Ultraviolet Spectral Study of *o*- and *p*-(Halomercurio)phenols

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The ultraviolet spectra of *o*- and *p*-(halomercurio)phenols, *o*- and *p*-OHC_6H_4HgX (X=F, Cl, Br, or I) have been recorded in ethanolic solution and λ_{max} and log ε_{max} have been recorded. The spectra of these compounds have been interpreted in terms of the correlation with the spectra of benzene. HgX group is shown to be having electron-withdrawing effect on the benzene ring. Variation in the values of λ_{max} and log ε_{max} on changing from *o*- to *p*-derivative for a particular (halomercurio)phenol and on changing the halogen attached to mercury has been explained.

A very large number of organomercury compounds are known but only a few of them have been subjected to UV spectral study; such a study is specially limited when one considers aromatic organomercurials. Leandri and Tundo[1] have reported and interpreted the UV spectral data (220 to 350 nm) of *p*-XC_6H_4HgCl and $XC_6H_4HgC_6H_4X$ where X=OH, CH_3, Cl, NO_2, and NH_2. Gowenlock and Trotman[2] restudied the *p*-XC_6H_4HgCl compounds in a wider range (200 to 350 nm) and also included compounds where $X=O^-$ or NH_3^+. In addition, they have reported the spectra of some ortho derivatives ($X=O^-$ or OH). Baliah and Subharayan[3] have reported the spectral study of some of the *o*- and *p*- compounds reported earlier and they have enlarged their list to include compounds where $X=(CH_3)_2N$, $(C_2H_5)_2N$, and CH_3O; however, their data were collected upto 220 nm and they have referrred to the work of Leandri and Tundo only but not that of Gowenlock and Trotman.

The spectral study of *o*- and *p*-(halomercurio)phenols reported so far have been confined to the chloromercurio derivatives only. Gowenlock and Trotman[2] predicted from their spectral analysis of *o*- and *p*-chloromercurio derivatives that the spectra of bromo- and iodomercurio derivatives would be more complicated because of the interference from HgBr and HgI groups as observed in the case of HgCl group. In the present work the spectra of *o*- and *p*-OHC_6H_4HgX where X=F, Cl, Br, or I are reported and interpreted.

Experimental

o- and *p*-(Halomercurio)phenols were prepared according to a method reported earlier.[4] The spectral data were recorded using ethanolic solutions of these compounds (ethanol was purified by treating with clean and dry magnesium turnings and a little iodine and refluxing for half an hour; the fraction distilling at 78.3 °C was collected). Solutions of concentration varying from 1×10^{-4} to 7×10^{-5} M were employed. The spectra were recorded on Unicam SP 700 UV and visible spectrophotometer. The spectra are shown in Figs. 1 and 2.

All the eight compounds studied showed three bands in the UV region. λ_{max} was recorded for each band and the corresponding value of log ε_{max} was also calculated. These

Table 1. UV Spectral data of *o*- and *p*-(haromercurio)phenols

Compound	λ_{max} (nm)	log ε	λ_{max} (nm)	log ε	λ_{max} (nm)	log ε
o-OHC_6H_4HgF	210	3.86	225	3.49	284	3.25
p-OHC_6H_4HgF	207	4.05	232	3.51	282	3.23
o-OHC_6H_4HgCl	212	4.13	225	3.80	282	3.51
p-OHC_6H_4HgCl	207	4.14	234	4.05	275	3.30
o-OHC_6H_4HgBr	210	4.16	225	3.82	284	3.52
p-OHC_6H_4HgBr	208	4.17	234	4.07	282	3.39
o-OHC_6H_4HgI	209	4.38	232	4.05	284	3.60
p-OHC_6H_4HgI	208	4.39	237	4.27	282	3.54

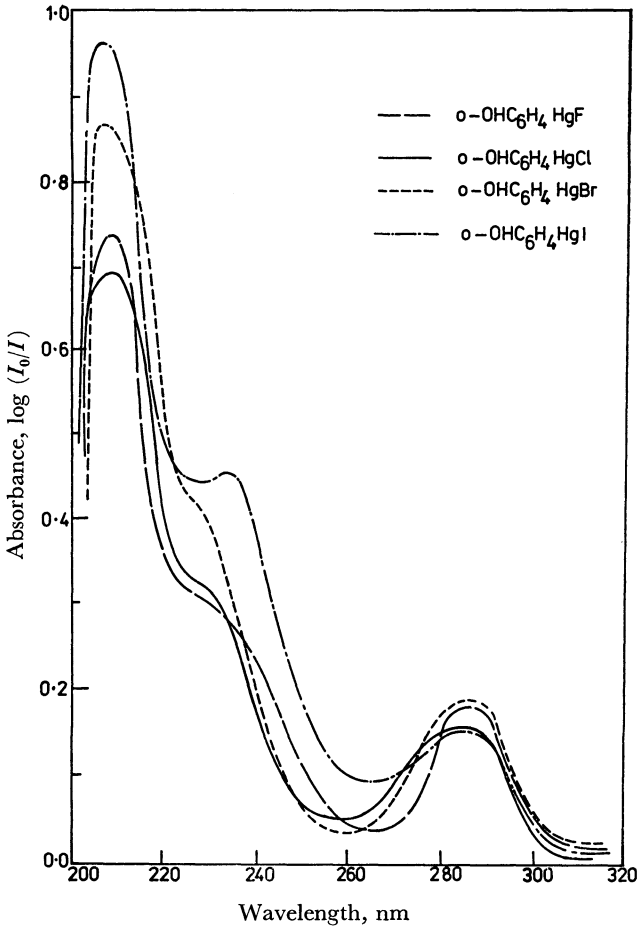

Fig. 1. UV spectra of *o*-(halomercurio)phenols.

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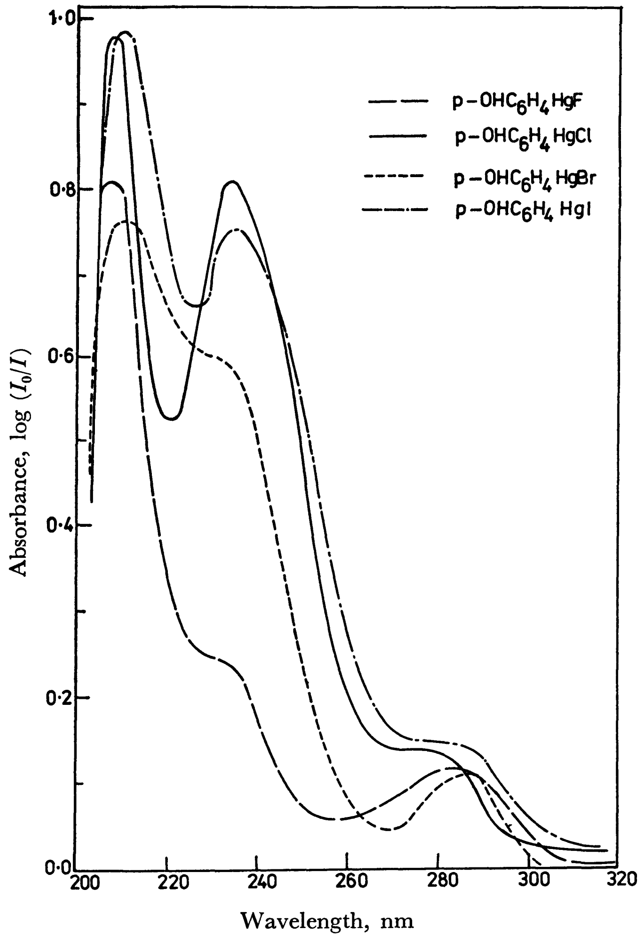


Fig. 2. UV spectra of *p*-(halomercurio)phenols.

values are shown in Table 1. In certain cases, *viz.* *o*-derivatives the band at 225 nm was not distinct, rather observed as an inflection point (Fig. 1).

Discussion

As *o*- and *p*-(halomercurio)phenols are disubstituted benzene derivatives, their spectral data may be correlated with those of benzene. Benzene shows three absorption bands at 256, 203, and 180 nm attributed to $^1B_{2u} \leftarrow {}^1A_{1g}$ $^1B_{1u} \leftarrow {}^1A_{1g}$, and $^1E_{1u} \leftarrow {}^1A_{1g}$ transitions respectively.[5)] The 256 and 203 nm bands usually called secondary and primary bands respectively have been studied extensively in benzene derivatives. These bands are usually present in the spectra of substituted benzenes, though shifted due to substitution.[6)]

Effect of HgCl Group on the Spectra of Benzene. The two bands of phenylmercury(II) chloride at 210 and 258 nm may be considered as bathochromically shifted primary and secondary bands of benzene.[1–3)] It is difficult to assess the amount of shift in the primary band because HgCl group itself absorbs in this region. In fact most of the mercury compounds (though not derivatives of benzene) have absorption bands in this region, *e.g.* $HgCl_2$ 211 nm, $HgBr_2$ 206 and 234 nm, HgI_2 215 and 273 nm,[2)] and CH_3HgCl 206 nm.[7)] Thus, the bands in the first column of Table 1 may be ascribed to HgX groups and the bands in the second and third columns may be treated as the shifted primary and secondary bands of benzene respectively.

In spite of the overlap of the primary band of C_6H_5-HgCl by that of HgCl group, it is possible to estimate a value of λ_{max} for the former using the observation by Doub and Vandenbelt[6a)] that the ratio of λ_{max} (secondary) to λ_{max} (primary) in monosubstituted benzenes is nearly constant, *viz.* 1.19 to 1.28. Taking an average value of 1.23 for this ratio and the known value of λ_{max} (secondary) for C_6H_5HgCl, 258 nm, the value of λ_{max} (primary) for C_6H_5HgCl comes out to be 258/1.23= 210 nm.

Electronic Effect of HgCl Group. It is not possible to conclude from the shifts alone in phenylmercury(II) chloride (203→210 nm, 256→258 nm) whether HgCl group is acting like electron acceptor or electron donor since both electron acceptor and electron donor groups are known to cause shift (bathochromic and hyperchromic) in the primary and secondary bands of benzene.[6,8,9)] Gowenlock and Trotman[2)] have concluded by comparing the effect of ionization $OH \rightarrow O^-$ on the secondary band for both *o*- and *p*-substituted phenols that HgCl group is *o*-, *p*-directing. However, their conclusion is not very convincing; for example, for the *p*-substituents SMe, Cl, HgCl, CHO, COMe, and NO_2 the ionization leads to a displacement of λ_{max} to a longer wavelength by 7, 19, 30, 46.5, 49, and 85 nm respectively and from this observation they conclude that HgCl group is similar to Cl group and is *o*-, *p*-directing. However, the value of the shift for HgCl, 30 nm, happens to be between the value for an *o*-, *p*-directing group (Cl, 19 nm) and that for a *m*-directing group (CHO, 46.5 nm) and thus it is not possible to say definitely whether HgCl group is *o*-, *p*-directing or *m*-directing. Unfortunately there is no direct experimental evidence of the *o*-, *p*-directing or *m*-directing nature of HgCl group in literature since most reagents used in substitution in the benzene ring remove the HgCl group from the ring.

Some idea about the electron withdrawing or electron releasing nature of HgCl group may be obtained by using the observation of Doub and Vandenbelt[6)] that in a *p*-disubstituted benzene, the shift in the primary band is not much different from the sum of the shifts by

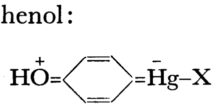
Table 2. Effect of para disubstitution $A-C_6H_4-B$ on the primary band of benzene

A	Shift (nm)[a)] for A	B	Shift (nm) for B	Ref.	Shift for *p*-A–C_6H_4–B: Calcd Sum A+B	Obsd	Ref.
HgCl	7.0	NO_2	57.0	1	64.0	66.0	1
HgCl	7.0	CH_3	3.5	1	10.5	21.5	1
HgCl	7.0	Cl	6.5	1	13.5	23.0	1
HgCl	7.0	NH_2	31.0	1	38.0	50.0	1
HgCl	7.0	OH	7.0	1	14.0	31.0	Table 1
HgCl	7.0	OCH_3	13.5	10	20.5	30.0	3
HgCl	7.0	$N(CH_3)_2$	47.5	10	54.5	76.0	3
HgCl	7.0	O^-	31.5	10	38.5	43.0	2

a) Calculated from the present work.

the individual substituents (as observed in corresponding monosubstituted derivatives) if the substituents are of the same character (*i.e.* both electron withdrawing or both electron releasing) but the shift is larger than the sum of the two shifts if the substituents are of opposite character. Table 2 shows that when HgCl group is in *p*-position to *o*-, *p*-directing groups (OH, NH_2 *etc.*) the shift is much larger than the sum of the shifts due to two substituents individually. Further when HgCl group is in *p*-position to an electron withdrawing group, namely NO_2, the shift is nearly the same as the sum of the shifts due to NO_2 and HgCl groups individually. These two observations clearly indicate that HgCl group acts like an electron withdrawing group.

The electron withdrawing capacity of Hg group can be ascribed to the fact that mercury has two vacant p orbitals in its valence shell which can accommodate the withdrawn electrons. These must be a conjugative interaction of HgCl group with the electron-releasing group, for example, the following structure would make an important contribution to the excited state of *p*-(halomercurio)phenol:


(I)

which causes a considerable bathochromic shift in the primary band of benzene.

Comparison of the Spectra of o- *and* p-*(Halomercurio)phenols.* It is observed in Table 1 that the shift in primary band is greater in *p*-compounds than in *o*-compounds and also that the intensities of these bands are greater for *p*-compounds than for *o*-compounds. In fact, for *o*-compounds usually inflection points are observed rather than peaks which are distinct for the *p*-compounds (Figs. 1 and 2). The decrease in the shift and intensity of the primary band in *o*-compounds can be ascribed to the steric interference with coplanarity. The steric overlap between the *o*-substituents sets up appreciable interference which prevents the attainment of uniplanar configuration by the benzene derivatives. Steric inhibition of electronic interaction thus raises the energy level of the ground state but since the phenyl-oxygen and phenyl-mercury links postulated in the excited state contain a larger amount of double bond character and since the interplanar angle cannot from theoretical consideration (Franck-Condon principle) change during transition, the energy level of the excited state will be raised even more than that of the ground state. Thus the transition energy is increased in *o*-compound as compared to *p*-compound resulting in a smaller bathochromic shift and also a reduced transition probability, resulting in a loss of absorption intensity.

In case of secondary bonds *p*-compounds show lesser bathochromic and hyperchromic shifts as compared to *o*-compounds. A reason for such a behaviour is not apparent since one might expect that the secondary bands would be effected in a similar way as the primary bands in changing from a *p*-isomer to *o*-isomer.

Effect of Change in Halogen Atom on the Spectra of o- *and* p-*(Halomercurio)phenols.* It may be noted that the prediction by Gowenlock and Trotman[2] regarding the complex nature of the spectra of bromo and iodo derivatives compared to that of chloro derivatives does not appear to be correct. Table 1 shows that the spectra of all the halo derivatives are similar and there are only three bands in each case.

It is seen in Table 1 that for the *o*-derivatives the intensity of the primary band increases in the order $F<Cl<Br<I$. The secondary bands behave in a similar way. However, the λ_{max} values for the secondary bands remain nearly constant (282—284 nm) and λ_{max} values for primary bands are also constant except for *o*-iodo derivative which has a longer λ_{max} value than other *o*-halo derivatives. For *p*-derivatives the situation is similar.

The excited state of *p*-(halomercurio)phenol may be represented by the structure I mentioned earlier where HgX group is acting like an electron acceptor. Since the iodo derivative shows the maximum intensity of the primary band, the excited state must be stabilized most in its case and stability of the excited state should decrease in the order $I>Br>Cl>F$. On the basis of inductive effect of halogen atoms it would appear that the excited state should be most stable in the case of fluoro derivatives (fluorine being the most electronegative amongst the halogens) and the order should be $F>Cl>Br>I$. Thus, the inductive effect cannot be used to explain the observed order. No other explanation is apparent for the observed order.

References

1) G. L. Leandri and A. Tundo, *J. Chem. Soc.*, **1954**, 3377.
2) B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, **1955**, 1554.
3) V. Baliah and P. Subharayan, *J. Ind. Chem. Soc.*, **40**, 638 (1963).
4) P. L. Yadav, N. K. Jha, and V. Ramakrishna, *Ind. J. Chem.*, **13**, 1095 (1975).
5) H. H. Jaffe and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," 4th ed, John Wiley & Sons, Inc., London (1966), p. 244.
6) L. Doub and J. M. Vandenbelt, a) *J. Am. Chem. Soc.*, **69**, 2714 (1974); b) *ibid.*, **71**, 2414 (1949).
7) K. Hartley, H. O. Pritchard, and A. A. Skinner, *Trans. Faraday Soc.*, **46**, 1019 (1905).
8) W. F. Hammer and F. A. Matsen, *J. Am. Chem. Soc.*, **70**, 2842 (1948).
9) F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5243 (1950).
10) A. E. Gilman and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy," 2nd ed, Edward Arnold Publishers, London (1957), p. 140.