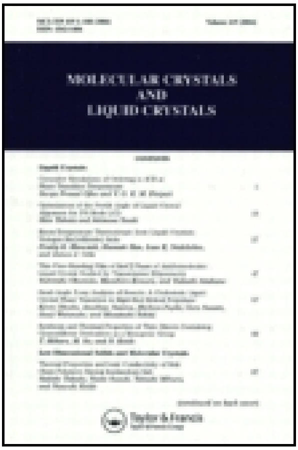

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Reactions of Solid Organic Compounds with Metal Species

Gleb B. Sergeev [a], Tatyana I. Shabatina [a], Victor N. Solov'ev [a] & Vyacheslav V. Zagorskii [a]

[a] Department of Chemistry, Moscow State University, 119899, Moscow, Russia

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Reactions of Solid Organic Compounds with Metal Species

GLEB B. SERGEEV, TATYANA I. SHABATINA, VICTOR N. SOLOV'EV and VYACHESLAV V. ZAGORSKII

Department of Chemistry, Moscow State University, 119899 Moscow, Russia

The results on chemical reactions of metal atoms, small clusters and nanoparticles with different organic and inorganic substances in the temperature range 12–300 K are presented. Complexation and reactions of atoms and clusters of magnesium, samarium and silver with alkyl halides, carbon dioxide, ethylene and some mesogenic cyanophenyls were studied by the technique of matrix isolation and low temperatrure co-condensation of metal and ligands vapours, low temperature UV-Vis, IR- and ESR-spectroscopy in the combination with quantum chemistry calculations. In some cases the reaction products were analysed by high performance gas chromatography. It was shown that cryochemical reactions of metal particles of different size reflected the system redundant energy.

Keywords: solid phase reactions; nanosize metals; condensate films; liquid crystals; low temperature spectroscopy

INTRODUCTION

Low and superlow temperatures give new possibilities to obtain small metal species and to study their reactions in solid co-condensates [1],which are highly nonequillibrium thermodynamic systems. The size of metal particles forming such systems and their reactivity are determined by the combination of different experimental conditions. The main experimentally controllable factors are the support temperature, the metal/ligand ratio, reagent condensation rate and the sample annealing rate. It was shown that the lower is the temperature of support surface, the less are diffusion controlled interactions between reactive particles and the more possible is the formation of high energetic low temperature co-condensates.

The metal/ligand ratio highly effect on the size of metal particles obtained via low temperature co-condensation. Rising this ratio ordinary leads to increasing of the part of clusters and higher aggregated metal particles. The component condensation rate produces the complex effect on the properties of low temperature co-condensate. The life time of exited species (metal atoms, their dimers or trimers) condensed at the cooled surface is inversely with the condensation rate. It depends on the nature of relaxation processes in the co-condensate.

Different parallel and sequential stages occur during the annealing of the co-condensate system: aggregation of metal atoms, surface adsorption and chemisorption of ligands, chemical reactions of the components. It was found that metal atoms, clusters and nanoparticles could react by pathways, which do not realise at room temperatures. The results on chemical reactions of metal atoms, small clusters and nanoparticles with different organic and inorganic substances in the temperature range 12-300 K are presented

EXPERIMENTAL

The interaction of magnesium with carbone dioxide was studied in metal co-condensates with carbone dioxide and its mixtures with argon 1/20. Co-condensates were formed on the KBr window, mounted on the bottom of conventional closed cycle refrigerator MSMR-100A-3,2/20 (Omsk Manif. Co.). Temperature was measured by Au-Cu thermocouple and was 10-80 K during the deposition. Magnesium of type MG-1 (99.9%) was used in our experiments. Magnesium in pieces was vaporised from stainless steel tube at a temperature ≈360-380°C. Condensation rate was about 1-2 μg/min per cm^2 according to quartz crystal microbalance. CO_2 was synthesized from $NaHCO_3$. Gas mixtures were introduced into the cryostat through the needle regulator. Typical deposition rate was about 1 mmol/hour.

Thermal behavior of silver cyanobiphenyl co-condensate films of 20-100 μm was studied by low temperature IR-spectroscopy at 77-330 K using special evacuated cryostat. The film samples (l=2-50 μm) were obtained by cyanobiphenyl molecular vapor deposition or metal and cyanobiphenyl vapors co-deposition on polished surface of copper cube, salt (KBr, CaF_2) or quartz windows ,cooled by liquid nitrogen (77 K) and then annealed upto 300-350 K. The deposition rates were 10^{17-18} molecules/cm s. The residual gas pressure in the system did not exceed $5\cdot10^{-4}$Torr at all temperatures upto 350 K.

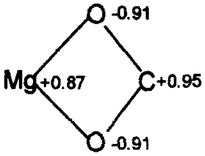
The IR-spectra of the samples were recorded using reflection mode on Specord IR-75 for film condensate samples and using transmission mode on Specord 80 for bulk samples and solutions. Spectroscopic accuracy was upto 0.5 cm^{-1} The temperature of the samples was maintained within ±1 K interval at 77-270 K and ± 0,5K at 290-350 K.In some cases the molecular vapor of cyanophenyl substance were co-deposited with inert matrix molecules: decane (at 80-100 K).

RESULTS AND DISCUSSION

It was shown that magnesium clusters reacted with methylhalides during light irradiation and formed Grignard reactives. We found that in the solid phase in temperature range 10-40 K single magnesium atom introduced into carbon-halogen bond. The influence of carbon-halogen binding energy value on chemical interaction was studied on the example of the reaction of magnesium particles with alkyl halides [2]. In the similar conditions samarium reduced methylhalides to methane during low temperature co-condensation.

The interaction of magnesium with carbone dioxide was studied in metal co-condensates with carbone dioxide and its mixtures with argon 1/20. The IR spectra of Mg and CO_2 containing co-condensates at 10 K were recorded. In the all cases three new weak absorption peaks at 1594 (C=O st.), 1378 (C-O st.) and 860 (OCO def.) cm^{-1} are visible. Argon matrix annealing up to 40 K, and also neat Mg/CO_2 sample annealing upto 80 K, increases the intensities of these bands. Variations of CO_2 concentrations and changes in condensation temperature (10 and 80 K) did not influence the spectrum.

The absence of spectral changes during annealing allows us to suppose that carbon dioxide only co-ordinates by magnesium. In order to determine the co-ordination type the quantum chemical calculations were carried out. The geometry optimization of the $Mg-CO_2$ system followed by the harmonic vibrational analysis have been performed at the MP2/6-311G*(2d,2p) level. The optimized complex structure and atomic charges are shown bellow.



The values of charges suggest this compound can be viewed as an ion-radical pair $Mg^{+}CO_2^{-}$. The calculated dipole moment of $MgCO_2$ is 2.6D.

The UV-Vis spectra of Mg-CO_2 condensate in comparison to the spectrum of small magnesium clusters in argon showed the the absence of the absorptions from Mg_2, Mg_3 and Mg_4 . The absorptions attributed to the higher aggregates and to the atomic S-P transition are prevailing and are more intensive than the corresponding bands in the spectra of Mg/argon systems.

Annealing at 27K led to a complete disappearance of cluster Mg_x absorptions and to decrease of the atomic ones, thus suggesting the higher magnesium cluster reactivity and the higher redundant energy than magnesium atoms.

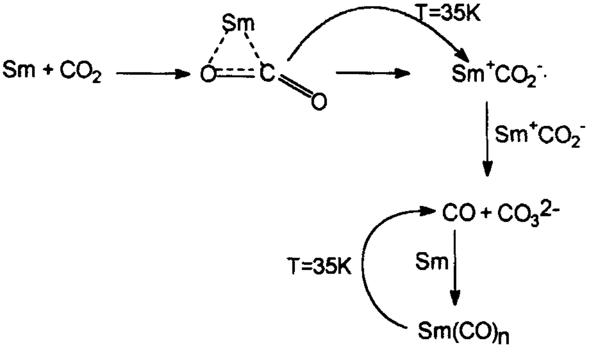
Two new weak and broad absorptions appear at 318 and 350 nm. By annealing these new bands grow in intensity and the absorption of magnesium particles decreases. Thus all magnesium absorption bands are well known, and matrix shifts due to CO_2 existence are negligible, the new bands may be attributed to the product of Mg and CO_2 interaction, anion-radical $CO_2^{-\cdot}$. Intense absorptions of unreacted magnesium even in neat CO_2 suggest very low reactivity of magnesium atoms and clusters in the ground state.

Co-condensates of samarium and CO_2/Ar mixture with ratios of 1/20 and 1/200 were studied in the temperature range 10-40 K. Thick co-condensate films were dark yellow or brown and transparent.

Samarium is more active than magnesium in the reaction with carbon dioxide . Just after the co-condensation it formed nor only complexes, and also secondary products. The IR spectra of Sm/CO_2/Ar (CO_2 : Ar = 1 : 20) after co-condensation and further heating to 35 K showed that some products are unstable and upon heating are converted into another products.

Absorption bands at 1586, 1370 and 862 cm^{-1} are very close to the data obtained for anion radical CO_2^{-}, produced by the reaction of magnesium : 1594, 1378, 860 cm^{-1}, and can be considered as anion radical pair $Sm^{+}Co_2^{-\cdot}$, which is stable upon annealing to 35K.

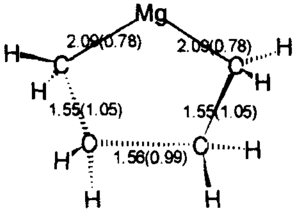
Besides anion radical samarium forms one more complex with carbon dioxide, which is unstable upon annealing. The absorption bands at 1795 (ν C=O), 1016 (ν C-O), 765 (δ OCO), 550 (ν Sm-C) cm^{-1} disappeared by annealing upon 33 K. Thus, data obtained on products identification and transformation suggest the following reaction scheme :.



UV-Vis spectra of the Sm/CO_2/Ar condensates obtained show at higher CO_2 concentration (1/20) only atomic absorptions after co-condensation. At lower CO_2 concentration (1/100) dimer and higher Sm aggregates are present in significant amounts in matrice immediately after deposition, but annealing to 21K decreases their amount almost in three times. Thus samarium aggregates also as for magnesium possess higher reactivity than atoms.

The interaction of magnesium with ethylene was studied in co-condensates with neat ethylene and with C_2H_4/Ar (1/20) mixture. The stepwise matrix annealing led to the appearance of a big number of new absorption bands at 3050-2800 cm^{-1} and 800-400 cm^{-1}. The geometry optimization of the MgC_2H_4 and $Mg(C_2H_4)_2$ species has been performed at the MP2/6-311G*(2d,2p) level. The complete optimization of MgC_2H_4 shows that the interaction of magnesium with ethylene realised in Wan-der -Waals complex formation. There is a small system energy minimum (0.8 kcal/mol) at Mg...C_2H_4 distance of about 4 Å. In this case the geometry of ethylene molecule is not disturbed and ethylene vibrations are shifted on 1-2 cm^{-1}. The IR spectra of ethylene at various dilutions in argon matrices revealed that ethylene forms relatively stable dimers in the matrix. So we analyzed the interactions of magnesium atom with two ethylene molecules [2].

Our calculations show that there is no global minimum associated with the C_{2v} symmetry on the potential energy surface of Mg + $2C_2H_4$. The global minimum of the system can be achieved by canceling of the symmetry restrictions. At the MP2 level it corresponds to the 5-member cyclic structure with the binding energy of 20.6 kcal/mol relative to the separated magnesium and two ethylene moieties [3].



The pairs of bands in 1400-1500 and 1100-1200 cm^{-1} regions are characteristic for the π-complexes of metals with ethylene and correspond to the coupled stretch C=C and def. CH_2 vibration modes of the distorted ethylene molecule. However, no absorption bands were found in the $\nu_{C=C}/\delta_{CH2}$ region during experimental studies of the Mg/C_2H_4 and MgC_2H_4/Ar cocondensates, according to the calculations the vibrational bands at 1145 and 1158 cm^{-1} are low intensive ones. On the other hand, the stretching modes of the C-H bonds and those of low-frequency intramolecular motions which include vibrations of magnesium are consistent in the theoretical and experimental data confirming the formation of the predicted structure $Mg(C_2H_4)_2$. The additional confirmation of the proposed structure gave the results of chromatographic analysis of the reaction products.

The interaction of samarium with ethylene in co-condensates with neat ethylene and with C_2H_4/Ar (1/25 and 1/250) mixture was studied by IR- and UV-spectroscopy. In order to obtain the more complete information the experiments with deuterated ethylene and with C_2D_4/Ar (1/20 and 1/200) mixtures. A big number of new absorption bands were obtained in different IR-regions, indicating that samarium as magnesium is the element, which interacts with ethylene intensively .

Absorptions, appearing in the co-condensate vibrational spectrum, can be devided in the following groups: νC-H bond stretch mode at 3000 -2800 cm^{-1} (νC-D 2200-2000 cm^{-1}), νC=C & δ CH_2 at 1500 - 1400 cm^{-1} and 1250 - 1100 cm^{-1} (C=C & δ CD_2 1350-1250 cm^{-1} and 1000 850 cm^{-1}), δ SmCH at 1000-700 cm^{-1}(δ SmCD 750-600 cm^{-1}), and νSm-C stretch mode at 600 - 500 cm^{-1}. It was concluded from spectra analysis that complexes $Sm(C_2H_4)$ and $Sm(C_2H_4)_2$ were formed with metal atom co-ordinated on ethylene π - system. The absorptions of complexes were also visible in the electronic spectra at 480 and 529 nm. Similar to the thermal behavior of samarium co-condensates with carbon dioxide rising of ethylene concentration leads to the decrease of metal clusters contents, and matrix annealig fully dispose of them.

The assignment of the absorptions, belonging to different complexes, were made using the band intensities dependence of ethylene concentration in matrix. The more ethylene molecules are in the complex, the weaker is metal interaction with each of them and less complexes band shift in respect to the band of unbounded ethylene. Predominant complex type was noticed to change with ethylene : argon ratio. In pure ethylene complex $Sm(C_2H_4)$ was practically absent. Complexes of composition 1:1 and 1:2 were observed at ethylene:argon ratio 1:25. Complex $Sm(C_2H_4)_2$ disappears in the system with ethylene:argon ratio 1:250. Annealing of the matrix did not lead to the transformation from lower complex to the higher one.

Isotopic ratios for samarium complexes are in good agreement with the data obtained for nickel and lithium. Maximal value (1.3-1.36) has been obtained for C-H/C-D stretching, and for low frequency ν C=C/δ CH_2 /CD_2 vibration. High frequency vibration ν C=C/δ CH_2/CD_2 and stretching vibration Sm-C possess the isotopic ratio 1:1, deformation vibrations $\delta_{SmCH/CD}$ possess the isotopic ratio of 1.25. Thus, we have obtained and characterised π-complexes of samarium with ethylene.

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The results obtained for the reactions of samariun and magnesium species are summarised in the Table1.

Table 1.

Reactions of magnesium and samarium species in matrices at 10-40 K.

Metal species	CO_2-ligand	C_2H_4/C_2D_4-ligand	CH_3X (X=Cl,Br)-ligand
Mg	Mg + $CO_2^{\cdot-}$ by matrix annealing	Cycle $Mg(C_2H_4)_2$ by matrix annealing	CH_3MgX by irradiation ($\lambda \approx$ 280 nm)
$Mg_{2\text{-}4}$	Mg + $CO_2^{\cdot-}$ by co-condensation		CH_3MgX by irradiation (λ>300 nm)
Mg_x	Mg + $CO_2^{\cdot-}$ by matrix annealing		
Sm	$Sm^{+}\cdot CO_2^{\cdot-}$,CO,$SmCO_3$ By matrix annealing	Complexes $Sm(C_2H_4)$/C_2D_4) and $Sm(C_2H_4)_2$/$C_2D_4)_2$	-
Sm_2	$Sm^{+}\cdot CO_2^{\cdot-}$,CO,$SmCO_3$ By co-condensation		
Sm_x			

The analysis of the data, presented in Table 1 shows that Sm atoms and clusters possess the higher redundant energy and reactivity than magnesium clusters in the same reactions. In the case of Sm all the reaction products are formed during the co-condensation process. The reaction of samariun with carbon dioxide does not stop after coordination of CO_2 molecule, as in the case of magnesium, and the secondary products are produced by annealing or irradiation of the system.

The different reactivity of Sm and Mg species appears also for the reaction with ethylene molecule. In the case of magnesium the results of ab initio quantum chemical calculations and IR-spectroscopic study allow us to propose the formation of 5-member structure including ethylene dimer. IR-spectra for samarium system under similar conditions show the formation of 1:1 and 1:2 complexes. The complex of samarium with ethylene dimer possesses, probably, sandwich-like structure.

Thus, the results on reactions of magnesium and samarium under low temperatures demonstrate the possibilities of the chemical reaction using as sensitive probe on the redundant energy stored by the system.

Co-condensation of samarium and silver with mesogenic cyanophenyls led to formation of π-complexes stable up to 200 and 120 K correspondly [4,5]. The complexes were characterized by IR-, UV-Vis and ESR-spectroscopy. The formation of nanosize metal particles during thermal degradation of the complexes took place. In the case of silver besides globular metal particles of 10-15 nm size highly anisotropic rods of 100 nm length were formed [6]. The reaction with the third component was proposed for trapping of high energetic species during complex decomposition.

CONCLUSIONS

The results on the interactions of the solid ligads with different metal species, obtained via low temperature co-condensation of metal and ligand vapors, demonstrate the effect of metal particle size on their reactivity. The use of low temperatures, matrix isolation technique and preparative cryochemistry in combination with the results of quantum chemistry calculations allowed us to reveal some peculiarities of nanometal's cryochemistry and to establish the molecular structures of nonstable and metastable reaction products.

Acknowledgments

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