

INFRARED SPECTROSCOPIC STUDY OF HYDROGEN BONDING: HYDROGEN BOND ASSOCIATION OF PHENOLS WITH DIOXAN*

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Introduction

A number of studies have been made on the frequency shifts that occur when phenol is dissolved in dioxan. Many of these have attempted to attribute shifts in O-H stretching frequency to hydrogen bond association between phenol and dioxan. This approach is illustrated by the studies of Freymann,¹ Gordy and Nielsen,² and Lindeberg.³ Hydrogen bond association of phenol and dioxan in carbon tetrachloride was studied from infrared spectra by Flett,⁴ Tsuboi,⁵ and Allerhand and Schleyer.⁶ Flett evaluated free energies and heats of formation of hydrogen bonds between phenol and dioxan, while Tsuboi estimated the dissociation energy of intermolecular hydrogen bonds between proton donor (phenol) and proton acceptor (dioxan). Allerhand and Schleyer studied the variation of frequency shift due to change in concentration of dioxan. It appears that no systematic study has been made so far about the effect of the substituent in the proton donor on the frequency shift. The present study was taken up with a view to examine the substitute effect on frequency shift due to hydrogen bond formation between substituted phenols and dioxan.

Experimental

Purification of Materials

The phenols (obtained from Riedel) employed were all liquids except phenol and *p*-chlorophenol. All the liquid phenols were dried over anhydrous sodium sulphate for about 24 hr and then distilled. If a preliminary spectrum indicated impurities, the compounds were redistilled. Phenol (Rhodia sample) and *p*-chlorophenol (E. Merck) were used without further purification.

Dioxan (B.D.H.) and carbon tetrachloride (E. Merck) were purified by the methods reported earlier by Naidu and Krishnan.⁷ The spectral purity of these compounds was ascertained from infrared spectra.

The spectra of phenols in dioxan were studied at low concentration to minimize solute-solute interactions. Infrared spectroscopic measurements were made with a Perkin-Elmer 221 infrared spectrophotometer. The spectral resolution in O-H stretching frequency is of the order of 2 cm^{-1} and the results are accurate to within $\pm 5\text{ cm}^{-1}$ for the broad bands of hydrogen bonded groups. All the measurements were made at room temperature (25°). Since the stretching frequency of phenolic O-H bond in the mixtures of phenols in dioxan was close to the stretching

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¹ Freymann, R., *C. r. hebd. Séanc. Acad. Sci., Paris*, 1937, **204**, 41.

² Gordy, U. W., and Nielsen, A. H., *J. chem. Phys.*, 1938, **6**, 12.

³ Lindberg, J. J., *Acta Soc. Sci. fenn.*, 1957, **20**, 5.

⁴ Flett, M. St. C., *J. Soc. Dyers Colour.*, 1952, **68**, 59.

⁵ Tsuboi, M., *J. chem. Soc. Japan (pure Chem.)*, 1951, **72**, 146.

⁶ Allerhand, A., and Schleyer, P. R., *J. Am. chem. Soc.*, 1963, **85**, 371.

⁷ Naidu, P. R., and Krishnan, V. R., *Trans. Faraday Soc.*, 1965, **61**, 1347.

frequency of phenolic O-H in phenol polymers, the spectra of phenols in dioxan and carbon tetrachloride were studied with a view to distinguish the stretching frequency of O-H bond in phenol polymer from that present in phenol-dioxan polymer.

Results

Hydrogen bonded O-H stretching frequencies and "free" O-H stretching frequencies in mixtures of phenols with dioxan in carbon tetrachloride are presented in Table 1.

TABLE 1
STRETCHING FREQUENCIES (cm^{-1}) IN CARBON TETRACHLORIDE

Substance	$\nu(\text{O-H})$ "Free"	$\nu(\text{O-H})$ Phenol-Dioxan	$\Delta\nu$
Phenol	3612	3378	234
<i>o</i> -Cresol	3613	3380	233
<i>m</i> -Cresol	3612	3380	232
<i>p</i> -Cresol	3613	3380	233
<i>o</i> -Chlorophenol	3542 <i>cis</i> 3608 <i>trans</i>	3340	268*
<i>m</i> -Chlorophenol	3604	3334	270
<i>p</i> -Chlorophenol	3609	3350	259

* Calculated on basis of *trans* form.

Hydrogen bonded O-H stretching frequencies of phenols in mixtures with dioxan are presented in Table 2.

TABLE 2
STRETCHING FREQUENCIES (cm^{-1}) IN DIOXAN

Substance	$\nu(\text{O-H})$ Phenol-Dioxan	$\Delta\nu$
Phenol	3338	272
<i>o</i> -Cresol	3340	270
<i>m</i> -Cresol	3340	270
<i>p</i> -Cresol	3340	270
<i>o</i> -Chlorophenol	3295	313
<i>m</i> -Chlorophenol	3290	314
<i>p</i> -Chlorophenol	3310	299

Values of $\Delta\nu$ listed in Table 2 are obtained as the difference between "free" O-H stretching frequencies observed in the spectra of phenols in carbon tetrachloride and the hydrogen bonded stretching frequencies given in Table 2.

Discussion

The shifts in O-H stretching frequencies of the different phenols in dioxan and of the phenols-dioxan mixtures in carbon tetrachloride indicate hydrogen bond association between phenols and dioxan. The variation in $\Delta\nu$ values listed in Tables 1 and 2 shows that the strength of the hydrogen bond in each case depends on the

electron density on the oxygen of the O-H group which is influenced by the substituent present in the different phenols. In the three isomeric cresols, while we expect the methyl group to enhance electron density on phenolic oxygen by an inductive effect and consequently to decrease the strength of the hydrogen bond with dioxan, as compared to that between phenol and dioxan, the observed values of $\Delta\nu$ rule out any appreciable effect of methyl groups.

The shifts in O-H stretching frequencies observed in mixtures of the three isomeric chlorophenols with dioxan differ appreciably from the $\Delta\nu$ value of phenol-dioxan system, as is to be expected due to the influence of chloro group on the polarization of O-H group in the chlorophenols. Chlorine in the chlorophenols pulls electrons inductively from the nucleus, causing a net decrease in electron density on oxygen in O-H group conducive to the formation of a stronger hydrogen bond between chlorophenols and dioxan than between phenol and dioxan. The observed value of $\Delta\nu$ in mixtures of chlorophenols in dioxan supports this contention, in the order expected of *ortho*, *meta*, and *para* chloro substituents.

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