Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

THE INVESTIGATION OF THE BIS(TRIETHYLGERMYL)MERCURY OXIDATION WITH OXYGEN

G. A. RAZUVAEV, YU. A. ALEXANDROV, V. N. GLUSHAKOVA AND G. N. FIGUROVA
Department of Chemistry, Gorky State University, Gorky (U.S.S.R.)

(Received April 15th, 1968)

SUMMARY

The formal kinetics of auto-oxidation of bis(triethylgermyl)mercury liquid phase, and its oxidation in the presence of ammonia are investigated.

The molecular character of the process and its catalysis by triethylgermyl-oxide, triphenylphosphine, triethylamine and ammonia are established.

The mechanism of the auto-oxidation of bis(triethylgermyl)mercury is discussed.

Oxygen is known to react rapidly at room temperature with organometallic compounds that have M–Hg–[1–4], M–Sb–[5,6], M–As–[7,8] and M–Cd–[9] bonds, where M is an element of Group IVB of the periodic system. The results of these experiments, however, are only qualitative as the products of the reactions have not been studied in detail.

Our studies of these reactions are based on the oxidation of bis(triethylgermyl)-mercury in n-octane. This solvent has been chosen in order to compare the oxidizing conditions of bis(triethylgermyl)mercury with those of dialkylmercury that have already been fully investigated[10]. The oxidation of bis(triethylgermyl)mercury was followed by measuring the amount of oxygen absorbed. The quantity of oxygen absorbed was calculated in mole (N) for each initial mole of bis(triethylgermyl)-mercury, for a given period of time of reaction.

The initial pressure of oxygen over the reaction mixture was usually 250–300 mm. The oxidation of bis(triethylgermyl)mercury in octane solution proceeds very rapidly at as low a temperature as $-20°$ as shown by the disappearance of the yellow colour of bis(triethylgermyl)mercury from the solution.

The rate of oxidation of bis(triethylgermyl)mercury is not dependent on the addition of 2,6-di-tert-butyl-4-methylphenol at the beginning of the reaction (Fig. 1); addition of 2,4,6-tri-tert-butylphenol to the solution gave similar results. These compounds are very effective inhibitors in free radical oxidation processes of organometallic compounds of the Group IVB elements and of dialkylmercury[10,11]. Consequently, the oxidation of bis(triethylgermyl)mercury must proceed without the participation of free radicals.

At 0° and above, the products of the oxidation of bis(triethylgermyl)mercury are triethylgermyl oxide and free mercury. The yields are 90–100 and 92%, respectively. These results fall into line with earlier data[1,2].

At temperatures below −10°, a considerably smaller amount of mercury is deposited as the free metal. Immediately after the completion of the reaction at −20° (c, 0.09 mole·l^{-1}), the reaction mixture contains only about 0.2 g-atom of free mercury (per one mole of oxidised bis(triethylgermyl)mercury). In this case, the liquid reaction solution (1) contains the mercury-containing product which is thermally unstable and also unstable in the presence of water.

If solution (1) is maintained at the experimental temperature an additional amount of mercury is gradually formed. Increasing the solution temperature accelerates this process. When the solution temperature is raised to 0° and maintained at this figure for one hour, an additional 0.74 g-atom of mercury precipitates (per one mole of oxidized bis(triethylgermyl)mercury). There is a rapid separation of mercury on treating solution (1) with water; the yield of mercury is approximately theoretical. After the separation is complete, solution (1) contains triethylgermyl oxide in approximate theoretical yield.

A note of interest is that the amount of oxygen absorbed by the reaction mixture during oxidation of bis(triethylgermyl)mercury in all cases is approximately equal to 0.5 mole per mole of bis(triethylgermyl)mercury taken for the experiment. It is concluded from these experiments that auto-oxidation of bis(triethylgermyl)mercury results in the formation of an intermediate compound, triethylgermyloxytriethylgermylmercury. Thermal decomposition of this compound gives mercury and triethylgermyl oxide.

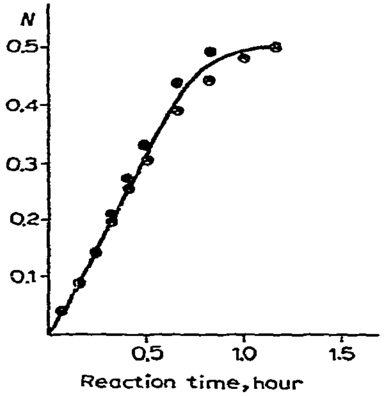


Fig. 1. Bis(triethylgermyl)mercury oxidation in n-octane (c, 0.1 mole·l^{-1}) at 0° without other additions and in the presence of 2,6-di-tert-butyl-4-methylphenol (0.01 mole·l^{-1}).

$$Et_3GeHgOGeEt_3 \rightarrow Et_3GeOGeEt_3 + Hg \qquad (1)$$

It is reasonable to suppose that the primary product of oxidation of bis(triethylgermyl)mercury is a peroxide compound [reactions (2) or (3)].

$$Et_3GeHgGeEt_3 + O_2 \rightarrow Et_3GeHgOOGeEt_3 \qquad (2)$$

$$Et_3GeHgGeEt_3 + O_2 \rightarrow Et_3GeOOGeEt_3 + Hg \qquad (3)$$

However, the reaction mixture after auto-oxidation of bis(triethylgermyl)mercury does not contain free peroxide.

$$\mathrm{Et_3GeHgOOGeEt_3 + Et_3GeHgGeEt_3 \rightarrow 2\,Et_3GeHgOGeEt_3} \quad (4)$$

$$\mathrm{Et_3GeOOGeEt_3 + Et_3GeHgGeEt_3 \rightarrow Et_3GeOGeEt_3 + Et_3GeHgOGeEt_3} \quad (5)$$

Apparently this is caused by the high reactivity of the peroxide product relative to that of the initial compound.

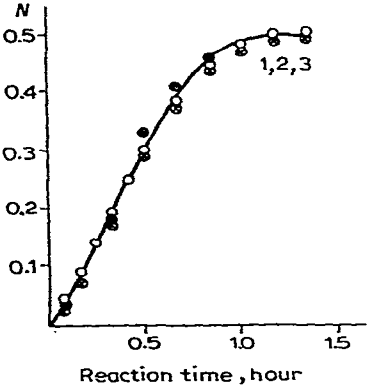
In order to appreciate the role of triethylgermyl peroxide in the bis(triethylgermyl)mercury auto-oxidation process, experiments were carried out in which an equimolar quantity of triethylgermyl peroxide was added to the mixture before the treatment with oxygen. If the peroxide compound is an intermediate product of bis(triethylgermyl)mercury reaction (5) should proceed rapidly and bis(triethylgermyl)mercury will react before coming into contact with oxygen. Therefore, oxygen absorption will not take place on further contact of the reaction mixture with oxygen. However, we have shown that even at room temperature triethylgermylperoxide does not interact with bis(triethylgermyl)mercury; there is no separation of mercury and the solution colour does not alter.

In the above experiments, after the equimolar bis(triethylgermyl)mercury (c, 0.01 mole$\cdot$l^{-1}) triethylgermylperoxide mixture is kept in n-octane for 30 min at room temperature, the appearance of the reaction mixture is not altered, and further oxidation at $-20°$ results in the absorption of 0.5 mole of oxygen per one mole initial bis(triethylgermyl)mercury. Hence, auto-oxidation of bis(triethylgermyl)mercury is not accompanied by the formation of large amounts of triethylgermyl peroxide.

The results obtained enable the oxidation of bis(triethylgermyl)mercury to be presented schematically by reactions (2), (4), (5) and (1). According to this scheme, the rate of oxidation should be directly proportional to the concentration of bis(triethylgermyl)mercury and the pressure of oxygen above the reaction mixture.

We established that the auto-oxidation of the bis(triethylgermyl)mercury is a first-order reaction in respect to the initial bis(organometallic) compound.

The log $N \sim i$ kinetic curves verify this result (Fig. 2). Unexpectedly, the order of the process in respect to oxygen is zero (Fig. 3); investigations were carried out with different oxygen pressures in the range 250–600 mm. This is apparently caused by catalysis of bis(triethylgermyl)mercury auto-oxidation by triethylgermyloxide,



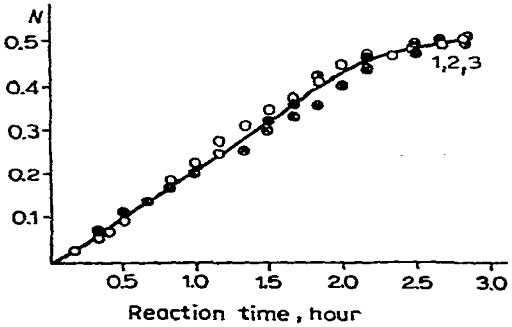
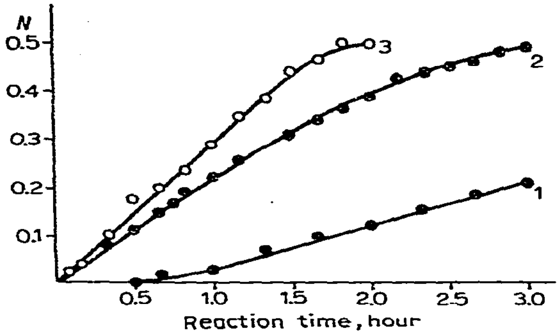


Fig. 2. Bis(triethylgermyl)mercury oxidation in n-octane (c, 0.1 mole$\cdot$l^{-1}) at 0°.

Fig. 3. Bis(triethylgermyl)mercury oxidation in n-octane (c, 0.1 mole$\cdot$l^{-1}) at $-10°$ with initial oxygen pressure above the reaction mixture equal to 250, 300, 540 mm.

one of the final reaction products. The addition of this oxide to the reaction mixture before the beginning of the reaction considerably accelerates the oxidation of bis(triethylgermyl)mercury (Fig. 4). However, triethylgermyloxide is extremely stable thermally and also stable to oxygen.



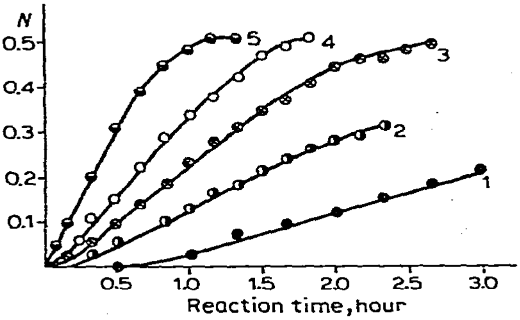


Fig. 4. Bis(triethylgermyl)mercury oxidation in n-octane (c, 0.1 mole·l^{-1}) at $-20°$; (1), without additions; (2, 3) with addition of triethylgermyloxide (c, 0.1 and 0.2 mole·l^{-1}).

Fig. 5. The effect of temp. on bis(triethylgermyl)mercury oxidation in n-octane (c, 0.1 mole·l^{-1}). (1), -20; (2), -15; (3), -10; (4), -5; (5), 0°.

The auto-catalysed oxidation of bis(triethylgermyl)mercury by triethylgermyl oxide explains why intermolecular oxidation of bis(triethylgermyl)mercury (free radical reactions are absent) proceeds with auto-acceleration, particularly at temperatures below 0° (Fig. 5). The catalytic action of triethylgermyloxide is obviously due to the formation of a complex of bis(triethylgermyl)mercury and triethylgermyl oxide (II).

$$Et_3GeHgGeEt_3 + Et_3GeOGeEt_3 \rightleftarrows \underset{(II)}{Et_3GeHgGeEt_3 \cdot Et_3GeOGeEt_3} \text{ (II)} \qquad (6)$$

The structure of this complex has not been established. In connection with this, a paper recently published by Eaborn and coworkers[12] is of interest. In this paper it was shown that at a relatively high temperature (185°) bis(trimethylsilyl)mercury interacted with some ethers forming an intermediate complex. In the case of ethers of the R_3SiOR' type (R and R' are alkyl radicals) a four-membered intermediate complex in which mercury- and silicon-bis(trimethylsilyl)mercury form transition bonds with R' and the oxygen of the alkoxytrialkylsilicon, respectively, is suggested. It follows that bis(triethylgermyl)mercury may form a similar complex with triethylgermyl oxide.

With this as the mechanism of the process, the oxidation rate (W) of bis(triethylgermyl)mercury is given by the following equation

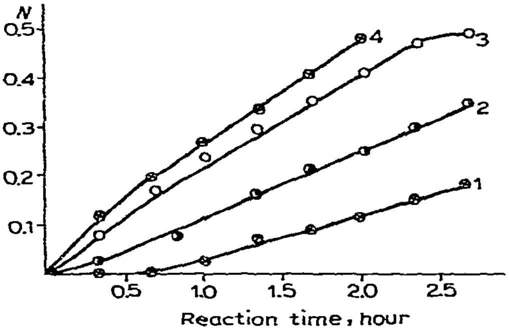
$$W = k[O_2]\,\frac{k_6'[MOC][OK]}{k_6''+k[O_2]} \qquad (7)$$

where k, k_6' and k_6'' are reaction rate constants of oxygen interaction with complex II, formation of complex II and the decomposition to its initial compounds; [MOC], $[O_2]$ are concentrations of bis(triethylgermyl)mercury and oxygen for a definite time.

Equation (7) shows that $k[O_2] \gg k_6''$, the order in respect to oxygen and bis(triethylgermyl)mercury is in agreement with experiment.

The acceleration of oxidation of bis(triethylgermyl)mercury was established experimentally by adding to it other compounds (known as nucleophilic reagents, *e.g.* triphenylphosphine, triethylamine, ammonia). These results are illustrated in Fig. 6.

The oxidation of bis(triethylgermyl)mercury in the presence of ammonia was investigated in more detail. In the presence of small amounts of ammonia (about 0.25 mole of ammonia in oxygen above the reaction mixture, per one mole of bis(triethylgermyl)mercury) the oxidation proceeds with the formation of triethylgermyloxytriethylgermylmercury. However, in this case the reaction mixture contains traces of the peroxide compound. This is shown by the fact that the liquid reaction mixture separated from the mercury metal at the end of the bis(triethylgermyl)mercury oxidation, gives a positive reaction with sodium iodide for active oxygen.



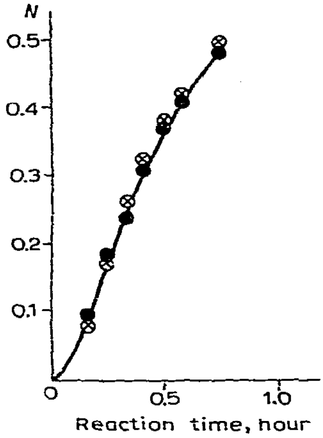
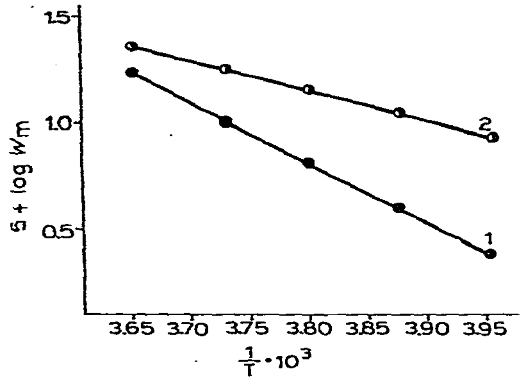


Fig. 6. The effect of some compounds on bis(triethylgermyl)mercury oxidation in n-octane (c, 0.09 mole·l^{-1}) at −20°. (1), without additions; (2, 4), with triethylamine and triphenylphosphine (for both, c, 0.01 mole·l^{-1}); (3), ammonia, approx. 0.1 mole ammonia/mole of initial bis(triethylgermyl)mercury.

Fig. 7. Bis(triethylgermyl)mercury oxidation in n-octane (c, 0.19 mole·l^{-1}) at 0° in presence of 2,6-di-tert-butyl-4-methylphenol (c, 0.019 mole·l^{-1}) and in presence of ammonia without additions.

During these experiments, this peroxide compound was not investigated in more detail, because of its small yield (about $1 \cdot 10^{-3}$ mole per one mole of initial bis(triethylgermyl)mercury). In order to obtain favourable conditions for a larger yield, bis(triethylgermyl)mercury was oxidized in the presence of a large amount of ammonia (2–5 moles of ammonia per mole of bis(triethylgermyl)mercury). The peroxide product yield was then 0.2–0.3 mole per mole of bis(triethylgermyl)mercury oxidized at a reaction temperature of −20°.

In an experiment with a similar ammonia addition at −50°, the peroxide compound yield is about one mole per mole per mole of absorbed oxygen and per mole of initial oxidized bis(triethylgermyl)mercury. In this case, the liquid reaction mixture does not contain combined mercury. The peroxide product was concentrated and identified as triethylgermyl peroxide by comparing its IR absorption spectrum with that of synthesized triethylgermyl peroxide. The formal kinetics of the oxidation of bis(triethylgermyl)mercury in the presence of small amounts of ammonia was studied as stated above and the experimental results are shown in Figs. 7, 9, 10 and partly in Fig. 8.



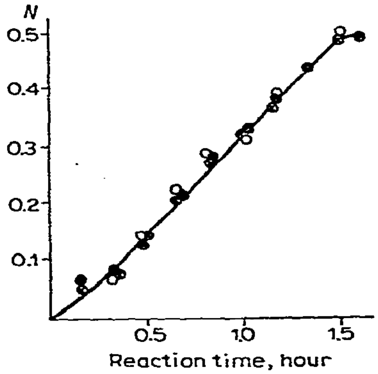


Fig. 8. W_m as function of temperature during bis(triethylgermyl)mercury oxidation in n-octane (c, 0.09–0.1 mole·l^{-1}). (1), without additions; (2), in presence of ammonia.

Fig. 9. Bis(triethylgermyl)mercury oxidation in n-octane (c, 0.045; 0.09; 0.019 mole·l^{-1}) at $-20°$ in presence of ammonia.

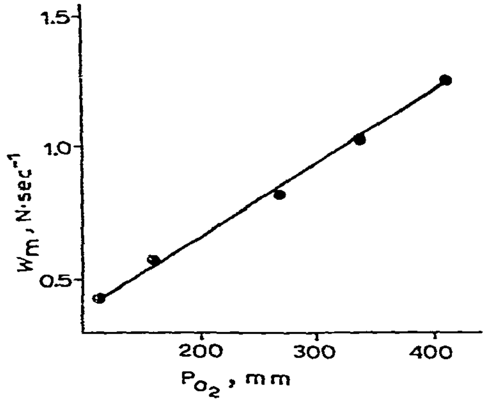


Fig. 10. W_m as function of oxygen pressure above the reaction mixture during bis(triethylgermyl)mercury oxidation in n-octane (c, 0.19 mole·l^{-1}) at $-20°$ and in presence of ammonia.

Figure 7 shows that additions of 2,6-di-tert-butyl-4-methylphenol have no effect on the oxidation of bis(triethylgermyl)mercury in the presence of ammonia. The temperature-dependence of the maximum rate (W_m) of this reaction, as well as of W_m of bis(triethylgermyl)mercury auto-oxidation satisfy the Arrhenius equation (see Fig. 8). The activation energy value (E) of the oxidation of bis(triethylgermyl)mercury in the presence of ammonia, is less than the E of auto-oxidation of this compound (6, 8 and 13.7 kcal·mole^{-1}, correspondingly) as expected.

Kinetic curves of the catalysed oxidation of bis(triethylgermyl)mercury at various initial concentrations are transformed to a one-line coordinate N reaction time (Fig. 9). These results indicate that the studied process is a first order reaction respecting initial organometallic compounds.

The maximum rate of oxidation of bis(triethylgermyl)mercury is proportional to the increase of oxygen pressure above the reaction mixture (Fig. 10). Consequently, the oxidation of bis(triethylgermyl)mercury in the presence of ammonia is a first-order reaction also in respect to oxygen.

The mechanism of the oxidation of bis(triethylgermyl)mercury in the presence of ammonia is unresolved and requires further investigation.

EXPERIMENTAL

Bis(triethylgermyl)mercury was synthesized by the hydride method[1]. The product obtained was purified by careful fractionation at low pressures in oxygen-free nitrogen (b.p. 123.5–124 at 1 mm).

n-Octane was conventionally purified and degassed by thrice-freezing in liquid nitrogen and re-freezing at low pressures.

Triethylgermylperoxide was synthesized by the method given in ref. 13. Oxygen was obtained by the thermal decomposition of potassium permanganate and was purified. Nitrogen was purified of oxygen by the copper–ammonia method[14], ammonia and water being finally removed by conventional means.

Bis(triethylgermyl)mercury was dissolved in n-octane in oxygen-free nitrogen.

The prepared solution was poured into ampoules with the aid of a special apparatus (see Fig. 11a) as follows. Ampoule (1), with the aid of a ground joint (2), was placed at the entrance cell (3) of box (4) which was filled with pure nitrogen. Then, by means of stopcock (5), the entrance cell and ampoules were evacuated and the ampoules were flushed with nitrogen three or four times. The entrance cell and ampoules were filled with nitrogen, after which the lid (6) was removed and a known volume of bis(triethylgermyl)mercury solution in n-octane was poured into the ampoule through the ground joint (2). The entrance cell lid was closed, nitrogen was

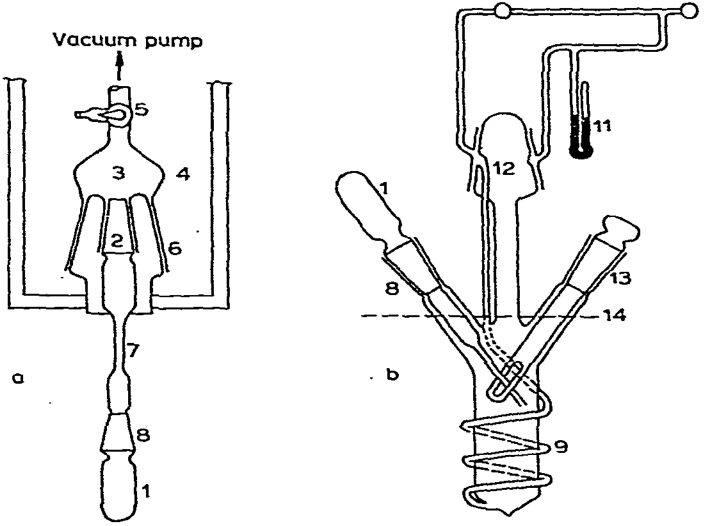


Fig. 11. (a), Sketch of apparatus for pouring of bis(triethylgermyl)mercury solution into ampoules; (b), sketch of apparatus for bis(triethylgermyl)mercury oxidation with oxygen.

evacuated from the ampoule, the solution being previously cooled to the temperature of liquid nitrogen.

The reaction solution was carefully purified from ammonia, which, as we established, was obviously present in nitrogen purified by the copper–ammonium method. Ammonia was removed by repeated freezing in liquid nitrogen and re-freezing in vacuum (not less than six times). Ampoules containing solutions prepared in this manner were kept in a dark place at room temperature until required.

The oxidation of bis(triethylgermyl)mercury was carried out with the evacuated glass apparatus, the principal scheme of which is shown in Fig. 11b. This apparatus consists of the reaction vessel (9), the circulating pump (10) and a mercury manometer (11). The reaction vessel is separated from the apparatus by the stopcock (12).

The procedure usually consisted of the following operations*. Ampoule (1) was connected to the reaction vessel (9) by the ground joint (8) so that its soldered needle-like end entered the eye of the pivoted breaker (13). The system was then evacuated and the reaction vessel (9) was tipped to close the stopcock. The apparatus was filled with the necessary amount of ammonia and the purified oxygen was brought to a pressure, P_0. The solution of bis(triethylgermyl)mercury was transferred into the reaction vessel (tip (1) was broken by the breaker (13)) and cooled to the reaction temperature by immersing it in the thermostatic liquid to level (14).

When the stopcock (12) was opened, the oxygen pressure in the system fell abruptly to pressure P_1, which was regulated to P_0. This moment was taken as the beginning of the reaction.

The amount of oxygen used in the oxidation of bis(triethylgermyl)mercury was estimated by the pressure drop in the reaction system, which was checked by a manometer. Corrections were made for the fall in oxygen pressure due to the fact that static temperature conditions in the reaction system were not established immediately while the oxidizing gas was continuously circulated through the system.

The experimental method used stipulated a variable oxygen pressure above the reaction mixture during the oxidation of bis(triethylgermyl)mercury. However, this did not cause any complications, because the order of this reaction in regard to oxygen was equal to zero.

In the experiments on the oxidation of bis(triethylgermyl)mercury in the presence of ammonia, the pressure of oxygen was rather high, P_1. The decrease in oxygen pressure after the complete oxidation of the initial organoelemental compound was less than 10% of P_1. There was only a slight slowing down of the reaction rate owing to the decrease of oxygen pressure and this effect was, therefore, not taken into account.

REFERENCES

1 N. S. VYAZANKIN, G. A. RAZUVAEV AND E. N. GLADYSHEV, *Dokl. Akad. Nauk SSSR*, 151 (1963) 1326.
2 N. S. VYAZANKIN, G. A. RAZUVAEV AND E. N. GLADYSHEV, *Dokl. Akad. Nauk SSSR*, 155 (1964) 830.

---

* Air evacuation and intake of oxygen were accomplished by a system of stopcocks, marked (15).

A liquid thermostat was used, which enabled to the temperature to be kept constant in the range, room temperature to −70° with little expenditure of the cooling agent (liquid nitrogen).

3 N. S. Vyazankin, O. A. Kruglaya, G. S. Kalinina and E. N. Gladyshev, *Zh. Obshch. Khim.*, in press.
4 K. Kühlein, Diplomarbeit, Giessen Universität, 1963.
5 N. S. Vyazankin, G. A. Razuvaev, O. A. Kruglaya and G. S. Semchikova, *J. Organometal. Chem.*, 6 (1966) 474.
6 W. Stamm, *Trans. N.Y. Acad. Sci.*, 28 (1966) 396.
7 H. Schumann and M. Schmidt, *Inorg. Nuclear Chem. Letters*, 1 (1965) 1.
8 H. Schumann and M. Schmidt, *Angew. Chem.*, 76 (1964) 344.
9 N. S. Vyazankin, G. A. Razuvaev and V. T. Bychkov, *Dokl. Akad. Nauk SSR*, 158 (1964) 382.
10 Yu. A. Alexandrov, O. N. Druzhkov, S. F. Zhiltsov and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, 157 (1964) 1395.
11 Yu. A. Alexandrov, T. G. Brilkina and V. A. Shushunov, *Tr. Khim. i Khim. Tekhnol.*, 1 (1961) 3.
12 C. Eaborn, R. A. Jackson and R. W. Walsingham, *J. Chem. Soc.*, (1967) 2188.
13 A. Rieche and J. Dahlmann, *Monatsber. Deut. Akad. Wiss. Berlin*, 1 (1959) 491.
14 Yu. V. Karyakin, *Pure Chemical Reactives, SSSR*, State Chemical Publ. Office, Moscow, 1947.