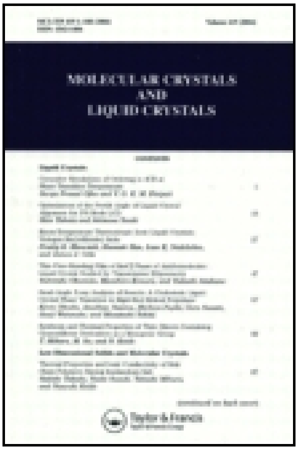


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Size Effects in Reactions of Solid Organic Compounds with Metal Particles

Gleb B. Sergeev [a] & Mikhail Yu. Efremov [a]
[a] Moscow State University, Chemistry Department, 119899, Moscow, Russia

Version of record first published: 24 Sep 2006.

To cite this article: Gleb B. Sergeev & Mikhail Yu. Efremov (1996): Size Effects in Reactions of Solid Organic Compounds with Metal Particles, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 278:1, 17-25

To link to this article: http://dx.doi.org/10.1080/10587259608033653

*Mol. Cryst. Liq. Cryst.*, 1996, Vol. 278, pp. 17–25
Reprints available directly from the publisher
Photocopying permitted by license only

# SIZE EFFECTS IN REACTIONS OF SOLID ORGANIC COMPOUNDS WITH METAL PARTICLES

GLEB B. SERGEEV, MIKHAIL YU. EFREMOV
Moscow State University, Chemistry Department, 119899, Moscow,
Russia

Abstract The influence size of different metal particles with solid organic compounds at low temperature have been investigated. It was shown that reactions depends on the thickness of films and generation of mechanical energy in growing film surface.

The chemistry under low (77K) and superlow (4K) temperature enlarge fundamental knowledge about the nature of elementary acts and opens the new possibilities of producing different chemical compounds. Most of the chemical substances are in a solid state at low temperatures. The initial compounds are usually in a gaseous or liquid state. During the preparation of samples by freezing of the reaction compounds, some specific features appear. This permits us to consider the low temperature reactions as a special branch of the solid state organic chemistry.[1]

In our paper we will discuss size effects in reactions of solid organic compounds with nanosize metal particles. The samples are prepared by vapour codeposition on a cold surface. Nanoscale particles are not studied well yet. It's connected with high reactivity of such particles. Atoms and small clusters of metals aggregate and react with other particles practically without activation energy.

The analysis of the data lets us summarize some peculiarities of nanoscale particles.[2]

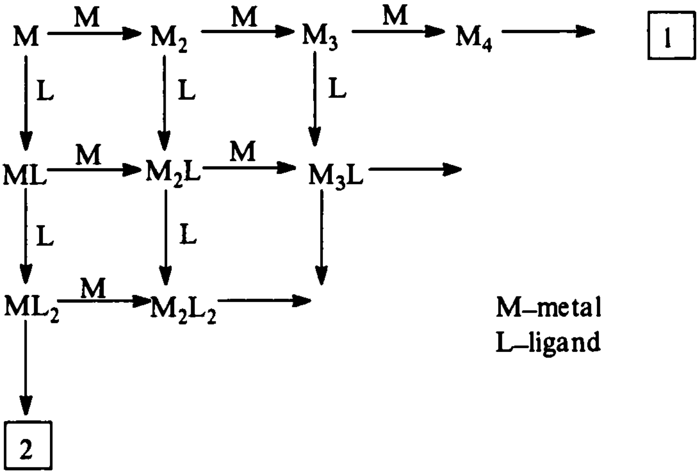
Nanosize metal clusters are energy-saturated or energy containing particles with redundant energy. The redundant energy is defined as energy of non-compensated atomic bonds of major part of atoms at surface and near surface layers, contribution of metastable states, latent heat of phase transitions, energy of defects.

There are problems when we apply classic thermodynamics and statistical physics for description of particles less then 1 nm. The application of thermodynamics is made difficult by the fundamental problem of determination of border line size between the different phases, and also the demarcation line between homogeneous and heterogeneous states.

Energy capacity could be increased by the extension of dispersion in a system. Traditional way is to increase temperature. So, the size of particles could be considered as active thermodynamic value instead of temperature.

To our opinion the all mentioned properties of nanoclusters should be taken into account when we analyze reactions of metal particles with different ligands.

The competition processes take place in system metal-ligand at low temperatures. These processes are described by the following Scheme (1).



(1)

First way is aggregation of metal particles. Second way is formation of metalloragnic compounds. Competition between two ways depends on many different factors. Most important are: reagents ratio, condensation rate, support temperature, chemical properties of particles.

At present we may formulate a problem "dependence of chemical activity on size of particles". To solve this problem it's necessary to obtain particles with definite size to stabilize them and to introduce them into chemical reactions. It's possible to use co-condensation of metal and ligand vapours at low temperatures.

We used glass vacuum cryostat for low temperature IR spectroscopy. The main part of this reactor is polished copper block cooled by liquid nitrogen. The vapours of metal and reactive ligands were codeposited onto copper surface. The block with matrix was rotated on $180^{\circ}$ after deposition and IR spectrum was measured. The temperature of the surface was monitored by a copper - constantan thermocouple.

Low temperature codeposites are the specific solid state samples. Low temperature co-condensates are extremely nonequilibrium systems. They are the systems with energetic, kinetic or thermodynamic inequivalence of the stabilized particles.

It is possible to distinguish some forms of accumulated energy:

redundant energy of nonequilibrium state (metastable and amorphous phases) with values about 5-20 kJ/mol;

energy of mechanical stresses with value about 1 kJ/mol;

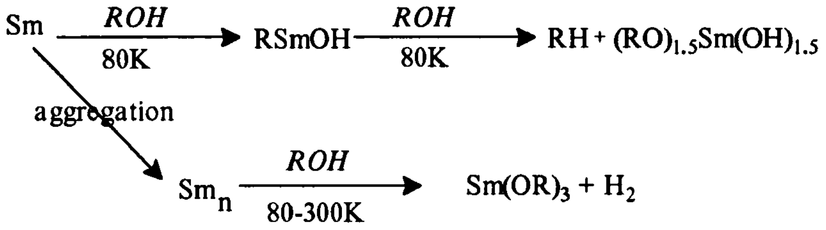
thermal effect of chemical reactions with values about 100 kJ/mol;

energy of stabilized active particles (atoms, radicals) - recombination energy app. equal to energy of chemical bond.

Our investigations allowed us to make a suggestion that stresses generation during the cocondensation and formation of the sample is a very important property. The measurements of stresses give additional information about structural processes. We measured the mechanical stresses in a special cryostat with electric capacitor.

It was very important to compare at first the reactions of metal clusters and bulk at low and room temperatures. We compared reactions of series of metals with acetone in cocondensates and bulk. There are different directions of reaction. The result depends on the nature of metal and particle size. For example magnesium clusters give enolytes. Bulk magnesium gives pinaconate. It's interesting that rare earth elements don't react with acetone at room temperature. Cocondensates of rare earth elements give pinaconates. The decrease of cluster size enforces their activity and increases the yield of secondary products.[3]

New reaction was found when we were studying the interaction of sodium, magnesium and samarium particles with aliphatic alcohols. If ratio metal:alcohol was large (1:5, 1:10) we obtain alcoholates. Decreasing of ratio to 1:500 or even less leads to the alcohol reduction to hydrocarbons. For example, methyl alcohol produces methane. The interaction with samarium was studied most carefully. Scheme (2) of this reaction is shown below.[4]



(2)

Several special experiments showed that hydrocarbons are obtained only at 80K. When the cocondensate is heated the formation of alcoholates occurs. The yield of hydrocarbon depends on alcohol-metal ratio or in other words on the cluster size. The kinetic analysis allows us to compare the experimental data with theoretical curves of hydrocarbon yield and makes possible the determination of ratio for effective rate constants, two competitive processes.

It was shown that interaction of samarium atom with other atom is more efficient then reaction with alcohol molecule. We observed also the alteration for molecule of alcohol with odd and even number of carbon atoms.[4]

During the investigation of interaction of samarium particles with hydrocarbons we found another interesting fact. We prepared two types of cocondensates: samarium -n-hexane and samarium -cyclohexane. Both systems were found to have catalytic activity in hydrogenation of olefines.

The system Sm-$C_6H_{14}$ was active in reaction with hexene and inactive with cyclohexene. System Sm-$C_6H_{12}$ on opposite was active with cyclohexene and inactive with hexene. It is possible to draw the conclusion that conditions of preparation of cocondensates are also important, along with the size of particles for the interaction.

The size of particles in our investigation was regulated by the reagents ratio. Direct measurements of particle size in reactive system practically impossible.

We used polymerization for estimation of particle size.[5] P-xylylene was the monomer we used to obtain poly-p-xylylene films at low temperatures. The formation of polymer restricts aggregation of metal particles.

The size of particles lead, zinc, cadmium, silver and some other metals was measured by Transmission Electron Microscopy. Metal particles, isolated in poly-p-xylylene matrix have globular form. Diameter of particles is almost independent upon weight percent of metal. Average values are 3-8 nm. IR spectroscopic data showed that there is no interaction with polymer matrix at 80K.

Magnesium particles readily react in solid state with different organic substances at low temperatures. We've studied carefully such reactions with alkyl- and aryl- halogens.[4]

Magnesium atom realizes a radical path. As a result we have great yield for recombination products (Wurtz reaction). Magnesium clusters give ion-radicals and form Grignard reagents. Both the particle size and bond strength are extremely important. Iodo- and bromo- alkanes (weak bonds) give radicals and recombination products. Chloro- and fluoro- compounds (strong bonds) give ion-radicals and Grignard reagents.

We obtained also in solid state at low temperatures compounds, similar to Grignard reagents with silicon. It's possible to describe the interaction with magnesium particles by Scheme (3):

$$2(CH_3)_3SiCl + Mg \Rightarrow (CH_3)_3\text{-}Si\text{-}Si\text{-}(CH_3)_3 + MgCl_2 \qquad (3)$$

Possible mechanism

$$R_3SiCl + Mg \Rightarrow [R_3SiCl^{-}Mg^{+}] \Rightarrow R_3SiMgCl$$

$$R_3SiMgCl + R_3SiCl \Rightarrow R_3Si\text{-}SiR_3 + MgCl_2$$

The first step is formation of ion-radical pair and silil-magnesium halogenide which interact then with initial reagent.

More size effects were found in the reactions of magnesium with alkyl and aryl halogens. There is a dependence of reaction rate, often explosions, on the film thickness. Process may be realized by mechanical excitation, particularly by striking with a needle.[6]

More recently we've investigated the system magnesium - 1,2-dichloroethane in details.[7] Cocondensates of substances have black colour. When the thickness reaches some critical value $L_{cr}$ reaction starts and sample becomes clear very quickly. Dependence of critical values of explosion reaction on metal-ligand ratio is presented in Figure 1.

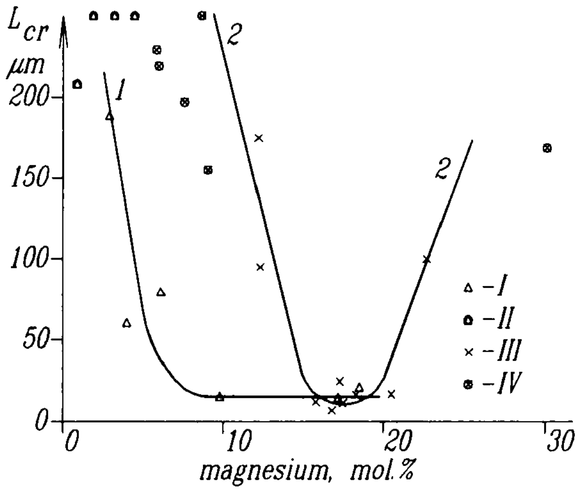


FIGURE 1 Dependence of critical values of explosion reaction on metal-ligand ratio. Cocondensation rate: $10^{16.8}$ $cm^{-2}s^{-1}$. Curve 1 - temperature 80K, Curve 2 - 90K.

We can see that increase of temperature decreases the field of critical values. Explosions were not observed at 0.1-20 mol% of magnesium at 110K. Curve 2 also shows the optimum behaviour of critical thickness value for explosion reaction on reagents ratio. It was found that the following factors favour the explosion reaction: decrease of temperature, increase of cocondensation rate, optimum of chemical composition. reagents ratio. In solid state at low temperature fast reaction is observed if content of magnesium in the composition was greater than 3 mol%. The critical value $L_{cr}$ decreases when the content of magnesium increases. Table I illustrates this fact:

TABLE I The critical value $L_{cr}$ in dependence on content of magnesium

| Content of Mg (mol%) | 10-20 | 20-25 | 25-30 | 30-50 |
|---|---|---|---|---|
| Mean critical thickness (μm) | 9.5 | 3.6 | 2.7 | 1.5 |

Cocondensation rate $10^{16}$ $cm^{-2}s^{-1}$. Support temperature 80K.

At low concentrations of metal in the cocondensate film we have atoms and small clusters. When the concentration of metal increases the ratio of large clusters increases too. For definite metal concentration it is possible to form percolate cluster. We observed the significant electric conductivity for the films with metal contents about 10 mol% at 80K.

So, we can assume that the specific chemical energy of co-condensate depends on the contents of metal, selforganized processes and interaction of particles. This is a subject of investigations in future.

We showed that accumulation of mechanical energy in growing co-condensate leads to plastic deformation in sample. In such films destruction are developed through crack formation.

The evaluation of film stressed state is presented in Figure 2.

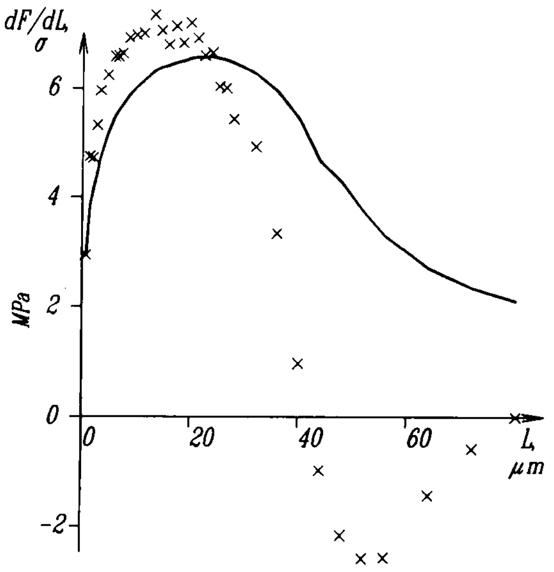


FIGURE 2 Typical dependence of mechanical stresses σ and dF/dL value vs L. Film of 1,2-dichloroethane. F - force of support action on the film. L - thickness of condensate. Conditions: Support temperature - 80K. Condensation rate $10^{16.7}$ $cm^{-2}s^{-1}$.

The dF/dL value means the value of stresses in freshly condensed layers of the film if the stresses in the volume of film are considered constant.

You can see that the plastic deformation probably takes place in the region of thickness 10-25 µm. The thickness near 25 µm probably correlate with reaching tensile strength and with crack formation and film destruction. This process initiates explosion reactions in the system magnesium-1,2-dichloroethane.

Recently we've found that critical phenomenon in low temperature solid state co-condensates is not connected only with reactions of metal particles. Analogous dependencies were found in reactions of two solid organic compounds: acetyl chloride and diethylamine.[8] The reaction has the same peculiarity as the interaction between magnesium with dichloroethane. The initial sample is in the glass state. After the reaction the sample is in crystalline state. The acceleration of reaction in this case is connected with increase of molecular mobility and transformation of growing film to the phase of plastic deformation.

General scheme of some processes connected with mechanical energy accumulation on surface of condensed film is presented in Figure 3.

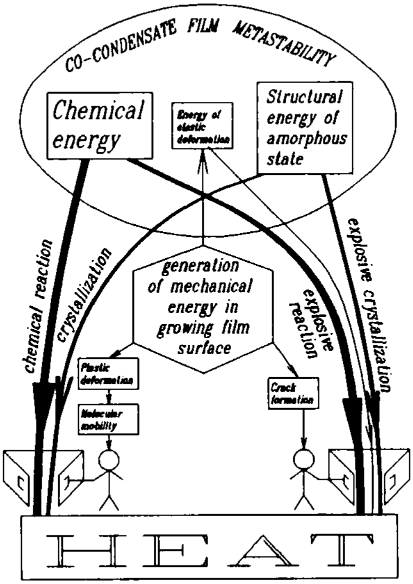


FIGURE 3 Mechanical energy generation and accompanying processes in growing solid co-condensate film.

Solid state co-condensates at low temperatures is a dynamic nonequilibrium system with redundant energy. The generation and accumulation of mechanical energy at the same time can lead to plastic deformation and molecular mobility and to crack formation. Both of these processes can open way for explosive reaction and explosive crystallization or in general to the reaction and crystallization.

The correlation of these pathways are multifactors phenomena. All our models are based on the idea that week interactions give rise to strong effects. The investigations at low temperatures in solid state help display these phenomena.

This work was partially supported by The Russian Fund of Fundamental Investigations (Grant No 94-0309987) and by Grant No MLS 300 from International Science Foundation and Russian Government.

## REFERENCES

1. G. B. Sergeev, Mol. Cryst. Liq. Cryst., 211, 439 (1992).
2. G. B. Sergeev, V. N. Solov'ev, in Modern Trends in Low Temperature Chemistry, (Moscow University Publishing House, Moscow, 1994), pp. 148-155.
3. V. V. Zagorskii, S. E. Kondakov, A. M. Kosolapov, V. N. Solov'ev, G. B. Sergeev, Metalloorganicheskaya Khimiya, 5, 533 (1992).
4. V. V. Zagorskii, G. B. Sergeev, Mol. Cryst. Liq. Cryst., 191, 289 (1990).
5. G. B. Sergeev, V. V. Zagorskii, M. A. Petrukhina, J. Mater. Chem., 5, 31 (1995).
6. G. B. Sergeev, V. V. Zagorskii, A. M. Kosolapov, Khimicheskaya Fizika, 1, 1719 (1982).
7. M. Yu. Efremov, V. S. Komarov, G. B. Sergeev, in Khimiya nizkikh temperatur i kriokhimicheskaya tekhnologiya, (Izdatel'stvo Moskovskogo Universiteta, Moscow, 1990), pp. 114-120.
8. M. Yu. Efremov, V. S. Komarov, G. B. Sergeev, Vestnik Moskovskogo Universiteta, Seriya 2, Khimiya, 33, 344 (1992).