[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

The Effect of Ortho Substitution on the Absorption of the OH Group of Phenol in the Infrared[1]

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Infra-red absorption that is characteristic of the presence of NH and OH groups in organic molecules exhibits in general a dependence upon the character of the rest of the molecule, particularly upon that of neighboring groups.[2] In the present researches the spectra of such molecules are being measured quantitatively, giving the results as curves of the molal absorption coefficient against position in the spectrum. This dependence of the spectra upon the constitution of the rest of the molecule indicates that this type of measurement will be powerful as a means of studying molecular structure, when a satisfactory theory of this type of spectrum is developed. Among the compounds showing the influence of neighboring groups on NH or OH absorption, the ortho substituted derivatives of phenol are, in some respects, the simplest.

Certain groups, when substituted ortho to the phenolic OH, lead to the formation of a hydrogen bond.[3] In these cases it has been shown that the absorption normally characteristic of the presence of the OH group in the region 6500–7500 cm.$^{-1}$ is absent, and this has been developed as an empirical criterion for the presence of such hydrogen bonds. On the other hand, other groups, when substituted ortho to the phenolic OH, do not cause the OH absorption to disappear, but they frequently do alter it in an interesting way. These cases are important in that they give positive results, that is, they afford some absorption which may be studied quantitatively to investigate this dependence on neighboring groups in the molecule. In a previous paper[2] the simplest representative of this latter class of compound was *o*-chlorophenol. In the present paper results are given for a number of ortho substituted phenols.

It is the purpose of this research to present as broad a survey as possible of this general type of absorption in organic molecules rather than to undertake as yet a detailed study of a few. It seems wiser to adopt this attitude, leaving an intensive study of single compounds until the theory of the absorption is developed to a point that warrants this. However, under these conditions it is necessary to emphasize, as has already been done, that minor characteristics of the absorption curves, such as slight displacements or dissymmetries, should not be given credence until an exhaustive study of the particular compound is made. Similarly, failure to show any absorption at some particular point must not be construed as meaning that very weak absorption may not be present there.

Experimental Procedure

The experimental details have already been described.[2] The absorption is measured in dilute carbon tetrachloride solution usually of the order of 0.01 molal. In the case of each compound presented below, at least two separate records were taken using two different solutions.

Certain of the compounds used were purchased from the Eastman Kodak Company and others were synthesized by methods already outlined in the literature. In every case some of their properties were checked with those recorded in the literature. In a few cases where there was some question as to the purity of the product, as was true in the case of pyrogallol and pyrogallol dimethyl ether, the absorption was studied before and after recrystallization and where no noticeable alteration in the spectrum was effected, it was assumed that the observed spectrum was essentially due to the compound itself. It is important to emphasize that the presence of very small amounts of impurities is not of great consequence in this work. Insofar as they do not contain the group being studied (*i. e.*, OH or NH) their presence can practically be neglected, while if they do contain such a group, their effect is simply proportional to the amounts present. If present in small amount, their effect will be a small alteration of the absorption curve, and minor characteristics, found in any of these curves, must be checked by further experimental work before being given importance, because of the rather wide limits of experimental error in the quantitative determination of the absorption coefficients themselves.[2]

Since pyrogallol and 1,8-dihydroxynaphthalene are only slightly soluble at room temperature, they were run at 60° as well, in order to secure an adequate concentration of the substance and hence of the absorption. Since no definite effect of temperature was observed, the runs at room temperature and at 60° were used together in determining the final or average curve.

Results

The curves, given in Fig. 1, present the results

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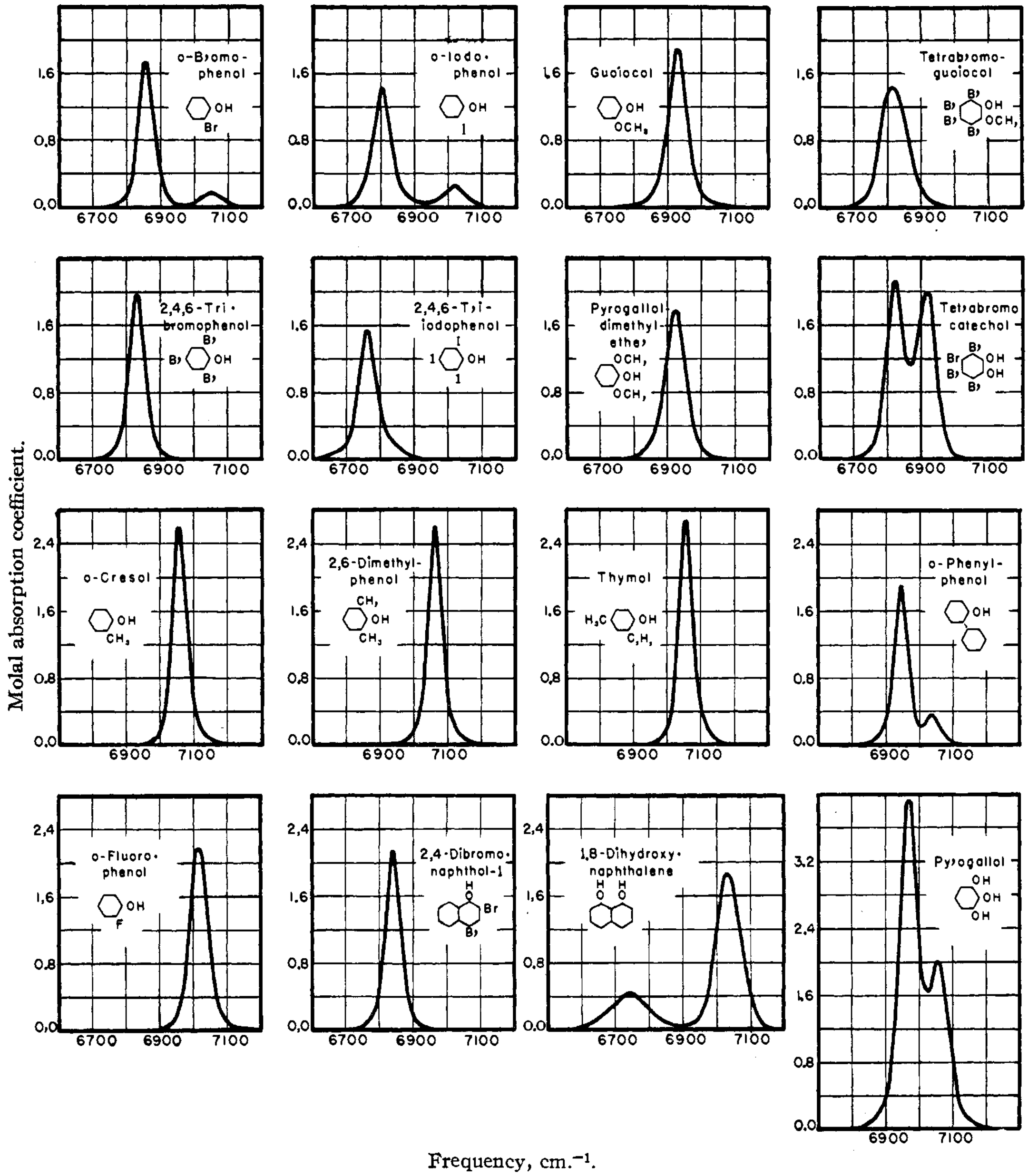
[1] Preliminary report of this work was presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at Kansas City, Mo., in April, 1936.

[2] Wulf and Liddel, THIS JOURNAL, **57**, 1464 (1935).

[3] Hilbert, Wulf, Hendricks and Liddel, *Nature*, **135**, 147 (1935); THIS JOURNAL, **58**, 548 (1936); **58**, 1991 (1936). See also Errera and Mollet, *Compt. rend.*, **200**, 814 (1935); *J. phys. radium*, **6**, 281 (1935).



Frequency, cm.$^{-1}$.

Fig. 1.—Molal absorption coefficients for some ortho substituted phenols.

in sufficient detail so that little further description need be given. In those cases where one of the ortho hydrogens of phenol remains, an absorption peak at approximately the phenol frequency is present. In most of the others this peak is missing, the evident exception being 2,6-dimethylphenol. In Table I the areas under the absorption curves are given, as was done in reference 2 where the areas for those compounds whose curves were published in that paper may be found.

A word must be said regarding the region 7100–7400 cm.$^{-1}$. Atmospheric water vapor absorption lies here, and makes observation difficult. Additional absorption of considerable strength would not be missed, and could be read though with less accuracy than that in other regions. It would, however, be possible to miss weak absorption, especially on days of high humidity, and therefore our curves must not be construed as indicating no absorption in this region. This applies to all results which we have published. Very weak absorption due to OH lies in this region. During an attempt to study in detail the effect of temperature upon the *o*-chlorophenol ab-

TABLE I

Substance	Molal absorption area, liter/sq. cm. mole
o-Bromophenol	125
o-Iodophenol	125
Guaiacol	145
Tetrabromoguaiacol	145
2,4,6-Tribromophenol	125
2,4,6-Triiodophenol	120
Pyrogallol dimethyl ether	140
o-Cresol	155
2,6-Dimethylphenol	150
Thymol	150
o-Phenylphenol	130
o-Fluorophenol	160
2,4-Dibromonaphthol-1	130
1,8-Dihydroxynaphthalene	235
Tetrabromocatechol	290
Pyrogallol	440

sorption, two further weaker peaks to higher frequencies were discovered while working on a very cold and dry winter day and at high concentrations. The weakest of these is probably due to OH, while the other might be ascribed to either OH or CH. There is indication that weak absorption in this region occurs in several if not all of the present compounds. It is not practical to measure this, however, at the concentrations used in this work, and no effort has been made to indicate its presence in the absorption curves. Hence reiteration of the words at the beginning of this paragraph must be made here to avoid misunderstanding.

Discussion

In reference 2 a simple theoretical discussion of the characteristics of this type of spectra was given, in which possible causes for the appearance of more than one single peak after substitution, as well as for pronouncedly broadened peaks, were mentioned. It was suggested that the appearance of several frequencies (peaks) of absorption was due to a coupling of the OH or NH group with a near-by group of similar frequency. Pauling has suggested recently[4] that the complexity of the spectra is due rather to two or more types of OH or NH groups having different characteristic frequencies. He points out that, because of resonance with other structures besides those of the Kekulé type, the C–O bond in phenol possesses some double bond character, which tends to cause the OH group to lie in the plane of the ring. The OH group then can orient itself stably in two positions which in phenol, however, are equivalent. Though different from phenol, these two positions are also equivalent for a symmetrical ortho disubstituted phenol, but not for the unsymmetrical case and are thus different for mono-ortho substituted phenols. In general, the OH group in the two forms of such a molecule, called by Pauling *cis* and *trans* forms, will lead to different characteristic absorptions. Furthermore, the amounts of the two different forms of molecule, present in equilibrium with one another, evidently will depend upon the difference in free energy between the two forms. There is, however, no evident quantitative relation between the free energy difference of any one pair of *cis* and *trans* forms and the frequency difference of their absorptions.

This interpretation is the only specific description of this type of absorption which we now have. It will therefore be helpful to attempt to interpret the present results as far as possible in accordance with it, in order to see to what extent it accounts for the observations.

Attempting now to interpret the absorption curves in terms of this picture, *o*-bromo- and *o*-iodophenol show in a similar way as does *o*-chlorophenol[2] two distinct peaks, one (*trans* form) approximately at the normal phenol frequency. The other peak (*cis* form) lies to lower frequencies and by a progressively increasing amount in the order *o*-chloro-, *o*-bromo-, *o*-iodophenol, indicating a progressively increasing proton attraction in this order. The increasing polarizability of the ortho substituent is the most evident way of accounting for this, and the result indicates that the dipole moments in the ortho groups $C^+ \text{---} {}^-X$, where X is the halogen, are relatively unimportant since the dipole moments for these groups are in the opposite order, thus that of C–Cl being considerably greater than that for C–I. This may seem reasonable from the circumstance that the dipole is oriented approximately at right angles to the direction toward the H atom. A rough measure of the increase in polarizability is given by the change in the molecular refractivities of the three monohalogen substituted benzenes, which are *o*-chloro 31.1, *o*-bromo 34.0 and *o*-iodo 39.2, respectively, for sodium D, these values being computed from data taken from the "International Critical Tables," Vol. VII, p. 34.

In the case of *o*-fluorophenol a single peak occurs but this peak is somewhat broad and has its maximum at about 7015 cm.$^{-1}$, an appreciably

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[4] Pauling, THIS JOURNAL, **58**, 94 (1936).

lower frequency than that of the *trans* peak in the other three analogous ortho substituted phenols. The broadening is in accord with the hypothesis that the *o*-fluorophenol absorption is comprised of two frequencies as in the case of the other three compounds, one at about 7050 cm.$^{-1}$ and the other at 7015 cm.$^{-1}$ and that in this case they largely overlap one another.

In the symmetrical 2,4,6-trichloro-, tribromo- and triiodophenols but one peak appears, the *cis* peak, since the two positions of the OH group are now the same, and are *cis* in character. The peak in each case lies moreover at approximately the same position as the *cis* peak of the respective three mono-ortho substituted derivatives. Actually in all three cases the peak in the symmetrical tri-substituted compounds is slightly but definitely at a lower frequency than the *cis* peak of the respective ortho substituted compound. The difference, while rather small, appears to be real.

Where the ortho substituent is a group of atoms rather than a single atom, the situation is more complicated. In this case it is difficult to see what the combined effect of polarizability and of the several variously oriented dipoles within the group might be. However, several such compounds were measured and it is interesting to consider the character of the absorption which they afforded.

o-Cresol and thymol show only a single prominent peak at about the normal phenol frequency. In the case of *o*-cresol it is probable that proton repulsion would characterize the *cis* form because of the rather close proximity of the hydrogen of the hydroxyl group to the hydrogen atoms of the methyl group. The single peak could be interpreted either as due to equal amounts of *cis* and *trans* forms of practically the same frequency, analogous with phenol, or as due to the *trans* form alone, the *cis* form being of different frequency and of much greater free energy, hence not present in appreciable amounts. From the geometry of *o*-cresol the first alternative presumably is the more reasonable. While the situation in thymol is not so simple as in *o*-cresol, the absorption appears to be of the same type. But the choice between the two possible interpretations in the case of *o*-cresol is substantiated by the absorption of 2,6-dimethylphenol. Here both positions of the O–H group are *cis* positions, and still a single peak of roughly the phenol area and at approximately the phenol frequency appears.

Again, in *o*-hydroxybenzonitrile[5] the absorption consists of two peaks, a small one (*trans*) at approximately the normal phenol frequency and a larger one (*cis*) at a somewhat lower frequency, indicating a small proton attraction by the substituent group.

The spectrum of *o*-phenylphenol (2-hydroxydiphenyl) interpreted in terms of the same picture, also shows appreciable amounts of both *cis* and *trans* forms of the molecule present. This is of considerable interest since it suggests a conclusion as to the structure of the rest of the molecule. If the two rings were coplanar as they are crystalline diphenyl, the hydrogen atoms of the hydroxyl group would be in very close proximity to the near-by hydrogen of the substituted ring, even allowing severe distortion of the valence angles. The strong resultant repulsion would ensure the presence of only a *trans* form. Since both forms are found it is to be concluded from the picture that the two rings do not lie in the same plane, and indeed, from the geometry of the system, that they are considerably removed from such position even as they are in optically active diphenyl derivatives. With the two rings swung far out of a common plane the first carbon atom of the ortho substituted ring lies closest to the hydroxyl hydrogen, and if this near-by carbon atom exercises an appreciable proton attraction, this would lead to a *cis* form of lower energy than the *trans* form, and could give rise to the two peaks.

Especial interest attaches, moreover, to guaiacol. Proton attraction by the oxygen of the methoxy group might be expected, and this appears to be present. A comparison with the absorption of catechol helps to make the guaiacol absorption more understandable. As presented in reference 2, catechol shows two peaks of equal intensity, one at the normal phenol frequency, the other at a considerably lower frequency. Pauling has interpreted these as arising from a *cis* and a *trans* form within the same molecule, the hydrogen of one of the hydroxyl groups being in the *cis* position owing to the proton attraction of the neighboring oxygen, but the hydrogen attached to this second oxygen having only the *trans* position left to it, strong proton repulsion presumably preventing both hydroxyls turning toward one another. This second (*trans*) OH group is thus essentially the same as the OH

[5] Hendricks, Wulf, Hilbert and Liddel, THIS JOURNAL, **58**, 1991 (1936).

group of phenol. In guaiacol one of the two hydroxyl hydrogens of catechol is removed, leaving, however, the corresponding hydroxyl oxygen in its old position. This leaves for the remaining hydroxyl group the *cis* position as the position of lowest energy. The guaiacol peak (*cis*) lies at a slightly lower frequency than the *cis* peak of catechol.

Important in a closely similar way is the absorption of 3-nitrocatechol, the curve for which has already been published.[3] Its absorption is very nearly the same as that of guaiacol. In 3-nitrocatechol the hydrogen of the hydroxyl group nearest the NO_2 group engages in a hydrogen bond, removing the OH absorption of this hydroxyl group. The remaining OH group shows the *cis* form absorption just as does guaiacol.

It appears, however, that in guaiacol and 3-nitrocatechol the difference in free energy between the *cis* and *trans* forms of the available OH group is greater than it is for instance in *o*-chlorophenol, *o*-hydroxybenzonitrile or even *o*-iodophenol, since no absorption due to a *trans* form can be seen. This is a necessary conclusion of the stereochemical interpretation *unless* the absorption coefficients for the two forms are greatly different from one another, in contrast to what is presumed to be true in the case of catechol. It has already been shown[2] that the absorption coefficient can be somewhat altered by the presence of another neighboring group.

In guaiacol the O–C of the methoxy group must be thought of as in the *trans* position, and this leaves an appreciable dipole moment (the O–C moment) so oriented as to give a resultant proton attraction. This might account for the deeper energy minimum in which the *cis* OH of guaiacol seems to lie as compared with the OH of *o*-iodophenol. Furthermore, it seems necessary to conclude that this greater free energy difference does not necessarily mean a greater shift in the absorption frequency for here the guaiacol peak is at a considerably higher frequency than is, for example, the peak of the cis form of *o*-iodophenol. It would appear that this could be the case. The form of the potential curve in which the vibrating hydroxyl swings will be different where simply the polarization of a near-by atom, such as the iodine atom, is concerned than it will where, as in guaiacol, the permanent dipole moment of another group, here the O–C moment, is so oriented as to exert attraction for the proton of the hydroxyl group. In this respect 3-nitrocatechol is similar except that here the active *cis* OH faces an OH locked in a hydrogen bond with the oxygen atom of the NO_2 group.

Pyrogallol shows a particularly interesting absorption. It is clear that, from the explanation suggested by Pauling for catechol, one would expect in pyrogallol a molecule possessing two *cis* OH groups and one *trans* group. In other words the third OH group when added to catechol finds the *cis* position available for it just as the *cis* position was available to the second group when added to phenol. The absorption of pyrogallol shows two peaks, one (*trans*) at approximately the normal phenol frequency and possessing an area approximately equal to phenol. The other peak (*cis*) is at lower frequencies and not far from the position of the *cis* peak of catechol. The area of this latter peak, moreover, is roughly twice that of phenol, and thus the absorption of this molecule is in rather striking accord with what might be expected, using Pauling's interpretation as a guide.

It is also interesting to compare the absorption of 1,8-dihydroxynaphthalene with that of catechol. It will be recalled that in catechol the configuration in which both OH groups were in *trans* positions appeared to occur in too small amounts to be noticeable, the two peaks possessing about the same area. That is, the catechol molecules were interpreted as being essentially all of one sort, this possessing one *cis* and one *trans* OH group. As mentioned above, this conclusion contained the assumption that the absorption coefficients of the two groups were the same. In 1,8-dihydroxynaphthalene the two OH groups are even closer together than in catechol, and the configuration in which the two groups turn toward one another is even more improbable than in catechol. The configuration possessing one *cis* and one *trans* group would certainly seem to be a possible one, and two peaks are indeed observed. However, while the total area is approximately that of two phenol-like OH groups, the area of the *cis* peak is considerably smaller than that of the *trans* peak. This would indicate that the configuration possessing two *trans* groups is also present in considerable amount, that is, that the difference in free energy between the *cis–trans* and *trans–trans* configuration is less than the corresponding free energy difference in catechol. It does not, however, seem probable that the hydrogen atom of the *cis*-hydroxyl group is sufficiently close to the oxygen atom of the adjacent group that repulsion offsets somewhat the proton attraction of this atom. Furthermore, the shift of the *cis* peak to lower frequencies is greater than that in catechol. It may be that here the absorption coefficients of the *cis* and *trans* forms are considerably different. If this is not the case, we are again confronted with the circumstance that a relatively large displacement of the *cis* peak from the normal phenol frequency does not necessarily mean a correspondingly large free energy difference between the *cis* and *trans* forms.

A further interesting opportunity to test the interpretation suggested by Pauling is to be had in some of the derivatives of the above mentioned compounds. In pyrogallol dimethyl ether the remaining hydroxyl group of pyrogallol would have only the *cis* position available to it, this *cis* position being similar to the *cis* position in guaiacol. The absorption does, indeed, consist of a single peak of approximately the area of a single OH group and at approximately the position of the guaiacol peak.

In tetrabromoguaiacol the position of the hydroxyl group which occurs in guaiacol itself (*cis*) presumably is not greatly changed, but in the position turned away from the oxygen atom of the O–CH_3 group, which position is essentially absent in guaiacol, the OH group finds a bromine atom adjacent in tetrabromoguaiacol. One would in first approximation expect proton attraction by the bromine atom similar to that in *o*-bromophenol and a *cis* peak at about the same position. The positions of the guaiacol peak and of the *cis* peak of *o*-bromophenol (or 2,4,6-tribromophenol) are not far removed from one another, and the broad peak observed for this compound may be interpreted as two overlapping peaks of approximately this frequency separation. It seems apparent, however, that, if this is the case, both peaks have been shifted somewhat to lower frequencies, recalling the observation that the *cis* peak in the monohalogen ortho substituted phenols seems to shift slightly to lower frequencies in the respective 2,4,6-trisubstituted phenols where both ortho positions are occupied by the halogen.

In 2,4-dibromonaphthol-1 the *cis* position of the OH group would be expected to be similar to the *cis* position of *o*-bromophenol, but in the *trans* position the adjacent hydrogen atom is considerably closer than in *o*-bromophenol, presumably leading to stronger proton repulsion. This would be expected to reduce the fraction of the molecules in the *trans* position, and indeed the *trans* peak is not observed, a single peak (*cis*) showing at approximately the position of the *cis* peak of *o*-bromophenol.

Finally in tetrabromocatechol the *cis* position of catechol should be present with roughly the same character, in first approximation, as in catechol itself, but the *trans* position no longer has a hydrogen atom adjacent, but a bromine atom, which exercises proton attraction, and which should lead to a *cis* peak at roughly the position of the *cis* peak of *o*-bromophenol. Two peaks are observed, but here again, as seemed probable also in tetrabromoguaiacol, the two peaks are shifted to somewhat lower frequencies than those occurring in the respective mono-ortho substituted compound, a characteristic apparently frequently to be found in phenols in which both ortho positions are occupied by a group exercising proton attraction. Moreover, it is to be noticed that here the configuration in which the two OH groups are turned away from one another would not be expected to possess as much excess free energy over the configuration one *cis*–one *trans* as was the case in catechol because of the attraction here exercised by the bromine atom. A similar remark applies of course to tetrabromoguaiacol as well. In other words, keeping in mind the suggested interpretation of the absorption of catechol, there seems to be no reason why the two peaks in these two compounds should be expected to possess the same area, and it may be that the small apparent difference in area of tetrabromocatechol is to be explained in this way. Finally, it is interesting to note that in both tetrabromocatechol and tetrabromoguaiacol, one quite definite prediction could be made beforehand on the basis of Pauling's interpretation, namely, that neither of these should possess characteristic OH absorption at the position of the normal phenol peak.

Thus the spectra of these compounds appear to possess characteristics which are rather strikingly in accord with Pauling's interpretation. At the same time they raise points which are not clear and which await further elucidation.

The authors are much indebted to Professor Linus Pauling for discussion of this type of spectra and for helpful advice as to its interpretation.

Summary

The absorption, characteristic of the presence of the OH group and in the region of its first vibrational overtone, has been measured quantitatively for certain ortho substituted phenols and the results have been presented as curves of the molal absorption coefficient against position in the spectrum.

The results have been discussed in the light of Pauling's recent interpretation of this type of spectra. For the most part the correspondence is remarkably close.

WASHINGTON, D. C. RECEIVED SEPTEMBER 10, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heat of Fusion and Vapor Pressure of Stannic Iodide

BY GEORGE R. NEGISHI

The investigations of Hildebrand and coworkers[1] in this Laboratory during recent years upon the subject of intermolecular forces and solubility have included a study of tetrahalides as examples of molecules having widely differing volumes and intermolecular fields but with a common highly symmetrical structure. Stannic iodide is one of the substances concerning which a considerable body of solubility data has been accumulated; however, its evaluation has been unsatisfactory on account of lack of accurate knowledge of its heat of fusion and vaporization. The work herein described has been carried out in order to fill this gap.

Preparation and Purification of Stannic Iodide.—This compound was prepared and purified by the method described by Dorfman and Hildebrand,[1] followed by two fractional distillations under high vacuum (10^{-5} mm.). The purity of the final product was undoubtedly high, as indicated by sharp breaks in the cooling curve, and by the absence of premelting in the heat of fusion determinations.

The Melting Point.—The sample was distilled under high vacuum into a Pyrex tube, in the center of which extended a narrow Pyrex tube almost to the bottom. The temperature of the freezing mixture was measured by means of an alumel-chromel thermocouple inserted into the central narrow tube. The couple was calibrated against the melting points of water and tin, the boiling point of water and the transition point of sodium sulfate decahydrate. The thermoelectric current was measured by means of a Leeds and Northrup Student Type potentiometer. A change in temperature of 0.1° could be detected. The sample was heated in a copper cylinder 20 cm. high, 5 cm. in diameter and 9 mm. thick, provided with a heating coil and thermally insulated with Sil-o-cel. The temperature was regulated by means of a rheostat. During the measurements the temperature of the furnace was lowered rather rapidly to the freezing point of the stannic iodide, after that at about 0.05° per minute. The apparatus was shaken continuously on a rocker except when the readings were taken. The melting point was determined from the "break" in the cooling curve. The plot of the curve is shown in Fig. 1. The melting point thus determined was 144.5°. This value is to be compared with the values of 143.5,[1] 145.3[2] and 146.2°,[3] from other sources.

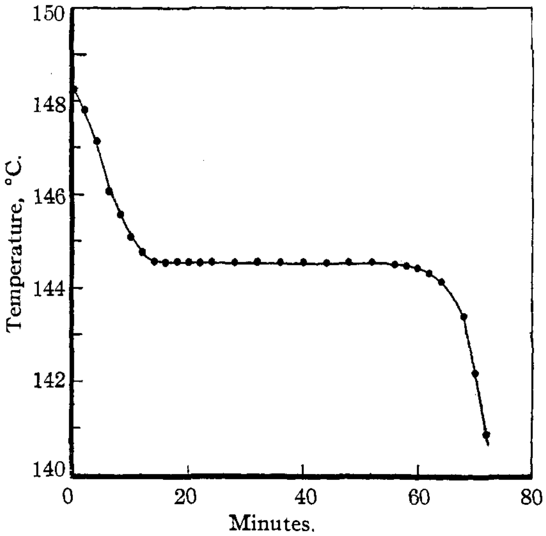

Fig. 1.

The vapor pressure was determined by means of a glass click gage as described by Smith and Taylor.[4] The click constant was determined at the pressures and temperatures of the actual runs. The constant increased with both increasing pressure and temperature up to a point where a permanent change set in. The "click-in" constant was found to be more reliable than that of "click-out," so only the former was calibrated. The space above the click gage (the manometer side) was evacuated to 10^{-2} mm. before each "click-in" was made. This was not necessary at lower temperatures, but above 200° it was essential.

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(1) M. E. Dorfman and J. H. Hildebrand, THIS JOURNAL, **49**, 729 (1927); Miriam E. Dice and J. H. Hildebrand, *ibid.*, **50**, 3023 (1928); J. H. Hildebrand and J. M. Carter, *ibid.*, **54**, 3592 (1932); J. H. Hildebrand, *ibid.*, **57**, 866 (1935).

(2) M. G. Raeder, *Z. anorg. allgem. Chem.*, **130**, 325 (1923).

(3) W. Biltz, *ibid.*, **203**, 277 (1932).

(4) D. F. Smith and N. W. Taylor, THIS JOURNAL, **46**, 1393 (1924).