CHEMISTRY

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1964

SovietRxiv

Figure 1

Figure 1: Figure 1

Abstract

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CHEMISTRY

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SOME REGULARITIES OF THE LIQUID-PHASE OXIDATION OF DIISOPROPYLMERCURY BY OXYGEN

Some alkyl organomercury compounds are readily oxidized by gaseous oxygen at comparatively low temperatures. The mechanism by which these processes proceed appears to us to be very complex. Thus, in studying the oxidation of dicyclohexyl-, ditritenoamyl-, dibenzyl-, and diisopropylmercury (DIPM) in a number of organic solvents, the reaction products were found to include mercury, alkoxyalkylmercury and alkylmercury hydroxide, products of oxidation of the alkyl radical of the initial organomercury compound (the corresponding alcohols and ketones), unsaturated and saturated hydrocarbons formed from the alkyl radical of the mercury compound, as well as products of oxidation of the solvent and—when halogenated hydrocarbons were used as solvents—products of interaction of the solvent with the initial organomercury compound ([1–3]).

In the present work we investigated the kinetics of the liquid-phase oxidation of DIPM, which is necessary in order to obtain a complete understanding of the mechanism of oxidation of all the above-mentioned organomercury compounds. *n*-Nonane was chosen as the solvent. The experiments were carried out in a special vacuum apparatus described in detail earlier ([4]). The experimental procedure made it possible to carry out the oxidation of DIPM at an oxygen pressure that remained constant throughout the experiment. The rate of the process was determined from the dependence of the number of moles of oxygen N, absorbed by the reaction mixture per mole of DIPM, on the reaction time (τ). Gaseous and volatile products of DIPM oxidation were frozen out during the experiment in special traps. The reaction products were analyzed as described previously ([1–4]).

Fig. 1. Effect of paraoxydiphenylamine on the rate of oxidation of DIPM in *n*-nonane solution at 70°.
$C^0_{R_2Hg} = 20$ mol.%, $P_{O_2} = 300$ mm Hg. Curve 1 was recorded without additives; curves 3 and 2 with addition of inhibitor at molar ratios to DIPM of 10^{-3} and 10^{-2}, respectively.

The oxidation of DIPM by oxygen proceeds with a clearly expressed self-acceleration (Fig. 1, 1). The amount of oxygen absorbed reaches up to 1.5 moles per mole of the initial organomercury compound. As the temperature of the experiment is increased, the oxidation of DIPM is regularly accelerated. The temperature dependence of the maximum rate of the process is satisfactorily described by the Arrhenius equation. The apparent value of the activation energy of the DIPM oxidation process calculated from this dependence proved to be 20 kcal/mole.

The rate of oxidation of DIPM drops sharply when small amounts of substances that are inhibitors of free-radical processes are introduced into the reaction mixture before the start of the experiment. This is clearly illustrated by kinetic curves 2-3 (Fig. 1), corresponding to the oxidation of DIPM in the presence of various concentrations of paraoxydiphenylamine. Such an influ-

the effect of inhibitor additions on the rate of oxidation of DIPM is due to the fact that DIPM is oxidized by oxygen by a chain free-radical mechanism. From Fig. 1, especially if it is plotted on a larger scale, it is seen that, at a ratio of the initial concentrations inhibitor : DIPM $\gg$ 1 : 1000, the rate of the process comparatively rapidly reaches a certain constant value, which does not depend on the concentration of inhibitor. The magnitude of this process rate apparently may be taken as the rate of non-chain oxidation of DIPM. The average chain length of the DIPM oxidation reaction, calculated from the ratio of the maximum rate of the process in the absence of inhibitor (Fig. 1, 1) to the rate of non-chain oxidation of DIPM, proved to be 160.

Fig. 2. Effect of isopropyloxyisopropylmercury and water on the rate of oxidation of DIPM in an *n*-nonane solution at 70°. $C^0_{R_2Hg} = 20$ mol.%, $P_{O_2} = 300$ mm Hg. Curve 1 was obtained without additives. Curve 2—with addition of isopropyloxyisopropylmercury (3.22 mol.%). Curve 3 was obtained when 5 ml of water was added to the reaction mixture before the experiment.

Oxidation of DIPM is accompanied by the formation of isopropyloxyisopropylmercury, isopropylmercury hydroxide, isopropyl alcohol, acetone, mercury, propane, and propylene (Table 1). Among the volatile and gaseous reaction products (in traps), the presence of water was established qualitatively by the formation of a crystalline hydrate with anhydrous copper sulfate.

In several special experiments it was established that acetone, isopropyl alcohol, mercury, and also solid products of deep oxidation of DIPM (over three hours at 90°) do not have a noticeable effect on the rate of oxidation of DIPM. To investigate the role of isopropyloxyisopropylmercury in the process of DIPM oxidation, we synthesized this previously undescribed compound. Isopropyloxyisopropylmercury proved to be a low-melting compound, readily soluble in hydrocarbons and very easily hydrolyzed. In an *n*-nonane solution, at temperatures corresponding to the temperature range in which DIPM oxidation was studied, the alkoxy compound undergoes thermal decomposition and is readily oxidized by oxygen. Additions of this oxygen derivative of the organomercury

compound completely eliminate the induction period of the process of DIPM oxidation by oxygen. This follows from comparison of curves 1 and 2 (Fig. 2), obtained respectively without additives and with addition of the alkoxy compound. Such an effect of isopropyloxyisopropylmercury on the rate of DIPM oxidation is explained by decomposition of isopropylmercury isopropylate into free radicals, which causes pronounced branching of the reaction chains in the process of DIPM oxidation.

Fig. 3. Transformation curve of DIPM oxidation at 70° in an *n*-nonane solution. Experiments 1, 2, and 3 were carried out with $C^0_{R_2Hg}$, respectively, 10, 20, and 30 mol.%; $P_{O_2} = 300$ mm Hg.

$$RHgOR \rightarrow RHg^{\cdot} + RO^{\cdot}. \quad (1)$$

This role of the alkoxy compound is confirmed by a study of the effect of water additions on the rate of oxidation of DIPM. During oxidation of DIPM in the presence of water the rate of the process drops sharply (Figs. 2, 3). The latter is caused by the very readily occurring hydrolysis of isopropyloxyisopropylmercury and, consequently, by removal from the reaction mixture of this compound formed during oxidation of DIPM.

The oxidation rate of DIPrHg under the conditions of the experiments carried out (P_{O_2} = 200–500 mm Hg) is practically independent of the magnitude of the oxygen pressure above the reaction mixture. This kinetic regularity indicates zero order with respect to oxygen for the DIPrHg oxidation process and points to quadratic termination of the reaction chains on peroxy radicals. The dependence of the DIPrHg oxidation rate on its concentration is more complex. Up to a reaction depth N = 0.5–0.75, the order with respect to DIPrHg is equal to 1.5. This follows from the transformation onto a single curve in the coordinates $\Delta v \cdot \gamma^{3/2} \sim \tau$ of the kinetic curves corresponding to experiments with different initial DIPrHg concentrations (Fig. 3). In this figure Δv is the amount of oxygen, in ml, absorbed by 1 ml of reaction mixture over the reaction time τ; γ is a coefficient showing by how many times the initial DIPrHg concentration (in mol/l) is smaller than the initial DIPrHg concentration in the experiment with its highest concentration. The observed reaction order with respect to DIPrHg is explained by the initiation of chains in the developed process as a result of the decomposition into free radicals of isopropoxyisopropylmercury, the formation of which during DIPrHg oxidation occurs proportionally to the initial concentration of the starting organomercury compound.

Of considerable interest are the initiation reactions of DIPrHg oxidation at the early stage of the process. This initiation may occur as a result of the molecular interaction of DIPrHg with oxygen, proceeding with the formation, apparently, of an intermediate organomercury peroxide. The latter, as noted earlier ([3]), reacts with DIPrHg to form isopropoxyisopropylmercury, or decomposes into isopropylmercury and isopropylperoxy radicals

$$R_2Hg + O_2 \rightarrow [RHgOOR] \begin{array}{l} \xrightarrow{R_2Hg} 2RHg(OR) \\ \longrightarrow RHg\cdot + RO_2\cdot \end{array} \quad (2)$$

Along with this reaction, initiation of DIPrHg oxidation at the early stage of this process may occur as a result of dissociation of DIPrHg molecules at the C –Hg bond, the energy of which is comparatively small (34 kcal/mol) ([5])

$$R_2Hg \rightarrow R\cdot + RHg\cdot \quad (3)$$

It seemed to us very interesting to estimate the contribution of each pathway of initiation. For this purpose we investigated the thermal decomposition of DIPrHg in the presence of paraoxydiphenylamine. The experiments were carried out in *n*-nonane solution at a temperature of 70°; the initial concentrations of DIPrHg and inhibitor were 20 and $2\cdot10^{-2}$ mol.% respectively. The reaction was carried out in sealed ampoules; the air was first thoroughly removed from the reaction mixture. The thermal decomposition of DIPrHg in *n*-nonane solution proceeds in the presence of the inhibitor (paraoxydiphenylamine) without self-acceleration and practically at a constant rate. The value of this rate ($2.4\cdot10^{-8}$ mol of gaseous products evolved in 1 min per 1 mol of R_2Hg) proved to be considerably lower than the rate of chain oxidation of DIPrHg ($7.4\cdot10^{-7}$ mol O_2 in 1 min per 1 mol of R_2Hg) in a solution of the same concentration and at the same temperature. This result indicates that initiation of DIPrHg oxidation at the early stage of the process occurs predominantly by reaction (2). The isopropylmercury radicals formed at the beginning of the development of the DIPrHg oxidation process by reaction (2) and then (in the developed process) by reaction (1) either decompose into mercury and isopropyl radicals, or react with oxygen with the formation of isopropylmercuryperoxy radicals:

$$RHg\cdot \begin{array}{l} \longrightarrow R\cdot + Hg \\ \xrightarrow{O_2} RHgO_2\cdot \end{array} \quad (4)$$

The comparatively small yield of mercury indicates that the latter reaction proceeds preferentially. Isopropylperoxy- and isopropylmercuriperoxy radicals oxidize DIPM with formation, as the main product, of isopropoxyisopropylmercury:

$$\begin{array}{ll} RHgO_2\cdot(RO_2\cdot) + R_2Hg \rightarrow RHgOR + RHgO\cdot(RO\cdot) & a) \\ RHgO\cdot(RO\cdot) + R_2Hg \rightarrow RHgOR + RHg\cdot(R\cdot) & b) \end{array} \quad (5)$$

This is confirmed by the high yield of isopropoxyisopropylmercury, despite its readily occurring oxidation by oxygen under the same conditions in which we

studied the oxidation of DIPM. In this process, the oxidation of isopropoxyisopropylmercury is accompanied by the formation of all the compounds that are products of DIPM oxidation.

Table 1

Oxidation of DIPM in an *n*-nonane solution at 70°

P_{O_2}, mm Hg	$C^0_{R_2Hg}$, mol. %	R_2Hg, mol · 10^2	N	R_H = RHgOR	O	ROH	RHgOH	Hg	C_3H_8	C_3H_6
200	20	0.972	0.87	62	13	7	9	3	0.3	5
500	20	1.104	0.76	36	9	3	4	3	0.4	3
300	30	2.21	0.97	45	21	16	16	8	0.3	2
300	10	1.1	0.93	61	16	7	5	8	0.1	1

A very interesting fact is the considerable excess of propylene yield over propane yield. Apparently, this is due to competition between the reactions:

$$\begin{aligned} \mathrm{RO}\cdot(\mathrm{RHgO}\cdot) + \mathrm{R_2Hg} &\rightarrow \mathrm{ROH(RHgOH)} + \mathrm{C_3H_6} + \mathrm{RHg}\cdot \quad \text{a)} \\ \mathrm{R}\cdot + \mathrm{R'H(R_2Hg)} &\rightarrow \mathrm{C_3H_8} + \mathrm{R'}\cdot(\mathrm{RHg}\cdot\mathrm{C_3H_6}) \quad \text{b)} \end{aligned} \tag{6}$$

During the oxidation of DIPM in an *n*-nonane solution, the solvent is oxidized to a significant extent. This follows from the fact that the DIPM oxidation products contain only about half of the oxygen absorbed by the reaction mixture. The oxidation of the solvent, initiated by the organomercury compound, is of independent interest and was not considered by us in the present work.

Received
27 IV 1964

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Note: Figure translations are in progress. See original paper for figures.