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Cryoreactions of magnesium atoms, clusters and nanoparticles with polyhalomethanes

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The reaction of magnesium particles with carbon tetrachloride at 12–40 K was observed for the first time.

Metal atoms, small clusters and nanoparticles possess high chemical activity. The new tendency of nanochemistry is the determination of the dependence of the chemical properties of particles on the number of atoms. The most successful achievements in this field were made in a gas phase and in low-temperatures inert matrices.[1,2]

The aim of this work was to determine difference in the chemical activity of magnesium particles with regard to CCl_4, $CFCl_3$ and $CHCl_3$ at 12–40 K. The reason for the selection of these substances was an increase in interest in magnesium reactions from both theoretical and experimental standpoints.[3,4] Polyhalogen-substituted hydrocarbons do not form organometallic compounds with magnesium. However, magnesium and carbon tetrachloride easily react in co-condensates at 80–150 K.[5] The reaction products were studied by IR and ESR spectroscopy. Grignard reagent, CCl_2, CCl_3 and products of their recombination were found. The suggested mechanism of the reaction includes two competitive processes. The first process is the elimination of chlorine atoms from carbon tetrachloride, and the other is the insertion of a magnesium atom into the carbon–chlorine bond.

Reactions of magnesium particles with polyhalomethanes at temperatures lower than 77 K and the influence of magnesium particle size on the reaction path was not studied previously. We were interested in the influence of carbon–chlorine bond energy on the possibility of chemical reactions at low temperatures.

Samples were obtained in a vacuum stainless-steel cryostat by the co-condensation of crossed beams of thermally vaporised magnesium and gas mixture on a cold salt window by the technique described elsewhere.[6] The films obtained at 12 K were heated up to 40 K stepwise at a rate of 5 K/min^{-1}. IR and UV absorption spectra were recorded after each temperature step of 12 K. Spectral changes were observed after heating for 10 min.

Magnesium chips were evaporated from a stainless-steel furnace at 650±20 K. The ratio of reagents and flow rates were controlled by a quartz crystal microbalance mounted near a salt window and maintained at the same temperature. The condensation time for UV and IR analysis was 4–7 min and 1–5 h, respectively.

$CFCl_3$ (ARKOS) was used without additional purification. GC analysis found 2% CCl_4 in it. Carbon tetrachoride and chloroform were purified by a known method.[7] GC analysis found 1% $CHCl_3$ and 1% CH_2Cl_2 in CCl_4 and $CHCl_3$, respectively.

Co-condensation of magnesium with argon at a ratio of 1/1000 led to red films containing metal atoms and clusters. The UV-VIS spectrum is shown in Figure 1(*a*). The assignments for atomic and cluster absorptions are taken from refs. 8 and 9.

The absorptions of magnesium atoms and clusters were stable at 12 K. The annealing of films lead to a simultaneous decrease of the absorption of all particles in the first 10 min. Spectra did not change on keeping at a higher temperature for 2 h. Figure 1(*b*) illustrates the temperature dependence of Mg/Ar condensate spectra. Absorptions of magnesium atoms and clusters were normalised to the absorptions at 12 K.

The co-condensates of magnesium with argon containing $CHCl_3$ or $CFCl_3$ are red, as well as films without polyhalomethane. The annealing of the co-condensates $Mg/CFCl_3/Ar$ or $Mg/CHCl_3/Ar$ (1/100/1000) resulted in a slower decrease of absorption of all metal particles than during the annealing of the argon–metal deposits (Figures 2 and 3). No new products were observed by IR spectroscopy at 12–40 K.

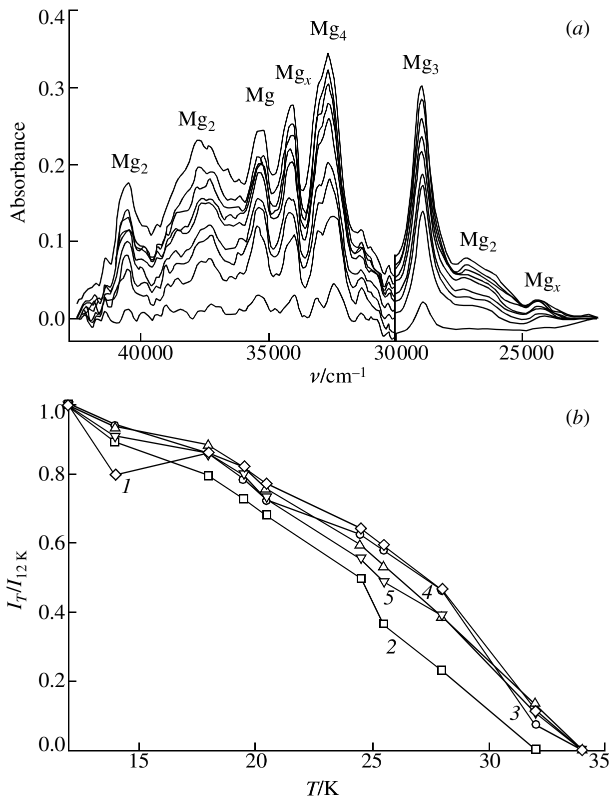

Figure 1 (*a*) Electronic absorption spectra of films (Mg/Ar = 1/1000) after annealing. Temperatures from top to bottom 12, 14, 18, 22, 25, 27, 28, 32 and 34 K. (*b*) Temperature dependence of the normalised integral intensity of magnesium atom and cluster bands (Mg/Ar = 1/1000). (*1*) Mg, (*2*) Mg_2, (*3*) Mg_3, (*4*) Mg_4 and (*5*) Mg_x.

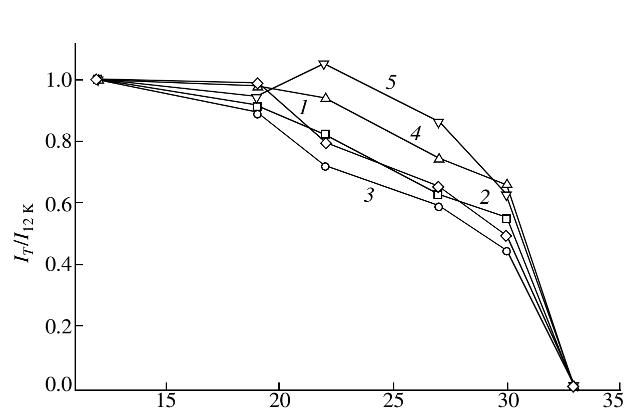

Figure 2 Temperature dependence of the normalised integral intensity of magnesium atom and cluster bands ($Mg/CFCl_3/Ar$ = 1/100/1000). (*1*) Mg, (*2*) Mg_2, (*3*) Mg_3, (*4*) Mg_4 and (*5*) Mg_x.

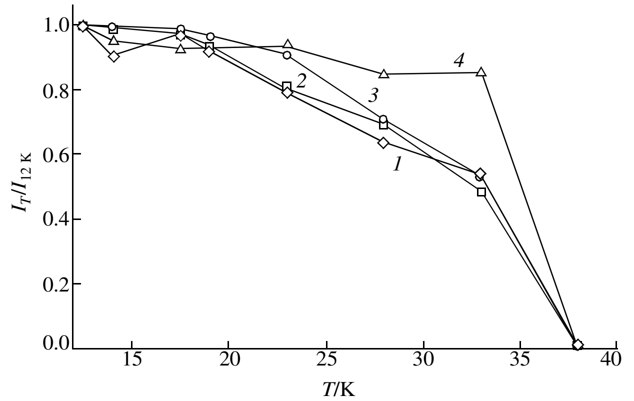

Figure 3 Temperature dependence of normalised integral intensity of magnesium atom and cluster bands ($Mg/CHCl_3/Ar$ = 1/100/1000). (*1*) Mg, (*2*) Mg_2, (*3*) Mg_3 and (*4*) Mg_4.

The co-condensates of $Mg/CFCl_3/Ar$ and $Mg/CHCl_3/Ar$ are argon films with cavities containing magnesium and polyhalomethane. The annealing of the films results in film crystallization and cracking. It is known that annealing displaces the admixtures on the surface of samples.[10] It is possible to assume that during heating atoms and small magnesium clusters are superseded on a surface of a crystal, and make larger metal particles.

The presence of polyhalomethane makes an argon film more rigid due to higher melting temperature and polarizability. This slows down diffusion of atoms and especially clusters, which explains higher temperature stability during sample annealing.

The presence of 10% polyhalomethane does not shift the positions of absorption bands of atoms and magnesium clusters that point to weak interaction of metal particles with polyhalomethane molecules. A band of S→P transition of magnesium atoms in co-condensates with $CFCl_3$ is twice wider than that in co-condensates with other polyhalomethanes. Probably, during condensation different complexes with the coordination of the metal to fluorine and chlorine are formed.

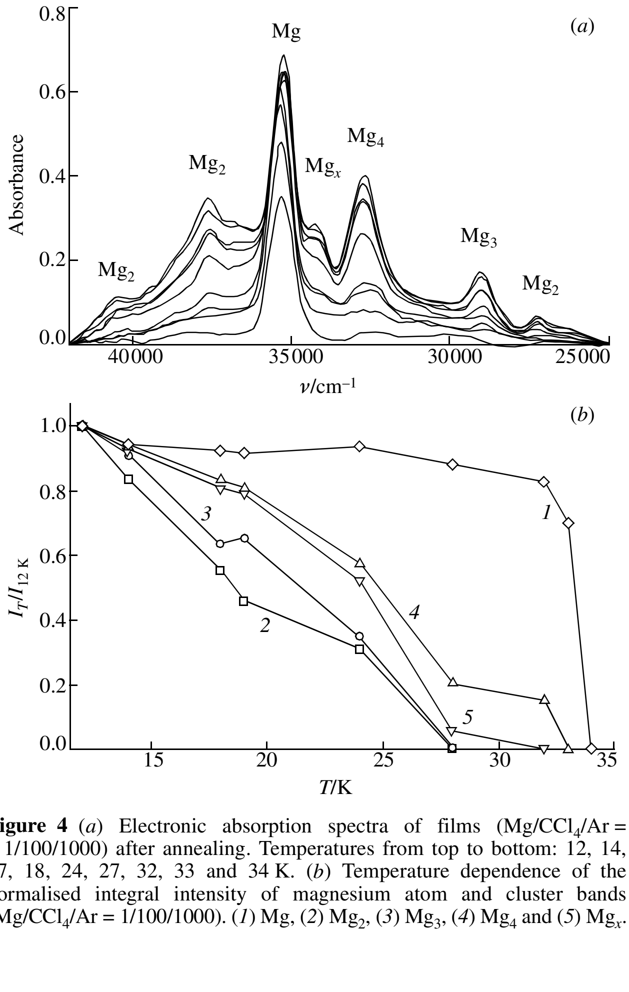

Figure 4 (*a*) Electronic absorption spectra of films ($Mg/CCl_4/Ar$ = 1/100/1000) after annealing. Temperatures from top to bottom: 12, 14, 17, 18, 24, 27, 32, 33 and 34 K. (*b*) Temperature dependence of the normalised integral intensity of magnesium atom and cluster bands ($Mg/CCl_4/Ar$ = 1/100/1000). (*1*) Mg, (*2*) Mg_2, (*3*) Mg_3, (*4*) Mg_4 and (*5*) Mg_x.

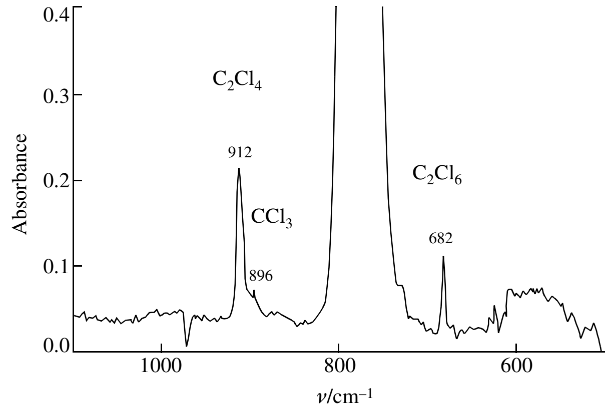

Figure 5 IR spectra of a co-condensate (Mg/CCl_4 = 1/100) at 70 K.

The absence of new products and the high thermal stability of magnesium atoms and clusters in matrices containing polyhalomethanes ($CHCl_3$, $CFCl_3$) are due to high C–Cl bond energy in $CHCl_3$, $CFCl_3$. According to published data,[11] the C–Cl bond in $CHCl_3$ is 78±4 kcal mol^{-1} and in $CFCl_3$ 81±3 kcal mol^{-1}.

Another behaviour of the system was found for the co-condensates of magnesium with an Ar/CCl_4 mixture. UV-VIS spectra of a $Mg/CCl_4/Ar$ (1/100/1000) film are shown in Figure 4. Complete expenditure of magnesium clusters was observed in the co-condensate of metal with mixed Ar/CCl_4 already at 27 K. The absorption of metal atoms remains constant and starts to decrease when less than 20% of the initial amount of clusters remains. One can also see (Figure 4), that the most stable clusters are Mg_4. Fast elimination of atoms and small cluster in a sample and the absence of colouring of a film we connect to a chemical reaction between magnesium and CCl_4. The C–Cl bond energy (70±5 kcal mol^{-1})[11] is less than in other polyhalomethanes and it can facilitate the course of reaction with magnesium. The reaction of magnesium with CCl_4 was confirmed by IR spectroscopy. IR spectra of samples (Mg/CCl_4 = 1/100) condensed at 12 and 70 K contain three new bands at 682, 896 and 912 cm^{-1} (Figure 5). Positions of bands are in good agreement with data[5] and relate to C_2Cl_6 (682 cm^{-1}), CCl_3 radical (896 cm^{-1}) and C_2Cl_4 (912 cm^{-1}). The product of insertion of magnesium atom into the C–Cl bond was not found.

The stability of magnesium atoms absorption in argon matrix with carbon tetrachoride can be caused by different activities of atoms and magnesium clusters or decomposition of metal clusters during interaction with polyhalomethanes.

The increase of absorption of magnesium atoms and the termination of cluster growth was observed earlier[12] in the Mg/MeCl system and related to higher activity of magnesium clusters. However, the addition of a methyl halide can result in the restriction of diffusion of magnesium atoms and a suspension of cluster growth without chemical reaction. We found earlier[6] that reaction of magnesium with MeCl proceeds only under UV irradiation.

Thus, we found the possibility of reaction of magnesium particles with carbon tetrachloride at 12–40 K and different behaviours of atoms and magnesium clusters in the reaction with CCl_4.

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