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THE POLARITY OF XH AND XM BONDS IN COMPOUNDS OF THE ArXH AND ArXM (X = O, S, NR; M = Hg, Sn, Pb, Sb) TYPES AND THEIR CAPACITY FOR COORDINATION AND DISSOCIATION

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Summary

The relationship between the values of the σ_R^+ constants of the XMR_n and XH groups, reflecting the polarity of the X–M and X–H bonds, and the capacity of these bonds for heterolytic dissociation in DMSO have been analysed. Linear relations have been established between σ_R^+ and log K_d. The factors responsible for the abnormal stability of the S–Hg and S–Pb bonds are discussed. It has been shown that the capacity of the X–M and X–H bonds for dissociation is not determined by the force of the coordination interactions (K_c) between the M or H atoms and DMSO. The parallel pattern of variations in σ_R^+ and K_c is observed only in the case of XH acids and their $SnPh_3$ and $PbPh_3$ derivatives.

Earlier we determined the values of the direct polar conjugation constants σ_R^+ for the XH and $XMPh_n$ groups in p-$NO_2C_6H_4$-$XMPh_n$ type compounds, where X = O, S, NR and M = Hg, Sn, Pb, Sb^V [1]. They were derived both in relatively inert media (C_6H_6, CH_2Cl_2) and in a coordinating solvent (DMSO) from the integrated intensities of the $\nu(NO_2)$ bands in the IR spectra.

Studies of the pattern of interaction between such compounds and DMSO have revealed that they yield, initially, molecular type complexes (II), which partially dissociate (III) without going through ion pair formation, which is not observed.

$$\underset{(I)}{ArXM + B} \rightleftarrows \underset{(II)}{ArXM\ldots B} \rightleftarrows \underset{(III)}{ArX^- + MB^+}$$

The complex formation (K_c) and dissociation (K_d) constants have been defined [2–4].

The present work is concerned with the relationship between the molecular structural features determined by the values of the σ^+ constants of the $XMPh_n$ substituents, on the one hand, and the capacity of the metal atom for coordination

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as well as that of the XM and XH bonds for dissociation, on the other.

The capacity of the heteroatom X for direct polar conjugation in organometallic derivatives is more pronounced than in the corresponding XH acids (Table 1). Since the organic groups at the metal atom remain the same, it may be assumed that the increase in the σ_R^+ constants is determined by the shift of the electron density from the metal atom and corresponds to an increase in the polarity of the X–M bond.

As can be seen from Table 1, in DMSO the σ^+ constants, which represent the polarity of the bond, increase in the series: X–H < X–Sn < X–Hg < X–Pb < X–Sb < X^- (X = O, S); X–H < X–Hg < X^- (X = NR).

The bond polarity in a coordinating solvent is more pronounced than in an "inert" one. Linear relations have been separately established between the values of the σ-constants in DMSO and CH_2Cl_2 for each class of compounds (Fig. 1). Superposition of the σ_R^+ values for X^- groups in DMSO on these regression lines gives a clear indication of the relative polarity of the bonds in terms of closeness to the purely ionic bond. Characteristically, as the bond approaches the purely ionic one, the capacity for heterolytic dissociation of the bond increases. Such an approach permits the degree of bond polarity to be associated with the values of K_d for compounds belonging to different classes.

Notably, the $SSbPh_4$ group, whose σ_R^+ is closest to that of the anionoid group, displays the most pronounced readiness to form an organometallic cation. Conversely, no bond dissociation is observed in the NHHgPh, $NHCH_3$ and NH_2 groups, whose σ_R^+ constants are the furthest away from that of the NH^- group. In the case of nitrophenol derivatives, the large difference between the σ_R^+ constant of the substituent and the charged group corresponds to the lesser capacity of the O–Sb bond for heterolysis, as compared to that of the S–Sb bond.

TABLE 1

VALUES OF σ_R^+, K_c, AND K_d IN DMSO FOR p-$NO_2C_6H_4XMR_n$ TYPE COMPOUNDS

	σ_R^+	$\Delta\sigma_R^+$ [a]	K_c(25°C)	$K_d \times 10^{-6}$(25°C)
SH	−0.17	−0.11	1.6	4.7
$SSnPh_3$	−0.49	−0.27	0.7	17
SHgPh	−0.60	−0.06	3.9	0.01
$SPbPh_3$	−0.65	−0.23	1.2	0.4
$SSbPh_4$	−2.60	−1.73	0.8	3300
S^-	−2.60	−0.12 [b]	–	
OH	−1.31	−0.57	790	0.2
$OSnPh_3$	−2.43	−0.77	140	7
OHgPh	−2.80	−1.54	1.4	10
$OPbPh_3$	−3.20	−1.31	230	90
$OSbPh_4$	−3.29	−1.31	0.5	400
O^-	−3.98	−0.75 [b]	–	
$NHSO_2Ph$	−1.11	0.09	432	8
$NHgPh(SO_2Ph)$	−1.20	−0.15	6.1	14
$N(SO_2Ph)^-$	−3.2	−0.3 [b]		
NH_2	−1.84	−0.42	11.9	0.01
$NHCH_3$	−1.91	−0.12	3.2	0.01
NHHgPh	−3.16	−1.24	2.0	0.01
NH^-	−5.25	−0.50 [b]	–	0.01

[a] $\Delta\sigma_R^+ = \sigma^+_{R_{DMSO}} - \sigma^+_{R_{CH_2Cl_2}}$. [b] $\Delta\sigma_R^+ = \sigma^+_{R_{DMSO}} - \sigma^+_{R_{CH_3CN}}$.

Linear relations between the σ_R^+ and the logarithm of the dissociation constants have been established separately for the O and S derivative (Fig. 2) *. The abnormally low capacity of the SHg and SPb bonds for dissociation should be noted. The values of K_d are much lower than expected from the pronounced polarity of the bonds. Moreover, in contrast to XH acids and their organo-tin and -antimony derivatives, the bonds between these metals and the sulfur atom are much less capable of heterolysis than their bonds with the oxygen atom.

In order to obtain a better insight into the bond features responsible for such results, let us consider some general relations.

By analogy with the enthalpy of heterolytic dissociation of the XH bond, ΔH^0 (eq. 1), let us determine that of the XM bond (eq. 2):

$$\Delta H^0 = DH_0(\mathrm{XH}) - EA(\mathrm{X}) + IP(\mathrm{H}) \tag{1}$$

$$\Delta H^0 = DH_0(\mathrm{XM}) - EA(\mathrm{X}) + IP(\mathrm{M}) \tag{2}$$

where DH_0 is the energy of homolytic dissociation of the XH and XM bonds, EA(X) is the affinity for the electron of the X atom, and IP is the ionization potential of the H atom and the MPh_n group, respectively.

If relations 1 and 2 are written for another heteroatom (X′) and the new relations are subtracted from eqs. 1 and 2, the result will give the expressions for the heterolysis-energy differences, $\Delta(\Delta H)$, as a function of the heteroatom:

$$\Delta(\Delta H) = [DH_0(\mathrm{XH}) - DH_0(\mathrm{X'H})] - [EA(\mathrm{X}) - EA(\mathrm{X'})] \tag{3}$$

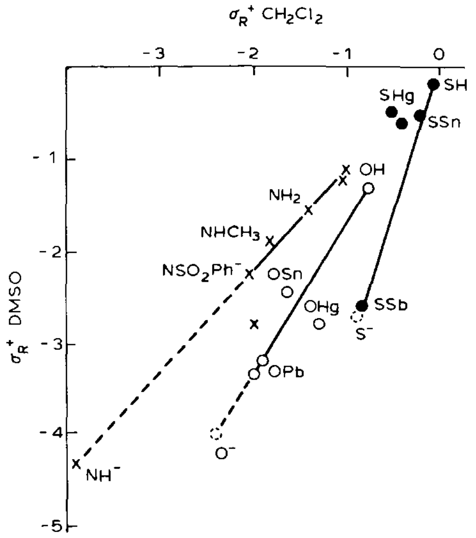

Fig. 1. Linear relations between the values of the σ_R^+ constants of the XH and XMPh_n groups (X = S (●), O (○), NR (×)) in DMSO and in CH_2Cl_2.

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* In the case of NSO_2Ph derivatives exhibiting a pronounced capacity for dissociation, the points do not lie on these straight lines. Further investigations are required to establish whether the N derivatives form an intermediate straight line.

$$\Delta(\Delta H) = [DH_0(\mathrm{XM}) - DH_0(\mathrm{X'M})] - [EA(\mathrm{X}) - EA(\mathrm{X'})] \quad (4)$$

Comparison of eqs. 3 and 4 clearly indicates that the quantities $\Delta(\Delta H)$ are independent of the *IP* and have a common second term, $\Delta(EA)$, i.e. they are determined only by the differences in the strength of the bonds connecting the hydrogen or metal atom with the heteroatoms X and X′.

In the gas phase, the foregoing applies to free energies (ΔG) as well, and hence to log K_d, in view of the extremely low entropy effects [5]. These effects must be taken into account in solution. However, it can be easily shown that the entropy effects are not responsible for the observed anomalies. To be more precise, the main differences in the behaviour of the O and S derivatives in DMSO are displayed by structurally similar compounds with Ph_3Pb and Ph_3Sn groups, whose entropy contributions must be closely similar. Consequently, the reversal of the values of K_d in the case of XHg and XPb bonds (SM < OM) may be determined only by the higher strength of the bonds connecting these metals with the sulfur atom (SM > OM). Unfortunately, the literature lacks data on the strength of S–M bonds. Data on the energy of homolytic and heterolytic dissociation are available only for XH acids. It has been shown that the increase in the energy of heterolysis of the OH bond in phenol, as compared to the SH bond in thiophenol ($\Delta H_0(\mathrm{OH}) > \Delta H_0(\mathrm{SH})$), is determined primarily by the greater strength of the OH bond ($DH_0(\mathrm{OH}) > DH_0(\mathrm{SH})$) [6].

To explain the abnormal stability of the SHg and SPb bonds, one may resort to the Pearson principle. According to the literature, the "softness" of organometallic cations decreases in the series [7]: $PhHg^+ > Ph_3Pb^+ > Ph_3Sn^+ > H^+$. In other words, the softest $PhHg^+$ and Ph_3Pb^+ cations exhibit greater affinity to the soft heteroatom (sulfur).

Indirect proof of the especially high strength of the S–Hg bond is the maximal value of this bond's force constant obtained by normal coordinate analysis [8].

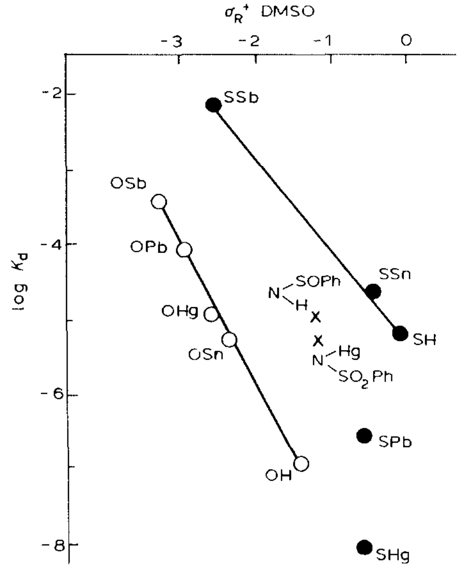

Fig. 2. Linear relations between the σ_R^+ constants of the XH and $XMPh_n$ groups and the logarithm of the dissociation constants of $p\text{-}NO_2C_6H_4XMPh_n$, (X = S (●), O (○), NR (×)).

Besides, according to our own findings and the published data, organic compounds of mercury form stronger coordination bonds with soft bases [9].

Thus, linear relations exist between the capacity for formation of an organometallic cation or proton and the polarity of the X–M and X–H (X = O, S) bonds. Only in the case of the softer MR_n groups are the S–M bonds abnormally stable, which is consistent with the Pearson principle.

Let us now consider the relationship between the capacity for heterolytic dissociation and the coordination capacity of the metal or hydrogen atom, as well as the relationship between the latter and the polarity of the XM and XH bonds.

As is known, in the case of XH acids, the relationship between the capacity for formation of hydrogen bonds and that for proton transfer involves compounds belonging to the same class [10]. For example, when the key atom X is varied, the sequence of K_c variations, namely $OH > NH_2 > SH$, is different from that of K_d values derived by us, namely $SH > OH > NH_2$, the latter being consistent with the known concepts of acidity [6,10].

The differences between the K_d and K_c sequences become apparent naturally in the case of MR_n derivatives. For instance, in the case of PhHg derivatives, the values of K_c decrease on going from the S–Hg bond to O–Hg, while those of K_d decrease dramatically on passing from O–Hg to S–Hg. For other MR_n derivatives, we are dealing with a different relationship between the coordination capacity and heteroatom. For example, in the case of Group IV elements, the capacity of O derivatives to form complexes is much more pronounced than that of the S analogues.

In some instances, the variations in K_c and K_d are anti-parallel. For example, *p*-nitrophenol and its Ph_3SnO derivative which form highly stable complexes dissociate weakly in DMSO.

At the same time, the $XSbPh_4$ groups exhibit the greatest capacity for dissociation and the lowest values of K_c, which must be due to steric hindrance.

Thus, the capacity for formation of organometallic cations is not determined by the force of the coordination interactions with the solvent.

Consequently, no direct relationship between the coordination capacity and polarity within the classes of O and S derivatives, similar to that described for K_d/σ_R^+, is likely to exist. A pronounced polarity effect on the coordination capacity is observed in the case of XH acids and their organometallic derivatives containing Group IV metals. OH acids and their derivatives form stable complexes with $K_c > 100$, whereas the complex formation constants of compounds with substantially less polar S–H and S–M bonds are lower by more than two orders of magnitude. In this case, the variations in K_c and σ^+ run in parallel:

$\mathrm{O{-}Pb}{\leq} > \mathrm{O{-}Sn}{\leq} > \mathrm{S{-}Pb}{\leq} > \mathrm{S{-}Sn}{\leq}$
$OH > NH_2 > SH$

Hence, only in the case of compounds whose complexing capacity varies within a wide range does the effect of bond polarity become predominant. Interestingly, the same applies to the increase in polarity in a coordinating medium ($\Delta\sigma_R^+ = \sigma^+_{R_{DMSO}} - \sigma^+_{R_{CH_2Cl_2}}$) (Fig. 3). In the literature, the medium-dependent variations in the electronic effect are usually attributed to the redistribution of the electron density in the complex. Our findings indicate that the relative contribution of another type of interaction, such as, possibly, dipole–dipole and dispersion ones, increases for

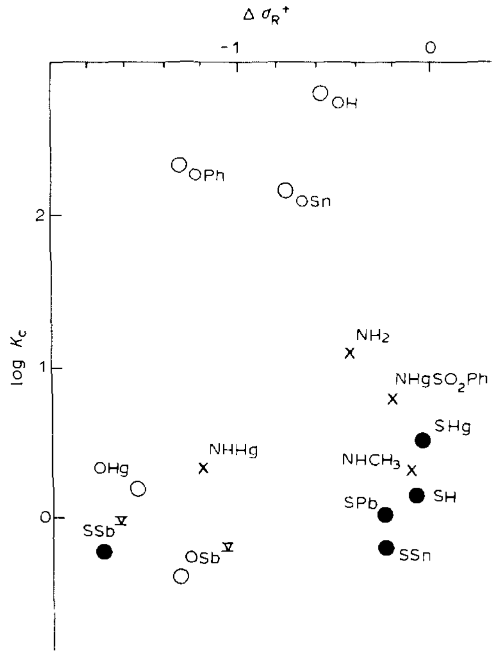

Fig. 3. Relations between the logarithm of the complex formation constants (log K_c) of p-$NO_2C_6H_4XMR_n$ (X = S (●), O (○), NR (×)) with DMSO and the values of $\Delta\sigma_R^+$ [$\Delta\sigma_R^+ = \sigma_R^+(DMSO) - \sigma_R^+(CH_2Cl_2)$].

compounds with larger substituents containing polar bonds (OSb, OHg, SSb). In the case of compounds with charged substituents (X^-) not capable of complexing, the values of σ_R^+ are also found to be solvent-sensitive, this sensitivity being determined only by polar interactions.

As a result, there is no common relationship between log K_c and σ_R^+. The parallel pattern of variations in these quantities applies only to XH acids and to compounds with $OPbPh_3$ and $OSnPh_3$ groups.

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