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THE INVESTIGATION OF COMPLEXING ORGANIC DERIVATIVES OF GROUP IV AND V ELEMENTS WITH OXYGEN BY ELECTRONIC EMISSION SPECTROSCOPY

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Summary

Electronic emission spectra of phenyl derivatives $(C_6H_5)_3M$ (M = N, P, As, Sb, Bi), $(C_6H_5)_4M$ (M = C, Si, Ge, Sn, Pb), $(C_6H_5)_3MH$ (M = Si, Ge) and tetraalkylstannanes R_4Sn (R = CH_3, n-C_4H_9, n-C_5H_{11}) have been studied at 77 K. The process of phosphorescence quenching by dissolved oxygen is predominant among other deactivation processes of triplet states. The oxygen quenches phosphoresence with the formation of labile donor—acceptor complexes. The bimolecular quenching process obeys Stern—Volmer equation. It has been shown that the compounds investigated and oxygen have donor as well as acceptor properties when they form complexes. Donor—acceptor properties of these compounds depend strongly on n,π-conjugation, energy of π- and σ-bonds with participation of *nd*-orbitals for the elements of phosphorus and silicon subgroups and on steric factors.

Introduction

The present literature data on autoxidation of organometallic compounds, for example [1], allow us to assume that the process consists of two stages. At the first stage a labile complex of organometallic compounds and oxygen is formed. At the second stage these complexes either transform into organometallic peroxide compounds or dissociate into initial compounds. The presence of two stages for the autoxidation process of organometallic compounds was found experimentally [2] for diethylcadmium autoxidation (eq. 1).

$$(C_2H_5)_2Cd + 2O_2 \rightleftharpoons (C_2H_5)_2Cd \cdot 2O_2 \rightarrow (C_2H_5OO)_2Cd \qquad (1)$$

In the case of diethylcadmium the initial reversible complex is rather stable in n-nonane solution, however in most cases the investigation of labile complexes of organometallic compounds and oxygen leads to certain difficulties due to the rapid second stage of the process. Therefore a sensitive method of investigation is required for studying labile complexes of organometallic compounds and oxygen. We have chosen electronic emission spectroscopy as a method of investigation. We assume that compounds which have no tendency to autoxidise may also form labile complexes with oxygen. Therefore phenyl derivatives of Group IVB elements, $(C_6H_5)_4M$ (M = C, Si, Ge, Sn, Pb), $(C_6H_5)_3MH$ (M = Si, Ge) and Group VB elements $(C_6H_5)_3M$ (M = N, P, As, Sb, Bi), as well as some tetraalkylstannanes, R_4Sn (R = CH_3, n-C_4H_9, n-C_5H_{11}), were chosen as subjects of our investigation.

It was found by methods of electronic spectroscopy that many organic compounds form reversible complexes with oxygen [3]. Complexes of electron-donor organic compounds with oxygen were studied fairly well in the works of Evans [5], Mulliken [4] and Tsubomura and coworkers [6].

Tsubomura and coworkers [7] found formation of reversible complexes between oxygen and strong electron-donor anion-radicals of tetracyanoethylene and tetracyanoquinodimethane (their ionization potentials are equal to 2.0 and 1.7 eV, respectively). Some theoretical aspects of quenching triplet states of aromatic compounds in solutions by oxygen are studied [8]. On the basis of theoretical considerations [3] the complexes given are charge-transfer ones. The donor is an organic compound and the weak acceptor is oxygen. Electron affinity of the oxygen molecule is less than 0.4 eV [7].

The influence of oxygen as well as other types of donor—acceptor interactions decrease the phosphorescence intensity due to the increasing spin—orbit interaction [3]. The phosphorescence quenching occurs as a result of an increasing role of radiationless deactivation of excited triplet states.

Results and discussion

We have shown that phenyl derivatives of Group VB elements as well as phenyl and alkyl derivatives of Group IVB elements also form reversible complexes with oxygen in n-hexane solution at the low temperature (77 K). The solutions of organometallic compounds were carefully degasssed by repeated freezing and unfreezing in vacuum up to 1×10^{-4} Torr. Firstly, we obtained the luminescence spectra of nonevacuated solutions and then the spectra of evacuated ones. The spectrum intensity changed strongly. After the addition of gaseous oxygen into an evacuated ampoule the spectrum becomes identical with the spectrum of a nonevacuated sample. Thus the addition of oxygen is reversible.

For all compounds studies the intensity of emission spectrum at 77 K is considerably reduced on the addition of oxygen. Thus, the oxygen dissolved has a significant effect on the electronic emission spectra of the compounds studied. In all cases the luminescence intensity decreases (quenching of luminiscence) on interaction of the compounds studied with oxygen (a quencher).

We have studied the rate of deactivation of the excited state of phenyl and alkyl derivatives while carrying out the experiments on luminescence. In the present work we studied the effect of oxygen on the intensity of the long wavelength band only in the luminiscence spectra. This band corresponds to phosphorescence of the compounds studied ($T_1 \rightarrow S_0$ transition).

Let's consider the process:

$$(T_1) + O_2(T_1) \rightarrow (S_0) + O_2(S_0),$$

in which the transition of the compound studied occurs from the excited state, e.g. the triplet state (T_1), into the ground state (S_0). The quencher (oxygen) makes a transition from the ground triplet state $O_2(T_1)$ into the excited singlet state $O_2(S_1)$ [8]. The rate of this bimolecular process $V_q = k_q[D(T_1)][O_2(T_1)]$ depends on the concentration of the substance $[D(T_1)]$ and the quencher $[O_2(T_1)]$.

The rate constant of phosphorescence quenching k_T may be obtained from Stern—Volmer equation:

$$\frac{I_P}{I_P^{O_2}} = 1 + k_q \tau_p [O_2],$$

where I_p is the intensity of phosphorescence in the absence of the quencher; $I_P^{O_2}$ is the intensity of phosphorescence in the presence of the quencher. The slope of a straight line plotted in the coordinates, $\frac{I_P}{I_P^{O_2}}$, $[O_2]$ is a product of $k_q \times \tau_P$, where τ_P is the real lifetime of the excited state T (measured experimentally) in the absence of the quencher. Knowing τ_P we may calculate the constant, k_q.

Stern—Volmer equation may also be written in the form:

$$\frac{I_P}{I_P^{O_2}} = 1 + K_q[O_2],$$

where $K_q = k_q\tau_P$ is a so-called "quenching constant ". The values of constants K_q are shown in Table 1. The dependence of $\frac{I_P}{I_P^{O_2}} = I_{rel}$ on oxygen concentration for the compounds studied are listed in Fig. 1 and 2. The analysis of the values of constants K_q, k_q and other kinetic parameters (shown in Table 1) permits one to draw some conclusions about the tendency of the compounds studied to form labile complexes with oxygen. For this purpose some features of phosphorescence quenching of organic compounds [10] are considered.

The quenching may be dynamic and static. With dynamic quenching the deactivation of the excited state of molecule occurs while approaching a quencher molecule. The possibility of approach is controlled by the rate of diffusion. With static quenching the molecule forms a complex with a quencher in the ground state.

Due to complexing the effectiveness of deactivation of excited states increases strongly. The static quenching occurs in dilute solutions (the experiment conditions of the present work) frozen at the low temperature (e.g. 77 K). Under these conditions the diffusion contact between the molecules of the substance and the quencher is practically impossible.

A fixation of the relative position of the substance and quencher molecules,

TABLE I

KINETIC PARAMETERS OF COMPLEX FORMING BETWEEN ORGANIC DERIVATIVES AND OXYGEN

Compound	λ_p (nm)	K_q (10^{-2} X l mol^{-1})	τ^a (s)	k_q (10^{-3} X l mol^{-1} s^{-1})	$\alpha = \frac{k_q}{k_q + k_q + k_{qt}}$
$(C_6H_5)_3N$	410	6.5	0.7	0.9	0.999
$(C_5H_5)_3P$	470	1.4	2.5×10^{-2}	5.6	0.993
$(C_6H_4)_3As$	490	2.5	3.2×10^{-3}	79	0.996
$(C_6H_5)_3Sb$	500	2.8	3.2×10^{-4}	340	0.996
$(C_5H_5)_3Bi$	495	4.1	3.6×10^{-4}	1100	0.997
$(C_5H_5)_4C$	500	0.8	4.2	0.02	0.987
$(C_6H_5)_4Si$	430	0.8	7.5×10^{-2}	1.1	0.988
$(C_5H_5)_4Ge$	430	0.9	5.1×10^{-2}	1.8	0.989
$(C_6H_5)_4Sn$	430	1.7	4.6×10^{-3}	38	0.994
$(C_6H_5)_4Pb$	420	3.4	3×10^{-4}	1100	0.999
$(C_6H_5)_3SiH$	360	2.3			
$(C_6H_5)_3GeH$	420	2.6			
$(CH_3)_4Sn$	520	1.3			
$(n\text{-}C_4H_9)_4Sn$	510	1.1			
$(n\text{-}C_5H_{11})_4Sn$	510	0.9			

[a] Ref. 9.

which existed in the liquid state at room temperature, occurs in the frozen solution. As the quencher concentration increases, according to Stern—Volmer equation, the luminescence quenchers decrease in accordance linearly. This is explained by the increase in concentration of nonluminescent complexes. The complex concentration also increases with the increase of equilibrium constant of complexing, i.e. with the increase of electron-donor and -acceptor properties of complex components.

The above confirms the supposition that the quenching constant, K_q, is a

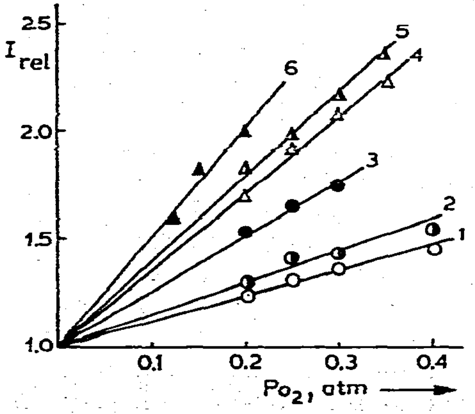

Fig. 1. The dependence of I_{rel} on the concentration of oxygen: $(C_6H_5)_4Si$, (1); $(C_6H_5)_4Ge$, (2); $(C_6H_5)_4Sn$, (3); $(C_6H_5)_3SiH$, (4); $(C_6H_5)_3GeH$, (5); $(C_6H_5)_4Pb$, (6).

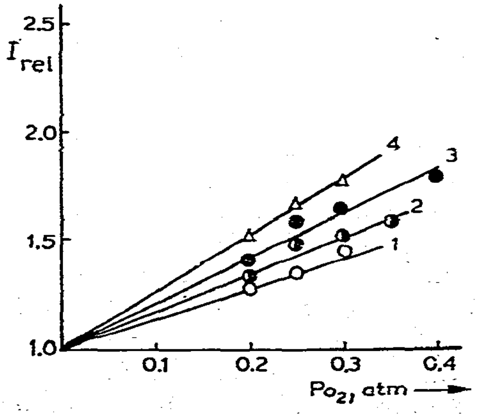

Fig. 2. The dependence of I_{rel} on the concentration of oxygen: $(n\text{-}C_5H_{11})_4Sn$, (1); $(n\text{-}C_4H_9)_4Sn$, (2); $(CH_3)_4Sn$, (3); $(C_6H_5)_4Sn$, (4).

measure of complexability of the organometallic compounds studied with oxygen in the ground electron state.

For the derivatives of Group VB elements, $(C_6H_5)_3M$, studied the value K_q decreases considerably when changing from M = N to M = P, and increases when changing from M = P to M = As, Sb and Bi; the irregularity of the changing values of K_q on successively increasing the atomic number of element M is due to the fact that on complexing both the compounds $(C_6H_5)_3M$ and oxygen have two functions, donor and acceptor ones. Therefore the formation of the complexes is probably susceptible to at least two influences, Firstly, the complexes are formed due to the formation of a charge-transfer complex between the derivatives, $(C_6H_5)_3M$, (electron-donor) and oxygen (electron-acceptor). In this case, phenyl derivatives may have properties of π- and n-donors. The relative π-donor ability depends on the extent of the π-electron density in the aromatic rings, which is, in turn, determined by the nature of element M. In phenyl derivatives of phosphorus the strong effect of d_π—p_π interaction is observed, i.e. a partial shift of π-electrons of the aromatic rings occurs onto the vacant $3d$-orbitals of the phosphorus atom [11].

As a result, the extent of π-electron density on the aromatic rings of triphenylphosphine and its π-donor ability decreases. The effect of d_π—p_π interaction weakens rapidly with increasing atomic number of element M and is practically absent for triphenylbismuth [12]. This d_π—p_π interaction is absent in triphenylamine due to the energy inaccessibility of d-orbitals in the nitrogen atom from the second period of the Periodic System. In addition to the effect of d_π—p_π interaction, π-donor ability is influenced significantly by the effect of n,π-conjugation between the unshared electron pair of the heteroatom and π-electrons of the aromatic rings. The effect of n—π-conjugation leads to an increase of π-electron density on the rings of triphenylamine. With increasing atomic number of heteroatom M, the effect of n,π-conjugation weakens sharply and the contribution of this effect is very small for triphenylphosphorus [13,14].

The relative n-donor ability of derivatives $(C_6H_5)_3M$ is determined by the presence of an unshared electron pair in the heteroatom M. The literature data [15] show that n-donor ability of Group VB derivatives decreases in the series of $N > P > As > Sb$. At the same time for derivatives $(C_6H_5)_3M$ this series shows increasing ionization potentials of [16]. The relative n-donor ability may also depend on steric factors which as it will be shown below, for Group IVB derivatives, have a significant influence on the values of K_q.

In summary, complexing under the form of above mentioned conditions (when derivatives $(C_6H_5)_3M$ are electron-donors and oxygen is an electron-acceptor) we may draw the following conclusion. The maximum complexing occurs with M = N, on changing to M = P we may expect a considerable decrease in complexing and in the series, P - As - Sb - Bi, an increase in complex forming ability. The experimental values of K_q agree well with this conclusion.

However, it should be noted that the values K_q probably reflect complexing under the latter conditions. In this case oxygen is an electron-donor and derivatives $(C_6H_5)_3M$ are electron-acceptors. The electron-acceptor properties are due to the presence of vacant d-orbitals in the Group VB elements, beginning with M = P. As was mentioned above, triphenylamine has no vacant d-orbitals. In contrast with the d_π—p_π interaction of π-type between elements with a direct chemical bond, the complexing of σ-type includes other d-orbitals of atom M (d_γ-orbitals). In the latter case it was shown for Group IVB compounds [17] that as the atomic number of the element in the group increases, the ability to form an additional σ-donor increases, i.e. down the group Bi > Sb > As > P. Thus, the second condition of complexing contributes towards increasing values of constants K_q on successively changing from M = P to As, Sb and Bi. By considering the relative contributions to complex formation of the first and second condition we may conclude that the first is predominant. Indeed, in spite of the fact that triphenylamine does not take part in complexing in the second case it has a maximum value of K_q. This fact apparently indicates the dominant role of π-donor properties of compounds $(C_6H_5)_3M$ to the nature of the complexing.

Now let us consider K_q values for Group IVB phenyl derivatives, $(C_6H_5)_4M$. These values increase on successively changing from M = Si to Ge, Sn, and Pb. The Group IVB elements have no unshared electron pairs, but like the Group VB elements, they have vacant d-orbitals. The vacant d-orbitals are involved in the formation of additional bonds of π- and σ-type. The effect of d_π—p_π interaction diminshes π-electron density on the aromatic rings which is a maximum for tetraphenylsilane. This effect is absent in carbon derivatives and also in triphenylamine. With increasing the atomic number of M the effect of d_π—p_π interaction is weakened and is partially absent for tetraphenyllead [12]. Thus, π-donor properties of $(C_6H_5)_4M$ derivatives decrease in series C > Si < Ge < Sn < Pb. This is the reason why the values of K_q increase with increasing the atomic number of M.

The second reason is complexing of σ-type which occurs at the expense of vacant d-orbitals of $(C_6H_5)_4M$ compounds (acceptors) and an unshared electron pair of oxygen (donor). Tetraphenylmethane is not involved in such a type of complexing as the central carbon atom has no vacant d-orbitals. The acceptor properties of tetraphenyl derivatives increase with increasing atomic number of Si-subgroup elements [17]. Due to this fact K_q values must increase with increasing atomic number of N. Thus, both mechanisms of complexing suggest an increase of K_q on changing from M = Si to Ge, Sn, Pb. The experimental data on K_q agree with this fact.

Let us state again that on formation of donor—acceptor complexes tetraphenylmethane exhibits π-donor properties only, acceptor properties are absent. Therefore tetraphenylmethane forms only one type of donor—acceptor complex in contrast to other derivatives of Group IVB elements and so has rather a low value of K_q.

When changing from $(C_6H_5)_4Si$ to $(C_6H_5)_3SiH$ and from $(C_6H_5)_4Ge$ to $(C_6H_5)_3GeH$, a considerable increase of K_q is observed. We believe that the increase of the complexability of triphenyl derivatives, as compared with tetraphenyl derivatives, is caused by a larger steric accessibility to the Si atom in triphenyl derivatives. This assumption was tested and proved correct when the influence of oxygen on the luminescence spectra of tetraalkylstannanes was investigated. For AlK_4Sn compounds K_q values decrease when changing from Alk = CH_3 to n-C_4H_9 and n-C_5H_{11}. We assume that this fact, in accordance with the data for $(C_6H_5)_3MH$ (M = Si, Ge) derivatives, points to a strong dependence of complexing on the steric accessibility of Group IVB elements. The increase in the size of alkyl radical in Alk_3Sn hinders the steric accessibility to the tin atom; in this case the complexing is also impeded and K_q values decrease.

Let us consider now the relative contribution of the processes resulting in deactivation of excited triplet states of organometallic compound molecules D * in the presence of oxygen. Deactivation occurs in three directions:

1. Phosphorescence: $D^* \rightarrow D + h$
   The rate of this process: $V_p = k_pD^*$
2. Radiationless deactivation: $D^* \rightarrow D$ + heat
   The rate of this process: $V_{qt} = k_{qt}[D^*]$
3. Deactivation in the presence of quencher (this process was considered above). The rate constant of this process is k_q.

The total value of $k_p + k_{qt}$ may be calculated from $k_p + k_{qt} = \frac{1}{\tau_p}$ according to the available literature or experimental values of τ_p.

We calculated the quantities $\frac{k_q}{k_q + k_p + k_{qt}} = \alpha$ (Table 1). α values indicate the relative contribution of the bimolecular quenching process into the totality of all the processes resulting in deactivation of the triplet state of organometallic compounds. As can be seen from Table 1 the α values are ~ 0.99 and > 0.99 for phenyl derivatives of Group IVB and VB elements, respectively.

Thus, the predominant deactivation process of excited triplet states of organometallic compounds is deactivation by means of interaction with oxygen quencher.

Experimental

Electronic emission spectra were measured with a DMR-4 or SF-16 spectrophotometer equipped with monochromators. The excitation of spectra luminiscence was performed with PRK-4 lamp. The photomultiplier FEU-79 served as an emission receiver, the signal of which was amplified with amplifier IMT-05 and registered with potentiometer KSP-4.

The solutions investigated were placed into an optical quartz vessel equipped with special taps. The sample was cooled to 77 K in a Dewar vessel of optical quartz. After recrystallization in alcohol the solid organometallic compounds were subjected to additional purification by high vacuum sublimation. The liquid compounds were subjected to repeated vacuum distillation and all compounds studied were kept in evacuated ampoules.

Chemically pure n-hexane, used as a solvent, was additionally purified in order to remove aromatic and unsaturated compounds by successive stirring with concentrated sulphuric acid (36 h), 10% H_2SO_4 saturated with potassium permanganate (4 h) and 10% alkali saturated with potassium permanganate (4 h). n-Hexane was then washed with distilled water until neutral, dried and distilled over metallic sodium of 4 Å molecular sieves. The solvent purity was controlled by UV-spectroscopy.

Luminescence spectra were obtained for evacuated solutions (10^{-3}—10^{-4} Torr) and for solutions in carefully dried oxygen. Oxygen was dried by passing over 4 Å molecular sieves, and kept in a balloon filled with 4 Å sieves. The concentration of the solutions studied was 10^{-3}—10^{-4} mol l^{-1}.

From calculations according to Stern-Volmer equation we assumed the oxygen concentration in n-hexane to be equal to 1.5×10^{-2} mol l^{-1} at room temperature and oxygen pressure above the solution to be equal to one atmosphere [10]. Under the present experimental conditions, quickly freezing to 77 K, the oxygen concentration approximated the oxygen concentration at room temperature.

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