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Quantum-chemical study of the Grignard reaction mechanism within the cluster model of reaction center

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ABSTRACT

Structure and energy of EtBr adsorption complexes on (0001) magnesium crystal surface in the surrounding of adsorbed solvent molecules L (L = *n*-pentane, acetonitrile, THF, DMF, DMSO, pyridine, HMPTA) as well as the most probable routes of their transformation with the Grignard reagent (EtMgBr) formation were studied by applying the DFT method (B3PW91/6-31G(d)). Surface complexes were modeled using the Mg_{50}–EtBr, Mg_{50}–L and Mg_{50}–EtBr–L_6 clusters. Thermodynamics of elementary reactions of Grignard reagent formation in aprotic solvents on the magnesium surface was studied. It is shown that the overall kinetic rate of the Grignard reagent formation is defined by the competition between the adsorption and desorption steps depending on the donor properties of solvents, while the oxidation step itself is fast. The magnesium oxidation rate correlates with the adsorption energy of oxidizer on a magnesium surface and product's desorption energy to the reaction mixture volume.

1. Introduction

The Grignard reaction that was discovered more than a hundred years ago, is one of the most convenient methods of obtaining organometallic and coordination compounds. The reaction is, to a large extent, a heterogeneous process that includes reagents adsorption, chemical reaction itself and products' desorption from the metal surface.

The oxidative dissolution of metals, in particular, Grignard reagent formation (1), has been subject of numerous publications [1–8].

$$RX + Mg + L \rightarrow RMgX \cdot L, \quad (1)$$

where RX is an alkyl- or aryl halide, L is an aprotic solvent. Kinetic studies of the reaction were conducted in many investigations [8–15]. Products and intermediates of the reaction between magnesium and hydrocarbon halides were characterized [6,15–18], the morphology of a metallic surface after the reaction was investigated [19]. The scheme of free radical formation with the participation of surface metal atoms was suggested [20]. Still, despite numerous studies done, the overall reaction mechanism remains a subject of discussions.

Two different mechanisms for the Grignard reagent formation were suggested: the radical and molecular ones. Walborsky [3,20,21] and Garst [5,7,22,23] assume that an intermediate radical R· is formed as result of the decomposition of an alkylhalide radical-ion pair adsorbed on a magnesium surface in accordance with the scheme:

$$RX + Mg \rightarrow R^{\cdot} + Mg^{\delta+} \ldots X^{\cdot\delta-}. \quad (2)$$

While Walborsky proposes that transformations of R· species occurs only on a magnesium surface ("A" model), Garst assumes the possibility of radical diffusion to the reaction volume ("D" model) where it can participate in different processes: interaction with solvent and alkylhalide molecules, recombination etc.

Quantum chemical calculations conducted up to date [24–26] support the formation of active radical intermediates.

Some of the conducted studies show that a high-symmetry compact cluster of magnesium atoms can be present in the Grignard reagent molecule RMg_nX. Such substances have been detected experimentally while quantum chemical studies demonstrate their higher thermodynamic stability as compared to mono-organomagnesium derivatives. For example, calculations performed in [27,28] confirm higher stability of bi- and tetra-organomagnesium derivatives CH_3Mg_nX (n = 2, 4; X = F, Cl). Rather high Mg—Mg bonding energy was noted within these studies. The cluster nature of the Grignard reagent is also claimed in Ref. [29]. It was shown that cluster-type Grignard reagents are more energetically favorable as compared to RMgX species. Based on results of this study, the stability of Grignard reagents is a function of the number of magnesium atoms and their configuration and is changing as following:

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$$CH_3MgF < CH_3Mg_2F \leqslant CH_3MgF(Mg_2) < CH_3MgF(Mg)$$

Obviously, Grignard reagent stability is determined by a number of atoms within the metal clusters and their space configuration. Thermodynamic stability and reactivity of the Grignard reagents containing the polyatomic magnesium clusters were studied experimentally as well as theoretically [30]. Cryochemical metal-vapor synthesis of the Grignard reagent was conducted in inert matrix [31,32]. The IR-spectra of the obtained products contained characteristic absorption bands typical for Grignard reagents with Mg—Mg bonds. Quantum-chemical calculations [33] at a high level of theory (MP2/6-311++G(d,p); B3LYP/6-31++G(d,p); B3P86/6-311++G(d,p); BLYP/TZ94P) also confirm the possibility of the existence of polyorganimagnesium derivatives.

Despite the long history of research in this field, a number of questions regarding Grignard reagent formation mechanism remains up to now unanswered. In particular, the rate-determining step of the process as well as the stationary point position corresponding to a transition state were not yet finally established. Possible Grignard reagent formation pathways were studied in detail in a number of theoretical studies [24–26,34]. A quantum chemical study of magnesium and methyl chloride interaction within a cluster model of reaction center was recently conducted [34]. The B3LYP/6-31G(d, p) basis was used for the calculation, with the addition of 6-311 + G(d) for selected precise evaluations. The authors note that an attempt to find the energy and geometry of the transition state with only one magnesium atom was not successful. They assume that that a transition state may contain more than one metal atom.

This conclusion is in agreement with the results of studies [30–32], where magnesium clusters containing 18 and 21 atoms showed minimum activation energies of 10.3 and 9.8 kcal/mol, respectively. The transition state corresponded to the breach of the C—Cl bond in the methyl chloride molecule with a simultaneous coordination of formed fragments to neighboring magnesium atoms in a way that one of the atoms remains between these two fragments. However, the mechanism of halogen—carbon bond breach was not considered. Also the presence of an electron-donor solvent (Et_2O, THF) close to the reaction center was not taken into account when the transition state was calculated. A possible solvation of the transition state was also not considered.

The cluster model was used in some studies [24–26] where quantum chemical calculations of the mechanism and transition state in the Grignard reagent formation on the interaction of RHal (R = CH_3, Ph; Hal = F, Cl, Br) with magnesium clusters Mg_4–Mg_{10} were performed. In these studies molecular-ionic and radical reaction mechanisms were considered. According to the results of Porsev and Tulub [26], the direction of the process is determined by the position of the C—Hal bond vs. the plane of the cluster surface. Parallel position leads to radical-free RMgHal formation, while a perpendicular one is responsible for the radicals formation in a homolytic dissociation of the C—Hal bond. The UB3LYP/6-31 + G(d) and CASSCF/6-31 + G(d) methods were used in a space of roughly 1.4×10^4 spin-symmetrized functions. It was shown that an activation energy is strongly dependent on the number of atoms in the cluster and is always lower in the case of the radical reaction pathway in comparison to the ionic one. The activation energy decreases by a factor of almost two when the number of atoms increases from 4 to 10. This fact is in good agreement with the conclusions of a study [34] where it was shown that reliable activation energy estimates can only be achieved for clusters containing more than 20 atoms.

The results of the calculations show that the separated $CH_3^{\cdot}$ and $^{\cdot}Mg_nHal$ species can be formed by C—Hal bond breakage after achieving the energy plateau on the potential energy surface. Thus, the rate-determining stage of the process (1), thermodynamic parameters of its separate stages, structure of adsorbed complexes and reaction centers as well as the effect of the surface coordinated solvent on the reaction kinetics require special consideration.

In the present work a quantum chemical study of the reaction (1) on an ideal magnesium surface was performed using the model cluster Mg_{50}. The purpose of our study has been manifold: (I) to determine the rate-limiting step of the reaction, (II) to establish the structure and formation energy of the reagent, solvent and product complexes formed at the surface Mg_{50}—L (L = ethyl bromide, ethyl magnesium bromide, diethyl ether, THF, DMF, pyridine) and (III) to reveal the influence of the adsorbed solvent molecules on the activation energy of separate reaction steps as well as the overall reaction.

2. Methods of calculation

DFT with B3PW91 (6-31G(d) basis) functional was used for the calculation of ethylbromide, solvent and Grignard reagent adsorption parameters. The choice of functional and basis was based on the fact that they were successfully earlier used for studies of stable magnesium clusters [35] and the good agreement with the available experimental data which was achieved. The reaction center of the magnesium surface where transformation occurs was modeled by a molecular cluster consisting of 50 magnesium atoms (Fig. 1).

The Mg_{50} cluster was taken as a fragment of the ideal magnesium crystal (space symmetry group $p\frac{6_3}{m}mc$) with the parameters of a compact magnesium lattice: $a = b = 3.21$ Å; $c = 5.21$ Å. The calculations were carried out for the ethyl bromide (oxidizer) molecule surrounded by *n*-pentane, acetonitrile, tetrahydrofurane (THF), N,N-dimethylformamide (DMF), dimethylsulphoxide (DMSO), pyridine and hexamethylphosphortriamide (HMPTA) which acted as typical aprotic solvents. Initially, the geometry of the isolated molecules was optimized using the same theory level B3PW91/6-31G(d).

For the adsorption complexes Mg_{50}–L, where L is a molecule of the adsorbed aprotic solvent, several conformations were studied. The coordination of the oxygen or nitrogen atom to the central atom of the cluster surface layer was considered. Mg_{50}–L complexes were partially optimized in the course of the calculation: all atoms of an adsorbed molecule, coordination center on metal and nine atoms surrounding it (six in outer and three in a middle layer) were free. Similar methodology was used for the calculation of the desorption energy of an organomagnesium product. To describe the solvent effects, the models of adsorbed complexes were built in a way that ethyl bromide and product molecules were surrounded by six molecules of the solvent located at peripheral atoms of the cluster. Full energy and electronic structure calculations of complexes Mg_{50}–L_6 also included preliminary partial optimization of the system geometry where all atoms of aprotic solvents molecules as well as all magnesium atoms of outer and inner layers remained free (see Fig. 3 below).

In fact, Mg_{50}–L_6 can be considered as models of magnesium surface reaction centers. L–Mg_{50}–L_6 and EtBr–Mg_{50}–L_6 complexes were constructed as adsorbed molecules of an alkyl halide and solvent on an active metal center in a solvent field (Fig. 4). This model is considered as a rather precise reflection of the real interaction of components upon Grignard reagent formation on a magnesium surface.

The calculations were performed with the Gaussian-03 software [36]. The original program MOLTRAN [37] as well as specialized software, developed by one of the authors [37], were used for the interpretation of the results and for choosing of the initial geometry.