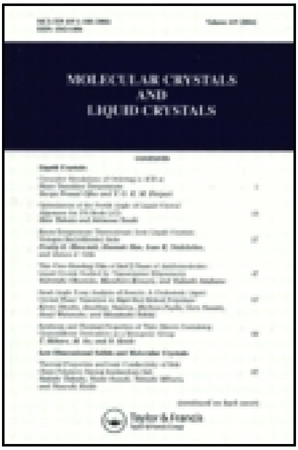

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Vladimir E. Bochenkov, Vyacheslav V. Zagorskii & Gleb B. Sergeev (2001): The Kinetics of Low Temperature Transformations of Samarium Complexes with 1,3,5-Tri-Tert-Butylbenzene in the Solid Phase, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 356:1, 299-303

To link to this article: http://dx.doi.org/10.1080/10587250108023709

Mol. Cryst. and Liq. Cryst., 2001, Vol. 356, pp. 299-303
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The Kinetics of Low Temperature Transformations of Samarium Complexes with 1,3,5-Tri-*Tert*-Butylbenzene in the Solid Phase

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Zerovalent samarium complexes with 1,3,5-tri-*tert*-butylbenzene were obtained by low temperature codeposition of metal and ligand vapours on the cold (77 K) surface under vacuum. The formation of two complexes was stated. The kinetics of thermal decomposition of complex with characteristic band at 967 cm^{-1} was investigated. It was shown that the retarded kinetics takes place. An effective activation energy was calculated from the initial rates. Its value is 8 kJ/mol, which is typical for diffusion controlled reaction.

Keywords: retarded kinetics; samarium lantanide complexes; solid phase reactions

INTRODUCTION

The technique of Metal Vapour Synthesis (MVS) allowed solving the problem of obtaining of zerovalent complexes of lanthanides [1]. Using bulky ligands, *e.g.* 1,3,5-tri-*tert*-butylbenzene (Bz*) for kinetic stabilisation of them lead to formation of complexes with a significant metal-arene bond enthalpy [2]. However, the metals with largest atoms and those with a high *f*→*d* promotion energy don't give stable complexes at convenient temperatures [3]. Specially developed cryostat allowed us to study instable at room temperature complexes by low temperature IR spectroscopy. The aim of this work was to investigate the kinetics of thermal decomposition of one of the less stable complexes – Sm-Bz* one.

EXPERIMENTAL DETAILS

An apparatus developed for preparation and investigation of film samples has been described elsewhere [4]. It consists of metal and ligand evaporators, copper cube, which can be cooled by liquid nitrogen and KBr window. The cryostat involves a thermocouple for layer temperature control and a mirror system which allows using this cryostat in an ordinary IR spectrometer for investigations of film samples by reflective method.

A typical experiment includes:

1) evacuation of the system to a vacuum of under 10^{-4} mbar
2) simultaneous evaporation of Sm (at 750-780 ^{0}C) and Bz* (at room temperature) and vapours co-condensation on the copper cube, cooled down to 77 K by liquid nitrogen.
3) rotating of the cube 180^0 so that the side with the film would face the KBr window
4) placing the cryostat in the IR spectrometer and
5) spectroscopic study in range 4000-400 cm^{-1}.

The cryostat for UV-visible spectroscopic investigations involves quartz cuvette and two optical windows instead of copper cube and KBr window.

Sm (99,9%) and Bz* (97%) were used without purification. The deposition of Bz* afforded a colourless glossy film, whereas the codeposition yields dark blue-green film. In codeposition of Sm with Bz* the deposition rates were adjusted to ensure an excess of ligand. The co-condensate is characterised by new peaks in the IR spectrum at 77 K. These peaks are a doublet at 967/973 cm^{-1} and a singlet at 1280 cm^{-1}.

Corresponding spectral investigations in UV-vis. region showed the appearance of new asymmetrical band with maximum at λ=690,4 nm, which is in agreement with published data (691 nm in pentane solution recorded at 180 K) [4]. We consider these new bands as the confirmation of Sm-Bz* π-complex formation.

DISCUSSION.

During the annealing process, there was no change in intensity of any absorption bands in both IR and UV-visible spectra of co-condensate to 160 K, at which temperature a decrease of intensity of the band at 967 cm^{-1} was detected. At 180 K equal intensity reduction was measured for both the 967 and 973 cm^{-1}. The intensity of all bands had decreased to zero by 200 K the bands have disappeared. We suppose the formation of two complexes that differ in metal:ligand ratio. The determination of the exact contents of these complexes requires additional investigations. The fragments of the spectra are presented on the figure 1.

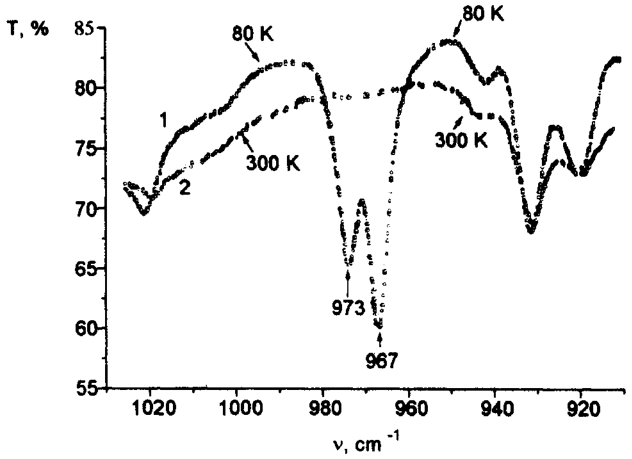

FIGURE 1. The IR-spectra fragments of Sm-Bz* co-condensate at 80 and 300 K.

Kinetic study was carried out for the most instable of these two complexes – of one with characteristic band art 967 cm^{-1}. The absence of changes in the sharps of peaks allowed observing the kinetics of decomplexation by peak intensity.

The film has been heated up to certain temperature followed by thermostatic control. At the same time we have been observed the change of peak intensity.

The kinetic curves thus obtained cannot be satisfactorily approximated by ordinary kinetic laws of the or second order, which is typical for processes in gas or liquid phase. Figure 2 presents the typical kinetic curve for Sm-Bz* complex decomposition at 200 K.

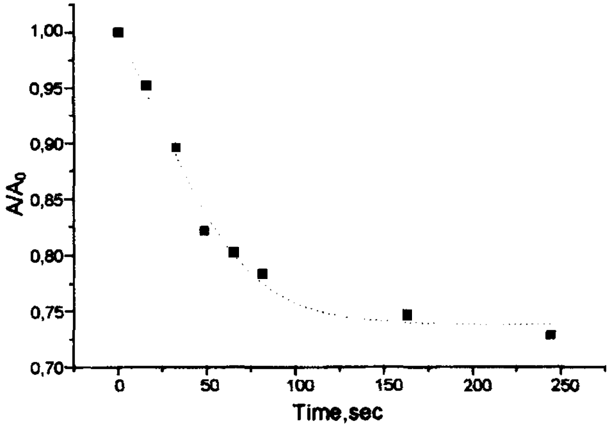

FIGURE 2. Typical kinetic curve for thermal decomposition of Sm-Bz* complex. T=200 K.

One can see that the retarded kinetics occurs for decomplexation. At constant temperature process slows down at the certain degree of conversion. This fact gives evidence that there is a distribution of rate constants (or, that is the same, the distribution of free activation energy). Such distribution can arise in the solid phase upon fast cooling. It is due to differences in a structure of environment.

Plotting of the dependencies in C/C_0 (or A/A_0) – ln(t) axes [5], where C is a *concentration*, A-*absorption*, *t-time*, *enable* well approximation by linear function, as it shown on the figure 3. This fact, as one can conclude from equation (1), indicates that the function of distribution of rate constants is rectangular with wide rate constant distribution.

$$\frac{1}{C_0}\frac{dC}{d\ln t} = -\varphi(G^*)\frac{dG^*}{d\ln t} = -RT\varphi(G^*) \qquad (1)$$

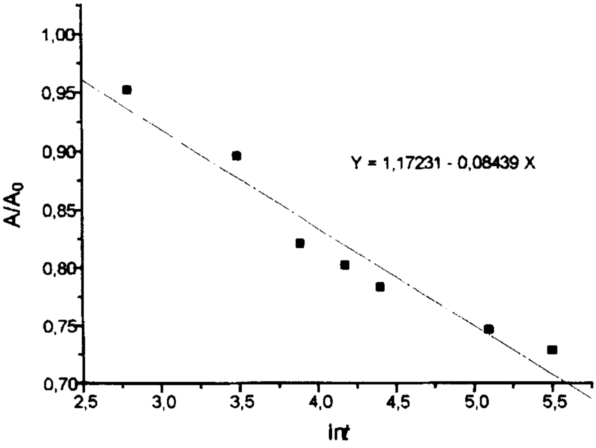

FIGURE 3. Linearization of the kinetic curve of Sm-Bz* complex decomposition. T=200 K.

Minimal and maximal values of rate constants were calculated using formula (2) for T=200 K.

$$\frac{C}{C_0} = \frac{(-\ln k_{\min}) - \ln t}{\ln k_{\max} - \ln k_{\min}} \tag{2}$$

The value of k_{min} is $9{,}3 \cdot 10^{-7}$ sec^{-1}, and $k_{max}=0{,}13$ sec^{-1}. The activation energy was estimated from the initial rates. Its value is 8±1 kJ/mol. This value is characteristic for the activation of the diffusion mobility required for transformation and decomposition of the complexes.

Acknowledgments
The work was partially supported by the Russian Foundation for Basic Research (grant 99-03-32206).

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