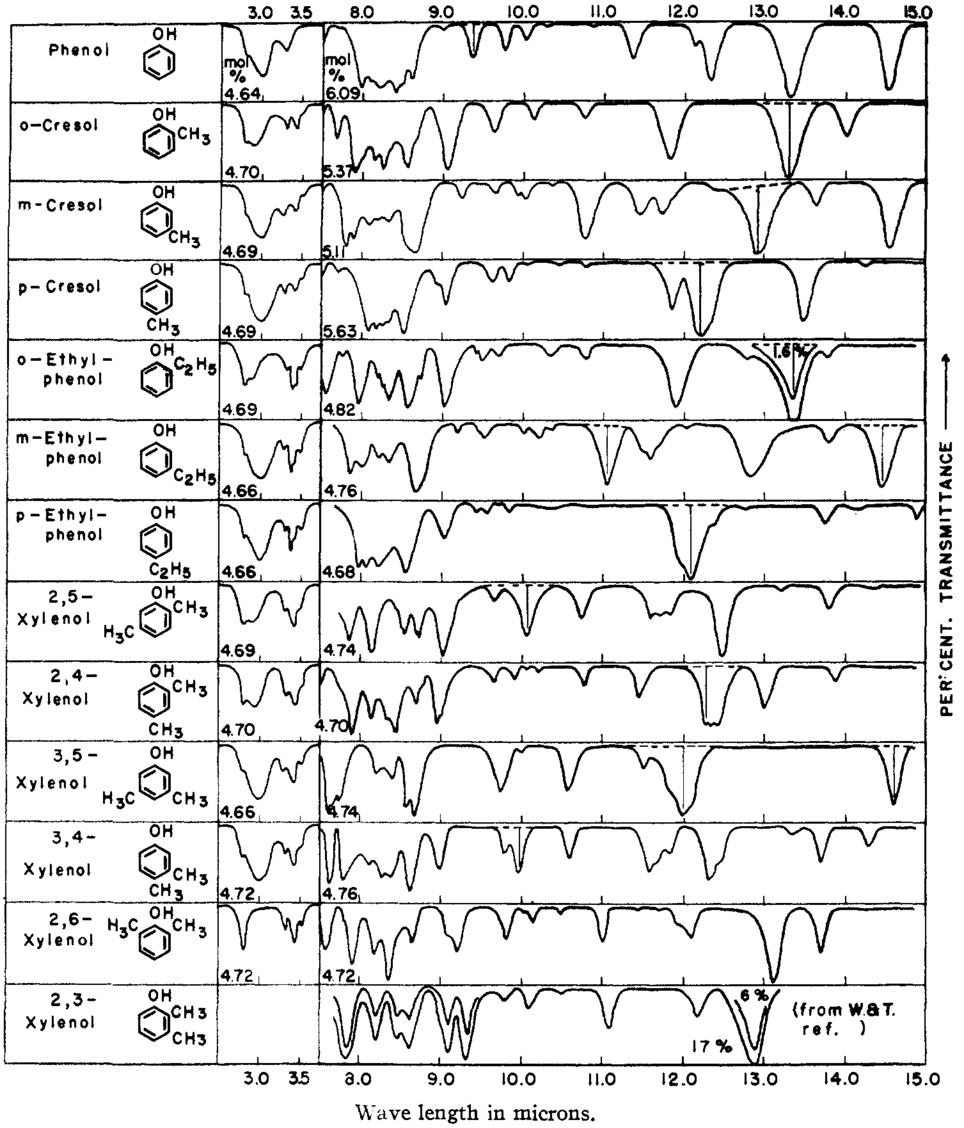

Fig. 1.—Infrared spectra of phenol, $C_7$, and $C_8$ alkylphenols in $CS_2$ solutions (concentrations in mole per cent. as indicated); absorption bands and base lines used in analysis are indicated.

absorption values in the hydroxyl region were obtained by comparison with the cell filled with pure $CS_2$. Values for the spectra from 7.5 to 15 microns were obtained by the base line technique.[4]

## Discussion

**Wave Length Shifts Due to Association.**—In this Laboratory the hydroxyl region of the spectra of phenols have been investigated in solution (about 4.70 mole per cent. in $CS_2$). Variations of wave length shifts with steric hindrance of substituents were found similar to those reported by others. For example, hindered *o*-cresol at this concentration produces a sharp free-OH band at 2.80 and a broad associated-OH band near 2.90 microns. Unhindered *m*- and *p*-cresols have weak bands at the 2.80 micron free-OH position but larger broad bands at the associated-OH position that lies at 3.01 microns. Wave length positions of the associated-OH bands for all the phenols investigated are given in Table I along with differences (shifts) between these and the free-OH band positions (2.79–2.80 microns).

**Band-intensity Correlation.**—The principal point in this investigation was the search for possible correlations of band intensities. It was found that phenol, the three $C_7$'s (cresols), 8 of the $C_8$'s (xylenols and ethylphenols—series complete except for 2,3-xylenol), and most of the more complex phenols correlated satisfactorily. They were classified into four major groups, varying from no hindrance to strong hindrance according to substituents ortho to the hydroxyl group: (1) *No substituent ortho to the OH:* The broad associated-OH band occurs at 3.00–3.01$\mu$. The average absorption intensity for 10 phenols of this type is 73.2 ± 2.1%. (2) *$CH_3$ or $CH_2$ groups ortho to the OH:* The associated-OH band occurs at 2.89–2.93$\mu$. (a) *$CH_3$ or $CH_2$ in 6-membered ring:* Four phenols of this type show an average intensity of 54.1 ± 2.8%. (b) *$CH_2$ in 5-membered ring.* (3) *$C_2H_5$ or larger groups ortho to the OH:* A weak associ-

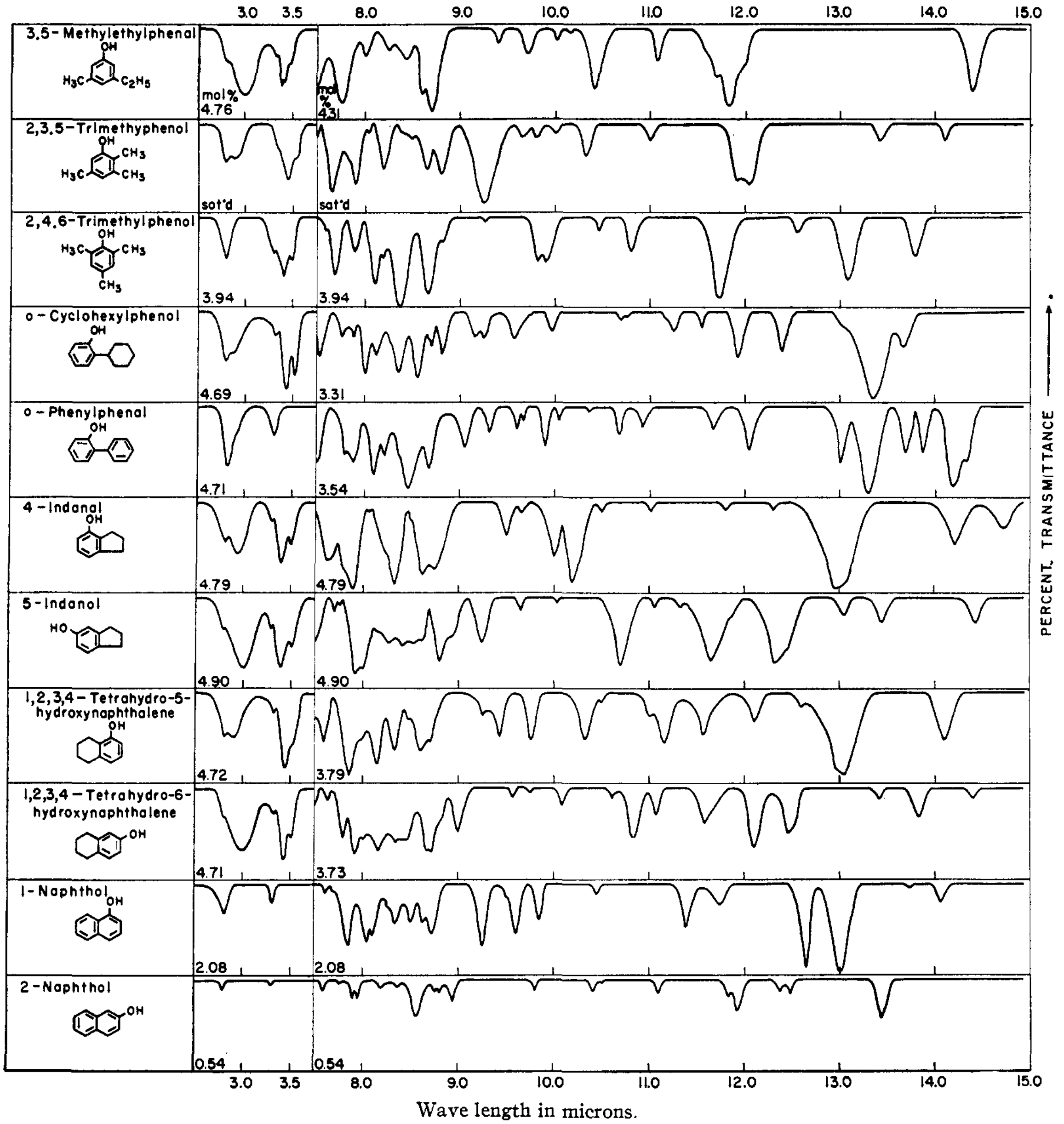

Fig. 2.—Infrared spectra of higher phenols; $CS_2$ solutions (concentrations in mole per cent. as indicated).

ated-OH band shoulder occurs at 2.89–2.93μ. (4) *$CH_3$ groups in both positions ortho to the OH:* No associated-OH band or shoulder occurs (at concentrations of 4.70 mole per cent.).

The absorption intensities are listed in Table I. The fair constancy found indicates that considerable qualitative and quantitative information concerning the OH bands in a phenol, or mixtures of some phenols, may be gained by determining the spectrum of the OH region at an appropriate concentration.

**Comparison of Meta and Para Band Intensities.**—Compounds having alkyl substituents para to the –OH produce slightly more intense OH bands than do the corresponding compounds with meta alkyl groups. Thus, the –OH bands for *p*-cresol and *p*-ethylphenol are more intense than those of the meta compounds; 2,4-xylenol produces greater intensity than 2,5-xylenol; 3,4-xylenol shows a slightly more intense band (nearly equal) than 3,5-xylenol.

**Polycyclic Phenols.**—Several additional correlations may be pointed out. Of the two $C_9$ dicyclic phenols studied, 5-indanol (Fig. 2), with the –OH group meta to both ends of the alicyclic five-membered ring, is similar to *m*- and *p*-cresols; that is, no hindrance exists. 4-Indanol (Fig. 2) is similar to, but shows more association than, *o*-cresol. This is due to the lesser hindrance of the 4-indanol $CH_2$ group which is bent away from the OH by the sharp angles of the 5-membered ring. In this connection it is interesting to compare 4-indanol with the corresponding dicyclic $C_{10}$ phenol, 5-hydroxyl-1,2,3,4-tetrahydronaphthalene, which has the –OH ortho to the 6-membered ring. The stronger 3.0 micron band, which indicates greater

TABLE I

ASSOCIATED-OH BANDS OF PHENOLS. CORRELATION OF BAND INTENSITY AND WAVE LENGTH POSITION WITH STERIC HINDRANCE OF ORTHO-SUBSTITUENTS

Concentrations, 4.70 ± 0.06 mole per cent. in $CS_2$[a]

| No ortho-substituent | Wave length, microns | Wave length shift from free-OH band | Absorption (1 − transmittance) at 2.89–2.93μ band, % | Absorption (1 − transmittance) at 3.00μ band, % |
|---|---|---|---|---|
| Phenol | 3.01 | 0.21 | .. | **69.4** |
| *m*-Cresol | 3.01 | .21 | .. | 72.6 |
| *p*-Cresol | 3.01 | .21 | .. | 76.8 |
| *m*-Ethylphenol | 3.00 | .21 | .. | 71.9 |
| *p*-Ethylphenol | 3.00 | .21 | .. | 73.7 |
| 3,5-Xylenol | 3.01 | .21 | .. | 72.4 |
| 3,4-Xylenol | 3.00 | .21 | .. | 72.6 |
| 3,5-Methylethylphenol | 3.01 | .21 | .. | 74.8 |
| 5-Indanol | 3.00 | .21 | .. | 78.0[b] |
| 5,6,7,8-Tetrahydro-2-hydroxynaphthalene | 3.00 | .20 | .. | 69.6[c] |
| | | | Average | 73.2 ± 2.1 |
| $CH_3$ or $CH_2$ in ortho position $CH_3$, $CH_2$ in 6-membered ring | | | | |
| 5,6,7,8-Tetrahydro-1-hydroxynaphthalene | 2.90 | 0.10 | 52.0 | .. |
| *o*-Cresol | 2.90 | .11 | 56.9 | .. |
| 2,5-Xylenol | 2.90 | .10 | 50.5 | .. |
| 2,4-Xylenol | 2.93 | .13 | 57.0 | .. |
| 2,3,5-Trimethylphenol | 2.90 | .10 | 42.0[d] | .. |
| | | Average (of first 4) | 54.1 ± 2.8 | |
| $CH_2$ in 5-membered ring | | | | |
| 4-Indanol | 2.93 | 0.14 | 67.5 | .. |
| $C_2H_5$ or larger in ortho position | | | | |
| *o*-Ethylphenol | 2.90 | 0.10 | 46.9 (sh) | .. |
| *o*-Cyclohexylphenol | 2.89 | .09 | 45.5 (sh) | .. |
| *o*-Phenylphenol | 2.89 | .07 | 37.7 (weak sh)[e] | .. |
| | | Average (of first 2) | 47.2 ± 0.7 | |
| $CH_3$ in both ortho positions | | | | |
| 2,6-Xylenol | .. | .. | .. (2.80 only) | .. |
| 2,4,6-Trimethylphenol (3.95%) | | .. | .. (2.80 only) | .. |

[a] Data for 1- and 2-naphthol are not included in the table, since low solubility in $CS_2$ prevented obtaining their spectra at concentrations comparable to those of the other phenols. [b] Value high, partly because of concentration, 4.90 mole per cent. [c] Purity questionable. [d] Saturated solution; less than 4.70 mole per cent. [e] Aromatic substituent.

association for 4-indanol, again may be attributed to the sharper angles and therefore less hindrance of the $C_5$ ring.[7]

**Solvent Effect.**—The effect of solvent on compounds containing OH groups is well known from the work of Gordy,[8] Fox and Martin[9] and others. Recently Tuttke and Mecke[10] have reported on infrared investigations which show that the association effects on phenol due to various solvents increase in the order: polychloromethanes and ethanes (including chloroform) < carbon disulfide < benzene. All of this work has been done in dilute solutions in which intermolecular association between solute molecules is not a factor. In the present work the concentrations are sufficiently great so that intermolecular association is the predominant occurrence. The magnitude of the effect of three solvents on the OH band of 2,5-xylenol is indicated in Fig. 3; association increases in the order: benzene < chloroform < carbon disulfide. These results may be correlated simply with the atomic dimensions of the solvent molecules. The larger benzene molecule is, as expected, the best "insulator" for the prevention of intermolecular association between solute molecules.

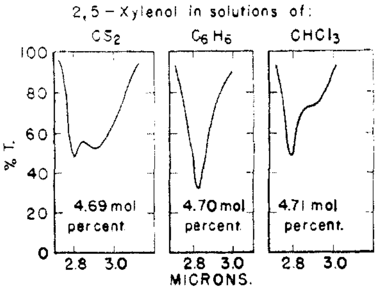

Fig. 3.—Variation with solvent of infrared absorption in the OH region.

**Acknowledgments.**—Thanks are due Marion Springer and Robert Zange for determination of the spectra.

BRUCETON, PENNA. RECEIVED AUGUST 2, 1950

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(10) V. W. Tuttke and R. Mecke, *Z. Elektrochem.*, **53**, 241 (1949).