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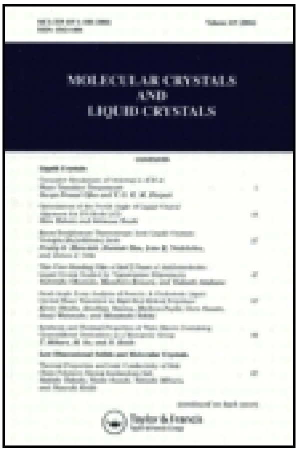

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Mechanical Stresses and Past Reactions in Organic Solid States Formed by Co-Deposition Op Reagent Vapours

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MECHANICAL STRESSES AND FAST REACTIONS IN ORGANIC SOLID STATES FORMED BY CO-DEPOSITION OF REAGENT VAPOURS.

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Abstract Fast critical processes are investigated in co-condensates of chemically active substances formed at low temperatures. The connection of mechanical state of co-condensate films and parameters of critical processes is discussed. An approach to understanding critical effects is proposed.

Keywords: mechanical stress, co-condensate films, solid-state reactions

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Chemical reactions in solid samples formed by co-deposition of chemically active components on surfaces at low temperatures have been investigated for more than 35 years.[1,2] One of the main interests in this field is to find new ways to synthesize known and unknown new compounds on the basis of unusual phase state and chemical activity of reagents in such mixtures.

In a number of such systems, critical effects were found. During the co-condensation of vapours of reagents on cold surfaces, fast processes were observed in prepared films at certain critical thicknesses. These processes had the appearance of an explosion on all of the film or just on part of the film. This effect is of interest for different reasons. One of them concerns new possibilities to influence the activities of reagents, and the direction and degree of interaction. Another one is to understand the origins of fast processes to avoid them when it is necessary.

Here we discuss examples of four systems that are chemically different: cyclopentadiene - $TiCl_4$, 1,2-dichloroethane - magnesium, acetyl chloride - diethylamine, benzoyl chloride - piperazine.[3-7]

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The vapours of reagents were deposited on a copper plate in a vacuum not less than 0.1 Pa. The rate of deposition varied from $5x10^{14}$ to $7x10^{16}cm^{-2}s^{-1}$. The temperature of the plate during co-condensation was between 77 K and 120 K. IR spectra were registered during co-deposition or immediately after preparing the sample. Mechanical stresses were determined by measuring the positional deviation of the substrate on a copper plate attached to a copper block at one end.

Critical processes in co-condensates are accompanied by a number of signs:

- rapid increase of the temperature of the film;
- change of mechanical states of the film;
- chemical reaction and crystallization;
- changes of outward appearance of film in colour and transparency.

Similar effects can be observed in the samples when their thickness is slightly less than the critical one. Fast processes may be realized by mechanical excitement, and in particular, by striking with a needle or by fast heating of the sample. Sometimes fast processes occur spontaneously even when the film is kept at a constant temperature. The time required before initiation varied from several seconds to several hours.

Specific signs of critical effects mentioned above were found in all investigated systems.

A number of factors influence the critical effects of investigated samples. These include temperature of the cold surface, the rate of vapour co-deposition and the ratio of reagents.

One of the methods for characterizing the critical effects involved measurement of the critical thickness when explosive process was observed.

Critical thicknesses of the films of cyclopentadiene - $TiCl_4$ and benzoyl chloride - piperazine were as a rule approximately several microns, but the critical thicknesses of films of 1,2-dichloroethane - magnesium and acetyl chloride - diethylamine were tens or even hundreds of microns.

It was discovered that in the investigated systems critical thicknesses depended upon the conditions of formation in an analogous manner. The ratio of components had a decisive effect on the critical thickness. For these samples the critical thickness was increased when the temperature of the cold surface was increased, and when the rate of vapour co-deposition was decreased.

It must be emphasized that the explosive effects described above were found in systems of very different chemical nature. In the system cyclopentadiene - $TiCl_4$ chemical reactivity is realized as a chain process of polymer formation. In the system 1,2-dichloroethane - magnesium, metalloorganic compounds are formed via radical and ion-radical interaction. In the chemical pairs acetyl chloride - diethylamine and benzoyl chloride - piperazine, the reaction of nucleophilic substitution occurs.

One of the most important conclusions is that in spite of the dramatic differences of the investigated systems in terms of the chemical nature of the components and the types of chemical interactions, the critical behavior of the films displayed many common features.

The attempts to consider these critical effects in terms of typical thermal or chain chemical explosions[2] were not successful.[4,6] In our point of view, more appropriate models of critical processes may be created by considering the mechanical states of co-condensate films.[4]

It is necessary to note that for all of the present systems mechanical stresses were found. These stresses arose in samples in the process of their formation.

Furthermore, there were clear correlations between the conditions used to form the films, the mechanical stresses and the critical thicknesses.

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In our opinion a plausible model of critical effects may be based on the ideas of theory of destroying of solid state. Destructive processes initiated by mechanical stresses may depend upon the developing structure of the growing film. For certain optimal relationships between mechanical disturbance, solidity of the sample, its structure and physicochemical activity, fast processes may begin and spread around the sample. In this case exothermic processes, for example chemical reactions,cause the destructive effects, which in their turn accelerate exothermic processes.

It is now clear that the generation of fast reactions in the samples during their formation has several consequences. One of them is the full reaction of reagents in these cases. In all investigated systems, the degree of conversion was nearly 100 %.

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