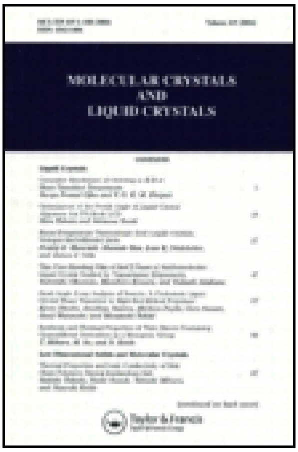

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The Specific Features of Low Temperature Organic Reactions in Differently Organized Media

Gleb B. Sergeev [a]

[a] Chemical Department, Moscow State University, Moscow, 119899, USSR

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THE SPECIFIC FEATURES OF LOW TEMPERATURE ORGANIC REACTIONS IN DIFFERENTLY ORGANIZED MEDIA.

GLEB B. SERGEEV.
Chemical Department, Moscow State University,
Moscow 119899, USSR.

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Abstract. It was shown that for the interpretation of results in the samples made by co-condensation of reagents from a gaseous phase on a cold surface, the molecular organization of system, its nonequilibricity and energetic, kinetic, thermodynamic inequivalence should be taken into account.

Keywords: low temperature reactions, co-condensation, energetic inequivalence, thermodynamic inequivalence

The chemistry under low (77K) and superlow (4K) temperatures enlarges our 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. A theoretical approach of chemical transformations (elementary act) at low temperatures is discussed in an earlier paper[1]. In our paper we undertake to discuss those features which are important for performing selective chemical syntheses.

The initial preparation techniques influence the process of carrying out chemical reactions at low temperatures. The differences between systems are especially distinct if the samples are prepared by vapor co-condensation on a cold surface. Researchers in the field of matrix isolation use this technique widely[2]. The usage of the same technique gives us a way of performing a number of new chemical reactions and of specifying the mechanism of some processes. Information concerning this research is available in a review[3] and references therein.

We believe it is necessary to regard the following features in the analysis of chemical transformations in low temperature co-condensates of two or more substances:

- mechanically tensed nonequilibrium states with exciting energy;
- molecularly organized or disordered systems at low temperatures;
- systems with energetic, kinetic or thermodynamic inequivalence;
- systems with high mobility of reagents.

The chemical transformations at low temperatures are carried out in crystals, polymers, amorphous and glass states, mesogenic crystals, frozen solutions, clathrates, molecular complexes as well as metal clusters with different organic and inorganic ligands[3].

The degree and kind of molecular organization certainly influences chemical processes. In our opinion these influences are most obvious in processes with molecular complexes in olefin halogenation and hydrohalogenation[4]. The rate of co-condensation of reagents defines the very possibility of complex production, their composition, and the presence or absence of reactions within the system. The complexes' transformation into the final product in the solid state at low temperatures is performed by a mechanism, that usually involves a six-membered intermediate state. We designate this as the "molecular mechanism"[4].

The processes with molecular complexes give a good example of the reactions in a solid state. They have kinetic, energetic and thermodynamic inequivalence. It is possible to create two types of complexes Cl_2-C_2H_4

and $Cl_2 \cdot 2C_2H_4$ in a system ethylene - chlorine. After the 1:1 complex is formed, an intermediate (gauche - 1,2 dichloroethane) is transformed slowly into the final product (staggered 1,2 dichloroethane). The addition of an inert solvent to the system influences the kinetics. During the transformation of the complex to the final product, first order, dispersive and step-wise kinetics were observed in different instances. We think that this is the result of the energetic inequivalence of sites[5].

In a solid state at low temperatures, hydrohalogens, halogens, interhalogens maybe oriented differently toward the same molecule. For example the ClF molecule makes different complexes with π and σ electron donors[6]. It has been shown that with bromobenzene, it yields two isomeric complexes. One has the ClF molecule coordinated to the bromine atom, while the other has it complexed with π electrons. We find it possible in this situation to talk about about thermodynamic inequivalencies. If a complex undergoes a chemical transformation, its reaction site configuration can be very important. For example the hydrogen chloride addition reaction in a styrene ring does not reveal the hydrohalogenation reaction of double bond. Styrene is not hydrochlorinated at low temperatures even though it has a low ionization potential compared with other olefins[4].

It should be emphasized that the creation of structures like donor-acceptor complexes plays the main role in the reactions of two components. The complex may be considered as a "storage site" where diffusion and energetic difficulties are significantly reduced.[7] The intermolecular interactions are decisive for reactions in donor-acceptor systems. For an interpretation of the reactions in a solid state at low temperatures, it is important to know the phase diagram for the system. It is a matter of common knowledge that in formally solid phases that are below the solvent freezing point, molecular mobility for one of the components in a two substance system can remain generally the same as in a liquid phase. The rate of freezing, and connected with this, the state of equilibrium or nonequilibrium, can influence this mobility decisively.

The reactions in solid phases at low temperatures are characterized by strong dependence on the concentration of reagents and their ratio. Changes in concentration lead to changes in the melting point, vitrification point and molecular mobility of the mixture. The influence of the initial ratio of reagents on the yield of final products is typical of reactions with molecular complexes[4], of clathrate production and diene synthesis and of systems forming with formation of intermediate metastable states like porous crystals[8]. The differences in hydrocarbon chlorinations in solid amorphous mixtures for systems enriched by hydrocarbon or chlorine is shown in a previous article[9].

Thus, the extent of system ordering and its non-equilibrium behavior constitutes the bulk of our research. Besides, it should be taken into account that well organized media like crystals are usually delocalized, while for disordered systems like glasses localization is common. During their production the low temperature co-condensates undergo different stages of molecular organizations and that make them inequivalent in kinetic, energetic and thermodynamic properties. In some co-condensates, there exists the possibilty of high molecular mobility, high rate chemical reactions, and even explosions at low temperature.

One obtains samples in a glass nonequilibrium state as a result of the cocondensation of initial compounds on cold surface. In these samples, mechanical strains generated in the film during it condensation can influence the reaction dramatically. Critical phenomena, formed in low temperature co-condensates and their connection to the mechanical strains are discussed in detail in a previous paper[10].

The reactions in low temperature co-condensates with metal atoms and their clusters permit us to raise the question of influence of particle size and shape on chemical reactivity. It has been shown that samarium atoms and clusters undergo different reactions with alcohols[11]. The most distinct difference in reactivity of metal atoms occurs for clusters containing up to ten atoms.

In general, for the reactions with metal atoms and clusters and for the reactions of organic compounds it is necessary to optimize the reaction particles' degrees of freedom. Thus, to carry out different reactions in a solid state at low temperature one can vary the co-condensaton rate, reagent ratios, temperature, material used in the cold surface, the rate of medium relaxation and diffusion rate of reagents.

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