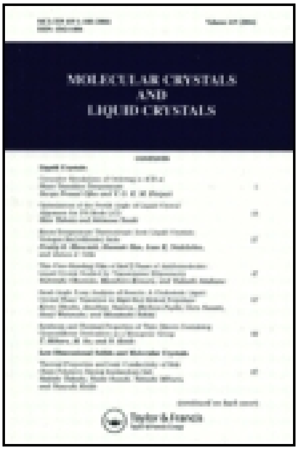

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ORGANIC REACTIONS IN THE SOLID PHASE PREPARED BY CO-DEPOSITION OF REAGENT VAPOURS ONTO COLD SURFACE

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Abstract New approach is proposed to influence reactivity and selectivity of organic reactions. It is based on structural ordering conditions for reagents using solids prepared from vapour phase.

As a rule, the organic solid-state reactions are restricted to isomerization, dimerization and polymerization, i. e. to processes in which only molecules of one kind take part.[1,2] At present the selective two-component reactions with the participation of organic crystals are being actively studied.[2,3] The most promising is the investigation of the inclusion compounds[4] and the difference in the selectivity of interaction at various faces in single crystals.[5,6] On the whole however, the organic solid-state chemistry of two-component reactions is only at the beginning of its development. Therefore, it is rather important to look for new prospective directions and create conditions under which the organic reactions could be selectively conducted with the participation of the solid phase.

In our opinion, non-equilibrium solid bodies produced by co-deposition of vapours of various compounds that serve both as potential reagents and structuring substances may be of great importance for the organic synthesis.

The reactive solid phase prepared by co-deposition of reagent vapours on a cold surface provides the following opportunities:

1. There are appears the fundamental possibility of structuring a system before its chemical activity is manifested.
2. It may be expected that metastable or extremely rare inclusion compounds are produced so that the mutual inclusion of the most different guest molecules can be carried out.
3. The range of organic species known as clathrate-forming substances may be drastically extended.
4. Metastable solid solutions can be produced for a whole range of systems.
5. Metastable porous structures can be produced on the basis of both clathrate-forming and conventional organic substances.

The co-condensation of vapours of urea and thiourea with organic compounds enabled us to obtain not only the already described clathrates (e. g. urea with linear hydrocarbons and thiourea with cyclic compounds) but also the inclusion compounds previously unknown.[7-10] First of all, these are thiourea clathrates with linear hydrocarbons (pentane, hexane, nonane) and with such substances as naphtalene, p-xylene. Urea compounds with cyclic molecules - cyclopentadiene, N-ethylmaleimide - were also produced. The combined inclusion of high-activity compounds in the channels of urea and thiourea was also carried out.[7,8] It should be mentioned that the combined inclusion of cyclopentadiene and maleic anhydride in thiourea channels can not be performed by classical clathrate-forming methods because even at 170 K this system is highly active. A similar reaction was accomplished for the system of cyclopentadiene - N-ethylmaleimide in the co-condensates with urea.

It is especially noteworthy since the cross-sections of the reagent molecules exceed the cross-sections of channel cavities in the crystal lattice of urea. It is evident that the obtained clathrate should be metastable.

In the above cases the reagent molecules were enclathrated within the channels in pairs, thus leading to the high degrees of transformation. The paired inclusion could be caused by complexation of reagent molecules that preceeds clathrate structuring. The formation of molecular complexes between the components of the diene synthesis is well known.[11] However, for the general case with no significant intermolecular interactions, it is difficult to predict, a priori, the distribution of molecules of the simultaneously included substances. Therefore to establish the regularities in the molecule distribution in combined clathrates, clathrate-formation was studied in the system of thiourea - cyclopentadiene - (1), where (1) is the reaction product of cyclopentadiene and maleic anhydride. In control runs no molecular complexes were detected for the two-component system of cyclopentadiene - (1) within the temperature range of 80--300 K. Therefore it was assumed that the intermolecular forces for the given system are determined only by Van der Waals interaction. The regularities of including molecules of cyclopentadiene and (1) into thiourea channels during clathrate-formation in the solid phase depend on the ratio of components. If the number of guest molecules is sufficient to fill completely the host structure, the molecules of cyclopentadiene and (1) are included separately. The combined inclusion of different molecules is only observed if the molar fraction of guest molecules is reduced.[12] It is important that we managed to obtain loose thiourea clathrates, while those formed by conventional techniques are always densely packed.[13] In our opinion, the intermolecular interaction (with the participation of included molecules) plays an important role in clathrate-formation. The effect of this interaction is proportional to the degree of channel packing. The dense packing of channels, i. e. minimal distance between guest molecules, corresponds to stronger intermolecular interaction as compared to loose packing. In the former case the distribution of guest molecules in host channels will tend to be thermodynamically controlled, thus, as a rule, resulting in separate inclusion.

It can be assumed that the crystallization in non-equilibrium conditions of multi-component organic systems even in the absence of clathrate-forming substances may proceed via metastable solid solutions where the components can interact provided the solution possessed adequate kinetic stability. To verify this assumption we have studied the reaction of maleic anhydride with tetraphenylcyclopentadiene (TPCD).[14-16] The reaction was studied in the samples produced by co-condensing reagent vapours and also in chloroform solution. We have founded that the lower rate of heating and deposition significantly decreased the reaction yield if the component ratios were close to equimolar ones and affected the transformation degree only slightly at the noticeable excess of one of the reagents.

To account for this regularity, we have considered two possible pathways with the relative contribution depending on the sample-forming conditions. The first pathway is the interaction of reagents in the metastable solid solution of equimolar composition. The second is the heterogenious interaction of maleic anhydride and TPCD crystals in the mixture. The closer these contitions are to thermodynamic equilibrium the more the reagents tend to follow the second route.

Thus, it becomes clear why at the reduced condensation rate of reagent vapours and the reduced rate of sample heating, the degree of transformation was lower. The fact is that by increasing the time of sample formation it is possible to produce a more stable sample, i.e., in our case the heterogeneous mixture of pure crystals.

It is essential that the selectivity to endo-exo isomers of interaction betmeen maleic anhydride and TPCD in samples produced by co-deposition of reagent vapours differs by 50% from the selectivity of their interaction in a solution.[16] This is evidently due to a planar molecular conformation of TCPD in solid phases, similar to many compounds with closely located phenyl rings.[17,18] In our opinion, in conditions of kinetic control of structuring the ability to accomodate guests is not limited only to such substances as clathrates, but can be extended to other organic crystals with loose packing of molecules.

The possibility of including guest species into the crystal lattice was studied for succinic anhydride and acrylamide as hosts. The packing density in the crystals of these compounds does not exceed 0. 65. Guest species were represented by alyphatic alcohols with varying size and shape of molecules: methanol, n-propanol, iso-butanol, sec-butanol, tert-butanol.

Naturally, it can be expected that the volatility of alcohols accomodated in acrylamide or succinic anhydride crystals will be lower than that of pure alcohol. Therefore, the temperature dependence of alcohol evaporation from co-condensates with acrylamide and succinic anhydride was studied. For the above alcohols the temperature intervals of evaporation were shifted to the region of higher temperatures as compared to evaporation of pure alcohols: for methanol - 8 K, for propanol, iso- and sec-butanol - 20-22 K. The observed retention of alcohol can only be due to the inclusion of alcohol molecules into the the crystal lattice and, consequently, their evaporation was complicated. It seems improbable that alcohol is retained in the intercrystalline space by capillary forces. To effectively retain alcohol, i. e. to decrease its volatility, the capillary cross-section should be commensurable with the size of alcohol molecules, in fact, to be equivalent to cavities inside the crystal lattice.

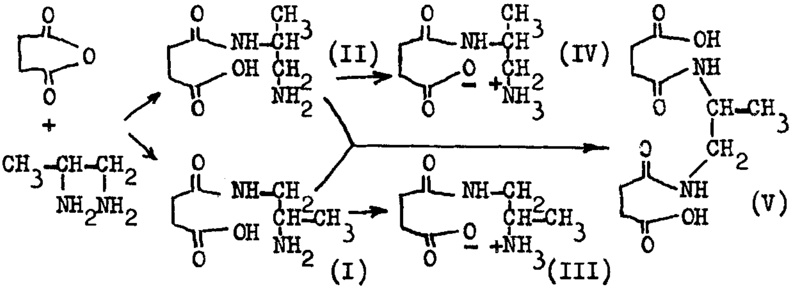
The most effective retention was observed at a molar fraction of alcohol in the starting co-condensate within 0.2-0.3. Outside this ratio the dependence of alcohol evaporation on heating acquires a step-wise character: alcohol partially evaporated at the evaporation temperature of free alcohol. Consequently, succinic anhydride and acrylamide crystals are capable of retaining only a certain quantity of alcohol as was observed during the formation of inclusion compounds.[9]

The IR spectra for co-condensate crystals of acrylamide and succinic anhydride differ from those for the individual crystals in the absence of alcohols. The IR spectrum of acrylamide in the presence of alcohols registered the following shifts in absorption band with the accuracy of ± 1 cm^{-1}: valence vibrations of C=O group from 1671 to 1680 cm^{-1}; deformational vibrations of NH_2 group from 1610 to 1614 cm^{-1} and of CH_2 group from 1425 to 1430 cm^{-1}. Valence vibration band of C=O group in succinic anhydride shifted from 1780 to 1790 cm^{-1}. Apparently, it is caused both by the changes in mutual orientation of host molecules in the sites of the crystal lattice and by the presence of alcohols in it. After the evaporation of alcohols and annealing of samples above 260 K the shifts of the absorption bands disappeared.

The X-ray diffraction analysis of low-temperature co-condensates of acrylamide and succinic anhydride with alcohols failed to detect scattering peaks other than those of thermodynamically equilibrated crystals of pure substances. It means that the location of sites in the lattice containing alcohol molecules remains unchanged. However, the packing of molecules in acrylamide and succinic anhydride crystals being rather loose, it can be assumed that molecules at the sites are partially reoriented without affecting the lattice structure. Then it is not impossible that cavities would form to accomodate guest molecules. The assumption was corroborated by the analysis of molecular Stewart-Brigleb models. Moreover, if the crystal lattice of the above substances is further assumed to accomodate one molecule (e. g. of propanol) for each four molecules of the crystal (molar fraction 0.25), the packing density would reach the optimal value of 0.75-0.80.

Thus, the results obtained testify to the possibility of forming the metastable porous acrylamide and succinic anhydride crystals capable of accomodating guests at low temperatures under the conditions of kinetic control. The shape and size of guest species should necessarily be considered. For example, the inclusion of tert-butanol was not detected, apparently, due to rather large cross-section of its molecules.

If the suggested mechanism is true, it enables us to affect the selectivity of organic reactions by a new method: by introducing a reactive molecule into the structure of another reagent. The system of succinic anhydride - 1,2-diaminopropane where the amine acylation reaction occurs was chosen to exemplify the above approach. The interaction of succinic anhydride with 1,2-diaminopropane yields the following products:



The reaction was conducted in samples produced by the consecutive deposition of Succinic anhydride crystals and 1,2-diaminopropane. The latter were prepared either by deposition of the vapours of pure substance on the solid surface at 80 K and further warming up to 220-230 K, or by co-condensing succinic anhydride with one of the alcohols in question at 80 K and subsequent removal of alcohol from the co-condensate at 230 K. At 80 K or 220 and 230 K the vapours of diamine were condensed on succinic anhydride crystals produced by either of the routes. The slectivity of interaction significantly depends on the technique of producing succinic anhydride crystals. The ratio of reaction products is given in Table 1.

Table 1

Reaction products	Crystals modified by: methanol	n-propanol	iso-butanol
III	0.30	0.18	0.65
IV	0.70	0.70	0.35
V	-	0.12	-

The observed differences in the alcohol-modified crystals, apparently, can be accounted for by the fact that the cavities in succinic anhydride lattices remaining after the evaporation of alcohol are occupied by 1,2-diaminopropane molecules taking part in the reaction. It is essential that the nature of alcohols affects the product ratio and, consequently, the structure of starting crystal. The selectivity is also determined by the conditions of producing succinic anhydride crystals in the presence of a given alcohol. For instance, when the succinic anhydride - n-propanol ratio in the starting co-condensate was changed from 2-3:1 to 1:2-3 the selectivity to the III and IV isomers sharply changed from 1:3 to 1:1.6.

Hopefully, the application of low-temperature co-condensates in the organic synthesis offers much scope for future experiments. It enables us to drastically extend the range of reactive systems employing the organic solid-state reactions, i. e. to realize one of the main advantages of the solid-state chemistry - selective interaction.

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