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RADICAL FORMATION ON EXCHANGE INTERACTION OF SOME NON-TRANSITION ALKYLMETAL COMPOUNDS *

Yu.A. ALEXANDROV, S.A. LEBEDEV, and N.V. KUZNETSOVA
Chemistry Institute at N.I. Lobachevsky State University Gorky (U.S.S.R.)

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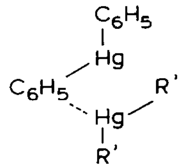
Summary

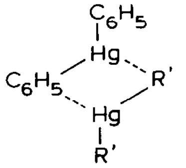
Radical formation on the exchange interactions of some cadmium, zinc and mercury compounds has been investigated. The kinetic parameters of these reactions and their role in the auto-oxidation processes of the compounds mentioned above have been determined.

Ligand exchange on the metal atom in organometallic compounds (OMC) represents one of the fundamental properties of these compounds and covers a wide variety of their reactions [1]. The study of such exchange interactions has been the subject of systematic investigations by Ingold, Hughes, Reutov and other scientific schools and this has led to the formulation of basic statements for the mechanisms of nucleophilic (Ingold and co-workers) and electrophilic (Reutov et al.) substitution on the OMC metal atom [1,2].

The exchange interactions between "complete" organic metal derivatives are of particular interest; these were investigated in great detail with organomercury compounds. The electrophilic substitution mechanism was proposed in the case of the electron-accepting group on mercury [3]. For example, the exchange between diphenyl mercury and HgR'_2, where R' is an electron-accepting group ($C{=}CC_6H_5$, CCl_3, $CH_2C(O)OCH_3$, $CH(F)C(O)OC_2H_5$, CN), was suggested to proceed through a transition state in which the mercury atom from HgR'_2 attacks the more nucleophilic carbon atom of diphenyl mercury (complex I), the simultaneous coordination or R' with the mercury atom of diphenyl mercury being possible (complex II):



(I)



(II)

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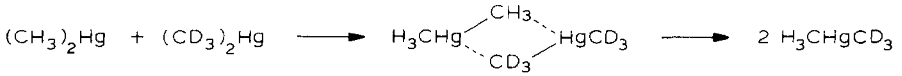
* Dedicated to Professor O.A. Reutov on the occassion of his 65th birthday on 5 September 1985.

It is more difficult to explain the exchange mechanism of organometallic compounds which have less polar metal–carbon bonds. Dessy et al. have studied the exchange in the $(CH_3)_2Hg/(CD_3)_2Hg$ system and have proposed a cyclic transition state for this reaction [4]:



$$(CH_3)_2Hg + (CD_3)_2Hg \longrightarrow H_3CHg\overset{CH_3}{\underset{CD_3}{\rightleftarrows}}HgCD_3 \longrightarrow 2\,H_3CHgCD_3 \quad (1)$$

Bremser et al. [5] have found "Homoexchange" in dimethylcadmium to represent a bimolecular reaction and at a temperature of about 100°C the activation energy (E_a) is 15.7 kcal/mol and $\Delta S^{\neq}$ -9.8 e.u. The exchange rate increases in tetrahydrofuran (at about -10°C E_a 6.8 kcal/mol and $\Delta S^{\neq}$ -28 e.u.) and in diethyl ether (E_a 5.6 kcal/mol, $\Delta S^{\neq}$ -38 e.u. [6]).

According to Ham et al. [7], methyl(methylperoxy)cadmium, the product of dimethylcadmium oxidation, increases the homoexchange process of dimethylcadmium substantially and the addition of H_3COH, in amounts of about 1 mol%, to dimethylcadmium results in a 20 to 30-fold increase in the exchange rate. It should be noted that H_3COH reacts readily with dimethylcadmium to form methyl(methoxy)cadmium, i.e. in the case mentioned above with H_3COH additions, it is the methyl(methoxy)cadmium which affects the reaction rate of homoexchange. The E_a of dimethylcadmium homoexchange catalyzed by "methanol" was determined; it proved to be equal to 16 kcal/mol in toluene and 13 kcal/mol in pyridine. By analogy with eq. 1, the cyclic 4-centre transition state is assumed in all cases of homoexchange in dimethylcadmium.

So, as a result of investigations on the exchange interaction mechanism between OMC molecules, specific theoretical concepts have been formed, the basis for which is a non-radical, "molecular" exchange mechanism.

In connection with this, the radical formation on OMC exchange interactions, which we have established, seemed to be of great interest. These results were obtained in studies of the primary reactions on auto-oxidation of some alkyl mercury [8], cadmium [9–11,16–25] as well as zinc [12,15–18,22–24] derivatives.

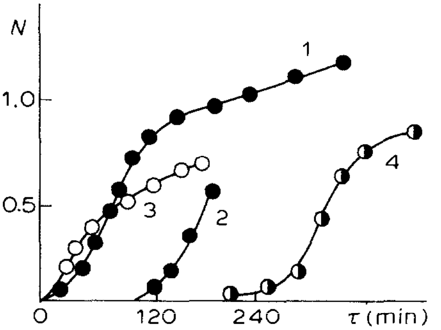


Fig. 1. Kinetic curves for auto-oxidation: Me_2Cd in n-decane (c^0 0.06 mol l^{-1}, T 50°C, $c^0_{O_2}$ 5.6×10^{-3} mol l^{-1}) without additions (curve 1), in the presence of phenthiazine* (c^0 1.3×10^{-5} mol l^{-1}, curve 2) and $Et(Et_3Si)Hg$ in n-decane (c^0 0.085 mol l^{-1}, T 60°C) without additions (curve 3) and with the addition of *o*-phenylene diamine* (c^0 5×10^{-4} mol l^{-1}, curve 4). * In Figs. 2 and 3 the present inhibitors are denoted by IH.

The data obtained indicate that in parallel with the OMC exchange interaction proceeding rather quickly through a non-radical mechanism, a substantially slower exchange reaction which proceeds through a radical mechanism takes place. Yet, this direction of the reaction is of crucial importance in chain OMC transformation processes.

The auto-oxidation of complete alkyl compounds of cadmium and zinc, as well as ethyl(triethylsilyl)mercury, proceeds through a chain, free-radical mechanism. This follows unambiguously from the fact that the additions of some compounds that are well known as inhibitors for free-radical processes of OMC and organic compound auto-oxidation efficiently hinder the auto-oxidation of the cadmium, zinc and mercury compounds mentioned above (Fig. 1). We made use of this to investigate chain initiation reactions in the auto-oxidation processes of complete alkyl compounds of cadmium, zinc and ethyl (triethylsilyl)mercury by the "inhibitor method", which was approved comprehensively by examples of organic compound [26] and OMC [27] auto-oxidation.

The kinetic characteristics of the chain initiation reaction on auto-oxidation of ethyl(triethylsilyl)mercury (second order with respect to OMC and zeroorder with respect to oxygen [8]) indicate generation of chain-leading radicals as a result of the interaction of two molecules (with each other) of the initial OMC. Formally the same interaction, but at higher temperature, results in disproportionation of ethyl(triethylsilyl)mercury [28]:

$$2Et(Et_3Si)Hg \rightarrow Et_2Hg + (Et_3Si)_2Hg \qquad (2)$$

In studies of chain, free-radical auto-oxidation processes of complete alkyl compounds of cadmium and zinc, we have established that the chain initiation in these cases also proceeds as a result of the interaction of two molecules (with each other) of the initial OMC.

The kinetic reaction order with respect to the initial OMC is equal to 2 (Fig. 2). The order with respect to oxygen is either zero or negative (Fig. 3).

The expression for the temperature dependence of the chain initiation rate on the auto-oxidation of the above-mentioned compounds of cadmium, zinc and mercury are listed in Table 1.

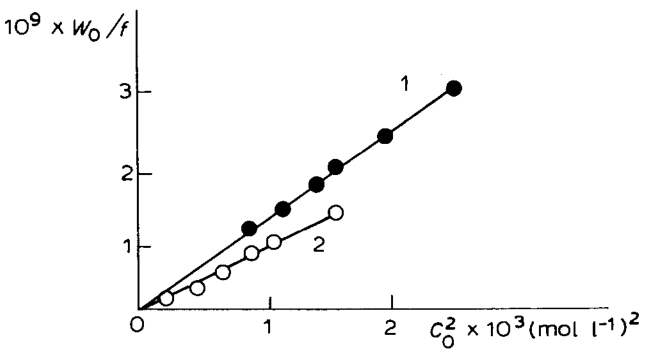


Fig. 2. Dependence of the chain initiation rate (W_0) of the Me_2Cd auto-oxidation process in n-decane (straight line 1, 50°C, c^0 5.3×10^{-3} mol l^{-1}, c^0_{IH} 1.5×10^{-5} mol l^{-1}) and that of Me_2Zn in toluene (straight line 2, T −50°C, c_{O_2} 5.3×10^{-3} mol l^{-1}, c^0_{IH} 8.1×10^{-6} mol l^{-1}) on the initial concentration (c^0) of the original OMC.

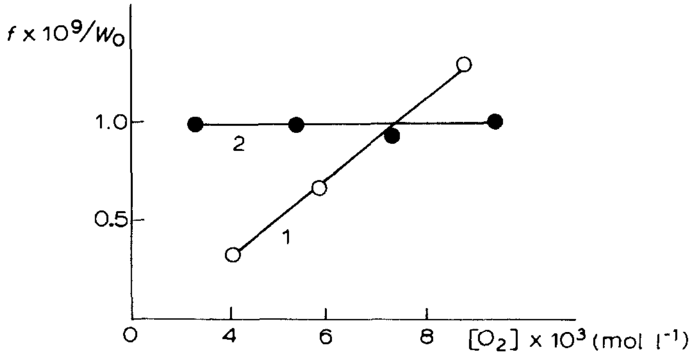


Fig. 3. Dependence of the chain initiation rate (W_0) of the Me_2Cd auto-oxidation process (straight line 1, 50°C, c^0_{MOC} 0.035 mol l^{-1}, c^0_{IH} 1.5×10^{-5} mol l^{-1}) and that of Me_2Zn (straight line 2, −50°C, c^0_{MOC} 0.1 mol l^{-1}, c^0_{IH} 8.1×10^{-6} mol l^{-1}) on the oxygen concentration in the reaction mixture.

As mentioned above, the exchange interaction of Me_2Cd with Me_2Cd is characterized by a considerably smaller activation energy than the energy of the Cd–C bond in this OMC (15.7 against 35 kcal/mol [29]), and by a negative activation entropy value ($\Delta S^{\neq} = -9.8$ e.u.). The positive kinetic effect of the solvent is determined by the decrease of E_a and the increase of $-\Delta S^{\neq}$, i.e. in reaction 1, a "harder" transition state causes a greater rate of the proceeding exchange interaction.

As would be expected, similar relationships are also characteristic of the radical formation reaction on the exchange interaction of R_2M with R_2M (Table 1).

It should also be noted that the additions of compounds accelerating the exchange interaction of an OMC with an OMC facilitate radical formation as well [9,12–18,23].

Using Me_2Cd as an example, it seems to be possible to compare the reaction of an exchange interaction proper (k_{exch}) with the accompanying radical formation reaction (k_{rad}).

According to Bremser et al. [5], for reaction (1) E_a 15.7 kcal/mol and $\Delta S^{\neq}$ −9.8 e.u., which at 50°C corresponds to K_{exch} 10 l mol^{-1} s^{-1}.

According to our data on the exchange interaction of Me_2Cd with Me_2Cd, the

TABLE 1

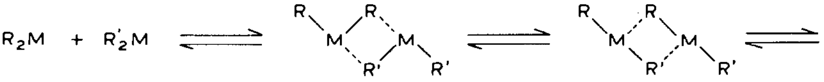
RATE CONSTANTS (k) AND ACTIVATION ENTROPIES ($\Delta S^{\neq}$) OF THE CHAIN INITIATION REACTION AS A RESULT OF AN "EXCHANGE" INTERACTION OF AN OMC WITH AN OMC IN HYDROCARBONS

OMC	$f^a \cdot k$ (l mol^{-1} s^{-1})	$-\Delta S^{\neq}$ e.u.	$[O_2]$-value in reaction mixture
$Et(Et_3Si)Hg$	$8.2 \times 10^{12} \exp\{-19700/RT\}$	3.7	does not depend on $[O_2]$
Me_2Zn	$10^{11.6} \exp\{-18000/RT\}$	9	does not depend on $[O_2]$
Me_2Cd	$10^{11.8} \exp\{-25200/RT\}$	8.7	5.6×10^{-3} mol l^{-1}
Et_2Cd	$10^{7.7} \exp\{-14900/RT\}$	27	5.6×10^{-3} mol l^{-1}
$n\text{-}Pr_2Cd$	$10^{7.0} \exp\{-14500/RT\}$	30	5.6×10^{-3} mol l^{-1}
$n\text{-}Bu_2Cd$	$10^{5.8} \exp\{-13500/RT\}$	36	5.6×10^{-3} mol l^{-1}

[a] f is the stoichiometric inhibition coefficient.

radical formation reaction has $\Delta S^{\neq}$ -8.7 e.u. (which is naturally somewhat lower than $\Delta S^{\neq}$ for an exchange proper) and k_{rad} $10^{-5.2}$ l mol^{-1} s^{-1} at 50°C, i.e. under comparable conditions, $k_{\text{exch}} \gg k_{\text{rad}}$.

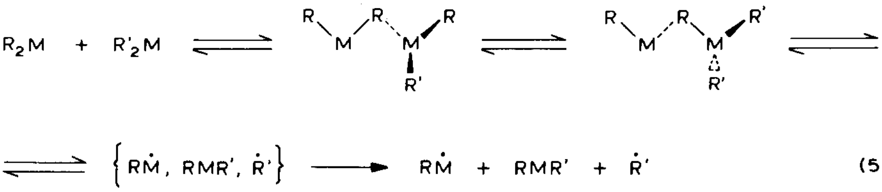
For the proper exchange interaction of an OMC with an OMC [1], convincing proof of a synchronous reaction mechanism proceeding through a 4-membered transition state was obtained:


(3)

In the case of Me_2Cd, $\Delta H^{\neq}$ of this reaction is of the order of 15.7 kcal/mol; it is a combination of the Cd transition energy from the *sp* to the *sp*^{2} state ($-\Delta H_1$), the formation energy of the additionally activated Cd–C bond (ΔH_2) and the activation energy of the Cd–C bond in $Me_2Cd(-\Delta H(Cd\text{–}C) + \Delta H_2)$:

$$-2\Delta H_1 - 2(\Delta H(\text{Cd–C}) - \Delta H_2) + 2\Delta \text{H}_2 = -15.7 \qquad (4)$$

The exchange interaction resulting in radical formation seems to proceed through a non-cyclic type of transition state:


(5)

According to our data (Table 1) for reaction 5 in the case of Me_2Cd, $\Delta H^{\neq}$ is about 25.2 kcal/mol. Analysis of the different variants for calculation of the $\Delta H^{\neq}$ constituents in reaction 5 results as shown in eq. 6:

$$-\Delta H_1 - 2(\Delta H(\text{Cd–C}) - \Delta H_2) + \Delta H_2 = -25.2 \qquad (6)$$

From the correlation of eqs. 4 with 6 and taking into account the fact that ΔH(Cd–C) is 43.5 kcal/mol, we obtain ΔH_1 16.6 and ΔH_2 26.6 kcal/mol.

It should be mentioned that the literature does not contain data on the $sp \rightarrow sp_2$ transition energy of a cadmium, zinc or mercury atom. According to Semyonov [30], the energy of the $s \rightarrow sp$ rearrangement for cadmium and zinc atoms is about 50 kcal/mol.

There is information [31] on the $sp^2 \rightarrow sp^3$ rearrangement energy of heteroatoms in BX_3, AlX_3 and GaX_3 (where X is F, Cl, Br, I and for B, H as well). The energies of this rearrangement are in the range 50 to 10 kcal/mol; they decrease in the range of values mentioned for the derivatives: F > Cl > Br > I > H, respectively; i.e. the resultant ΔH_1 and ΔH_2 values seem to be acceptable.

The negative kinetic effect of triplet oxygen on the formation of chain-leading radicals is due to the composition of reaction 5, "departure" of radicals from a radical pair (RP), with reaction 7, RP destruction by triplet oxygen [13]:

$$\{R\dot{M},RMR',\dot{R}'\} + O_2 \rightarrow RMOOR' + RMR' \qquad (7)$$

To check this assumption, we investigated the influence of the magnetic field on both the rate of reaction 5 (W_0) and its competition with reaction 8 [20,21,23,25].

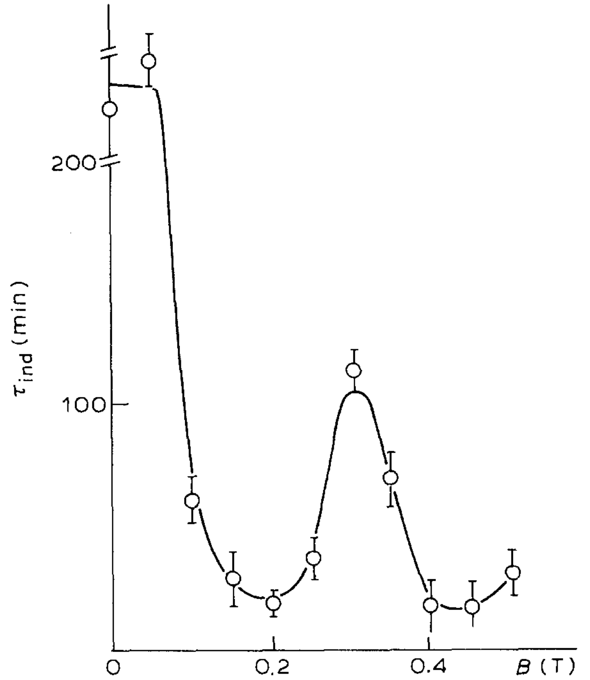


Fig. 4. Influence of the magnetic field the induction period $\tau_{ind} = f\frac{[IH]_0}{w_0}$ of Me$_2$Cd auto-oxidation inhibited by phenthiazine in n-decane (50°C, c^0_{MOC} 0.027 mol l^{-1}). The data are taken from [20].

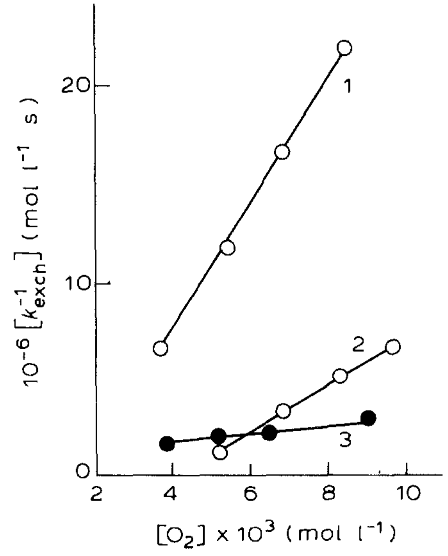


Fig. 5. Influence of the dissolved oxygen concentration on the experimental chain intitiated rate constant (k_{exp}) in a magnetic field with induction of 0, 0.2 and 0.4 T (curves 1–3, respectively). The data are taken from [25].

The dependence of W_0 on the magnetic field strength is of a resonance character (Fig. 4). In this case, an increase of the magnetic induction causes a decrease of the sensitivity of W_0 to the negative kinetic effect of oxygen (Fig. 5).

The magnetic field effect found may be explained within theoretical ideas by the magnetic field influence the singlet-triplet (S–T) transitions in radical pairs. Between radicals coordinated on one former complex (RP), a strong exchange interaction appears, which is responsible for a small probability of S–T transitions in non-radical fields. In this cases, the departure of radicals from a radical pair is hindered, therefore the probability of recombination of singlet RP is close to unity. On increasing the magnetic inducation, a "cross-section" of S and T_{-1} levels is possible, i.e. resonance increase of the probability for S–T transitions and an appropriate increase of the probability for the departure of radicals from RP occur.

The estimation indicated [20] that the scale of the field effect on W_0 in the Me_2Cd auto-oxidation process may be achieved provided the lifetime of RP exceeds 10^{-8} s. Such an RP lifetime seems to be sufficient for S–T "superposition" of RP evolution (under the action of magnetic inducation) and RP destruction by triplet oxygen.

We have also confirmed radical formation on the exchange interaction of R_2Cd with R_2Cd by another independent way, we investigated the thermal decomposition of Me_2Cd in n-decane [32] and Et_2Cd in the gaseous phase [33]. As a whole, the mechanisms of these processes are intricate and independent; therefore a comprehensive treatment of them here does not seem to be expedient. Yet, it should be mentioned that in both cases radical generation as a result of R_2M interaction with R_2M was confirmed, and methane and an organocadmium compound of net composition $(CdCH_2)_n$ were determined as the decomposition products of Me_2Cd in n-decane.

The radical formation reaction on the exchange interaction of an OMC with an OMC "accompanies" the exchange interaction proper, well known practically for OMC's of all types [1]. Therefore the fundamental property of an OMC, its ability to exchange intermolecular interactions, determines radical formation on an OMC. We believe that this OMC property is noteworthy because the ease of radical formation on an OMC (kinetic stability of the OMC, respectively) is corresponding to the ease of the exchange interactions mentioned above and is not always determined directly by the bond strength in the OMC.

This offers possibilities of controlling radical formation in OMC-containing systems (a rather difficult process to control) by means and techniques which control the intermolecular exchange interaction (a process which is easier to control).

Experimental

The technique of the experiments and primary experimental data have been described earlier [8,12,13,18,20].

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