IR spectroscopic study of the interaction between trimethylgallium and arsine in the liquid phase

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The formation of a donor-acceptor complex $Me_3Ga \cdot AsH_3$ in a solution in liquid krypton at 130 K and in a binary liquid solution of those substances at 263 K was established by IR spectroscopy. In the latter case, Me_3Ga and AsH_3 react at an appreciable rate to form an amorphous product of composition $Me_{3-x}GaAsH_{3-x}$.

Key words: trimethylgallium, arsine, solution, donor-acceptor complex; IR spectroscopy.

Vapor-phase chemical precipitation is widely used to obtain semiconductor epitaxial structures.[1] Volatile organometallic compounds (as a rule, of elements of groups III, V, and VI) as well as volatile inorganic hydrides of elements of groups IV—VI are commonly used as starting substances. Gallium arsenide is one of the most important structures obtained by this method. Its synthesis from traditionally used trimethylgallium (TMG) and arsine can be described by the following scheme:

$$Me_3Ga(g) + AsH_3(g) \rightarrow GaAs(s) + 3\ CH_4(g). \qquad (1)$$

The mechanism of this reaction has been discussed for more than a decade (see, for instance, Ref. 2). The peculiarities of the electron structure of TMG molecules (a strong acceptor of electrons, a Lewis acid) and arsine (a weak donor of electrons, a Lewis base) allow one to assume that reaction (1) proceeds *via* the formation of an intermediate donor-acceptor complex with subsequent elimination of gaseous methane. Similar complexes of TMG with strong Lewis bases (NMe_3, PhCN, PMe_3, OMe_2, *etc.*) are known;[3] however, data on isolation of a free adduct with arsine (which is a weaker base even than phosphine[4]) are not available. Attempts failed to detect the formation of the $Me_3Ga \cdot AsH_3$ complex in the gas phase at increased temperatures (~400 K), *i.e.*, under conditions close to the real conditions of reaction (1).[5,6] At the same time, the results of recent *ab initio* quantum-chemical calculations[7] point to satisfactory thermodynamic stability of this complex. It seems likely that the content of the complex under equilibrium conditions in the gas phase is lower than the limiting concentration that can be detected using spectroscopic[5] and mass spectral[8] methods.

Matrix IR spectroscopy is an informative technique for studying intermediates of chemical reactions and weak molecular complexes. Therefore, this method was used for studying the interaction between TMG and AsH_3 molecules when they coprecipitated from a mixture with argon onto a support cooled to 14 K.[10] It is believed[10] that the substantial (by 10—50 cm^{-1}) shift of all the spectral bands, including both the high-frequency shift of the band of AsH_3 stretching vibrations and the low-frequency shift of the band of antisymmetrc stretching vibrations of the Ga—C bond, $\nu_{as}(GaC_3)$, in TMG, is evidence for the formation of the $Me_3Ga \cdot AsH_3$ complex. In addition, a new band in the region 520 cm^{-1} assigned to $\nu_s(GaC_3)$ vibrations, which are usually forbidden by the selection rules, appears in the spectrum of a mixture of TMG with AsH_3. At this time these data[10] are likely the only direct experimental evidence for the existence of the $Me_3Ga \cdot AsH_3$ complex; however, they were obtained under specific non-equilibrium conditions of the low-temperature matrix.

The aim of the present work was to perform an IR specroscopic study of the interaction between trimethylgallium and arsine in the liquid phase when they are directly mixed in a solution in liquid krypton at 130 K and in a binary solution at a temperature close to room temperature.

Experimental

Specially developed cuvette-cryostats were used to obtain IR spectra of mixtures of TMG with arsine and of individual TMG in solution in liquid Kr and in the liquid state (analogous arsine spectra have been studied previously[11,12]).

The experimental installation for registration of the IR spectra of solutions of the substances under study in liquid krypton has been described previously.[11] A cuvette with l = 10 cm was used. The spectra in the region of 5000—400 cm^{-1} with resolution of 2 cm^{-1} were recorded on a Perkin-Elmer 325

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Table 1. Positions of the bands of the fundamental vibrations (ν/cm^{-1}) in the IR spectra of pure TMG and AsH_3 and in the $Me_3Ga \cdot AsH_3$ complex in the gas phase, in an Ar matrix at 12 K, in a solution in liquid krypton at 130 K, and in the liquid phase at 263 K

Type of vibration	TMG				AsH_3				Complex $Me_3Ga \cdot AsH_3$			
	Gas[10]	Ar-matrix[10]	Solution in Kr	Liquid phase	Gas	Ar-matrix[10]	Solution in Kr[11]	Liquid phase[12]	Gas[7]	Ar-matrix[10]	Solution in Kr	Liquid phase
$\nu_s(GaC_3)$									540	520	511	525
$\nu_{as}(GaC_3)$	550	576	552	570					589	565	545	575
			537								532	
$r_1(CH_3)$	715	723	699	731					713	722	695	726
$r_2(CH_3)$	823	768	741	768					818	753	735	762
$\nu_s(AsH_3)$					2321	2140	2123	2116	2354	2175	2132	2142
$\nu_{as}(AsH_3)$					2327	2150			2360	2191		
$\delta_s(AsH_3)$					1020	912	900	905	1006	892	904	908
$\delta_{as}(AsH_3)$					1123	1003	994	980	1116	989	989	980

spectrometer. To obtain solutions of a mixture of TMG and arsine in liquid Kr, two procedures were used: (1) dissolution of the crystalline phase of a previously prepared gaseous mixture of the substances under study; (2) dissolution of the crystalline phase of gaseous TMG and AsH_3 successively frozen onto the inner walls of the cuvette.

The spectra of pure liquid TMG and its mixtures with arsine in the liquid phase were studied by using a cuvette 16 μm thick developed previously for recording spectra of liquid hydrides.[12] This presented some problems in loading liquid TMG because of the low pressure of its saturation vapor. Therefore, TMG was fed into a cuvette under the action of excess argon pressure (2 atm). An indentical inlet was used then to supply gaseous arsine. Zinc selenide windows were attached to the case of a stainless steel cuvette by means of flanges through an indium gasket. The thickness of the cuvette was determined by a silver gasket (aluminum gaskets react with TMG at an appreciable rate even at room temperature). The spectra in the region of 4000—500 cm^{-1} with resolution of 2 cm^{-1} were recorded on a Specord M80 spectrometer.

TMG and AsH_3 were purified by distillation.

Results and Discussion

IR spectra of a solution of a mixture of TMG and AsH_3 in liquid krypton. Bands corresponding to the fundamental vibrations of the Ga—C_3 and C—H bonds of the TMG molecule and of the As—H bond of arsine (Table 1) remain in the spectrum of a solution containing Me_3Ga and AsH_3 in a 1 : 2 ratio at 130 K (Fig. 1). However, their intensities are substantially lower than in the spectra of the individual substances. Simultaneously, a considerable shift of all the bands is observed (Table 2). The character of the shift of the studied fundamental bands of Me_3Ga and AsH_3 in solution in liquid Kr is analogous to that observed for the Ar-matrix (experiment) and for the gas phase (calculations). The characteristic low-frequency shift of the $\nu_{as}(GaC_3)$ band points to weakening of the Ga—C bond, while the high-frequency shift of the bands of the stretching vibration of the As—H bond points to strengthening of this bond in the course of the interaction between TMG and AsH_3 (in solution as well as in the matrix and in the gas phase). The position of the bands of arsine deformation vibrations in the mixture in the cryosolution differs slightly from that observed in the spectrum of the individual compound. One of the most important changes in the spectrum of TMG after it is mixed with arsine in a solution in Kr is the appearance of a new band at 511 cm^{-1}. We have assigned this band to symmetric bond vibrations of the GaC_3 fragment, which are usually forbidden in IR spectrum. The appearance of this band along with the above-mentioned small spectral shifts (which produced no radical change in the shape of the fundamental bands of the individual components) points to the formation of the donor-acceptor $Me_3Ga \cdot AsH_3$ complex at 130 K in the cryosolution. The existence of a similar complex was predicted by calculations for the gas phase and observed experimentally under the nonequilibrium conditions of the low-temperature matrix.

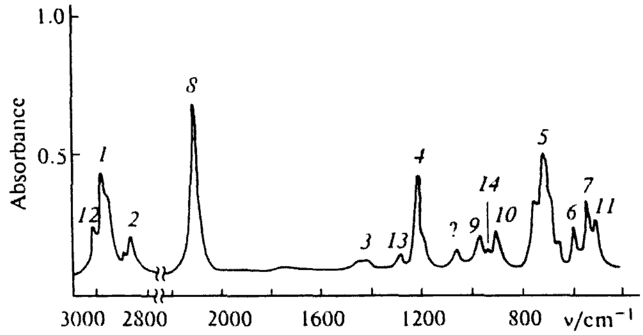

Fig. 1. IR spectrum of a solution of a mixture of TMG with AsH_3 in liquid Kr (T = 130 K, l = 100 mm): *1*, $\nu_{as}(CH_3)$; *2*, $\nu_s(CH_3)$; *3*, $\delta_{as}(CH_3)$; *4*, $\delta_s(CH_3)$; *5*, *6*, $r(CH_3)$; *7*, $\nu_{as}(GaC_3)$; *8*, $\nu_s(AsH_3)$, $\nu_{as}(AsH_3)$; *9*, $\delta_{as}(AsH_3)$; *10*, $\delta_s(AsH_3)$; *11*, $\nu_s(GaC_3)$; *12*, $\nu_s(CH_4)$; *13*, $\delta_{as}(CH_4)$; *14*, $\delta(C{=}C)$.

The weak bands at 3016 and 1304 cm^{-1} (see Fig. 1) are assigned to the stretching and deformation vibrations of the methane molecule formed in reaction (1), respectively. The weaker band in the region of 940 cm^{-1} can be assigned to the non-planar deformation vibrations of the olefin fragment (for instance, in the ethylene molecules); however, this assignment calls for further investigation. It should be emphasized that the above-listed

Table 2. The shift of the bands of the fundamental vibrations ($\Delta\nu$/cm^{-1}) in the IR spectra of a mixture of TMG with AsH_3 in different aggregate states relative to free molecules

Type of vibration	Gas (calculations)[7]	Ar-matrix[10]	Solution in Kr	Liquid phase
$\nu_{as}(GaC_3)$	+10	+7	+7	−5
$r_1(CH_3)$	+2	+1	+4	+5
$r_2(CH_3)$	+5	+15	+6	+6
$\nu_s(AsH_3)$	—	−38	−9	−26
$\nu_{as}(AsH_3)$	—	−46		
$\delta_s(AsH_3)$	+14	+17	+4	−3
$\delta_{as}(AsH_3)$	+7	+13	−2	0

Note. The plus sign means a low-frequency shift, the minus sign means a high-frequency shift.

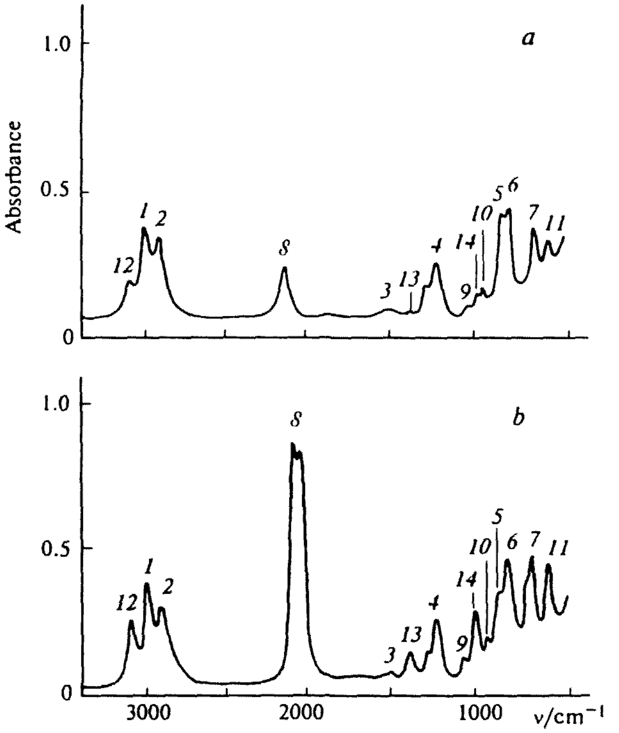

Fig. 2. IR spectrum of a mixture of liquid TMG and AsH_3 (T = 263 K, l = 16 μm) 40 min (*a*) and 20 h (*b*) after the start of observation. For the notation of the bands, see Fig. 1.

new bands are observed even when the cryosolution is prepared according to the second procedure (by dissolution of the crystalline phase of gaseous TMG and AsH_3 successively frozen onto the inner walls of the cuvette). This points to partial chemical interaction between the components already in the solid phase at low temperature. A similar phenomenon was observed in the course of preparation of the Ar matrix.[10] The spectrum of a mixture of TMG with AsH_3 in liquid Kr after 10 h showed no considerable changes in the intensity of the bands including the methane bands. The character of the time dependence of the spectrum of the mixture of TMG with AsH_3 in the liquid phase at a temperature close to room temperature was found to be more complicated.

IR spectra of a mixture of liquid TMG and AsH_3. To study the IR spectra of a mixture of liquid TMG with AsH_3, a cuvette exploited previously for recording spectra of pure TMG and AsH_3 in the frequency region of their fundamental vibrations was used. Under a pressure of 15 atm, gaseous arsine was fed into a cuvette prefilled with TMG and cooled to −20 °C. Then, the temperature was slowly increased to −10 °C. Under these conditions, AsH_3 was a liquid and in excess relative to TMG. However, because of the small thickness of the cuvette and the limited mutual solubility of the substances, arsine was fed into the cuvette gradually. That is why the spectrum of the mixture recorded, for instance, ~15 min after from the beginning of the introduction of AsH_3, is nearly the same as the spectrum of the starting TMG. The spectrum obtained 40 min after the beginning of the experiment at 260 K (Fig. 2, *a*) has much in common with the spectrum of the solution of TMG and AsH_3 in liquid Kr at 130 K (see Fig. 1). Thus, a band of stretching vibrations of AsH_3 appears at 2142 cm^{-1}. Its low-frequency shift far exceeds that for its solution in Kr, though it remains less than that in the matrix IR spectrum (see Table 2). The positions of the bands of the deformation vibrations of AsH_3 molecules are not different from those in the spectrum of individual arsine in the liquid phase. In contrast to the spectra obtained in the krypton solution as well as in the Ar matrix and in the gas phase, the $\nu_{as}(GaC_3)$ band in the liquid phase for uncertain reasons is shifted to a high-frequency region. A redistribution of the intensities of the components in favor of the low-frequency component is observed for the complex band of the rocking vibrations of methyl groups along with the general shift of the band to the long-wave region. A new band at 525 cm^{-1} corresponding to symmetric vibrations of $\nu_s(GaC_3)$ was observed in the spectrum of the liquid phase. The addition of arsine to the cuvette results in a substantial decrease in the intensity of the TMG bands as compared to the spectrum of the pure substance. All of the spectral peculiarities indicated can be evidence for the formation of the donor-acceptor complex $Me_3Ga \cdot AsH_3$ in the liquid phase.

Bands in the region of the stretching and deformation vibrations of the CH_4 molecule as well as the band at 940 cm^{-1} (as in the spectrum of the mixture of Me_3Ga with AsH_3 in the krypton solution) are clearly seen in Fig. 2, *a*. However, in contrast to the latter, the intensities of those bands increase substantially with time. Simultaneously, either a shift or a change in the contour of most of the bands assigned to TMG and AsH_3 molecules are observed. The spectrum of the liquid mixture obtained 20 h after the beginning of the experiment is shown in Fig. 2, *b*. The relatively high

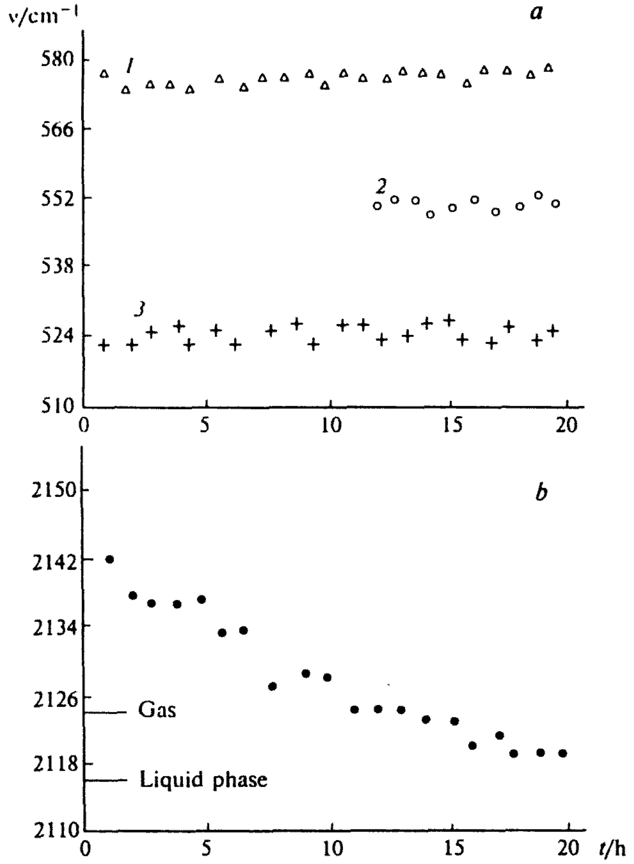

Fig. 3. Changes over time in the band frequencies in the IR spectra of a mixture of TMG with AsH_3 in the liquid phase: *a*, $\nu_{as}(GaC_3)$ (*1*), $\nu_{as}(GaC_3)$ after splitting (*2*), and $\nu_s(GaC_3)$ (*3*); *b*, $\nu_s(AsH_3)$, $\nu_{as}(AsH_3)$.

intensity of the $\nu_s(AsH_3)$ band (*cf.* Fig. 2, *a*) is explained by the constant supply of excess arsine to the cuvette while its rate of consumption in the course of the reaction is not high. The diagram in Fig. 3, *a* shows that the positions of the $\nu_{as}(GaC_3)$ and $\nu_s(GaC_3)$ bands remain nearly constant in the course of observation. However, 2.5 h after the beginning of the experiment the ν_{as} band splits into two components, which points to an essential change in the symmetry of the TMG molecule. Presumably, the low-frequency maximum of this band (in the region of 552 cm^{-1}) can be assigned to the products of reaction (1) while the high-frequency maximum (at 570 cm^{-1}) can be assigned to starting TMG molecules that are either free or in the AsH_3 complex. Substantial changes are observed for the band of stretching vibrations $\nu_{as}(AsH_3)$, which was found to be shifted to the low-frequency region by more than 20 cm^{-1} after 20 h and to be simultaneously split into two components (see Fig. 3, *b*). The low-frequency shift of the band points to a decrease in the energy of the As—H bond, which eventually favors the formation of methane. By the end of the observations, the $\nu_s(AsH_3)$ band is a superposition of bands of the stretching vibrations of the As—H bonds which might be present in both the product of reaction (1) and in arsine molecules.

Thus, a relatively fast reaction (1) with the formation of an intermediate donor-acceptor complex at its initial stage is observed when there is excess arsine in the liquid phase at 10 °C. After disassembling the cuvette, a yellow-brown amorphous substance was found. According to IR spectroscopy and electron-sonde microanalysis data, this product is $Me_{3-x}GaAsH_{3-x}$, which is in agreement with the literature data.[13]

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