Journal of Organometallic Chemistry, 202 (1980) 363—378
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

MOLECULAR COMPLEXING AS THE INITIAL STAGE OF SOME REACTIONS OF ORGANOMETALLIC COMPOUNDS

G.A. RAZUVAEV *, A.V. SHABANOV, A.N. EGOROCHKIN, V.A. KUZNETZOV and S.F. ZHILTSOV

Institute of Chemistry, Academy of Sciences, Gorky (U.S.S.R.)

(Received June 10th, 1980)

Summary

Complexing of molecular oxygen with arylmercury compounds and phenyl derivatives of Group IV and V elements has been studied by electronic spectroscopy. The type of complexing appeared to depend on the nature of the central heteroatom in the organometallic compounds.

The chemical model for the reaction of R_2Hg (R = Et, n-Pr, n-Bu, Ph) with CCl_4 indicates that the complex $R_2Hg \cdot L$ (L = molecular oxygen, aromatic compound) is formed in the initial stage of the interaction. By studying the influence of π-donors on this process the correlation between the yield of alkylmercuric chloride and the donor properties of the ligand has been determined.

Introduction

Molecular complexes of donor-acceptor type play an important role in many chemical processes. Thus it is known, for example, that certain electron donor substances (hexamethylphosphoric triamide, dimethylformamide, pyridine, tetrahydrofuran, molecular oxygen) catalytically affect reactions of organic compounds of mercury [1—3], tin [4—6] and lead [4] with CCl_4 and ozone. The catalytic action of L comprises the formation of a labile complex $R_nE \cdot L$ (R = alkyl, aryl; E = Hg, Sn, Pb etc.) in the first stage of the process.

The formation of new donor—acceptor bonds results in an increase of polarity of the E—C [7—10] bond which leads to a change of reactivity of R_nE.

It is known [11] that the complex $R_nE \cdot O_2$ not only effects spontaneous homolytical decomposition of an organometallic compound but is also the initial stage of the autoxidation of the latter.

The properties of the complexes $R_nE \cdot L$ depend on the nature of the organometallic compound, ligand and solvent. Investigation of the properties of these complexes is very important not only for the understanding of the mechanisms of the chemical processes and for their control but also for the study of intramolecular interactions in organometallic compounds. However, complexing trends have not been studied well enough [12]. Difficulties in studying the properties of these complexes are presented by their lability and low values of equilibrium constants of complexing reactions, K_c.

$$R_nE + L \overset{K_c}{\rightleftharpoons} R_nE \cdot L \qquad (1)$$

For a given L, the stability of the complexes, and hence the K_c value, can be increased by introducing into the R_nE molecule electron-acceptor substituents or by reducing the temperature [13]. Analysis of literature data on complexing of mercury, tin and lead derivatives (these organometallic compounds served as the subjects of studies of reactivity with respect to CCl_4) showed that the majority of authors preferred the first method of increasing K_c, i.e. studying the complexes formed by organometallic compounds, containing electron-acceptor substitutes [14—30]. Formation of complexes by compounds possessing substituents with weak acceptor properties (for example, phenyl derivatives [9,12,24] is cast into doubt in some publications. We consider that it is caused by the non-availability of reliable methods of complex characterisation. Therefore, the aim of this work (studying the influence of complexing on the reactivity of R_nE) could be achieved by solving at least two interrelated problems.

The first was the development of a method for studying labile complexes formed by organometallic compounds. The second was the study of complexing effects on the course of chemical processes.

Results and discussion

K_c constant values for alkyl and aryl organometallic compounds were increased by reducing the temperature at which the complexes were studied down to 77 K.

We have shown previously [31,32] that electron emission spectroscopy is an suitable method for studying labile $R_nE \cdot L$ complexes at 77 K. It was found that molecular oxygen and tert-butyl peroxide cause a decrease (quenching) of R_nE luminiscence. The experiments were run under conditions of static quenching and obey the Stern-Volmer equation [33]:

$$\frac{I_0}{I} = 1 + K_q[Q]$$

where I_0 and I are emission intensities in the absence and in the presence of a quenching agent, respectively, [Q] is the quenching agent concentration and K_q the quenching constant. The assumption [33] that K_q for static quenching represents the equilibrium constant for $R_nE \cdot Q$ complex formation was verified on model systems [35]. For the latter the typical charge-transfer complexes of π,π-type formed by naphthalene (π-donor) and tetracyanoethylene (π-acceptor) were chosen. Complexing equilibrium constants K_c determined by spectrophotometry at room temperature are related to K_q constants determined at 77 K by the equation: $K_q \times 10^{-4} = 2.56\ K_c + 0.50$. This relation suggests that the quenching constants K_q are also proportional to the equilibrium constants K_c in the case of complexing of organometallic compounds with electron donors (molecular oxygen, peroxides, etc.). Therefore, values of K_q must be dependent on the donor-acceptor properties of the complex components and represent the complexing ability of the organometallic compound.

Complexing of the R_nE compounds studied, phenyl derivatives of mercury and Group IV and V elements, depends on two factors. Firstly, they possess an aromatic system and can therefore display π-donor properties. In this case oxygen, owing to its antibonding π_g^*-molecular orbitals, is a π-acceptor and as a result π,π-complexing can occur. Secondly, due to the availability of vacant *np* or *nd* orbitals of the central atoms E (V-acceptor) in R_nE and the bonding molecular π_u-orbitals of oxygen, a donor-acceptor element—oxygen bond can be formed by π,V-complexing. Complexing of tert-butyl peroxide depends on both factors in this way. The K_q value characterises the total complexing process according to the π,π- and π,V-mechanisms.

We shall now discuss in detail the relationship between reactivity and complexing for the aryl mercury compounds studied. An increase in electron donor character of substituent X in the aromatic ring of organomercury compounds [32] such as $(XC_6H_4)_2Hg$ (X = H, F, EtCOO, Me, MeO, Me_2N) is accompanied by a decrease of K_q quenching constant values for oxygen and tert-butyl peroxide (compounds 1—4, Table 1). The highest values of K_q are observed for $(C_6F_5)_2Hg$ and C_6H_5HgCl with electron-acceptor substituents on the mercury atom. Thus, analysis of K_q values (Table 1) allows us to conclude that organometallic compounds when complexing with oxygen and tert-butyl peroxide primarily show themselves as V-acceptors, forming π,V-complexes. From the data of Table 1 it can be inferred that quenching constants for peroxides ($K_q{}^2$) have lower values compared with quenching constants for oxygen ($K_q{}^1$). One of the main reasons for this, in our opinion, is steric hindrance caused by the tert-butyl groups bonded with the oxygen atom.

Referring now to the reactivity data, it should be noted that molecular oxygen and tert-butyl peroxide substantially change the reactivity of diphenylmercury with respect to CCl_4 [36,37]. Diphenylmercury reacts with CCl_4 only

TABLE 1

QUENCHING CONSTANTS FOR MOLECULAR OXYGEN (Kq^1) AND TERT-BUTYL PEROXIDE (Kq^2) AND FREQUENCIES OF CHARGE-TRANSFER BANDS IN CHARGE-TRANSFER COMPLEXES OF ORGANIC MERCURY COMPOUNDS WITH TETRACYANOETHYLENE (ν_{ct}) [a]

	Compound	$Kq^1 \times 10^{-2}$ (l mol^{-1})	$Kq^2 \times 10^{-2}$ (l mol^{-1})	$\nu_{ct} \times 10^{-3}$ (cm^{-1})
1	$(p\text{-}CH_3OC_6H_4)_2Hg$	2.5	0.15	17.9
2	$[p\text{-}(CH_3)_2NC_6H_4]_2Hg$	2.9	0.05	19.5
3	$(p\text{-}CH_3C_6H_4)_2Hg$	3.8	0.45	23.9
4	$(C_6H_5)_2Hg$	3.8	0.55	24.4
5	$(p\text{-}FC_6H_4)_2Hg$	3.9	0.70	24.4
6	$(p\text{-}C_2H_5COOC_6H_4)_2Hg$	4.0	0.80	23.8
7	C_6H_5HgCl	4.4	1.05	25.0
8	$(C_6F_5)_2Hg$	4.8	1.15	—

[a] Ref. 44.

TABLE 2

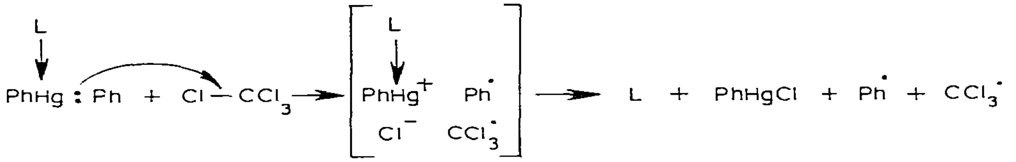
MAIN PRODUCTS FROM THE INTERACTION OF ORGANO-MERCURY COMPOUNDS WITH CCl_4 IN THE PRESENCE OF EQUIMOLAR AMOUNTS OF MOLECULAR OXYGEN

Experiment no.	Compound	Reaction condition	Conversion (%)	Yield of products in moles per mole of reacted R_2Hg									
				$RHgCl$	Hg	Hg_2Cl_2	$CHCl_3$	RCl	$R{-}H$ [a]	$RClCCl_3{-}H$ [b]	RH	ROH	CO_2
1	$(C_2H_5)_2Hg$	150°C, 30 h	91	0.66	0.30	0.02	0.50	0.66	0.55	—	0.15	—	—
2	$(C_2H_5)_2Hg$	O_2, 100°C, 50 h	96	0.83	0.11	0.03	0.33	0.60	0.40	0.02	0.04	—	0.20
3	$(n\text{-}C_3H_7)_2Hg$	150°C, 60 h	78	0.05	0.95	trace	1.00	0.96	0.91	—	0.05	—	—
4	$(n\text{-}C_3H_7)_2Hg$	O_2, 100°C, 60 h	100	0.50	0.40	0.05	0.39	0.58	0.28	0.32	0.03	0.10	0.10
5	$(n\text{-}C_4H_9)_2Hg$	150°C, 25 h	46	0.07	0.89	0.02	1.05	0.87	0.76	—	0.04	—	—
6	$(n\text{-}C_4H_9)_2Hg$	O_2, 85°C, 15 h	65	0.63	0.15	0.11	0.30	0.62	0.20	0.36	0.02	0.05	0.21

[a] Olefin. [b] Adduct of CCl_4 with olefin.

after heating to 473 K but the temperature of interaction is reduced to 373 K after introduction of tert-butyl peroxide into the reaction mixture. The rate of the reaction is accelerated upon increasing the molar ratio of peroxide to diphenylmercury. The rate of reaction can be judged by the amount of phenylmercuric chloride formed after 12 hours of reaction. The yield of PhHgCl was 7, 19 and 60% at a molar ratio of peroxide to Ph_2Hg of 1 : 10, 3 : 10 and 1 : 1, respectively. It should be noted that tert-butyl peroxide is practically not consumed in the reaction. Molecular oxygen similarly affects the interaction of diphenylmercury with CCl_4.

The catalytic action of tert-butyl peroxides and oxygen on this reaction can be explained by the formation of a labile complex $Ph_2Hg \cdot L$ (L = oxygen or tert-butyl peroxide) of π,V-type in the first stage of the reaction. Organomercury compounds with low ionization potentials can react directly with CCl_4 by the one-electron transfer mechanism [38,39,41]. Complexing leads to an increase of the polarity of the C—Hg bond [7—10] which must promote one-electron transfer in the reaction of diphenylmercury with CCl_4. Interaction of the coordination complex $Ph_2Hg \cdot L$ with CCl_4 is accompanied by generation of radicals. The formation of radicals by non-solvated organometallic compounds was observed in the interaction with tetracyanoethylene [42]:



(2)

The influence of molecular oxygen on reactions of alkylmercury compounds R_2Hg, in contrast to the reactions of phenyl derivatives was explained by oxidation of the organic mercury compounds [43]. This conclusion was reached on the ground of the formation of oxidation products of R_2Hg (the reactions were carried out at 2.3-fold molar excess of oxygen with respect to R_2Hg). At the same time, the interaction of R_2Hg with CCl_4 is catalysed by electron donor compounds L (hexamethylphosphoric triamide, pyridine, tetrahydrofuran) [2]. We conducted similar reactions at 358—373 K in the presence of an equimolar ratio of oxygen to R_2Hg in order to study in detail the role of molecular oxygen in these processes (Table 2). In this case the mercury derivatives R_2Hg (R = Et, n-Pr, n-Bu), stable with respect to oxygen, were used [43].

The organomercury compound initially dissociated into radicals in the thermal reaction of R_2Hg with CCl_4 in the absence of oxygen (exps. 1, 3, 5; Table 2):

$$R_2Hg \rightarrow RHg^{\bullet} + R^{\bullet} \qquad (3)$$

The radicals formed react with the solvent:

$$R^{\bullet}(\text{or } RHg^{\bullet}) + CCl_4 \rightarrow RCl(\text{or } RHgCl) + C^{\bullet}Cl_3 \qquad (4)$$

or with the original organomercury compound, inducing decomposition of the latter [36,38,40].

$$C^{\bullet}Cl_3 + RHgR \rightarrow CHCl_3 + [(R-H)^{\bullet}HgR] \qquad (5)$$

$$(\mathrm{R-H})^{\cdot}\mathrm{HgR} \left\{ \begin{array}{l} \xrightarrow{(a)} (\mathrm{R-H}) + \mathrm{Hg} + \mathrm{R}^{\cdot} \\ \xrightarrow[(b)]{} \underset{(\text{olefin})}{(\mathrm{R-H})} + \mathrm{RHg}^{\cdot} \end{array} \right. \qquad (6)$$

The presence of Hg_2Cl_2 in the reaction products is due to further dealkylation of the resulting alkylmercuric chloride. The main product from thermal reactions of dipropyl- and dibutylmercury with CCl_4 is mercury (~0.90 mol per 1 mol of the decomposed organomercury compound, see Table 2, exp. 3 and 5). Mercury formation is the result of induced decomposition of R_2Hg according to reactions 5 and 6a. Introduction of O_2 into the reaction mixture results in a decrease of the reaction temperature and the yield ratio of mercury and alkylmercuric chloride (cf. exp. 1 and 2, 3 and 4, 5 and 6; Table 2) is drastical changed. The higher value of RHgCl yield as compared to mercury (exps. 2, 4, 6; Table 2) can be explained by the important role of process 2 in these reactions. The catalytic action of oxygen in this case is also due to the formation of the labile complex $R_2Hg \cdot O_2$ which reacts directly with CCl_4 in the first stage of the reaction. Transformation of the complex with the formation of the products of R_2Hg oxidation practically did not take place. The corresponding alcohol or aldehyde were found in the reaction mixture in only insignificant amounts.

Hence, the increase in reactivity of diphenyl- and dialkylmercury by the action of oxygen is accounted for by the formation of a π,V-type complex in the first stage of the reaction. Spectroscopic data on complexing of arylmercury compounds with molecular oxygen not being available, an alternative mechanism for the change of reactivity of Ar_2Hg with formation of π,π-type complexes might be suggested. In this case transfer of the electron density from the aromatic ring of Ar_2Hg (π-donor) onto the oxygen molecule (π-acceptor) also presupposes a polarity increase of the Hg—C bond, but on the basis of ref. 32 this alternative π,π-mechanism is either completely non-existent or plays a substantially subordinate role as compared to the π,V-type complexing. When varying the central element E in the phenyl derivatives of Ph_nE type, the relation between the π-donor and V-acceptor properties of these compounds may be expected to change. In this connection we have studied the dependence of the complexing mechanism on the nature of the heteroatom E. Determination of the molecular oxygen coordination centre and of its role as a component of the donor-acceptor complex is a relevant to a more fundamental understanding of the oxidation mechanism of organometallic compounds as well as to the study of the dependence of R_nE reactivity on molecular oxygen and other electron donors.

The coordination of molecular oxygen was studied on Group IV and V element complexes of Ph_4E (E = C, Si, Ge, Sn, Pb) and Ph_3E (E = N, P, As, Sb, Bi) types with molecular oxygen. These compounds differ from the organomercury compounds by the fact that the substituents in the latter were varied for a given heteroatom.

Molecular oxygen coordination onto the phenyl ring is promoted by increasing π-electron density on the aromatic ring. The data on the magnitude of the π-electron density, i.e. on the π-donor ability of Ph_nE can be obtained, for example, from absorption spectra of charge-transfer complexes of organometal-

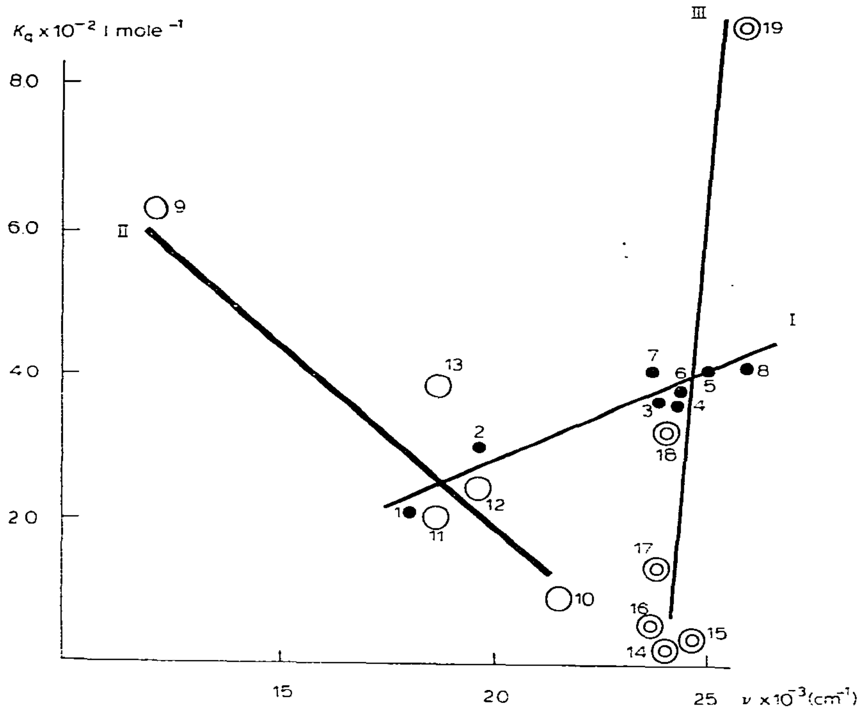


Fig. 1. The interdependence of K_q and ν_{ct}. Line I refers to compounds listed in Table 1. Lines II and III refer to compounds listed in Table 3.

lic compounds with tetracyanoethylene. These complexes are of π,π-type, where the π-acceptor is tetracyanoethylene which, as in the case of molecular oxygen, makes use of antibonding molecular orbitals when forming a donor-acceptor bond. The charge transfer frequency ν_{ct} characterises the π-donor ability of Ph_nE and permits qualitative evaluation of the contribution of the π,π-type complexing mechanism to the quenching constant K_q(Ph_nE-oxygen system). ν_{ct} values decrease as the donor properties of Ph_nE compounds increase. Fig. 1 shows K_q as a function of ν_{ct} for the compounds studied.

For the series of organomercury compounds (Fig. 1, linear function I) the decrease in ν_{ct} (increase of π-donor properties) is accompanied by a decrease in K_q values. Hence, the organomercury compounds which show themselves as strong electron donors in complexing with tetracyanoethylene are characterised by the lowest values of K_q when interacting with molecular oxygen. This confirms the above conclusion that arylmercury derivatives display V-acceptor properties when complexing with molecular oxygen.

The ν_{ct} values for derivatives of Group V elements (Table 3) reveal a high π-donor ability for triphenylamine (ν_{ct} ~11400 cm^{-1}), a much lower π-donor ability for Ph_3P (ν_{ct} ~21400 cm^{-1}) and approximately the same π-donor properties for Ph_3As, Ph_3Sb and Ph_3Bi, for which ν_{ct} is 18500, 19000 and 18600 cm^{-1}, respectively. Weak donor properties for triphenylphosphine are due to the effect of p_π—d_π interaction [47] resulting in delocalization of π-electron density of the aromatic ring onto the vacant 3d orbitals of the phosphorus

TABLE 3

K_q AND ν_{ct} VALUES FOR PHENYL DERIVATIVES OF GROUP IV AND V ELEMENTS

	Compound	$K_q^1 \times 10^{-2}$ (l mol^{-1})	$\nu_{ct} \times 10^{-3}$ (cm^{-1})
9	Ph_3N	6.5	11.4
10	Ph_3P	1.4	21.4
11	Ph_3As	2.5	18.5
12	Ph_3Sb	2.8	19.0
13	Ph_3Bi	4.1	18.6
14	Ph_4C	0.8	24.3
15	Ph_4Si	0.8	24.4
16	Ph_4Ge	0.9	24.0
17	Ph_4Sn	1.7	24.0
18	Ph_4Pb	3.4	24.3
19	Ph_2GeH_2	8.8	25.6
20	$PhGeH_3$	20	25.6

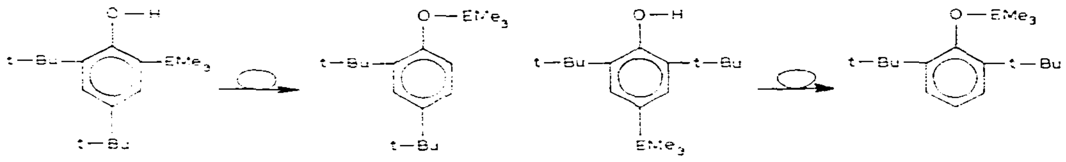
atom. This effect does not occur in triphenylamine as there are no energetically accessible vacant orbitals on the nitrogen atom. With increase of the central element E atomic number on changing from Ph_3P to Ph_3Bi, the effect of p_π—d_π interaction disappears almost completely. K_q values for Group V compounds change simultaneously with the change in their π-donor ability (Table 3) [45]. This is an indication of the predominant role of π,π-type complexing (Ph_nE—π-donor) for these compounds. The K_q value is the highest for triphenylamine, which exhibits high π-donor ability and does not possess V-acceptor properties, among these compounds of Group V elements.

The fact that K_q values for triphenylbismuth are much higher than for Ph_3As and Ph_3Sb, although the π-donor properties of these compounds are approximately equal (see Table 3), is an indication of a significant contribution to K_q from V-acceptor properties in the case of Ph_3Bi. The deviation of point 13 (Fig. 1, linear function II), representing Ph_3Bi, in the direction of higher values of K_q points to an increase of V-acceptor properties with increasing atomic number of the central element E. This relationship clearly shows itself for phenyl derivatives of Group V elements. The π-donor properties of these elements are almost the same (ν_{ct} values are approximately equal, Table 3) but the K_q values increase with increasing atomic number of E (linear function III, Fig. 1). The points representing tetraphenylmethane and tetraphenylsilane are located on the straight line for organic compounds of Group V elements (Fig. 1), but the points representing tetraphenyltin and tetraphenyllead deviate from this line towards higher values of K_q. High values of K_q for Ph_4Sn and Ph_4Pb are an indication of a significant contribution from V-acceptor properties for these compounds when complexing with molecular oxygen.

Tetraphenylgermane exhibits weak acceptor properties for complexing. K_q values for diphenylgermane and further for phenylgermane are much higher as compared with the values for tetraphenylgermane although the π-donor properties of these compounds, as judged by ν_{ct} values, are weaker than that of Ph_4Ge (Table 3). This experimental fact indicates that with a decrease of steric hindrance for the germanium atom (substitution of three-dimensional phenyl rings by hydrogen atoms) the V-acceptor properties of the organometallic compound increase substantially.

Thus, increasing of atomic number of Group IV and V element E in Ph_nE compounds results in a gradual change from the π,π-type complexing mechanism to the π,V-type. Therefore the catalytic action of electron donor substances on the interaction of tetraphenyllead with CCl_4 [4] can undoubtedly be treated on the basis of π,V-type complexing. If complexing in the reactions is postulated for Ph_4C, Ph_4Si, Ph_3N, Ph_3P, $PhER_3$ (E = Si, Ge; if E = Ge, R $\neq$ H) with molecular oxygen or other ligands possessing commensurable donor and acceptor functions, this complexing will primarily follow the π,π-mechanism.

In this connection we considered the rearrangement of screened organometallic phenols caused by molecular oxygen [44].

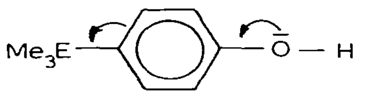


E = Si, Ge

Oxidised phenols were not found among the reaction products.

We found that all the phenols 21—27 form complexes with O_2 (Table 4). It is also known [45] that phenylsilanes Ph_nSiX_{4-n} (X = H, Cl, Me, Et, OMe; n = 1—3) form π,π-type complexes with molecular oxygen. In this case, K_q values for phenols (Table 4) are much higher than for phenylsilanes. This indicates that phenols as well as phenylsilanes form π,π-type complexes with molecular oxygen since the acceptor properties of phenols are markedly weaker than those of phenylsilanes.

The increase of K_q values for phenols from 21 to 22 and 27, and also from 23 to 24 and 27 (Table 4) is accounted for by the increase of electron donor properties of the *ortho* or *para* substituents of EMe_3 type in the following series: $SiMe_3 < GeMe_3 < CMe_3$. Indeed σ_p constants for these substituents are +0.07, —0.01 and —0.19 respectively. Thus, the $SiMe_3$ group possesses acceptor properties and the $GeMe_3$ and CMe_3 groups possess donor properties. Hence, with variation of E, K_q values increase in the series Si < Ge < C. However, when passing from phenol 21 to 23 and from 22 to 24, the K_q values decrease (Table 4). This relationship seems to result from a decrease of π-electron density on the aromatic ring due to the effect of direct polar conjugation



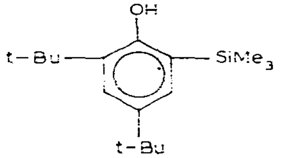
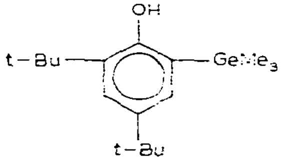
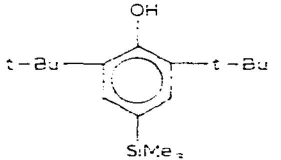
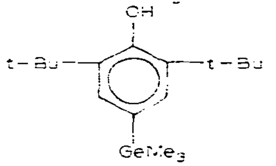
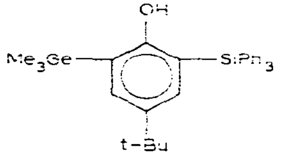
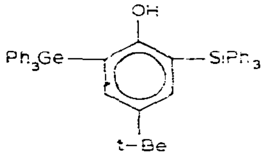
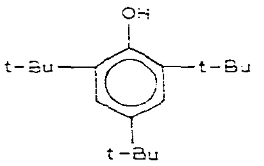
The decrease of π-donor properties (low values of K_q in comparison with phenol 27) for the mixed phenols 25 and 26 (Table 4) can be accounted for by the substitution of typically electron donor tert-butyl groups by Ph_3E fragments.

The stabilities of the phenols increase in the following order: 22 < 21 < 23 ~ 24. Phenols 25 and 26 do not rearrange in air. The K_q values decrease in the same order (Table 4).

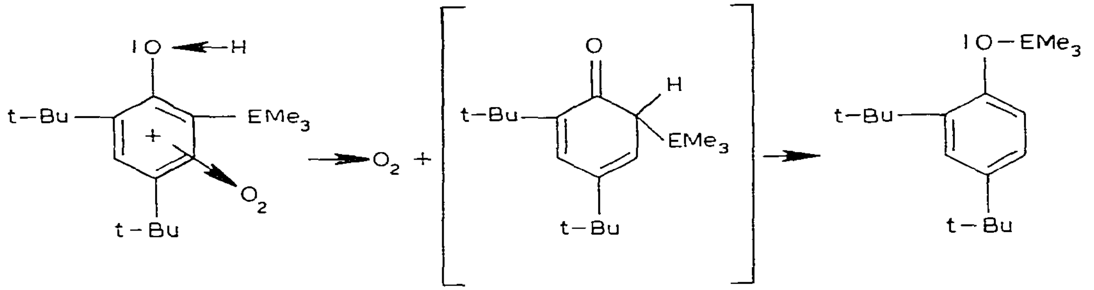
The existence of a correlation between the stability of organometallic phenols and K_q values and absence of oxidised phenols allows us to draw a con-

TABLE 4

K_q VALUES FOR SILICON AND GERMANIUM-CONTAINING PHENOLS

Number	Compound	$K_q \times 10^{-2}$ (l mol^{-1})
21		3.0
22		3.5
23		2.8
24		3.0
25		2.7
26		2.8
27		3.8

clusion about the significant role of molecular oxygen as a component of a donor-acceptor complex. In the process of complexing of a phenol with molecular oxygen a partial positive charge appears on the aromatic ring, causing increasing n,π-conjugation of the lone electron pair of the oxygen atom of the OH group with the π-system. As a result, the hydroxyl hydrogen atom of the phenol becomes more mobile.



Thus the initial stage of the molecular oxygen-induced rearrangement of sterically hindered phenols is the formation of the labile complex ArOH · O_2. The tendency to rearrange increases with increasing equilibrium constant for the complexing, i.e. with increasing π-donor ability of the phenol.

The complex $R_nE \cdot O_2$ also participates in reactions of organomercury compounds with CCl_4. Molecular oxygen, when forming a π,V-type complex, increases the polarity of the C—Hg bond, raising the reactivity of the original organometallic compound with respect to CCl_4. The degree of polarization of the C—Hg bond must be highly dependent on the ligand donor properties. In this connection it might be expected that the degree of conversion of the organomercury compound could be correlated with the π-donor properties of the ligand. But when using hexamethylphosphoric triamide, dimethylformamide, tetrahydrofuran, pyridine etc. [2,4] as ligands, this simple relationship does not hold. This can be explained by the participation of different donor centres of ligands L (oxygen and nitrogen atoms) in the formation of the donor-acceptor bonds Hg ← L. It should be noted that the donor properties of pyridine and to a lesser extent of hexamethylphosphoric triamide and dimethylformamide are weakened by their coordination with CCl_4 [49—53]. When hydrocarbons of C_6H_5X (X = H, Me, Et, OMe, OEt) type, possessing π-donor properties, are used as L, the π-donor ability of the ligand can be widely varied by changing the substituent X. The σ_p^+ Brown-Okamoto constants for the substituent X can serve as a parameter reflecting the influence of X on the basicity of the aromatic hydrocarbons [54].

The influence of aromatic hydrocarbons on the reaction of dipropylmercury with CCl_4 was studied. This organomercury compound was chosen because of possibility of separating the products from the induced decomposition of Pr_2Hg (processes 5 and 6) from the molecular interaction with participation of $Pr_2Hg \cdot L$ (equation 2) in this case.

The addition of equimolar quantities of aromatic hydrocarbons increases the conversion of Pr_2Hg. In this case the yield of propylmercuric chloride (the product of complex reaction according to equation 2) approaches (exps. 3—7, Table 5) and even exceeds (exps. 8 and 9, Table 5) the yield of mercury (induced decomposition product according to equations 5 and 6). Fig. 2 shows the yield of PrHgCl as a function of $\Sigma\sigma_p^+$ constants of the substituents in C_6H_5X. As can be seen from Fig. 2, the influence of *p*-xylene (exp. 4) and durene (exp. 2) on the reaction is abnormally low as compared with the influ-

TABLE 5

YIELD OF MAIN PRODUCTS FROM THE REACTION OF n-Pr_2Hg (0.0017 mol) WITH CCl_4 (0.03 mol) IN THE PRESENCE OF π-DONORS (0.0017 mol) AT 130°C AFTER 50 h. ν^1_{ct} AND ν^2_{ct} REPRESENT THE CHARGE-TRANSFER FREQUENCIES OF CHARGE-TRANSFER COMPLEXES OF DIPHENYLMERCURY AND TETRACYANOETHYLENE, RESPECTIVELY, WITH π-DONORS

Number	π-donor	$\nu^1_{ct} \times 10^{-3}$ (cm^{-1})	$\nu^2_{ct} \times 10^{-3}$ (cm^{-1}) [a]	Conversion (%)	Yields (moles per mole of n-Pr_2Hg)				
					RHgCl	Hg_2Cl_2	Hg	RCl	$CHCl_3$
1	—	—	—	36	0.01	—	0.35	0.37	0.41
2	1,2,4,5-$(CH_3)_4C_6H_2$	—	20.8	50	0.03	—	0.47	0.40	0.49
3	C_6H_6	37.0	26.0	66	0.15	—	0.51	0.45	0.60
4	p-$(CH_3)_2C_6H_4$	36.2	24.1	62	0.22	—	0.40	0.38	0.51
5	$C_2H_5C_6H_5$	36.6	24.3	70	0.18	0.02	0.48	0.41	0.50
6	$CH_3C_6H_5$	36.5	24.7	73	0.16	0.04	0.49	0.58	0.72
7	m-$(CH_3)_2C_6H_4$	35.9	22.8	83	0.20	0.06	0.51	0.55	0.78
8	$CH_3OC_6H_5$	34.9	19.7	98	0.35	0.10	0.43	0.75	0.83
9	$C_2H_5OC_6H_5$	34.7	19.3	97	0.39	0.09	0.40	0.73	0.79

[a] Ref. 54.

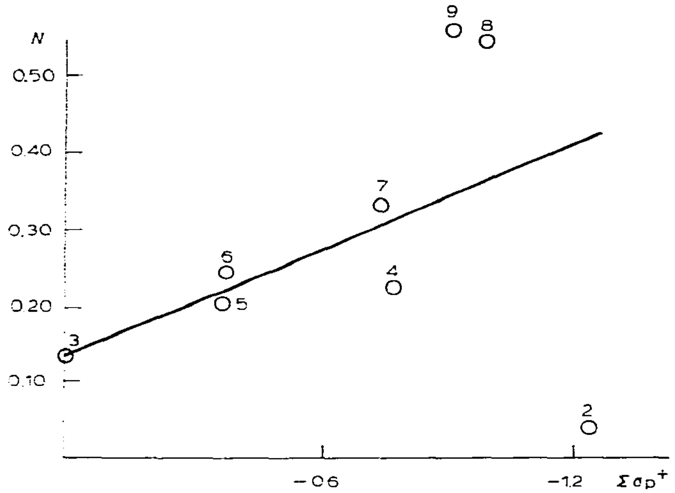


Fig. 2. The dependence of propylmercuric chloride yield N (with regard for formation of Hg_2Cl_2) on $\Sigma\sigma_p^+$ constants for the substituents of the π-donor.

ence of compounds in experiments 3, 5, 6 and 7 (Table 5). At the same time anisole and phenetole (exps. 8 and 9) exhibit abnormally high donor properties. These data suggest that anisole and phenetole act in the reaction with CCl_4 not as π- but as n-donors due to the lone electron pairs of the oxygen atom. Therefore, for the purpose of getting a deeper insight into the initial stage of the process studied we investigated the trends in complexing of diphenylmercury with aromatic hydrocarbons by electronic absorption spectroscopy. The absorption spectra showed that addition of benzene to a diphenylmercury solution in methylene chloride causes the appearance of a new absorption band at about 37000 cm^{-1} which was not present in the spectra of the separate compounds. We assign this long wavelength band to the charge-transfer transition. Introduction of electron donor substituents into benzene ring increases the energy of the highest occupied molecular orbital of donor closer to the lowest vacant orbital of the acceptor (Ph_2Hg) and causes an increase in energy $h\nu^1$ of charge transfer (exp. 3—9, Table 5). The charge-transfer frequency, ν_{ct}, characterises the ligand donor properties in this case. It should be noted from the spectrophotometric study of complexing the π-donor properties of p-xylene are much weaker than those of m-xylene (cf. exps. 4 and 7, Table 5). Weak donor properties of p-xylene are also observed for charge-transfer complexing with tetracyanoethylene [54].

The spectra of complexes of π-donors with tetracyanoethylene are well studied [e.g. 55]. The following correlation between ν_{ct} for π-donors with Ph_2Hg and tetracyanoethylene

$$\nu_{ct}^1 = 0.32\nu_{ct}^2 + 28660 \ (r = 0.98) \qquad (7)$$

allows us to draw a conclusion about the close nature of donor-acceptor interactions in these systems. That is why we correlated ν_{ct}^1 values with propylmercuric chloride yield in the reaction of n-Pr_2Hg with CCl_4 (Fig. 3).

$$\text{Number of moles PrHgCl} = 7.57 - 0.0002\nu_{ct}^1 \ (r = 0.97) \qquad (8)$$

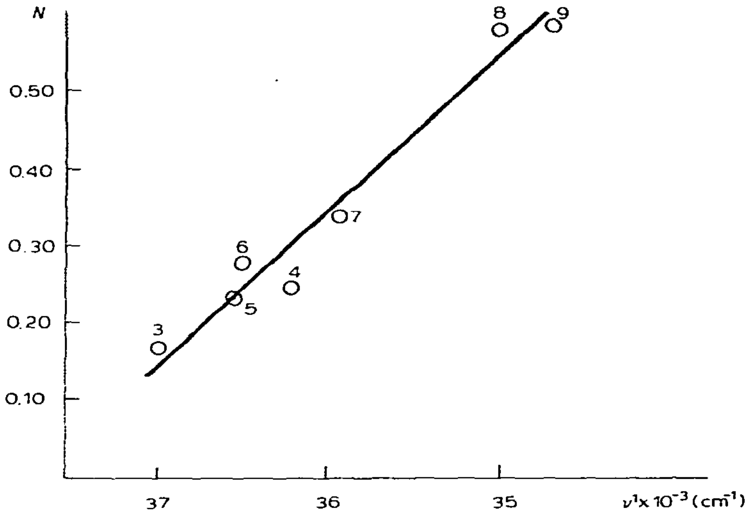


Fig. 3. The interdependence of propylmercuric chloride yield N and ν^1_{ct}.

This correlation confirms the above conclusions about the participation of complexes $R_nE \cdot L$ in reactions of R_nE with CCl_4. The non-existence of a durene complex with Ph_2Hg (absence of the charge-transfer band) and the weak π-donor properties of *p*-xylene can be explained by a decrease of basicity resulting from a symmetric arrangement of methyl groups [56]. For example, *p*-xylene and *m*-xylene basicities as determined by complexing with Ag^+ are 1.04 and 1.23, respectively, (the basicity of benzene is taken as 1.0). For durene the basicity equals 0.80 and for its non-symmetric isomer it is 1.54.

Thus, simultaneous analysis of data on the reactivity and electronic spectroscopy of complexes with reagent participation allows us to draw important conclusions on the role of molecular complexes in the initial stage of reactions of organometallic compounds.

Experimental

The starting organomercury compounds were obtained by the Grignard reaction. Their purity was checked by determination of their boiling (melting) points and by means of IR spectroscopy. Tert-butyl peroxide, CCl_4 and other solvents were purified in accordance with literature procedures [57,58]. After the reaction had been completed the gaseous products were separated and analyzed by means of a MI-1305 mass spectrometer. The highly volatile products and solvent were recondensed in vacuum cold traps cooled by liquid nitrogen. This fraction was analyzed by means of a Tsvet-100 chromatograph employing a heat conductivity detector. Carbon tetrachloride was added to the reaction residue after distillation of the highly volatile fraction. The obtained solution was filtered from mercury, alkylmercuric chloride and calomel. Associated polychloroalkanes were found in the filtrate. Alkylmercuric chlorides were separated from calomel and mercury by dissolving in chloroform. They were identified from their melting points. Calomel was identified by the reaction with aqueous ammonia.

Complexes of organometallic compounds with oxygen [31] and tert-butyl peroxide were studied at 77 K in optical quartz vessels. Oxygen was dried over 4 Å molecular sieves. It was assumed that under normal conditions and with rapid freezing to 77 K the oxygen concentration in n-hexane was 1.5×10^{-2} mol l^{-1} [33]. The absorption spectra were recorded on a Perkin-Elmer 402 spectrophotometer. The quartz cells were 1 cm thick. The concentration of solutions studied was 10^{-4} mol l^{-1}.

References

1 G.A. Razuvaev, S.F. Zhiltsov, G.I. Anikanova and T.V. Guseva, Dokl. Akad. Nauk SSSR, 225 (1975) 336.

2 G.A. Razuvaev, S.F. Zhiltsov, A.V. Shabanov and L.F. Kudryavtsev, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 1331.

3 G.A. Razuvaev, S.F. Zhiltsov, A.V. Shabanov and A.A. Lavrentyev, Zh. Obshch. Khim., 50 (1980) 567.

4 G.A. Razuvaev, S.F. Zhiltsov, G.I. Anikanona and T.V. Guseva, Zh. Obshch. Khim., 49 (1979) 2020.

5 M.L. Pereplyotchikov, B.I. Tarunin, Yu.Yu. Alexandrov and E.G. Pomerantseva, Zh. Obshch. Khim., 47 (1977) 1222.

6 M.L. Pereplyotchikov, B.I. Tarunin, Yu.A. Alexandrov, T.I. Lyohonkaya, E.G. Pomerantseva, Zh. Obshch. Khim., 49 (1979) 160.

7 J.C. Milles, H.S. Preston and G.H. Kennard, J. Organometal. Chem., 14 (1968) 33.

8 R.S. Seccomble and G.H. Kennard, J. Organometal. Chem., 18 (1969) 243.

9 Y. Farhangi and D.P. Gradnard, J. Organometal. Chem., 71 (1974) 17.

10 L.A. Fyodorov and E.I. Fedin, Dokl. Acad. Nauk SSSR, 195 (1970) 856.

11 Yu.A. Alexandrov, Jidkofaznoye Avtookisleniye Elementoorganicheskikh Soyedineniy, Nauka, Moscow, 1978, p. 7.

12 I.P. Beletskaya, K.P. Butin, A.N. Ryabtsev and O.A. Reutov, J. Organometal. Chem., 59 (1973) 1.

13 E.N. Guryanova, I.P. Goldshteyn and I.P. Romm. Donorno-aktseptornaya svyaz, Khimiya, Moscow, 1973, p. 100.

14 V.S. Petrosyan, N.S. Yashina, O.A. Reutov, E.V. Bryuchova and G.K. Semin, J. Organometal. Chem., 52 (1973) 321.

15 L.A. Fyodorov, D.N. Kravtsov, A.S. Peregudov, E.I. Fedin and E.M. Rockhlina, Izv. Akad. Nauk SSSR, Ser. Khim., (1971) 1705.

16 L.L. Fridman, T.N. Ivshina, V.A. Tartakovskiy and S.S. Novikov, Izv. Akad. Nauk SSSR, Ser. Khim., (1968) 2839.

17 S.A. Bhattacharya, Raj. Prem. J. Inorg. and Nucl. Chem., 40 (1978) 1699.

18 L.A. Fyodorov, Z.A. Stumbrevichyute, B.I. Martinov and B.L. Dyatkin, Zh. Org. Khim., 11 (1975) 489.

19 L.A. Fyodorov, Z.A. Stumbrevichyute and E.I. Fedin, J. Org. Khim., 11 (1975) 913.

20 M. Gielen and J. Nasielski, J. Organometal. Chem., 1 (1963) 173.

21 L.A. Fyodorov, Z.I. Stumbrevichyute, A.K. Prokofyev and E.I. Fedin, Dokl. Akad Nauk SSSR, 209 (1973) 134.

22 E.T. Bogoradovskiy, V.S. Zavgorodniy, B.I. Rogozeev, V.I. Cherkasov and A.A. Petrov, Zh. Obshch. Khim., 47 (1977) 2630.

23 G. Naselskiy, Usp. Khim., 41 (1972) 1229.

24 H. Warren and H.F. Henneike, J. Phys. Chem., 77 (1973) 558.

25 A.G. Canty and J.B. Deacon, J. Organometal. Chem., 49 (1973) 125.

26 L.A. Fyodorov, Z.A. Stumbrevichyute and E.I. Fedin, Zh. Strukt. Khimii, 15 (1974) 1063.

27 V.S. Petrosyan, A.S. Voyakin and O.A. Reutov, Zh. Org. Khim., 6 (1970) 889.

28 V.S. Petrosyan, N.S. Yashina, V.I. Bakhmutov, A.V. Permin and O.A. Reutov, J. Organometal. Chem., 72 (1974) 71.

29 L.A. Aslanov, V.M. Ionov, V.M. Attiya, A.B. Permin and V.S. Petrosyan, Zh. Strukt. Khimii, 18 (1977) 1103, 1113; 19 (1978) 109, 185, 315.

30 V.S. Petrosyan, N.S. Yashina, O.A. Reutov, E.V. Bryuchova and G.K. Semin, J. Organometal. Chem., 52 (1973) 321.

31 G.A. Razuvaev, A.N. Egorochkin, V.A. Kuznetsov, V.N. Glushakova, Yu.A. Alexandrov, A.V. Shabanov and Yu.Yu. Baryshnikov, J. Organometal. Chem., 148 (1978) 147.

32 A.V. Shabanov, V.A. Kuznetsov, A.N. Egorochkin, S.F. Zhiltsov and G.A. Razuvaev, Dokl. Acad. Nauk SSSR, 239 (1978) 617.

33 A.N. Terenin, Fotonika Molekul Krasiteley i Rodstvennykh Organicheskikh Soyedineniy, Nauka, Moscow, 1967, p. 455.

34 G.A. Parker, Photoluminescence of Solutions, Elsevier, Amsterdam-New York, 1968.

35 P.G. Sennikov, V.A. Kuznetsov, A.N. Egorochkin and D.V. Muslin, Dokl. Acad. Nauk SSSR, 248 (1979) 123.

36 S.F. Zhiltsov, Zh. Obshch. Khim., 43 (1973) 586.

37 S.F. Zhiltsov, L.F. Kudryavtsev, O.N. Drujkov and G.G. Petukhov, Zh. Obshch. Khim., 39 (1968) 2276.

38 W.A. Nugent and I.K. Kochi, J. Organometal. Chem., 124 (1977), 327, 349, 371.

39 P. Fehler, I. Shman, W.A. Nugent and I.K. Kochi, Inorg. Chem., 15 (1976) 2544.

40 W.A. Nugent and I.K. Kochi, J. Amer. Chem. Soc., 98 (1976) 5405.

41 C.L. Wongand and I.K. Kochi, J. Amer. Chem. Soc., 101 (1979) 5593.

42 S. Fukuzumi, K. Moshida and I.K. Kochi, J. Amer. Chem. Soc., 101 (1979) 5961.

43 G.A. Razuvaev, S.F. Zhiltsov, O.N. Drujkov and G.G. Petukhov, Dokl. Akad. Nauk. SSSR, 152 (1963) 633.

44 G.A. Razuvaev, E.P. Oleynik, I.L. Knyazeva, V.A. Kuznetsov and A.V. Shabanov, Izv. Akad. Nauk SSSR, Ser. Khim., (1980) 634.

45 A.V. Shabanov, A.N. Egorochkin, V.A. Kuznetsov, S.F. Zhiltsov and G.A. Razuvaev, Dokl. Akad. Nauk SSSR, 250 (1980) 1161.

46 V.A. Kuznetsov, A.N. Egorochkin, S.E. Skobeleva, G.A. Razuvaev, N.A. Pritula and G.Ya. Zueva, Zh. Obshch. Khim., 45 (1975) 2439.

47 A.N. Egorochkin and S.E. Skobeleva, Usp. Khim., 48 (1979) 2216.

48 A.N. Egorochkin, V.A. Kuznetsov, A.N. Artyomov, N.I. Sirotkin, V.G. Kirilicheva and G.A. Razuvaev, Dokl. Akad. Nauk SSSR, 227 (1976) 878.

49 Ya. M. Tsikanchyuk, P.G. Makitra and V.M. Lukyanets, Zh. Obshch. Khim., 47 (1977) 1690.

50 S. Kennard and P.A. Gusker, J. Amer. Chem. Soc., 70 (1948) 3375.

51 D.F. Grey, I.D. Watson and A.G. Williamson, Austr. J. Chem., 21 (1968) 379.

52 K.W. Marcom and D.H. Travers, Trans. Farad. Soc., 62 (1966) 2063.

53 V.M. Lukyanets, P.G. Makitra and Ya.M. Tsikanchyuk, Zh. Obshch. Khim., 47 (1977) 506.

54 V.A. Kuznetsov, A.N. Egorochkin, G.A. Razuvaev, S.E. Skobeleva and N.A. Pritula, Dokl. Akad. Nauk SSSR, 216 (1974) 812.

55 L. Andrews and R. Keefer, Molecular Complexes in Organic Chemistry. Holden Day Inc., San Francisco and London, 1964.

56 N. Ogimachi, L. Andrews and R. Keefer, J. Amer. Chem. Soc., 77 (1955) 4202.

57 Organikum. VEB Deutscher Verlag der Wissenschaften Berlin, 1964.

58 E.S. Stern, C.I. Timmons, Gillam and Stern's Introduction to Electronic Absorption Spectroscopy in Organic Chemistry, Edward Arnold, Publishers, London, 1970.