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A CNDO Treatment of the Strucures of the Grignard Reagents

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Although many experimental studies of the structures of Grignard reagents have been accumulated[1], there have been few approaches from the point of view of the molecular orbital consideration of the structures of these organomagnesium compounds.[2]

The purpose of this note is to examine the plausible

1) E. C. Ashby, *Quart. Revs.* (London), **21**, 259 (1967); G. E. Parris and E. C. Ashby, *J. Amer. Chem. Soc.*, **93**, 1206 (1971).

2) K. Ohkubo and F. Watanabe, This Bulletin, **44**, 2869 (1971).

structures of Grignard reagents on the basis of their energies obtained by the CNDO/2 method[3], which does not consider the outer d-AO of the Mg atom. The following monomer-dimer equilibrium has been observed as the composition of Grignard reagents in diethyl ether[1]:

$$\underset{\text{(III)}}{R\text{-}Mg\langle{}^{X}_{X}\rangle Mg\text{-}R} \rightleftharpoons \underset{\text{(I)}}{2RMgX} \rightleftharpoons \underset{\text{(IV)}}{R\text{-}Mg\langle{}^{X}_{R}\rangle Mg\text{-}X}$$

$$\underset{\text{(VI)}}{\left(X\text{-}Mg\langle{}^{R}_{R}\rangle Mg\text{-}X\right)}$$

$$\rightleftharpoons \underset{\text{(II)}}{R_2Mg} + MgX_2 \rightleftharpoons \underset{\text{(V)}}{{}^{R}_{R}\rangle Mg\langle{}^{X}_{X}\rangle Mg}$$

$$\underset{\text{(VII)}}{\left({}^{R}_{R}\rangle Mg\text{-}X\text{-}Mg\text{-}X\right)}$$

$$\underset{\text{(VIII)}}{\left({}^{R}_{R}\rangle Mg\text{-}Mg\langle{}^{X}_{X}\right)}$$

For the sake of simplicity, the smallest molecules showing the essential properties are chosen that is R=CH_3 and X=Cl. The geometries of the above compounds are taken to be Mg–Cl=2.5 Å, Mg–C=2.2 Å, and Mg–Mg=2.8 Å(bridge type)[6] through all the compounds considered (the adopted valence angle for R–Mg–R, R–Mg–X, and X–Mg–X in dimers and bent monomers are determined by the use of the above atomic distances).

The relative energies of various compounds appearing in the above equilibrium are illustrated graphically in Fig. 1, in which the total energies of linear and bent CH_3–Mg–Cl monomers are doubled for the sake of comparison with those of the dimeric species, and in which the sum of the energies of the linear $Mg(CH_3)_2$ and $MgCl_2$ is taken as a reference for the energy di-

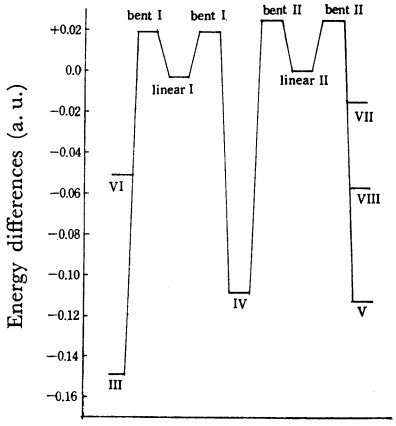

Fig. 1. The energy diagram of various compounds appearing in the equilibrium of Grignard reagents.

Table 1. The calculated results of the net charges of atoms and energy differences

Compounds	Net charges[a]			Energy differences ΔE (a. u.)
	Mg	R=CH_3	X=Cl	
MgR_2 linear (II)	+0.562	−0.281	——	0.0
MgX_2 linear (II)	+0.826	——	−0.413	
RMgX linear (I)	+0.689	−0.279	−0.410	+0.003
MgR_2 bent (II)	+0.603	−0.301	——	+0.025
MgX_2 bent (II)	+0.842	——	−0.421	
RMgX bent (I)	+0.711	−0.339	−0.401	+0.019
${}^{R}_{R}\rangle Mg^1\text{-}X^1\text{-}Mg^2\text{-}X^2$ (VII)	+0.439(+0.935)	−0.347	−0.309(−0.385)	−0.014
$X\text{-}Mg\langle{}^{R}_{R}\rangle Mg\text{-}X$ (VI)	+0.594	−0.183	−0.421	−0.051
${}^{R}_{R}\rangle Mg^1\text{-}Mg^2\langle{}^{X}_{X}$ (VIII)	+0.336(+0.548)	−0.135	−0.306	−0.057
$X^1\text{-}Mg^1\langle{}^{R^1}_{X^2}\rangle Mg^2\text{-}R^2$ (IV)	+0.602(+0.464)	−0.109(−0.274)	−0.420(−0.264)	−0.109
${}^{R}_{R}\rangle Mg^1\langle{}^{X}_{X}\rangle Mg^2$ (V)	+0.208(+0.884)	−0.301	−0.244	−0.113
$R\text{-}Mg\langle{}^{X}_{X}\rangle Mg\text{-}R$ (III)	+0.498	−0.275	−0.223	−0.149

a) The values in parentheses are referred to the atoms with the number 2.

3) J. A. Pople, D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **43**, s 129 (1965); J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966); D. P. Santry and G. A. Segal, *ibid*, **47**, 158 (1967).

4) The SCF procedures for many solvated compounds did not converge.

5) Some results for the energy differences in solvated species which are calculated to be considerably unstabilized by the coordinated water molecules, are given as as follows:

$$\left[{}^{R}_{R}\rangle Mg\langle{}^{OH_2}_{OH_2} + {}^{H_2O}_{H_2O}\rangle Mg\langle{}^{X}_{X}\right]\left[{}^{H_2O}_{X}\rangle Mg\langle{}^{X}_{R}\rangle Mg\langle{}^{R}_{OH_2}\right]$$

ΔE 0.0 −0.068

$$\left[{}^{H_2O}_{R}\rangle Mg\langle{}^{X}_{X}\rangle Mg\langle{}^{R}_{OH_2}\right]$$

−0.081 (a. u.)

where the energy reference is the one-half of the sum of the total energies of the two monomers in the first bracket. From the above results, the solvated states seem to be situated in the narrower energy region than the isolated state as in Fig. 1.

6) These distances are taken as the sum of the covalent radius estimated by Prithard and Skinner (*Chem. Rev.*, **55**, 177 (1955)).

agram (in atomic units). The dimer types are energetically more favored than the monomer types, as is indicated in Fig. 1. The calculated results for the net charge of the atoms are presented in Table 1, together with their energy differences. It seems in this table that the net charges of Mg atoms coordinated by three or four atoms in dimers are generally smaller than in monomers, and that these excess charges are transferred from the bridge-head atoms or groups. That is, the stability of the dimer forms, especially of the bridge structures, is mainly dependent on the electro-dificient character of the magnesium atom as well as on the electron-rich character of the bridge-head atoms and the methyl groups which act as the electron donor. The exchange of alkyl groups can be explained by the existence of an intermediate mixed alkyl-halogen bridge structure(IV), as has suggested earlier.[1] Figure 1 indicates that the stability of this mixed bridged dimer is considerably larger than those of monomers; this is in accordance with the above experimental considerations. It should be noted, however, that our results are obtained by neglecting the solvent effects,[4] and also that the experiment shows that the dimer forms are present in equilibrium states in "weak" solvents such as diethyl ether, and not in "strong" solvents such as tetrahydrofuran. Thus, it may be said that both the experimental and calculated results prove that the mixed structure is favored at the monomer-dimer equibrium in the case of weak interaction with solvent molecules;[5] also, there is no doubt that the solvent strongly influences the structures of Grignard reagents.

For the solvated state in these compounds, further treatments are desired.

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