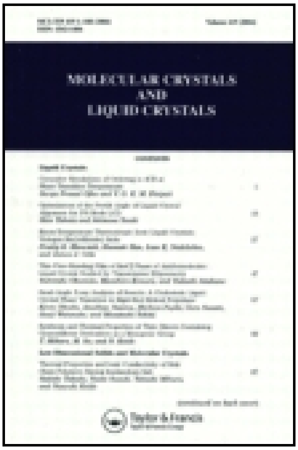

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CRYOSYNTHESIS OF ORGANOMETALLIC COMPOUNDS IN THE SOLID PHASE

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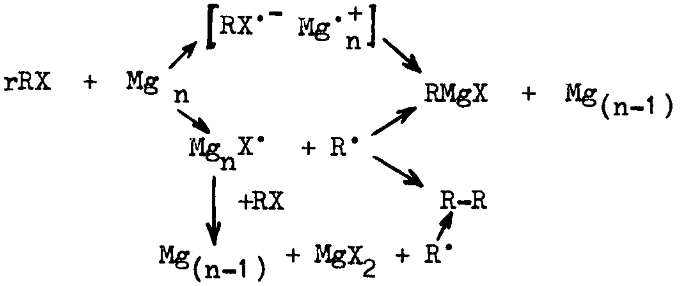
Abstract Under conditions of joint condensation of metallic vapour with organic substances, metal may participate in reactions in the form of atoms (mainly on the surface) or clusters in the solid-state cocondensate. The systems Mg-RHal and Sm-ROH have been considered as examples of different products from "atomic" and "cluster" mechanisms.

Simultaneous condensation of metal vapors with various organic compounds at 80-100 K results in the formation of solid phase cocondensates in which synthesis of organometallic compounds occurs. Explosive development of work on metalloorganic compound cryosynthesis began in the 70-ies (1, 2, 3.).

Most metals are single-atomic in vapors but, during the cocondensation processes with moderate excesses of reagents, clusters may form from the atoms and further enter into reactions: Applications of metal atoms and clusters in synthesis have some thermodynamic and kinetic advantages as compared with bulk metal. The atoms react with most compounds actually without any activations energy; reaction of bulk metal is usually limited by small specific surface and formation of barely penetrable product films.

Based on examples of some metal-ligand systems, we succeeded in demonstrating the possibility of adjusting, under conditions of solid state cryochemical synthesis, the reaction connected with metal atoms and clusters, to give different products for the same system. The relation between "atomic" and "cluster" reaction paths depend on a number of factors: metal and ligand nature, reagent ratio and condensation rate, temperature and nature of the surface where condensatoin occurs.

Based on the studies of magnesium interaction with halogenated hydrocarbons (4) we have proposed a reaction mechanism including different reaction paths for magnesium atoms and their aggregates (clusters):



At n=1 (atomic magnesium) a radical path is realised resulting in great yields of recombination products. At the same time, for metal-ligand ratios equal to 1 : 100-200 which is usual for cryochemistry, most of the magnesium reacts in aggregate (cluster) form giving the Grignard reagent. According to IR and ESR spectroscopic data, the reaction of atomic magnesium is realised mostly at cocondensate surfaces just at the moment of condensation. The ion-radical reaction occurs en masse when heating the specimen. With increase of metal dilution by ligand, the radical process becomes dominating - actually a Wurtz reaction proceeds instead of a Grignard one (4).

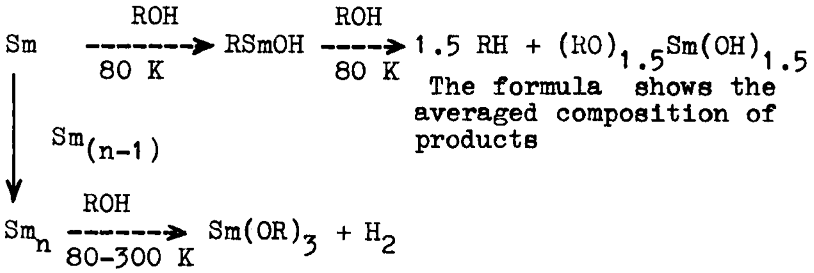
For mono derivatives of different halogens, the dependency of the radical path on the ratio of starting reagents is different. Such dependence is most pronounced for monoiodoalkanes. At the same time monofluoro- and monochlorobenzene do not give any remarkable amounts of radical products for any ratio with magnesium.

We have recently found one more example of different reaction paths for atoms and clusters of the same metal. When metals react with aliphatic alkohols under the usual conditions, as in simultaneous condensation (cryosynthesis), corresponding alcoholates of metal are generally obtained. But with decrease of the metal part in cocondensates down to ratios of 1 : 500 and lower, the yield of alcoholates of metal is decreased under conditions of cryochemical synthesis.

In that case alcohol is reduced to the corresponding hydrocarbon. We have proceeded to such as yet unknown reactions between normal and branched aliphatic alcohols, C_1-C_7, and three metals: sodium, magnesium and samarium. The interaction with Sm has been studied the most completely (5), e.g., after heating cooperative condensates of samarium with n-pentanol-1 at a ratio of 1: 1000 (surface temperature when condensing vapor was about 80 K), Sm (III) hydroxyalcoholate, n-pentane and traces of decane were observed with pentane yields of 1.5 moles to 1 mole of cocondensated samarium. At the same conditions and metal : alcohol ratio equal to 1: 50 the yield of pentane was less than 0.1 mol.

To explain the results obtained, we have used a kinetic model of reactions in vapors condensed together, which was first proposed by Moskovitz et al (6). According to the model, metal atom aggregations and their reaction with ligand on the surface of metal and ligand condensate films are competitive during the formation of the film. All the atom reactions in the case of active ligand are terminated on condensate surfaces. After finishing, the reaction specimens contain mostly products of the reaction of metal atoms and small aggregates with the ligand and also large metal aggregates reacting with less activity with excess ligand.

Special experiments have shown that in the alcohol- Sm system, hydrocarbons are obtained only in the condensation at 80 K. When the cocondensate is heated, formation of samarium alcoholates occurs. Based on the results obtained we have suggest the following reaction scheme:



$$\mathrm{Sm} \xrightarrow[80\ \mathrm{K}]{\mathrm{ROH}} \mathrm{RSmOH} \xrightarrow[80\ \mathrm{K}]{\mathrm{ROH}} 1.5\ \mathrm{RH} + (\mathrm{RO})_{1.5}\mathrm{Sm(OH)}_{1.5}$$

$$\mathrm{Sm} \xrightarrow{\mathrm{Sm}_{(n-1)}} \mathrm{Sm}_n$$

$$\mathrm{Sm}_n \xrightarrow[80\text{-}300\ \mathrm{K}]{\mathrm{ROH}} \mathrm{Sm(OR)}_3 + \mathrm{H}_2$$

The formula shows the averaged composition of products

This scheme includes the organometallic compound RSmOH similar to Grignard reagents as transition state. The experimental dependence of hydrocarbon yield on alcohol-metal ratio (Fig.1) agrees well with theoretic ones obtained on the basis of kinetic analysis of the reaction scheme proposed.

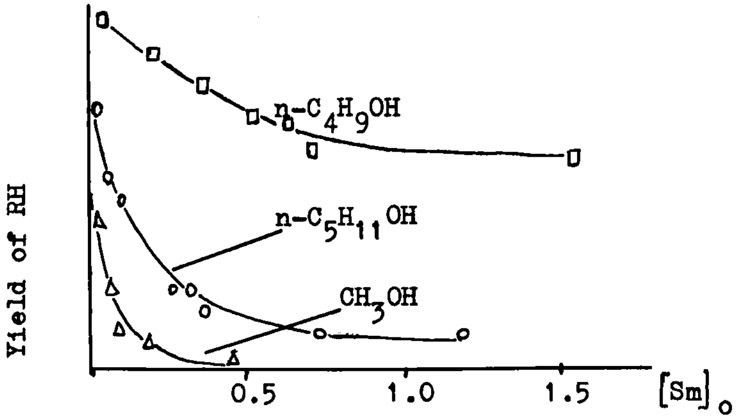


FIGURE 1 Theoretical curves and experimental data (points) for the yield of RH in Sm-ROH cocondensates.

The kinetic analysis makes it possible to determine also the ratio of effective rate constants for samarium atom dimerisation and for the Sm atoms inserting themselves into the C-O bond of the alcohol molecules. According to the kinetic model of Moskovitz, two rate constants, K_1 and K_2, are sufficient for the description of processes taking place in condensates:

$$Sm + ROH \xrightarrow{K_1} RSmOH$$

$$Sm + Sm \xrightarrow{K_2} Sm_2$$

$$-d[Sm]/dt = K_1'[Sm] + K_2[Sm]^2 \qquad (1)$$

$$K_1' = K_1[ROH]$$

$$Sm = [Sm]_0 \Big/ \left\{ e^{K_1' t} \left(1 + \frac{K_2[Sm]_0}{K_1'}\right) - \frac{K_2[Sm]_0}{K_1'} \right\} \qquad (2)$$

$$\text{if } t = 0 \Longrightarrow [Sm] = [Sm]_0$$

Because the vapor of Sm is single-atomic, the initial Sm concentration is equal to its full concentration in the cocondensate.

$$\varphi_{RH}[Sm]_o = 1.5\,\frac{K'_1}{K_2}[Sm]_o + 1.5\,\frac{K'_1}{K_2}\ln\left(\frac{K_2}{K'_1}\right) \qquad (3)$$

The solution of kinetic differential equation (1) gives the yield of hydrocarbons φ calculated by equation (3). The ratios of the effective samarium atom aggregation constant to the effective reaction constant with alcohols are given in the next table:

TABLE 1 Ratios of the effective constants, K_1/K_2

Alcohol	K_1/K_2
CH_3OH	$(5 \pm 0.5) \times 10^5$
$n\text{-}C_4H_9OH$	35 ± 5
$n\text{-}C_5H_{11}OH$	690 ± 20
$n\text{-}C_6H_{13}OH$	46 ± 5
$n\text{-}C_7H_{15}OH$	1660 ± 70

In solid cocondensates of samarium with alcohol, when heated from 80 K, the formation of Sm(III) alcoholate and hydrogen occurs. For this reaction, as for the magnesium - chloroalkane system (7), step-wise kinetics are characteristic. Reaction is accelerated during the heating process and progressively stops upon stabilising the temperature. The evaluation of activation energy gives 4 kJ/mol, which is characteristic for diffusion processes. The step-wise mode of the reaction seems to be connected with the presence of metal aggregates (clusters) in solid cocondensates, due to differences in their dimensions.

Hence, two reaction types have been found in studied systems of metal-halogenohydrocarbon and metal-alcohol: metal atoms react with ligand or with each other mostly during the cocondensation process. When heating solid cocondensate, metal clusters enter into reaction. If metal is condensed with small active ligand molecules, e.g. CCl_4 (7) or CO_2(8), most of the metal reacts as atoms at 80 K and after finishing the condensation the cocondensate does not contain metal clusters. When heating up to room temperature, chemical composition changes to a lesser degree - mostly at the expense of the transformation of primary unstable products.

True solid phase reactions proceed in condensates of metals with ligand molecules which generally have one reaction center connected with the inert (hydrocarbon) part. Activation energy of such reactions is very small and is associated with processes limited by diffusion in the solid state.

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