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THE STUDY OF CHARGE-TRANSFER COMPLEXES OF THIOPHENOLATES OF TIN AND MERCURY WITH TETRACYANOETHYLENE BY ELECTRONIC ABSORPTION SPECTROSCOPY

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Summary

CT electronic absorption spectroscopy has been used for the study of some electronic features of organotin, ArSuSAr′ (I), and organomercury, ArHgSAr′ (II), thiophenolates. The compounds I and II are stronger electron donors than the corresponding aromatic derivatives Ar_nM (M = Hg, Sn). Analysis of $\nu(CT) = \phi(\sigma_p^+)$ correlations has shown that the electron-donor ability of a number of sulphur-containing compounds decreases in the order:

$ArSC_6H_5 > ArSnSAr' \approx ArHgSAr' > ArSCH_2Ar > ArSH$

while the sensitivity of these compounds to substitution increases in the following order:

$ArSH > ArSHgAr' > ArSCH_2Ar' > ArSAr'$

Introduction

Electronic absorption spectroscopy of charge-transfer (CT) complexes is a source of valuable information on the influence of substituents on the electronic density distribution in the components of the CT complexes. It is well known [1,2] that the spectral characteristics of the band corresponding to the intermolecular CT transition can supply us with information on the new state of the complex components, i.e. on the charge-transfer state. This the intramolecular interactions in the ground electronic state do not differ drastically from those in the CT state. However, many fine electronic effects are more pronounced in the CT state. Linear correlations of

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the CT transition energies, $h\nu$(CT), corresponding to the λ_{max}^{CT} band in the absorption spectrum, with ionization potentials of the donor components and with the σ^+ constants of the substituents in the aromatic ring serve as the basis of the quantitative study of the substituent electronic effects by electronic CT absorption spectroscopy of the aromatic compounds (in the case of an unchanged acceptor) [1–3]. This approach has been used successfully for the investigation of electronic effects in monovalent mercury-containing groups of the XHg type (where X are functional substituents) [4].

The purpose of the present work is to study the CT complexes of symmetrical aromatic mercury and tin derivatives of the Ar_nM-type (M = Hg, Sn) (I–VI) and of the corresponding substituted thiophenolates, Ar_nMSAr' (M = Hg, Sn, CH_2) (VII–XVII; XXII–XXVII) with tetracyanoethylene (TCNE) (Table 1).

Results and discussion

We observed only one CT band in the electronic absorption spectra of CT complexes I–VI in the 24000–27000 cm^{-1} region. This λ_{max}^{CT} band is due to electron transfer from the π-molecular orbital of the benzene ring with the corresponding contribution from the atomic orbitals of the metal atoms [5] to the lowest unoccupied molecular orbital (LUMO) of TCNE. The dominating contribution of the π-MO of the benzene ring is confirmed by the similarity of spectral characteristics of $\lambda_{max\ I}^{CT}$ bands to λ_{max}^{CT} of benzene and its derivatives [2]. The transition from tetraphenyltin (I) to the tetrafluoro-substituted compound (III) is accompanied by a shift of the $\lambda_{max I}^{CT}$ band to the short-wave range of the spectrum in accordance with the stabilization of the highest occupied molecular orbital (HOMO) by electron-accepting substituents, i.e. by fluorine atoms. The stabilization energy is $\Delta\nu_{I-III}$ = 2800 cm^{-1}.

As can be seen from Table 1 the similar transition from V to VI for organomercury compounds does not lead to the shift of $\lambda_{max I}^{CT}$ band. Apparently, such low sensitivity of ν(CT) of Hg-containing derivatives to the influence of substituents in comparison with their Sn-containing analogues may be due to the different number of variable radicals in these systems.

Introduction of a sulphur atom into a molecule of organomercury and organotin compounds changes the CT spectrum drastically. In all cases a new $\lambda_{max II}^{CT}$ long-wave CT band appears in the 12500–20000 cm^{-1} region. In accordance with literature data [6] the appearance of the long-wave band in the spectrum is due to the electron transition from the HOMO which is localized mainly on the SAryl fragment. The main contribution to this HOMO is made by atomic orbitals of sulphur. Interaction of the lone electron pair of a sulphur atom with π-orbitals of aryl fragments facilitates the removal of the degeneracy of the e_{1g} molecular orbital of benzene and its strong splitting *.

Thus, comparing the energies of the $\lambda_{max\ I}^{CT}$ and $\lambda_{max\ II}^{CT}$ bands of compound VII with the $\lambda_{max\ I}^{CT}$ band of II one may conclude that the destabilization energy of the HOMO of VII is $\Delta\nu_{VII-II}$ = 7000 cm^{-1} and the destabilization energy of the

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* Apparently, introduction of organometallic fragments into the benzene molecule (compounds I–VI) also causes splitting of the e_{1g} orbital. However it is too weak to be observed in the CT spectra.

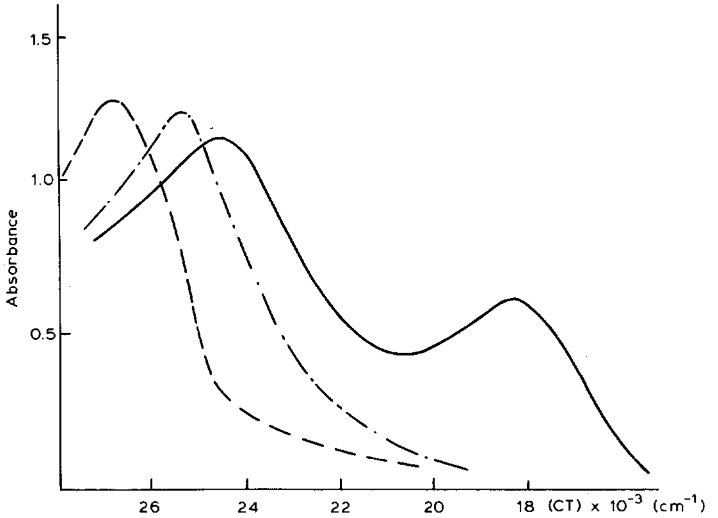

Fig. 1. UV spectra of CT complexes of $(C_6H_5)_3SnC_6H_4F$-4 (–··–), $(4\text{-}FC_6H_4)_3SnC_6H_4F$-4 (— —) and $(C_6H_5)_3SnSC_6H_4F$-4 (———) with TCNE.

"benzene orbital" is only $\Delta\nu_{VII-II} = 800$ cm^{-1}. Introduction of electron-withdrawing substituents in aryl fragments (compound VII) leads to insignificant stabilization of the HOMO, $\Delta\nu_{VIII-VII} = 100$ cm^{-1}. Thus sulphur-containing organomercury and organotin derivatives show themselves as stronger electron donors than I–VI. This follows from the appearance of the above-mentioned $\lambda^{CT}_{max II}$ long-wave band in the spectrum as well as from the bathochromic shift of the "benzene" $\lambda^{CT}_{max I}$ short-wave band. The latter is overlapped in most cases with the $\lambda^{CT}_{max II}$ band and therefore the corresponding values of ν(CT) are not given in Table 1 (except for VII–IX and XII). Analysis of the position of the $\lambda^{CT}_{max II}$ band allowed us to study the substituent effects in the aryl fragments of compounds VII–XVII, bearing in mind that for the derivatives containing the heteroatom with a lone electron pair the long-wave band is the most sensitive to the influence of substituents [1,2].

As it follows from Table 1 the frequences ν(CT) of sulphur-containing organomercury compounds as well as the ones of the corresponding substituted thiophenols (XVIII–XXI), *p*-fluorobenzyl arylsulphides (XXII–XXVII) and phenylaryl sulphides decrease gradually with replacement of electron-withdrawing substituents in the ring by electron-donating ones in accordance with the bathochromic shift of the $\lambda^{CT}_{max II}$ band. Satisfactory correlations between ν(CT) and the Brown-Okamoto σ^+ constants are observed for all cited series of compounds (eqs. 1–4 in Table 2). The intercepts of these correlations (b) represent values of ν(CT) corresponding to unsubstituted compounds and therefore characterize the relative electron-donor strength of compounds of this series.

The $ArSHgC_6H_4F$-4, $ArSCH_2C_6H_4F$-4 and $ArSC_6H_5$ compounds may be considered as thiophenol (ArSH) derivatives, in which the hydrogen atom is substituted. In accordance with the increase of the *b* intercept in eqs. 1–4 (Table 2) the donor ability of these compounds decreases in the series:

$$ArSC_6H_5 > ArSHgC_6H_4F\text{-}4 > ArSCH_2C_6H_4F\text{-}4 > ArSH \qquad (1)$$

TABLE 1

CHARGE TRANSFER FREQUENCIES (ν(CT)) OF CT COMPLEXES WITH TETRACYANOETHYLENE

No.	Compound	ν(CT) (cm^{-1})
I	$(C_6H_5)_4Sn$	24000 [a]
II	$(C_6H_5)_3SnC_6H_4F$-4	25400
III	(4-$FC_6H_4)_3SnC_6H_4F$-4	26800
IV	(4-$ClC_6H_4)_3SnC_6H_4F$-4	26800
V	$(C_6H_5)_2Hg$	24400 [4]
VI	(4-$FC_6H_4)_2Hg$	24400 [4]
VII	$(C_6H_5)_3SnSC_6H_4F$-4	18400 (24600) [b]
VIII	(3,4-$Cl_2C_6H_3)_3SnSC_6H_4F$-4	18500 (24800)
IX	$C_6H_5HgSC_6H_4F$-4	18400 (23800)
X	4-$OCH_3C_6H_4HgSC_6H_4F$-4	18200
XI	4-$CH_3C_6H_4HgSC_6H_4F$-4	18300
XII	4-$ClC_6H_4HgSC_6H_4F$-4	18500 (24800)
XIII	$C_6H_5SHgC_6H_4F$-4	17600
XIV	4-$(CH_3)_2NC_6H_4SHgC_6H_4F$-4	12400
XV	3-$FC_6H_4SHgC_6H_4F$-4	18600
XVI	3-$ClC_6H_4SHgC_6H_4F$-4	18700
XVII	3-$CF_3C_6H_4SHgC_6H_4F$-4	19300
XVIII	C_6H_5SH	19600
XIX	4-$OCH_3C_6H_4SH$	16500
XX	4-$CH_3C_6H_4SH$	18200
XXI	4-ClC_6H_4SH	19900
XXII	$C_6H_5SCH_2C_6H_4F$-4	17900 (28600)
XXIII	4-$(CH_3)_2NC_6H_4SCH_2C_6H_4F$-4	13500
XXIV	4-$OCH_3C_6H_4SCH_2C_6H_4F$-4	15900 (26400)
XXV	4-$CH_3C_6H_4SCH_2C_6H_4F$-4	16700
XXVI	4-$FC_6H_4SCH_2C_6H_4F$-4	18500
XXVII	3,4-$Cl_2C_6H_3SCH_2C_6H_4F$-4	19800
XXVIII	$C_6H_5SC_6H_5$	17100 [7]
XXIX	4-$OCH_3C_6H_4SC_6H_5$	16500 [7]
XXX	4-$CH_3C_6H_4SC_6H_d5$	16300 [7]
XXXI	4-$ClC_6H_4SC_6H_5$	17400 [7]

[a] Long wavelength CT frequency λ^{CT}_{maxI}. [b] Short wavelength CT frequency λ^{CT}_{maxII}.

TABLE 2

PARAMETERS OF $\nu(CT) = a\Sigma\sigma^+ + b$, CORRELATIONS FROM SPECTRA OF CT COMPLEXES WITH TETRACYANOETHYLENE

No.	Compound	a	S_a	b	S_b	r
1	$ArSC_6H_5$	1204	319	17120	135	0.936
2	$ArSHgC_6H_4F$-4	3052	84	17580	45	0.999
3	$ArSCH_2C_6H_4F$-4	2850	257	18170	206	0.984
4	$ArSH$	3800	147	19500	62	0.999
5	$ArHgSC_6H_4F$-4	313	61	18430	26	0.965

Since the donor ability of the compounds studied is in addition to other factors determined by the electron density on the C_6H_4S fragment we suggest that the polarities of the S–H bonds (where X = Ph, HgC_6H_4F-4, $CH_2C_6H_4F$-4,H) decrease in the same order.

It is interesting to note that in accordance with the *a* slope values of the correlations (eqs. 1–4 in Table 2) the same systems in comparison with eq. 1 above give the inverse decreasing order of the influence of substituents in the aromatic rings on the sulphur atom on ν(CT) of the corresponding CT complexes:

$$\text{ArSH} > \text{ArSHgAr}' > \text{ArSCH}_2\text{Ar}' > \text{ArSAr}'' \qquad (2)$$

where

$Ar' = C_6H_4F\text{-}4,\ Ar'' = Ph$

Apparently, this can be accounted for by the fact that in comparison with the substituted thiophenols, ArSH ($Ar = XC_6H_4$), in all the other systems studied the electron density shifts caused by the X substituents are localized to a smaller degree on the fragment concerned ($-C_6H_4S$) and are transferred to a greater degree beyond the fragment onto the other aromatic ring either directly or through Hg or CH_2 bridging groups. Then the greater the shift, or in other words the greater the electronic transmittance of the system, the less is the influence of substituents on this fragment. Thus, analysis of the data obtained shows that the transfer of substituent electronic influences to the aryl groups Ar′ or Ar″ increases when passing from ArSHgAr′ to $ArSCH_2Ar'$ and further to ArSAr″. This is in complete agreement with available literature data on the greater transmission ability of the non-bridging systems in comparison with similar systems with a CH_2 bridge [8], as well as data on a lower transmission ability of the Hg bridge atom as compared to the CH_2 group [9].

Furthermore, from the comparison of transmission abilities of the standard nonbridged series, $ArSC_6H_5$ (the slope of a_0 in eq. 1 in Table 2) and the similar series in which the indicator fragment is separated from the variable substituents by a mercury atom, $ArHgSC_6H_4F$-4 (the slope of *a* in eq. 5) it follows that the electron transmittance coefficient of mercury ($\pi' = a/a_0$) is 0.25.

To confirm the conclusions drawn on the basis of the data obtained from the CT spectra of organotin and organomercury compounds with TCNE we carried out a similar investigation of the CT complexes of these systems with another π-acceptor, i.e. with chloranil (CA) (Table 3). Analysis of the data obtained shows that the absorption bands of the CT complexes of $ArSHgC_6H_4F$-4 compounds with CA are shifted to shorter wave length with respect to the CT bands in the spectra of the CT complexes with TCNE. This is probably due to the weaker π-acceptor ability of chloranil as compared to TCNE (the electron affinity is $E(\text{CA}) = 1.37$ eV and $E(\text{TCNE}) = 1.80$ eV [10]). However, the dependence of the $\lambda_{\max}^{\text{CT}}$ band position on the nature of substituents in the aromatic ring on the sulphur atom is also clearly observed in the case of CT complexes with CA. Quantatively this is expressed in the good correlation between ν(CT) and σ^+ constants:

$$\nu(\text{CT}) = 2247\,\sigma^+ + 19310\ (r = 0.991) \qquad (3)$$
$$S_A = 202 \qquad S_B = 220$$

At the same time the comparison of energies of the long wavelength transitions in

TABLE 3

CHARGE TRANSFER FREQUENCIES (ν(CT)) OF $ArSHgC_6H_4F$-4 COMPLEXES WITH CHLORANIL

No.	Compound	ν(CT) (cm^{-1})
XX	$C_6H_5SHgC_6H_4F$-4	17600
XXI	4-$(CH_3)_2NC_6H_4SHgC_6H_4F$-4	15400
XXII	3-$FC_6H_4SHgC_6H_4F$-4	19900
XXIII	3-$ClC_6H_4SHgC_6H_4F$-4	20100
XXIV	3-$CF_3C_6H_4SHgC_6H_4F$-4	20400

the spectra of the CT complexes with TCNE and CA

$$\nu(\mathrm{CT})_{\mathrm{TCNE}} = 1.3\,\nu(\mathrm{CT})_{\mathrm{CA}} - 8211 \quad r = 0.992 \tag{4}$$

shows that the CT complexes with TCNE are more sensitive to the substituent electronic influences than the CT complexes with CA (the slope of $a = 1.3$ in eq. 4). The CT complexes with TCNE are more suitable for the investigation of the problems raised in this work.

In conclusion, we note that the information obtained on the electron density distribution in molecules of the compounds studied in the charge-transition state is in complete agreement with conclusions drawn when studying the same systems in the ground state by ^{19}F NMR spectroscopy [11].

Experimental

The electronic absorption spectra of CT complexes were measured on a Perkin-Elmer-402 spectrophotometer in the 300–850 nm region. A solution of the compound studied in CH_2Cl_2 (10^{-1} mol/l) and a solution of tetracyanoethylene in CH_2Cl_2 (5×10^{-2} mol/l) were mixed in 3 : 1 volume ratio to record the spectra. The cell path was 1 cm. The preparation of compounds studied was described previously [11].

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