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A MO-theoretical Account for the Molecular Structure of the Grignard Reagent

Katsutoshi OHKUBO and Fumio WATANABE
Department of Synthetic Chemistry, Kumamoto University, Kurokami-machi, Kumamoto

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Concerning the molecular structure of the Grignard reagent,[1] two representative chemical formulae (RMgX and $R_2Mg \cdot MgX_2$) have been proposed by Ashby[2] and Dessy.[3] However, the structure has not yet been strictly established. In view of the association of the reagent in such a solvent as ether, the structure of the reagent can also be characterized by the following equilibrium:

$$\underset{\text{I}}{(RMgX)_2} \rightleftarrows \underset{\text{II}}{2RMgX} \rightleftarrows$$

$$\underset{\text{III}}{R_2Mg + MgX_2} \rightleftarrows \underset{\text{IV}}{R_2Mg \cdot MgX_2}$$

We intend to clarify which is the most plausible structure among the reagents expressed by the above chemical formulae. The extended Hückel method[4] was applied to the discussion of this feature. For the discussion from the energetic point of view, R and X were taken to be C_2H_5 and Cl respectively.

First, let us discuss the change in the total energy (E_{EH}) of the symmetrical dimer, $(RMgCl)_2$, with the variation in the angle of Cl–Mg–Cl (named by θ) at the fixed distance of Mg–Cl (2.39 Å), together with the variation in the distance of Mg–Cl at the fixed angle ($\theta = 90°$). As Fig. 1 indicates, the most energetically stable structure of the symmetrical dimer can be found in the configuration of $\theta = 130°$ (Mg–Cl=2.39 Å).

Second, it is of interest to discuss this problem with respect to the structure of the anti-symmetrical dimer, $R_2Mg \cdot MgX_2$. The Mg–Cl distance of 1.80 Å gives the most stable structure of the anti-symmetrical dimer, as may be seen from Fig. 2.

Third, the extended Hückel-MO calculations were also performed on RMgX ($R = C_2H_5$ and $X = Br$), which is considered to take two distinct configurations, *i.e.*, an angular-type RMgX[5] and a linear-type RMgX. These configurations are presented below, together with

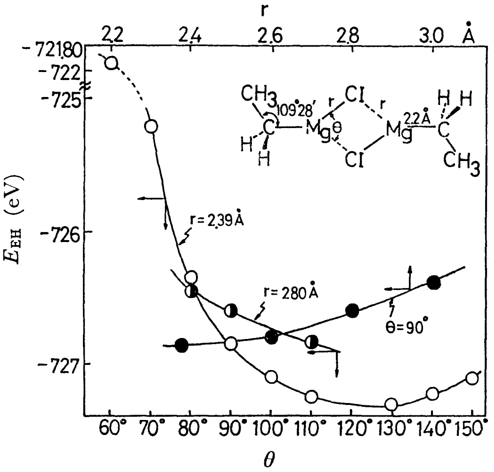

Fig. 1. Changes in the total energy (E_{EH}) of the symmetrical dimer, $(C_2H_5MgCl)_2$. (The bond length of Mg-C was cited from Ref. 8).

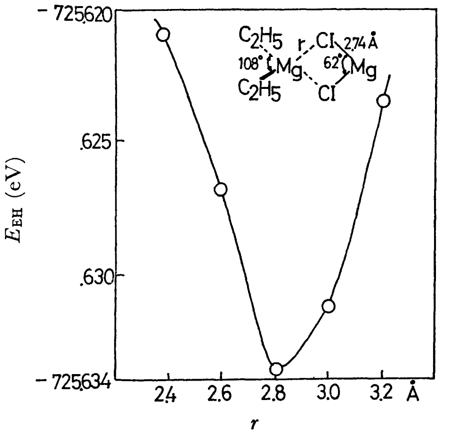

Fig. 2. Change in the total energy (E_{EH}) of the anti-symmetrical dimer, $(C_2H_5)_2Mg \cdot MgCl_2$. (The bond lengths and angles were cited from Ref. 9).

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[1] V. Grignard, *Ann. Chim. Phys.*, **24**, 433 (1901); Grignard has suggested the structure of the reagent by the chemical formula of RMgX.

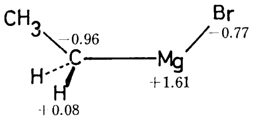
[2] E. C. Ashby, *Quart. Rev.* (London), **21**, 259 (1967), and the references cited therein.

[3] R. E. Dessy, *J. Org. Chem.*, **25**, 2260 (1960).

[4] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); *ibid.*, **40**, 2474 (1964). The Coulomb intergrals of Mg are −8.95 eV (for 3*s*) and −4.52 eV (for 3*p*).

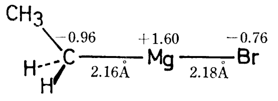
their atomic charges and total energies ($E_{\rm EH}$).

Angular-type RMgX



$E_{\rm EH} = -359.55$ eV

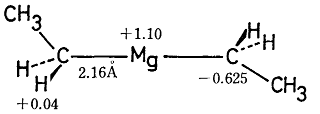
Linear-type RMgX



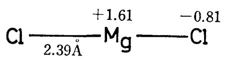
$E_{\rm EH} = -359.67$ eV

In view of the orientation effect of the solvent surrounding RMgX, the former structure of RMgX seems more possible than the latter one, although the value of $E_{\rm EH}$ in the latter structure is lower than that in the former. Accordingly, the angular-type RMgX ($R=C_2H_5$, $X=Cl$, and $E_{\rm EH} = -365.11$eV) was adopted for the structure of II.

Finally, we studied the system involving R_2Mg and MgX_2. Their atomic charges and total energies are shown below:



$E_{\rm EH} = -470.05$ eV



$E_{\rm EH} = -258.04$ eV

On the basis of the above discussions, the order of the energetic stability of the Grignard reagents expressed by I, II, III, and IV is as follows: II(−730.22eV)> III(−728.09eV)>I(−727.09eV)>IV(−725.63eV). In other words, the monomer-type structure of II is the most stable and the Schlenk's equilibrium reaction[6] between II and III can be accepted on the basis of some evidence.[7] However, the equilibrium mentioned before can be expected at a low concentration of the Grignard reagent (at least, below 0.3 mol/*l*). In the case of a high concentration, the reagent is apt to take a dimeric structure in a solvent, in particular in ether. Table 1 indicates the stabilization energy of RMgX as solvated by several solvents. Considering that RMgX exists as a monomer in tetrahydrofuran or triethylamine while, in ether, RMgX is present as a dimer at a high concentration, the number of the molecules interacting with the reagent may be different between the solvents according to the values of $E_{\rm EH}$ listed in Table 1.

TABLE 1. THE STABILIZATION ENERGY ($\Delta E_{\rm EH}$) IN THE SYSTEM OF RMgX AND SOLVENTS

RMgX[a] solvated	Mg–O or Mg–N (Å)	∠CMgO or ∠CMgN	$\Delta E_{\rm EH}$ (eV)	$\Delta E_{\rm calcd}$[c] (eV)
RMgX mono-etherate[b]	2.04	110°	1.13	1.19
RMgX mono-tetrahydrofuranate	2.04	110°	1.06	—
RMgX mono-trimethylaminate	2.1	110°	1.18	0.87

a) $R=C_2H_5$ and $X=Br$.

b) Methyl derivative was used for the simplicity of computations.

c) This stands for the stabilization energy estimated from a rough approximation: $\Delta E_{\rm calcd} = e^2(1-1/\varepsilon)/2a$, where a is taken to be 5.0 Å and ε is the dielectric constant of the solvent. The assumed value of 5 Å was estimated from the ionic radii of Mg and Br and van der Waals radius of CH_3CH_2 group.

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5) R. E. Rundle and L. J. Guggenberger, *J. Amer. Chem. Soc.*, **86**, 5344 (1964).

6) W. Schlenk and W. Schlenk, Jr., *Ber.*, **62**, 920 (1929).

7) E. C. Ashby and W. E. Berker, *J. Amer. Chem. Soc.*, **85**, 118 (1963).

8) E. Weiss, *J. Organometal. Chem.*, **4**, 101 (1965).

9) H. Schibilla and G. T. Le Bihan, *Acta Cryst.*, **23**, 332 (1967).