Correlation of O–H Stretching Frequencies in Phenols and Catechols with Chemical Reactivities

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The O–H stretching frequencies have been studied for a series of substituted catechols and phenols. The frequency shifts produced by substitution have been related to Hammett's σ values.

It has been shown[2a] that substances capable of intramolecular hydrogen bonding such as catechol may exhibit two O–H vibration frequencies, one corresponding to a hydrogen bonded or "bound" hydroxyl and the other to the non-hydrogen bonded or "free" hydroxyl. The effects of ortho-substituents which combine both steric and electronic effects on the frequency of the bound hydroxyl absorption have been extensively studied[2b] by infra-red spectroscopy. However, little is known concerning the electronic effects of substituents, *per se*, apart from steric effects. By studying substituents in other than the ortho position, steric effects can be largely eliminated. Some of the needed spectroscopic data for the evaluation of the electronic effects have become available from investigations carried on at this Laboratory on enzymatic browning of fruits. In these investigations various substituted catechols and phenols are being used as model substrates for tyrosinase. Infrared absorption data for these substrates allowed us to make an analysis of the electronic effects of substituent groups upon both the intramolecularly bound and free hydroxyl stretching frequencies.

Several investigators have shown relationships between stretching frequencies and chemical reactivities to exist for other types of compounds. Flett[3] has shown that the reactivities of substituted aromatic acids, amines and aldehydes are correlated with the infrared frequencies of the functional groups. The frequencies were found to be almost a linear function of Hammett's σ functions[4] used to relate the reaction rate and equilibrium constants of a series of *m*- and *p*-substituted benzene derivatives. Similar relations for O–H stretching frequencies have been found by Linnett,[5] who has shown that the O–H stretching force constant varies with the charge on the oxygen atom in the series water, methanol and phenol, and by Batuev, Meshcheryakov and Matveeva,[6] who noticed the O–H stretching frequency of three alcohols increased with decreasing acidity. The bound hydroxyl frequency of methanol-*d* has been shown to be a linear function of the basic *pK* of the solvent.[7]

It will be shown in this paper that the frequency shifts produced by substitution in phenols and catechols can also be related to Hammett's σ values.[4]

Experimental

Materials.—The catechols used in this study have been described in a previous paper.[8] The phenols are all commercially available. The *m*-cresol, *p*-chlorophenol, *m*-ethylphenol were purified by distillation under reduced pressure. The hydroquinone monobenzyl ether, hydroquinone monomethyl ether and *p*-hydroxybenzaldehyde were crystallized from water and dried over phosphorus pentoxide *in vacuo*. The *m*-aminophenol was crystallized from toluene. The other compounds were used without further purification. The solvents, carbon tetrachloride and tetrachloroethylene, were distilled from phosphorus pentoxide and used within three days after distillation.

Absorption Spectra.—Dilute (<0.006 *M*) solutions of the compounds in carbon tetrachloride and in tetrachloroethylene were examined at 27.7° in the 3 micron region of the spectrum with a Beckman Model IR-3 spectrophotometer using fluorite prisms and an absorbing path length of 1.15 cm. At these low concentrations intermolecular hydrogen bonding is unimportant.[9] The positions of the absorption maxima of the symmetrically shaped bands were reproducible to ± 1 cm.[-1]. Absolute accuracy of the band positions is ± 3 cm.[-1]. Tetrachloroethylene was used as a solvent in addition to carbon tetrachloride because of the limited solubility of several of the compounds in the latter.

Results and Discussion

The various O–H stretching frequencies of the compounds studied are listed in Table I. In Figs. 1 and 2 we have plotted the O–H stretching frequencies against Hammett's σ values.[4] The linear relationship

$$\nu = \nu_0 + \rho_\nu \sigma \qquad (1)$$

has been fitted to the data by the method of least squares[10] with the resulting standard differences between observed and calculated values of ν listed in Table II. The dotted lines represent an estimated uncertainty of ± 1 cm.$^{-1}$ in frequency and ± 0.06 unit[4] in σ. The majority of the σ values are those given by Hammett.[4] The acid dissociation constants of 4-benzyloxy,[11] 3-hydroxy[12] and the 4-carbalkoxy ester[13] derivatives of phenols and benzoic acids were used to calculate the corresponding σ values using Hammett's ρ-values[4] for acid dissociation. Either the meta or the para σ value, whichever was the larger (σ_1), was used for the bound hydroxyl and the smaller value (σ_2) was used for the free hydroxyl. This corresponds to assuming that of configurations I and II in equi-

(1) United States Department of Agriculture, Agricultural Research Administration, Bureau of Agricultural and Industrial Chemistry. Article not copyrighted.

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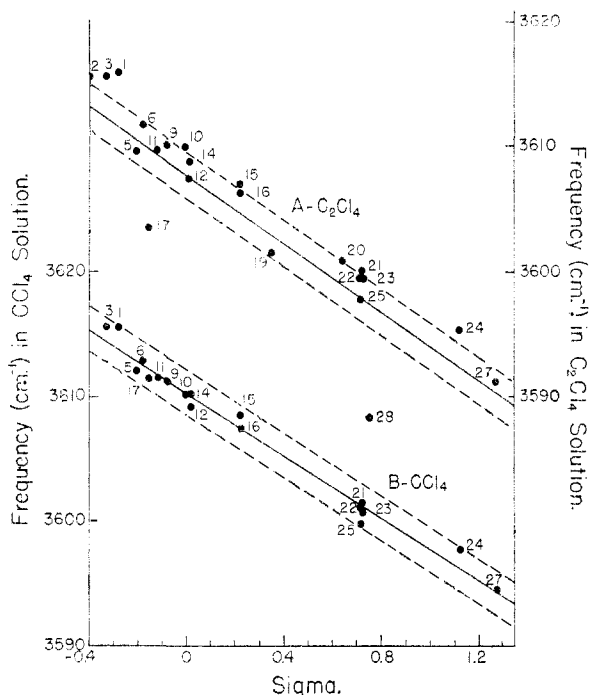(13) E. E. Sager, M. R. Schooley, A. S. Carr and S. F. Acree, *J. Research Natl. Bur. Standards*, **35**, 521 (1945).

Fig. 1.—Curve A, O–H stretching frequency of phenols in tetrachloroethylene *vs.* σ values; curve B, O–H stretching frequency of phenols in carbon tetrachloride *vs.* σ values.
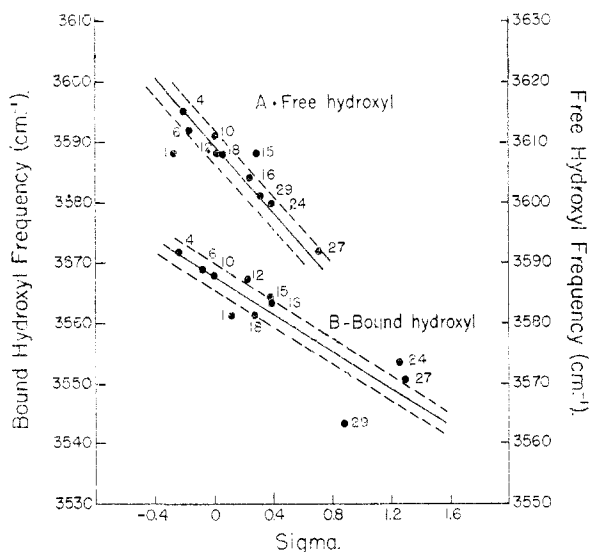

Fig. 2.—A, the frequency of the free hydroxyl of catechol in tetrachlorethylene *vs.* the smaller σ value; B, the frequency of the bound hydroxyl of catechol in tetrachloroethylene *vs.* the larger σ value.

librium, that form predominates in which the oxygen of the free OH group bears the greater effective negative charge. Thus a 4-substituted catechol
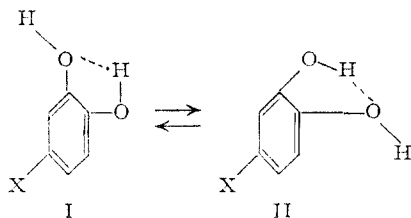

TABLE I
HYDROXYL FREQUENCIES (CM.$^{-1}$) OF VARIOUS SUBSTITUTED PHENOLS AND CATECHOLS

No.	Substituent	Phenol CCl$_4$	Phenol C$_2$Cl$_4$	Catechol (C$_2$Cl$_4$) Free	Catechol (C$_2$Cl$_4$) Bound
1	4-Methoxy	3615.6	3616.0	3608.5	3561.4
2	4-Hydroxy		3615.6		
3	4-Benzyloxy	3615.6	3615.6		
4	4,5-Dimethyl			3615.6	3572.1
5	4-t-Butyl	3612.1	3609.7	3612.5	3569.8
6	4-Methyl	3612.8	3611.7	3612.5	3569.0
7	4-Benzyl		3610.5		
8	3-Ethyl	3610.9	3610.1		
9	3-Methyl	3611.3	3610.1		
10	None	3610.1	3610.1	3611.7	3568.2
11	3,5-Dimethyl	3611.7	3609.7		
12	4-Phenyl	3609.3	3607.4	3608.5	3567.5
13	4-Trityl			3608.5	3568.2
14	3-Hydroxyl	3610.1	3608.9		
15	4-Chloro	3608.5	3607.0	3606.2	3564.4
16	4-Bromo	3607.4	3606.2	3604.6	3563.7
17	3-Amino	3611.7	3603.5		
18	4-Fluoro			3608.5	3561.4
19	3-Carboxy		3601.5		
20	4-Phenylazo		3600.7		
21	4-Carbo-n-butoxy	3601.5	3599.9		
22	4-Carboethoxy	3601.1	3599.2		
23	4-Carbomethoxy	3600.7	3599.2		
24	4-Formyl	3597.6	3595.3	3600.0	3553.8
25	3-Nitro	3599.9	3597.6		
26	4-Propionyl		3596.9		
27	4-Nitro	3594.5	3591.1	3592.2	3550.8
28	4-Carboxy		3588.3		
29	4-Acetyl			3601.5	3543.2
30	4-Benzoyl			3601.5	3537.2

TABLE II
CALCULATED ρ-VALUES FOR VARIOUS SERIES

Series	Independent variable	Standard difference[a,10] (cm.$^{-1}$)	ρ_ν
Catechol bound hydroxyl in C$_2$Cl$_4$	σ_1	±4.3	−15.9
Catechol free hydroxyl in C$_2$Cl$_4$	σ_2	±3.0	−27.0
Catechol free hydroxyl in C$_2$Cl$_4$	$\sigma_2 + 0.5\sigma_1$	±1.7	−11.9
Phenol free hydroxyl in CCl$_4$	σ	±0.8	−12.6
Phenol free hydroxyl in C$_2$Cl$_4$	σ	±3.0	−14.4[b]

[a] Difference in observed frequency and that calculated from equation 1 assuming no error in the σ value used. [b] When the compounds not studied in the CCl$_4$ solvent are omitted this value reduces to −13.2.

is assumed to exist primarily in form I if the para σ value exceeds the meta σ value for substituent X, or in form II if the meta σ-value is algebraically the larger.

The values of ρ_ν for Equation 1 (listed in Table II) depend upon the solvent and the parent compound of the series. The sign of ρ_ν should be a measure of the direction of the dipole in the bond to which the frequency refers.

Consideration of each O–H stretching frequency of 4-substituted catechols as a function of either the meta or para σ value only, neglects the modification of the interaction between the two hydroxyl groups[8] due to the introduction of the substituent. This is probably the reason why the ρ_ν value for the free O–H frequency of catechols differs so greatly from that for phenols in the same solvent. If we allow for this inductive effect across the hydrogen bond by using $\sigma_2 + \alpha\sigma_1$ as the independent variable, a

value of $\alpha = 0.5$ results in a ρ_ν value approximately equal to that for phenol. In addition, a better fit of experimental points is obtained, as shown by the standard differences in Table II.

It is of interest to note that the ρ_ν values for

phenols in carbon tetrachloride and tetrachloroethylene are found to be approximately the same (-12.6 and -13.2) when only data for the same compounds in each solvent are used.

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Carbanionic Copolymerization Studies

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Relative reactivity ratios have been determined for the carbanionic polymerization of vinyl butyl sulfone–acrylonitrile catalyzed by sodium in liquid ammonia. Similar data were obtained on the carbanionic copolymerization of styrene–acrylonitrile and methyl methacrylate–acrylonitrile; however, reactivity ratios could not be determined in these systems because of a side reaction in the former system and the large difference in monomer reactivities in the latter system. The relative reactivity of vinyl butyl sulfone in carbanionic copolymerization is consistent with the proposed effect of structure on reactivity. Steric effects have been suggested as a possible explanation of the tendency for alternation of monomer units in the vinyl butyl sulfone–acrylonitrile copolymerization.

Recent work[1] has clearly shown the large differences in relative monomer reactivities in the three mechanisms of vinyl polymerization: free radical, carbonium ion and carbanion. In fact, copolymer composition affords the most direct method of determining polymerization mechanism.

The free radical mechanism of polymerization has been so extensively studied that an adequate theory of monomer reactivity has been established which effects a theoretical correlation of these data and can be used to predict, fairly accurately, monomer reactivity ratios in systems that have not been experimentally investigated.

However, very little experimental work has been done on the determination of monomer reactivity ratios for copolymerizations catalyzed by ionic mechanisms. There are many reasons for this. The number of monomers that readily polymerize by either a carbonium ion or a carbanion mechanism is small. In addition, differences in reactivity between individual monomers are so large that few monomer pairs easily yield copolymers containing appreciable proportions of both monomers. Also, both carbanion and carbonium ion polymerizations yield low molecular weight polymers in a large proportion of the possible systems, especially when the less reactive monomers are used. All of these factors account largely for the general lack of technical interest in ionic catalyzed copolymers.

The present work includes studies on the carbanionic copolymerization of three monomer pairs using sodium in liquid ammonia as catalyst.

Experimental

Acrylonitrile obtained from American Cyanamide Corporation was distilled before use. Physical constants found were b.p. 77.0° at 740 mm., $n^{20}D$ 1.3916.

Methyl methacrylate obtained from Resinous Products and Chemical Co. was distilled before use. Physical constants found were b.p. 100.2° at 733 mm., $n^{20}D$ 1.4150.

Styrene obtained from Koppers Company, Inc., was distilled under reduced pressure. Physical constant found was $n^{21}D$ 1.5450.

Vinyl butyl sulfone was prepared in this Laboratory. Physical constants found were b.p. 115–116° (4 mm.), $n^{20}D$ 1.4632, molecular refraction 37.62 (calcd.), 38.04 (obsd.).

All monomers were tested for the absence of polymer before use by adding a sample to methanol.

The experimental procedure was the same as that described in a previous publication[2] with the following exceptions. The copolymerizations of acrylonitrile–vinyl butyl sulfone were conducted at $-78°$. The copolymerizations of styrene–acrylonitrile were conducted at $-40°$, and 140 cc. of ether was added as solvent. The higher temperature and the ether were necessary to make the reaction mixture one phase. The copolymerizations of acrylonitrile–methyl methacrylate were run at the temperature of the previous experiments, $-55°$. In the purification of the copolymers by reprecipitation, dimethylformamide was used as solvent and methanol as precipitant for many of the copolymers.

The compositions of all copolymers were determined by nitrogen analyses, using the theoretical per cent. nitrogen for acrylonitrile, 26.40.

An experiment was conducted to obtain evidence that some of the styrene monomer was not available for copolymerization in the reactions of styrene–acrylonitrile with sodium in liquid ammonia. The experiment was conducted like the other copolymerizations except that an excess of the catalyst was employed. The initial charge consisted of 23.31 g. of acrylonitrile and 23.31 g. of styrene. A yield of 24.29 g. of copolymer was produced. Duplicate nitrogen analyses yielded values of 24.10 and 24.22%, average value 24.16%. The copolymer accounts for 22.23 g. of acrylonitrile and 2.06 g. of styrene. This corresponds to 95.4% of the initial charge of acrylonitrile and 8.8% of the initial charge of styrene. The difficulty in obtaining a complete material balance on the acrylonitrile was probably due to the violence of the reaction. The above data indicate that a large portion of the styrene monomer is not available for copolymerization with acrylonitrile. These data, together with the published work[3] on the reaction of styrene with sodium in liquid ammonia, indicate strongly that a large portion of the styrene monomer is reduced to ethylbenzene under the conditions of the present experiments.

Results

Below, in tabular form, are the experimental results obtained in the three copolymerization systems.

TABLE I

STYRENE–ACRYLONITRILE

Initial styrene charge, g.	Initial acrylonitrile charge, g.	Yield, g.	N in copolymer, %
20.04	17.20	0.50	23.04, 23.00
29.08	12.60	3.35	23.22, 23.25
69.39	7.80	2.41	23.20, 23.08
26.32	11.04	0.83	22.95, 23.00
17.98	16.10	0.86	23.00, 23.20

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