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On the possibility of complex formation of Group IIIB organic compounds with molecular oxygen

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Abstract

The likelihood of the formation of $R_3E \cdot O_2$ complexes (E is an element of Group IIIB) in R_3E/O_2 systems has been shown experimentally and theoretically. The most probable energetic parameters, structure, problems of stability are discussed.

The results of quantum-chemical calculations for the Me_3B/O_2 system and those of experimental study of complexing Me_3Ga with molecular oxygen have been reported [1,2]. In the present paper these investigations are discussed in more detail, the new data of quantum-chemical calculations for Me_3Al/O_2 and Me_3Ga/O_2 systems are given.

The calculations for fragments of potential energy hypersurfaces (PEHS) for model Me_3E/O_2 systems, where E is B (I), Al (II), Ga (III), were carried out within the scope of standard versions of LCAO MO SCF INDO and MINDO/3 (for I, II), CNDO/2 (for III) in formalism of the unrestricted Hartree–Fock method [3–7] with an overall optimization of molecular geometry. The results of calculations of overall energy for systems I–III show that optimum inactivated directions of approach for molecules of coreagents combine in the solid angle which is closely spaced to C_3 symmetry axis of organoelement R_3E molecules (Fig. 1) and fall in $\sim \frac{2}{3}\pi - \pi$ steradian range. The detailed PEHS investigation of Me_3E/O_2 systems within the scope of INDO and CNDO/2 methods indicated that in the region of the configuration space which conforms to the initial interaction of reagents, three local minima (LM) can be selected. They are consistent with $Me_3E \cdot O_2$ intermediates (IM) of the classic donor–acceptor type of different structure and multiplicity. The major energetic, electronic and geometric characteristics of isolated molecules and intermediates are listed in Tables 1 and 2. The results show that for all IM mentioned above as well as for Me_3E/O_2 systems in the initial phase of interaction, the transfer of electron density from O_2 fragment onto Me_3E (up to 0.2 electrons) and the overall localization of spin density for systems with multiplicity

Table 1

Geometrical and electronic characteristics of isolated O_2 and Me_3B, Me_3Al, Me_3Ga molecules

Molecule	Symmetry	Method of calculation	Bond	Bond length (Å) [a]	W [b]	Atom, group	Effective charge
$O_2^3\Sigma_g^-$	$D_{\infty h}$	INDO	O–O	1.140 (1.207)	2.0	O	0.0
O_2	$D_{\infty h}$	CNDO/2	O–O	1.132 (1.207)	2.0	O	0.0
Me_3B	C_{3h}	INDO	B–C	1.530 (1.578)	1.085	B CH_3	+0.077 −0.026
Me_3Al	C_{3h}	INDO	Al–C	1.994 (1.957)	1.165	Al CH_3	+0.017 −0.006
Me_3Ga	C_{3h}	CNDO/2	Ga–C	1.920 (1.967)	1.067	Ga CH_3	+0.362 −0.121

[a] Experimental values are given in brackets (taken from [8,9]). [b] Modified Wiberg index of bond [10].

(M = 3) on oxygen atoms are typical. Thus it is necessary to note that the formation of intermediates is accompanied by distortion of atomic C_3E fragment planarity. The reaction enthalpies of IM formation (ΔH_r°) can be estimated as being between -17 and -100 kJ mol^{-1} *. For more correct calculation of energetic parameters of $Me_3E \cdot O_2$ intermediates (E = B, Al) in singlet electron state and to investigate their ability to tranform further the same regions of configuration PEHS space for Me_3E/O_2 systems have been considered within the scope of MINDO/3 method. The main results are presented in Table 3. Quantum-chemical analysis permits one to conclude that the intermediates formed are extremely labile and readily transform into the corresponding peroxide with an activation barrier which does not exceed 25 kJ mol^{-1} with respect to an intermediate.

Thus, the quantum-chemical calculations point to the possibility of the formation, without activation, of labile complexes, $Me_3E \cdot O_2$ intermediates, the existence of which solves the problem of the change of multiplicity formally prohibited by the selection rules in Me_3E/O_2 systems from M = 3 to M = 1 during the transformation. Furthermore the calculations definitely indicate that the C_3E fragment in the $Me_3E \cdot O_2$ intermediate has pyramidal structure. The change in OEC geometry in complexed OEC $\cdot$ O_2 from planar configuration into pyramidal one makes the application of IR spectroscopy for the experimental elucidation of this complex possible.

We investigated by IR spectroscopy the formation of the oxygen complex with organic compounds of Group IIIB elements, as exemplified by the Me_3Ga/O_2 system. The choice of trimethylgallium was due to the fact that in contrast to the boron and aluminum compounds, trimethylgallium autooxidation is not complicated by secondary reactions at temperatures below −50 °C. It has been found [11] that the object is resistant to oxidation of the second and the third Ga–C bond, and that the peroxide formed is thermally stable (however, it decomposes rapidly

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* With regard to the known reestimation of bonding in schemes of INDO and CNDO/2 type [3].

Table 2

Geometrical and electronic characteristics of $Me_3E \cdot O_2$ intermediates [a]

Intermediate:	$Me_3B \cdot O_2$			$Me_3Al \cdot O_2$			$Me_3Ga \cdot O_2$		
Multiplicity:	3	3	1	3	3	1	3	3	1
Symmetry:	C_{3v}	C_s	$\sim C_{3v}$	C_{3v}	C_s	C_s	C_{3v}	C_s	$\sim C_{3v}$
	Bond lengths (Å) and γ,α angles (°)								
O^1–O^2	1.140	1.155	1.142	1.139	1.146	1.145	1.132	1.153	1.133
E–O^1	1.655	1.794	1.644	2.284	2.456	2.434	2.011	2.111	2.008
E–O^2	2.795	1.794	2.778	3.423	2.456	2.434	3.143	2.111	3.141
C^1–E	1.557	1.560	1.558	2.016	2.019	2.023	1.936	1.940	1.933
E–$C^{2,3}$	1.557	1.565	1.557	2.016	2.018	2.018	1.936	1.939	1.936
γ	100.6	102.2	100.2	100.6	101.6	102.3	101.1	103.4	100.7
α	0.0	90.0	13.4	0.0	90.0	90.0	0.0	90.0	14.7
	Modified Wiberg indexes of bonds								
O^1–O^2	1.937	1.814	1.912	1.974	1.928	1.958	1.962	1.888	1.955
E–O^1	0.374	0.212	0.386	0.310	0.169	0.179	0.341	0.223	0.343
E–O^2	0.000	0.212	0.022	0.000	0.169	0.179	0.0	0.223	0.0
E–C^1	1.023	1.033	0.991	1.134	1.133	1.128	1.048	1.053	1.036
E–$C^{2,3}$	1.023	0.992	1.030	1.134	1.128	1.128	1.048	1.042	1.052
	Effective charges on atoms								
O^2	+0.050	+0.090	+0.030	+0.068	+0.089	+0.095	+0.109	+0.109	+0.103
O^1	+0.149	+0.090	+0.149	+0.106	+0.089	+0.095	+0.076	+0.109	+0.077
E	+0.022	+0.058	+0.028	−0.058	−0.052	−0.058	+0.237	+0.191	+0.238
C^1H_3	−0.074	−0.081	−0.060	−0.039	−0.042	−0.047	−0.141	−0.136	−0.142
$C^{2,3}H_3$	−0.074	−0.078	−0.073	−0.039	−0.042	−0.043	−0.141	−0.136	−0.138

[a] The model of nuclear frame for Me_3E/O_2 systems and the numeration of atoms in them are given in Fig. 1.

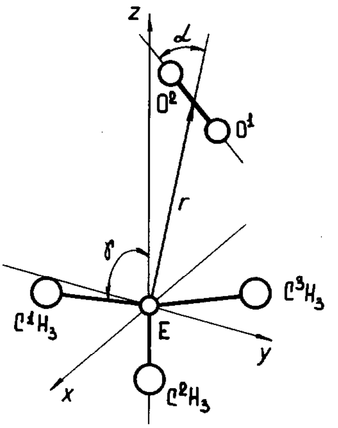

Fig. 1. A model of the nuclear frame and the atom numbering of the Me_3E/O_2 system.

above 100 °C), the reaction is almost completely absent at temperatures below −50 °C (eq. 1):

$$Me_2GaOOMe + Me_3Ga \rightarrow 2\ Me_2GaOMe \qquad (1)$$

In the low temperature region (down to −191° C), trimethylgallium undergoes no phase transitions [12] which could change its IR spectrum.

IR spectroscopy of Me_3Ga/O_2 reaction system was carried out in a special vacuum cell. Me_3Ga was frozen onto silicon plates the thickness of which was 0.05 cm. Its IR spectrum was entirely consistent with that given in ref. 13 and did not change over the temperature range of −120 to −60 °C (Fig. 2a). Dry oxygen (300 mmHg) was then let into the cell with Me_3Ga frozen over silicon plates at −110 °C. Trimethylgallium in the presence of oxygen was kept at this temperature for an hour. Under these conditions, the IR spectrum of Me_3Ga/O_2 system investigated did not differ from Me_3Ga spectrum in the absence of oxygen.

The temperature of the silicon plates was elevated to −92 °C. After 4 h at this temperature the IR spectrum of Me_3Ga/O_2 showed an absorption band at 545 cm^{-1} and a gradual increase of its intensity together with a negligible decrease in the intensity of the absorption band at 575 cm^{-1} (Fig. 2b). In addition very weak absorption bands were seen at 600, 815 and 1010 cm^{-1}.

After 4 h the increase in intensity of the band at 545 cm^{-1} ceased, so repeated impulsive heating of plates to −70 °C was carried out. It was found that the intensity of the bands at 600, 815, 1010 cm^{-1} increased and the band at 575 cm^{-1}

Table 3

The calculated enthalpies reactions of formation (ΔH_r°) and the main structural parameters of $Me_3E \cdot O_2$ intermediates with M = 1 multiplicity (MINDO/3 method)

Intermediate	Symmetry	$-\Delta H_r^\circ$, (kJ mol^{-1})	r (Å)	γ(°)	α(°)
$Me_3B \cdot O_2$	$\sim C_{3v}$	37	2.037	103.2	19.0
$Me_3Al \cdot O_2$	C_s	81	1.861	104.8	90.0

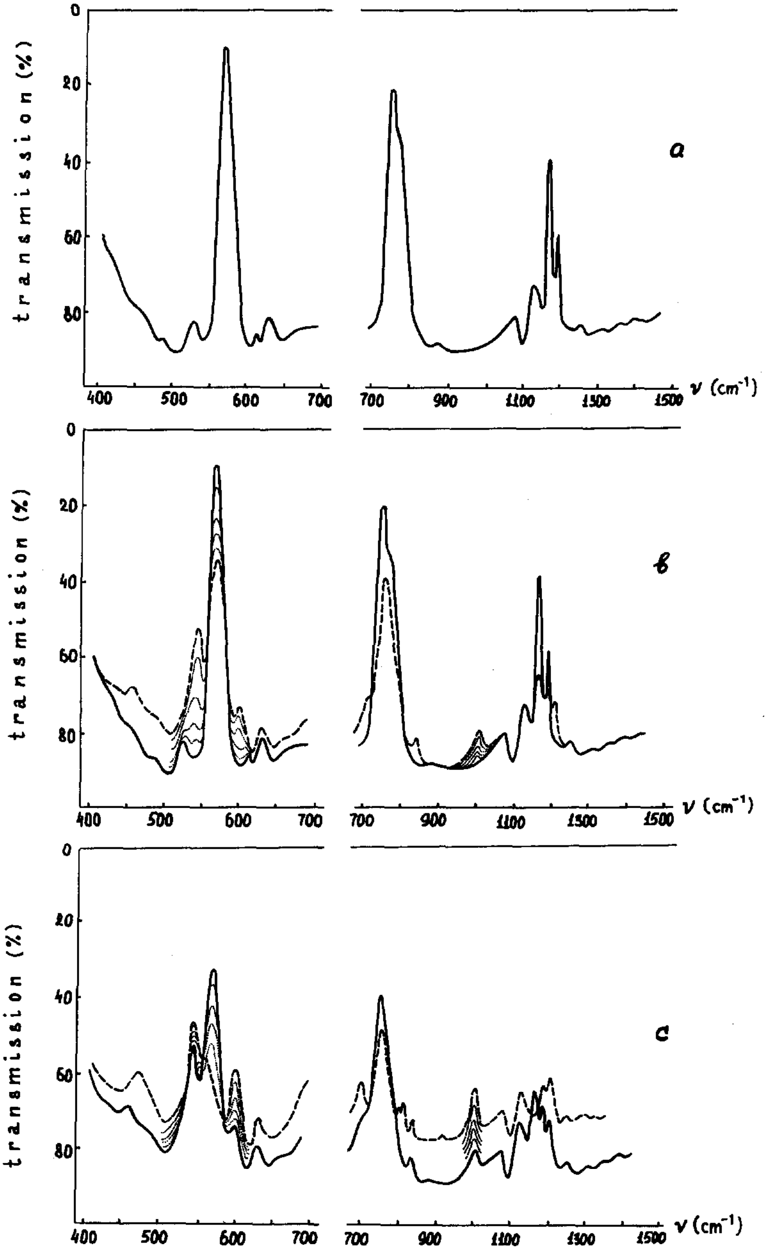

Fig. 2. IR spectrum of Me_3Ga in the absence of oxygen (−60−−120 °C) (a) and variation of IR spectrum for Me_3Ga/O_2 reaction system in the temporary c–d (b) and d–e (c) interval (see Fig. 3). Solid and dashed lines characterize initial and final points of temporary intervals, respectively. Variation in intensity of the most characteristic bands are denoted by successive dotted lines at equal intervals of time: 1 h (b), between temperature impulses (c).

disappeared completely (Fig. 2b). The effect of variation of temperature on the Me_3Ga/O_2 reaction system during the process investigated is represented graphically in Fig. 3.

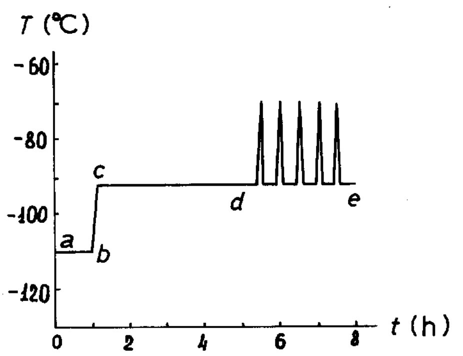

Fig. 3. The effect of the variation of temperature on the course of the transformation of the Me_3Ga/O_2 system.

To study this phenomenon in detail we obtained IR spectra of some possible oxygen-containing products of trimethylgallium autooxidation: $Me_2GaOOMe$, Me_2GaOMe, $MeGa(OMe)_2$ and were interpreted on the basis of frequency calculations and the form of normal vibrations. The results are listed in Table 4.

The absorption bands at 600, 815, 1010 cm^{-1} are consistent with valence vibrations of dimethyl(methylperoxy)gallium Ga–O, O–O and C–O bonds, respectively. After the disappearance of the band at 575 cm^{-1} (Fig. 2b) the final spectrum of the sample investigated is entirely consistent with the peroxide spectrum

Table 4

Fundamental frequencies of normal vibrations in IR spectra of oxygen-containing organogallium compounds (cm^{-1}) [a]

$Me_2GaOOMe$	Me_2GaOMe	$MeGa(OMe)_2$	Assignment of frequencies [b]
475w			
	585s		
	540s		ν(Ga–C), ν(Ga–O)
545s			
560m	560s	585s	ν(Ga–C)
600s		470s	ν(Ga–O)
700m	690m	725m	
750s	740m	745m	$\rho(CH_3)$
815w			ν(O–O), δ(C–O–O), δ(Ga–O–O)
1010s			ν(C–O), δ(C–O–O)
	1015s 1040m	1070m	ν(C–O), δ(C–O–Ga)
1185w 1215m	1210m	1210m	$\delta(CH_3)$

[a] IR spectra of $Me_2GaOOMe$ and Me_2GaOMe were obtained on a thin layer between KBr or $MeGa(OMe)_2$ windows in suspensions in Nujol mulls. [b] ν, ρ, δ are valent, torsional, deformation vibrations, respectively.

Table 5

Calculated and observed fundamental frequencies of normal vibrations in IR spectra of trimethylgallium

Experimental data (solid film, 110 °C)	Calculated frequencies		Assignment of frequencies
	planar C_3Ga configuration D_{3h}, ∠CGaC = 120 °	pyramidal C_3Ga configuration C_{3v}, ∠CGaC = 109.5 °	
527vw [a]	524 [b]	542	ν_s(Ga–C)
575vs	576	568	ν_{as}(Ga–C)
755s	742	741	$\rho(CH_3)$
780sh	750	750	
1175s	1207	1196	$\delta(CH_3)$
1200m	1208		

[a] The appearance of a band in IR spectrum of solid sample is due to a matrix effect. [b] Inactive in IR spectrum.

($Me_2GaOOMe$). The other oxygen-containing organogallium compounds were not found in large quantities during the process investigated.

The calculated IR spectra of various trimethylgallium structures: planar (D_{3h} symmetry, ∠CGaC = 120 °) and pyramidal (C_{3v} symmetry, ∠CGaC = 109.5 °), obtained by solving the vibrational problem directly are shown in Table 5.

In both cases the nuclear C_3Ga frame of trimethylgallium molecule is characterized by two normal ν(Ga–C) vibration frequencies: overall symmetrical (ν_s) and twice degenerated (ν_{as}). For planar structures ν_s(Ga–C) vibration is prohibited in the IR spectrum by selection rules. This absorption band, at 527 cm^{-1}, has a very low intensity in a firm Me_3Ga film spectrum, which is why the matrix effect cannot be assumed to distort the planar structure of the nuclear C_3Ga frame. At the same time the calculations (Table 5) indicate that a change in the geometry of the nuclear frame in the trimethylgallium molecule should have a substantial influence on IR absorption band location.

The absorption band at 545 cm^{-1} of the Me_3Ga/O_2 could be the superposition of the following two absorption bands. The first band can be assigned to full symmetrical vibrations in the nuclear C_3Ga frame of the Me_3Ga pyramidal (Table 5) and the second to vibrations of the Ga–C bonds of the $Me_2GaOOMe$ molecule (Table 4). To throw light on the components of the absorption band at 545 cm^{-1} the variation in intensity of the other peroxide absorption bands has been analyzed and compared with this band. For this purpose the intensities of the absorption bands for valence vibrations of the Ga–O (at 600 cm^{-1}) and C–O (at 1010 cm^{-1}) bonds of the peroxide molecule were used as the most typical and intense (see Table 4). The variation of the ratio of optical density in the absorption band at 545 cm^{-1} to optical density of dimethyl(methylperoxy)gallium absorption bands at 600 cm^{-1} ($D_{545/600}$) and at 1010 cm^{-1} ($D_{545/1010}$) for the duration of the process, c–d (see Fig. 3) is given in Fig. 4. The nature of $D_{545/600}$, $D_{545/1010}$ – temporary process relationship observed in Fig. 4 points to an essentially slower increase in intensity of the $Me_2GaOOMe$ absorption bands (600, 1010 cm^{-1}) compared with that of the absorption band at 545 cm^{-1} which indicates that in this period one more product appears; it is different from peroxide and shows a valence vibration band at 545 cm^{-1}.

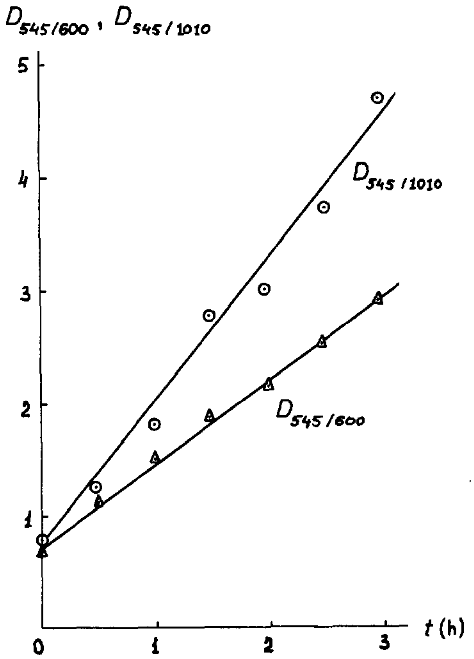

Fig. 4. The variation of $D_{545/600}$ and $D_{545/1010}$ in the temporary c–d interval of the trimethylgallium auto-oxidation process.

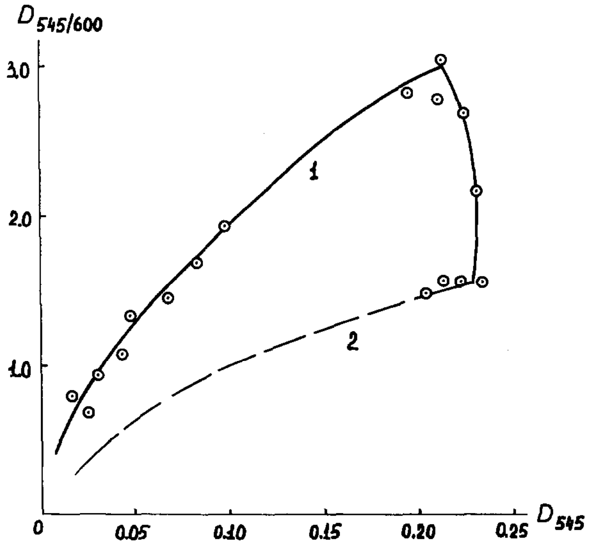

Fig. 5. The dependence of the optical density of $D_{545/600}$ on D_{545} in the IR spectra of the Me_3Ga/O_2 reaction system in the temporary a–e interval (1).
The expected dependence when no intermediate is formed (2).

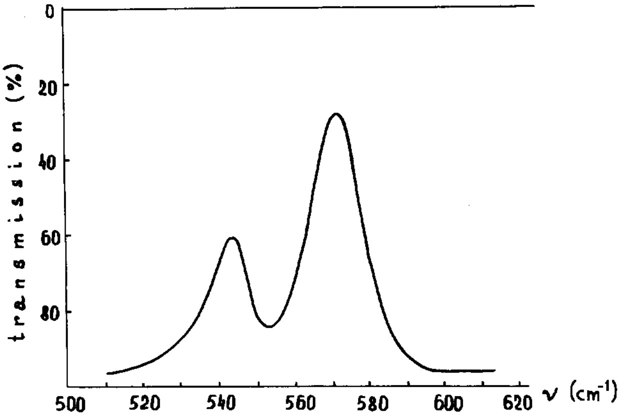

Fig. 6. The IR spectrum of an intermediate in the region of 500–620 cm^{-1}.

The dependence of $D_{545/600}$ magnitude of the Me_3Ga/O_2 system on the optical density of the band at 545 cm^{-1} (D_{545}) in all the temporary a–e points is given in Fig. 5. During the process in the temporary interval a–e, the regular shape of curve 1 points to the formation of an intermediate compound which has an absorption band at 545 cm^{-1}; this compound differs structurally from $Me_2GaOOMe$. This intermediate appears more rapidly in the temporary c–d period than peroxide. It disappears during the d–e period. In this case the sharp increase in the peroxide absorption bands at 600, 815, 1010 cm^{-1} occurs. The peroxide is a final reaction product. Thus the following transformation chain is presumed to take place in the temporary a–e interval:

$$Me_3Ga + O_2 \rightarrow IM \rightarrow Me_2GaOOMe \qquad (2)$$

By subtraction of the well-known trimethylgallium and dimethyl(methylperoxy)gallium spectra, the IR spectrum of the intermediate was obtained, this is given in Fig. 6. In this case the following assumptions have been made:

(i) the amount of final peroxide was taken to be equal to the amount of initial trimethylgallium;

(ii) the optical band density of silicon plate absorption in the region of 630–635 cm^{-1} was considered to be constant and on this basis the magnitude of background was determined which in the temporary d–e interval was found to increase slightly.

The IR spectrum of the intermediate given in Fig. 6 is consistent with the calculated IR spectrum of the compound in which the nuclear C_3Ga frame is a pyramid (C_{3v} symmetry, $\angle CGaC = 109.5$) (Table 5). In this case the approximate constancy of an absorption band at 575 cm^{-1} in the temporary c–d interval (Fig. 2b) can be due to a partial overlap of decreasing absorption bands of twice degenerated vibrations of Ga–C trimethylgallium bonds (575 cm^{-1}) with a similar intermediate band (568 cm^{-1}) increasing during this period. Under these conditions (−92°C) at low rates of intermediate decomposition the decreasing intensity of trimethylgallium band at 575 cm^{-1} will be compensated by the increase in intensity of the absorption band of the intermediate at 568 cm^{-1}.

Thus, variations in the IR absorption spectrum observed in the trimethylgallium autooxidation can be interpreted as evidence for the formation of a very unstable intermediate in which by the action of oxygen the rearrangement of the C_3Ga frame from planar to pyramidal one occurs. These conclusions agree well with results of quantum-chemical investigations for Me_3E/O_2 (E = B, Al, Ga) systems, which have shown the necessity of similar structural rearrangement for Me_3E molecules in the formation of dioxygen complex.

The result obtained characterizes the process which occurs in the Me_3Ga/O_2 system in solid film of trimethylgallium, when the mobility of the molecules and radicals is hindered. Up to now there are no reasons to suppose that the present process proceeds similarly in liquid phase, owing to peculiarities of reactions in liquid phase (the appearance of only the close order interactions viz. diffusion, solvation and so on) the conditions for the realization of another direction of the process can be created, which does not take place under the conditions studied.

Experimental

Trimethylgallium was synthesized by B.I. Kozyrkin (Moscow). Its purity was more than 99.9%.

The construction of vacuum IR spectroscopic cell to investigate Me_3Ga auto-oxidation has been described [14]. The temperature conditions were sustained automatically. The error in determination of temperature was $\pm 1°$C. IR spectra were recorded on a UR-20 spectrophotometer in the 400–4000 cm^{-1} region.

Dimethyl(methylperoxy)gallium was obtained by the method described [11]. Dimethyl(methoxy)gallium and methyl(dimethoxy)gallium were synthesized as in [15].

The calculations of frequencies and forms for normal vibrations of molecules were carried out on a BESM-6 computer in formalism of FG matrices by a modernized program previously described [16].

The detection of an intermediate spectrum was conducted to use a mathematical manipulation method of a series of spectrograms [17].

The quantum-chemical calculations were made using the amended system of mathematical software for the ES-1045 computer together with a modified program from the GEOMO/RV QCPE No. 350.

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