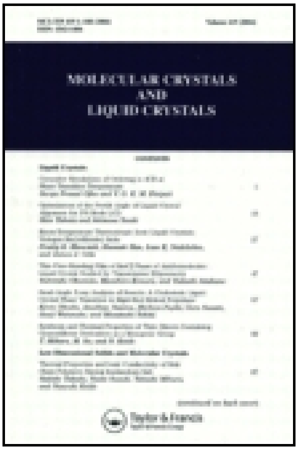

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Reactions in Solid Low Temperature Co-condensates

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We discuss the general peculiarities of low temperature co-condensates and influence of the sample preparation conditions on the chemical reactions in co-condensates. Hydrohalogenation of olefins and explosive reactions in solid co-condensates Mg-dichloroethan, acetylchlorid - diethylamin are condidered. The scheme of influence of mechanical stresses in growing films on the chemical reactions is suggested.

Keywords: low temperature co-condensate; mechanical stresses; reactions

The chemistry at low (77K) and superlow (4K) temperatures enlarges fundamental knowledge about the nature of elementary steps of chemical reactions and opens new possibilities of producing different chemical compounds with unusual properties. Most of the chemical substances are in the solid state at low temperatures while the initial compounds are usually in the gaseous or liquid state. During the transition to low temperatures, some specific features appear in the samples. The technique of sample preparation plays an important role in chemical reactions at low temperatures. Two methods are widely used nowadays[1,2]. The first one is based on the condensation of substances under an excess of inert gas. This is a well known method of matrix isolation. The second one is based on the co-condensation of the reagents in the conditions which exclude interaction in gas phase.

Different variations of these methods are given below:

- Condensation of particles of one type
- Condensation of particles with excess of inert substance
- Layer by layer condensation of two different types of particles
- Co-condensation of two different types of particles
- Co-condensation of more than 2 different types of particles

It's important to note that in all cases various types of initiation (light, X-ray, high frequency, heat) may be used to promote the interaction.

Matrix isolation is normally used for investigations of spectral properties of the individual active particles, such as atoms and free radicals.

Co-condesation of two different substances is usually the preferred method of preparative chemistry.

These two methods were previously considered as mutually exclusive. Any type of chemical interactions between the matrix and ligand was not suitable for matrix isolation. On the other hand the chemical interaction which proceeds at low temperatures excludes the stabilization and freezing of active substances. Many years ago we showed, that chemical reactions may occur at low temperatures and proceed with high rate, and very frequently explosively[2].

Previous studies of low temperature reactions of metal atoms with different organic and inorganic ligands have shown internal connection between matrix isolation and methods of preparative cryochemistry.

In this paper we will concentrate on the so called spontaneous reactions. These are the reactions which proceed at high rate without any external influence. These reactions utilize internal energy.

We have developed several types of cryostats for the studies of these reactions using ESR, UV and calorimetry techniques. Original cryostats were developed for the IR spectroscopic studies of co-condensates. The cryostats were designed for the IR study of the samples several micron thick, which practically eliminate temperature gradients. The main part of the cryostat is the polished copper block. Substances are condensed on one of the cold surfaces of the block and then the block is rotated to the opposite position and reflection IR spectra are recorded.

The cryostat for measuring mechanical stresses during the formation of low temperature co-condensate was constructed based on this setup. System based on a set of electric capacitors was used for measuring stresses. The movable cantilevered support of the capacitor was mounted in parallel to the copper block on the copper plate. The unmovable plate was located on the copper block. The system had several heaters and thermocouples. The displacement of the movable plate, caused by the mechanical stresses was measured through the change in capacity. Calibration process allowed us to determine the values of stresses in co-condensate films.

Lets consider the specifics of the chemical reactions in solid low temperature co-condensates. Homogenity and mixing should be ensured in such reactions. These conditions are fulfilled when the condensation is conducted in the regime of molecular beams. This regime excludes interaction in the gas phase and provides the formation of homogeneous "molecular" mixture on the cold surface.

One more peculiarity of the low temperature co-condensates occurs due to the difference of the reaction in "micro" and "macro" samples. Two examples demonstrate this statement:

a) Magnesium atoms and clusters react with sylilhalogens in the samples, obtained at 77K using the molecular beams is described by the scheme:

$$2(CH_3)_3SiCl + Mg \text{ -----> } (CH_3)_3Si\text{-}Si(CH_3)_3 + MgCl_2$$

The interaction of trimethylchlorosilane with magnesium was not found upon the conditions of preparative cryochemical synthesis[3].

b) No interaction was found for Silver and Acrylic acid in our molecular beams experiments. The polymerization of acrylic acid, induced by silver atoms and clusters proceeds in preparative cryostat at low temperatures.

Consequently the low temperature reactions are strongly dependent on the nature of reacting particles and methods of sample preparation.

The influence of experimental conditions on the chemical transformations can be divided into two groups. The processes during the condensation and the processes after condensation - took place postprocesses.

The vapors of the substances on the cold surface are in the quasiliquid state during condensation. The lifetime of the particles at these conditions depends on a number of factors: intensity of the particle beam and temperature of cold surface. Intensity of beam determines the number of collisions of the molecules with the surface and with each other. The temperature of the cold surface determines the relaxation processes. Together with the chemical nature of the reagents these factors determine the direction of processes leading or not leading to the reaction. The processes which occur during the real condensation are more complicated than the given scheme.

Complex processes take place as well after the condensation is completed, especially during the heating of the sample. The most important factors, influencing the chemical reaction on this stage are: (1) particle mobility, (2) different phase transitions and (3) conditions of heat exchange with surroundings, which depend on the rate of condensation and system heating after condensation.

The most difficult to understand features of the reactive low temperature co-condensates arise due to the inhomogenity and non-equilibricity of these systems. This leads to at least two consequences.

First, the particles in co-condensate are kinetically, thermodynamically and energetically inequivalent, and second: low temperature co-condensates possess accumulated energy[4].

It is necessary to mention the following types of accumulated energy in low temperature co-condensates:

- accumulated energy of nonequilibrium states, for example metastable and amorphous phases. Typical values 5-20 kJ/mol.
- Energy of donor-acceptor interaction. Typical values 4-20 kJ/mol.
- Heat effects of chemical reactions. Typical values 100 kJ/mol.
- Stabilization energy of active particles, such as atoms and radicals. Their recombination energy is in the order of chemical bond energy.
- Energy of mechanical stresses. Typical values are 1-10 kJ/mol.

It is possible to study different reactions in solid state at low temperatures. In this paper we discuss three reactions only. All these reactions have different mechanisms but one common feature - fast, practically explosive rates in the solid phase at low temperatures.

First example is a reaction of halogenation and hydrohalogenataion of olefines. This type of the reactions is studied in details[5,6]. It is shown that unstable donor-acceptor molecular complexes play crucial role in the mechanism of these reactions.

The formation of the complexes depends on the conditions of sample preparation. This is illustrated by solid co-condensates of hydrogen chloride and 2-methylbutene-2. The correlation between reactivity and the degree of complexation was found. The results are shown in the Table 1. The degree of complexation is controlled by IR spectroscopy and the choice of condensation regime.

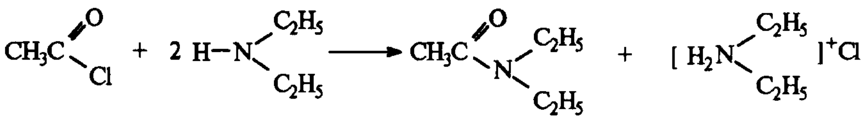
TABLE 1 The dependence of reaction rate in the system 2-methylbutene-2 - HCl on the degree of complexation (HCl:olefin=6:1, 80K)

Degree of complexation, %	Reaction rate during condensation %conversion/hour	Reaction rate during thermal treatment %conversion /hour
100	39	25
50	22	13
0	0	0

The main conclusion from the table is that absence of complexation leads to the absence of reaction.

The solid state hydrohalogenation is characterized by an interesting feature which cannot be otherwise observed in liquid or gas phase. The primary reaction product is not the corresponding alkylhalide, but its complex with hydrohalogen. Thus, it is possible to present the scheme of the reaction as a transformation of one molecular complex into another: Ol + 2HX ---> Ol·2HX ---> P·HX, where Ol is olefin, P is alkylhalide, X-chlorine or bromine atom. The formation of such complex causes the increase in thermal effects of the reaction by the value of complexation enthalpy usually by 3-4 kcal/mol. This can be considered as one of the reasons for high reactivity of the complexes of olefines and halogens or hydrohalogens in the solid phase.

The explosive reaction in co-condensates of acetylchloride and diethylamine has been discovered and studied in details for the first time[7]. Nucleofilic substitution in this system can be described by the following scheme



$$CH_3C(O)Cl + 2\ H{-}N(C_2H_5)_2 \longrightarrow CH_3C(O)N(C_2H_5)_2 + [H_2N(C_2H_5)_2]^{+}Cl$$

The co-condensate of acetylchloride and diethylamine is a colorless film. The explosion occurs at a certain critical thickness L_{cr}. The reaction yield after the explosion is nearly 100%. The dependence of the critical values of the explosion reaction on the reagents ratio is shown in the Fig.1.

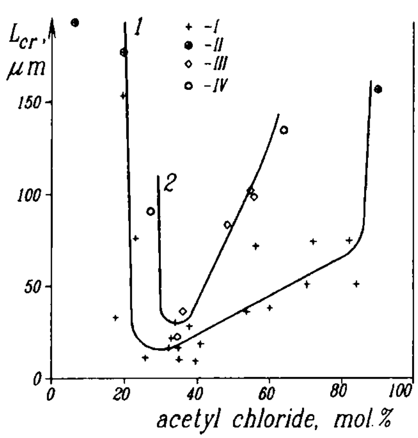


FIGURE 1 Curve 1- Temperature 80K, Curve 2 - 90 K

The critical thickness (Lcr) has a minimum. The minimum corresponds approximately to the stoichiometric composition 1/3 acetylchloride and 2/3 diethylamine. An increase in the temperature narrows the region of explosions.

The following new features should be mentioned for the reaction of acetylchloride and diethylamine:

- The initial sample is in an amorphous state. It is crystalline after explosion
- The reaction may affect only a part of the film. There is a defined interface between the reacted and inreacted parts of the sample.
- Process is heterogeneous. The self-propagating wave forms.
- The explosive process may repeat if the film formation is continued.
- Heat or mechanical impacts may initiate explosions

- Explosion may also occur during the storage of sample at isothermal conditions.

- The probability of explosion decreases with the increase of surface temperature and lowering the rate of reagents condensation.

Similar feature was found in the radical reaction of magnesium with 1,2-dichloroethane[8]. This reaction also proceeds explosively in low temperature co-condensates. When the thickness reaches some critical value L_{cr} reaction starts and the sample changes in color very rapidly. The dependence of the critical values of the reaction on metal-ligand ratio is shown in the Fig. 2:

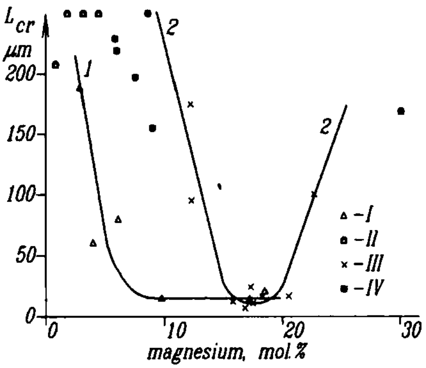


FIGURE 2 Cocondensation rate: $10^{16.8}$ molec./cm^2 sec. Curve 1- Temperature 80K, Curve 2- 90K

We can see that the increase in temperature decreases the field of critical values. Curve 2 also shows the optimum critical thickness for the explosion reaction. It was found that the following factors favor the explosion: decrease of temperature, increase of cocondensation rate, optimum reagents ratio. Fast reaction was observed if the content of magnesium in the composition was greater than 3 mol%. The critical value L_{cr} decreases when the content of magnesium increases. Atoms and small clusters were observed at low concentrations of metal in the cocondensate film. When the concentration of metal increases the ratio of large clusters increases as well. It is possible to form a percolate cluster at a certain metal concentration.

It has been shown that the accumulation of mechanical energy in growing co-condensate leads to plastic deformation in the sample. Destructions were developed through crack formation in such films. The plastic deformation probably takes place in the region 10-25μm. The thickness near 25 μm probably correlates with reaching tensile strength and with crack formation and film destruction. This process initiates explosion reactions in the magnesium-1,2-dichloroethane system. The most adequate model for the interaction in reactive co-condensates is a model of destruction. Crack formation in the sample most likely initiates the explosion.

Tenzometric measurements in the number of studied systems fits well in this assumption. Fig. 3 shows typical dependence of mechanical stress σ (curve 2) on thickness.

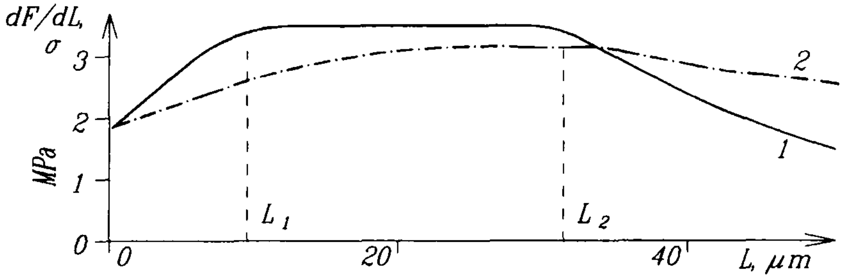


FIGURE 3 Dependence of mechanical stress on thickness.

Curve 1 demonstrates the dependence of the derivative of the force which influence the co-condensate film (dF/dL) from the thickness of the sample. It has the meaning of mechanical stress in the layer of condensate.

One can divide both curves into three sections. They are: increase during the initial stages of film formation, weak dependence of stresses in the middle part and fast decrease in the thick film.

Consequently mechanical stress may be used as an indicator of structure state of the sample. The dependence of the reaction rate on the sample thickness is called dimensional effect and is explained through the changes of stress. The changes in structure are connected with the possibility of initial critical effects. The net of cracks is visible in the film when $L >> L_2$. Therefore the L_2 value correlates with the crack formation.

Fig. 4 shows the correlation between values L_2 and L_{cr} for system acetylchloride - diethylamine.

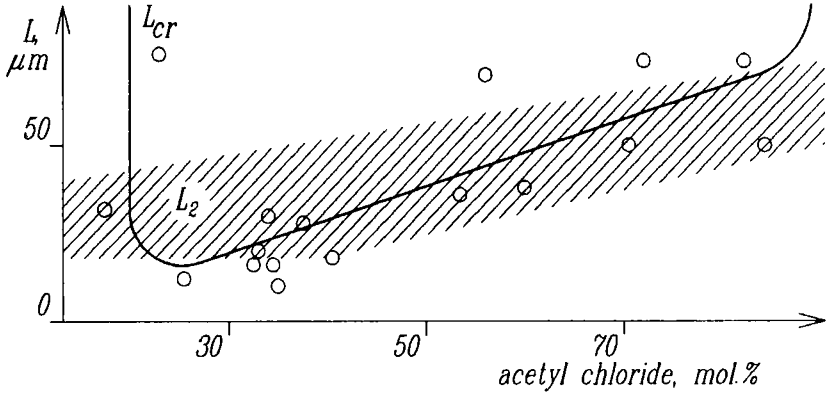


FIGURE 4 co-condensation rate: 10^{17} cm^2s^{-1}. Temperature 80K. Y axis - film thickness, X-axis mole% of acetylchloride.

Circles correspond to experimental values of L_{cr}. Values L_2 are in the shaded region. There is a good agreement between L_{cr} values, and L_2 values corresponding to the beginning of crack formation.

The same phenomena occurs in co-condensates of magnesium with 1,2-dichloroethane and cyclopentadien with $TiCl_4$.

We have compared the L_{cr} values for the samples containing 80-90% of organic component with values of L_2 for pure organic compound. Table 2 shows the correlation of L_{cr} (explosion) and L_2 (crack formation).

TABLE 2 The comparison of values L_{cr} and L_2

System/compound	ratio	L_2	L_{cr}	Co-cond. rate $cm^{-2}s^{-1}$	Temp.
Mg-dichloroethane	10:90		10-20μm	10^{16}-10^{17}	80K
dichloroethane		20-25μm			80K
Mg-dichloroethane	10:90		5-25μm		90K
dichloroethane		20-30μm			90K
$TiCl_4$-cyclopentadien	6:94		4.5μm	10^{17}	90K
cyclopentadien		2.5μm			80K

It is important to point out once again the importance of isothermal evolution of co-condensates structure in various physical-chemical processes. Solid state co-condensates at low temperatures are dynamic non-equilibrium systems with excessive energy.

The generation and accumulation of mechanical energy at the same time can lead to plastic deformation and molecular mobility and to the crack formation. Both of these processes as shown in Fig. 5 can open a way for explosive reaction and for explosive crystallization or in general to the reaction and crystallization.

The balance of these pathways is a multifactor phenomenon. Our models are based on the notion, that weak interactions give rise to the significant changes.

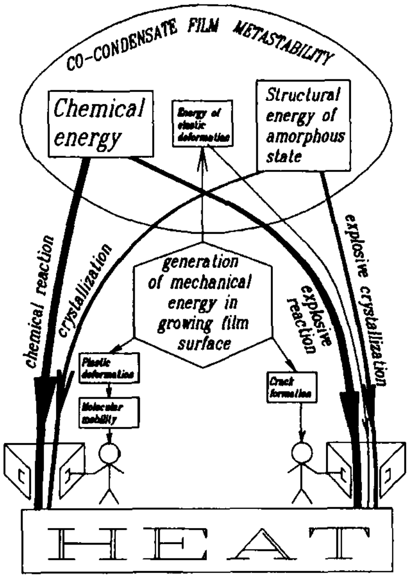


FIGURE 5 Mechanical energy generation and accompanying processes in growing solid co-condensate film.

Understanding of the reaction specifics in low temperature co-condensates allows us to solve a fundamental problem of determining the reaction mechanism by identifying the intermediate particles and eventually to synthesize new and unusual materials.

Acknowledgments

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