Journal of Organometallic Chemistry, 243 (1983) 123–129
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

MECHANISM OF THE SOLID-PHASE REACTION OF MAGNESIUM WITH ORGANIC HALIDES

G.B. SERGEEV *, V.V. ZAGORSKY and F.Z. BADAEV

Department of Chemistry, Moscow State University, Moscow 117234 (U.S.S.R.)

(Received August 19th, 1982)

Summary

Low-temperature solid-phase reactions of magnesium with monosubstituted benzene halides and primary alkane halides have been investigated. On the basis of EPR and chromatographic data on the reactions products it was found that the carbon–halogen bond energy substantially influences the mechanism of formation of Grignard reagents.

Reactions of atomic magnesium with organic halides in the solid phase result in the formation of unsolvated Grignard reagents [1–3]. The analysis of the EPR spectra indicates the formation of free radicals and presumably of ion-radicals in the reactions of magnesium atoms with organic chlorine derivatives at low temperatures [4,5].

In the present work the paramagnetic particles, generated in the low-temperature solid phase reactions of magnesium with monosubstituted fluoro-, chloro-, bromo- and iodo-alkanes and -benzenes, with carbon–halogen bond energies varying over a wide range from 54 to 122 kcal/mol [6], are investigated by means of EPR technique. In our view the nature of the intermediates generated in the formation of unsolvated Grignard reagents is strongly dependent on the bond strength. The increase in carbon–halogen bond energy makes the abstraction of the halogen atom by magnesium less probable and the reaction appears to occur via an ion-radical mechanism.

Analysis of the reaction products supplies us with valuable information on the nature of intermediates generated in the process. Since free radicals are formed during the formation of the Grignard reagents, a considerable amount of their recombination and disproportionation products can be expected. Therefore, we investigated the reaction products composition relative to the carbon–halogen bond strength in the initial compound by GL and GA chromatography.

0022-328X/83/0000–0000/$03.00

Experimental

The reactions were performed by cocondensation of atomic magnesium and a 50–100-fold excess of organic reagents onto a surface cooled with liquid nitrogen according to the molecular beam method. The EPR spectra were recorded following the technique described earlier [4].

Results and discussion

EPR spectra at a *g*-factor at about to 2 characteristic of free organic radicals were recorded for all the investigated systems at 77 K. The EPR spectra of the condensed magnesium with fluorobenzene (carbon–halogen bond energy 122 kcal/mol) and with chlorobenzene (94 kcal/mol) show only a singlet with a half-width of 10 ± 1 G (Fig. 1a). In the case of bromobenzene (75 kcal/mol) the EPR spectrum represents a wide signal where components of a triplet with a distance of 18 ± 1 G between the lines are observed (Fig. 1b). Each component of the main triplet splits into an additional three components with a distance of 7 ± 1 G between the lines. The EPR spectrum of the magnesium condensed with iodobenzene (63 kcal/mol) is similar to that of magnesium with bromobenzene but is less well resolved. The spectra of the magnesium condensed with bromo- and iodo-benzenes were compared with litera-

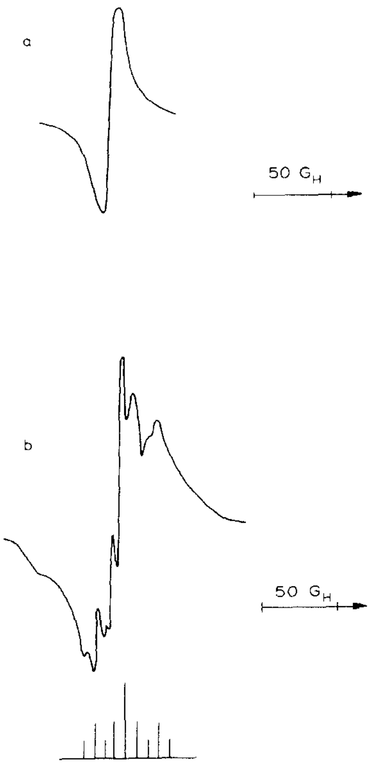


Fig. 1. The EPR spectra of condensates at 77 K: a) magnesium with fluorobenzene; b) magnesium with bromobenzene.

ture data [7,8] and identified with the EPR spectrum of phenyl radical generated upon abstraction of a halogen atom from the initial benzene halide with magnesium. These spectra also corresponded to that of phenyl radicals obtained by irradiation of condensed magnesium and chlorobenzene with unfiltered UV light and by joint condensation of sodium and chlorobenzene vapours. The EPR spectrum of magnesium condensed with bromobenzene (Fig. 1b) shows the superposition on the multiplet of another broad signal, which can be apparently assigned to the radicals of cyclohexadienyl type generated in such systems [8] upon addition of phenyl radical to benzene halide.

Two types of signals were also recorded in the systems of magnesium condensed with primary alkane halides. The EPR spectrum in magnesium-iodobutane (54 kcal/mol) and magnesium-bromobutane (68 kcal/mol) systems represent a sextet with a distance of 22 ± 1 G between the lines (Fig. 2a). In the magnesium-fluorooctane system (107 kcal/mol) a sextet with a distance of 22 ± 1 G between the lines and a superimposed singlet with a half-width of 10 ± 1 G (Fig. 2b) was observed. A similar EPR spectrum was recorded earlier in the magnesium-chlorobutane system (81 kcal/mol) [4,5]. The sextet in the EPR spectra belongs to the n-alkyl radical. The assignment is confirmed by comparison of our spectra with literature data [9]. Further evidence can be obtained on analysing the EPR spectra of radicals formed upon irradiation of primary monochloroalkanes with unfiltered ultraviolet light at 77 K. The EPR spectra of n-alkyl radicals generated in photolysis [9] are similar to that obtained for the systems of magnesium condensed with bromo- and iodo-butanes.

The singlet in the EPR spectra of magnesium condensed with fluoro and chloro derivatives can be assigned to a ion-radical pair of $[\mathrm{RX}^{\dot{-}}\ \mathrm{Mg}^{\dot{+}}]$ type. The absence of

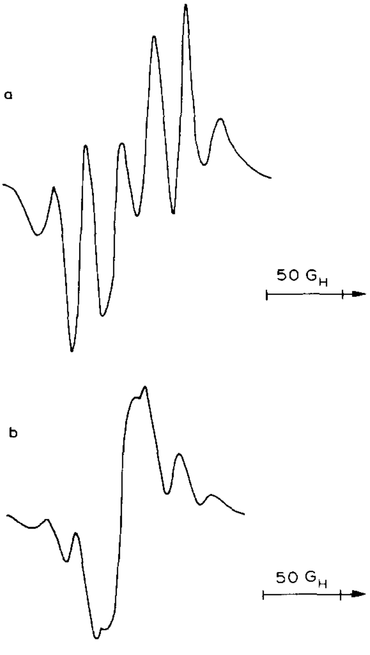


Fig. 2. The EPR spectra of condensates at 77 K: a) magnesium with bromobutane; b) magnesium with fluorooctane.

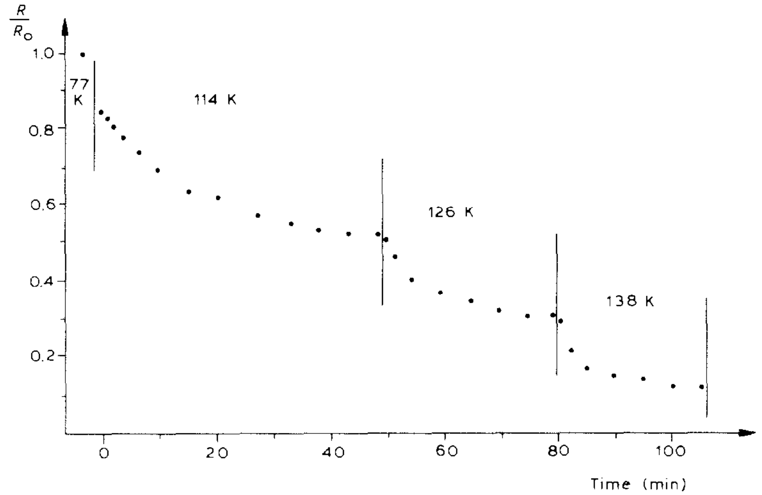


Fig. 3. Dependence of the relative concentration of paramagnetic particles in the condensate of magnesium with chlorobenzene on temperature and time.

hyperfine structure in the case of the ion-radical pair seems to be caused by exchange processes. This assumption is in a good agreement with the results obtained upon condensation of chloro, bromo and iododerivatives onto a predeposited film of compact magnesium. In this case a greater stabilization of the ion-radical pairs due to the delocalization of a positive charge on the metallic film may be expected. Indeed, the EPR spectra of such samples showed only the singlet whose half-width fitted within experimental error the half-width of the singlet obtained in the EPR spectra of magnesium condensed with organic fluoro and chloro derivatives.

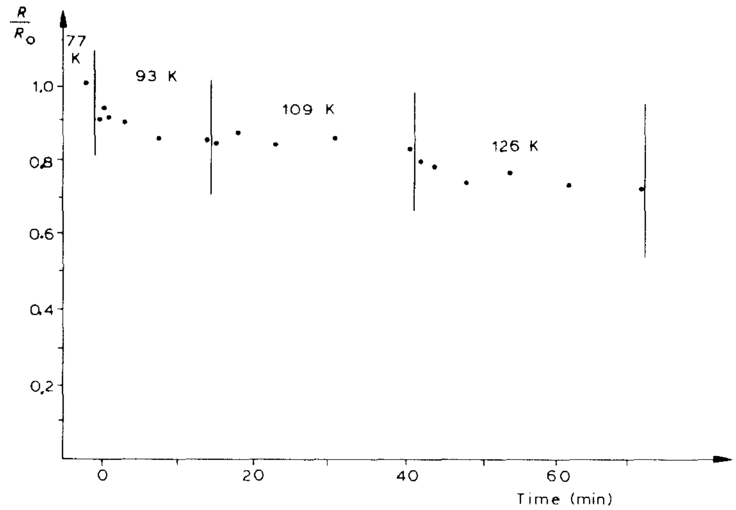


Fig. 4. Dependence of the relative concentration of paramagnetic particles in the condensate of magnesium with iodobenzene on temperature and time.

The experiments with the heated sample provide information concerning the stability and transformations of paramagnetic particles. Heating the magnesium condensed with chloro- and iodo-benzenes and iodobutane did not affect the shape of the initial EPR spectra. Increasing the temperature to 93 K gradually reduced the intensity of the singlet in the EPR spectrum of the magnesium condensed with chlorobenzene. Starting from 110 K the paramagnetic particles rapidly decay and their decay kinetics is presented in Fig. 3. Unlike chlorobenzene in the case of iodobenzene the phenyl radical signal intensity decreases upon increasing the temperature to 70–75% of the initial signal intensity (Fig. 4). This value remains constant up to 170 K. This constancy over a wide range of temperatures can be attributed to the fact that the decay of the active phenyl radicals [8] is compensated by their formation due to the diffusion of magnesium atoms and aggregates and their reactions with organic halides molecules.

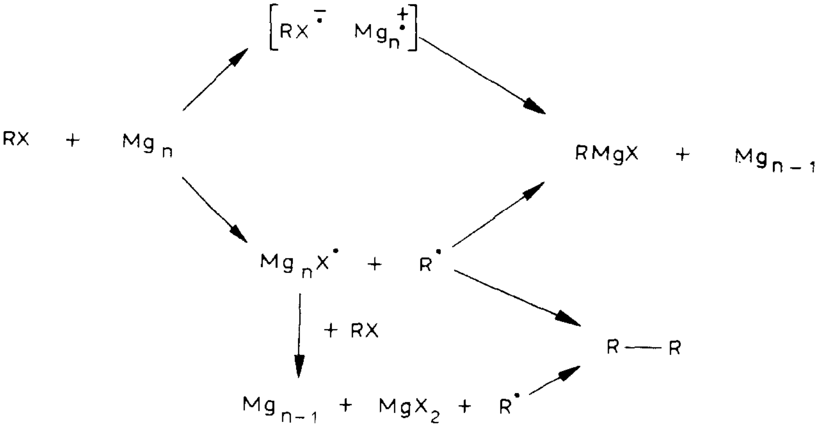
If formation of a Grignard reagent occurs directly via formation of radical, $R^\cdot$, relatively high yields of the Wurtz reaction products R–R can be expected. But if the process proceeds through addition of magnesium to the carbon–halogen bond in an ion-radical pair, then the formation of the Wurtz reaction product is, in our view, unlikely. An analysis of the products of the reaction of magnesium with iodobutane by GA and GL chromatography revealed a decrease in the relative yield of octane with increasing magnesium content in the system from 60–70% (Mg:RX ratio = 1:1000) to 5–6% (reagents ratio 1:10). This may be explained by greater stabilization of ion-radical pairs on aggregates of magnesium atoms, which facilitates the formation of the Grignard reagent. On the contrary, magnesium atoms, more active than aggregates, are able to abstract a halogen atom from the initial organic halide derivative yielding alkyl radicals. In this case the Wurtz reaction occurs along with the formation of the Grignard reagent. The absence in the EPR spectra of the singlet characteristic of ion-radical pairs in the system of magnesium condensed with iodobutane is most probably due to the weakness of the carbon–iodine bond. Magnesium adds to this bond immediately after formation of an ion-radical pair. The relative yield of octane in the magnesium-chlorobutane system (reagents ratio from 1:1000 to 1:10) is constant 3–5%. In this case the reaction probably occurs mainly through the ion-radical mechanism. The low radical yield leading to the low yield of the products of the Wurtz reaction seems to be related to the high strength of the carbon–chlorine bond.

With fluorobenzene, which is characterized by the strongest carbon–halogen bond (122 kcal/mol) a Wurtz reaction product, diphenyl, was not detected, unlike the case for bromobenzene and iodobenzene.

The investigation of the paramagnetic particles generated in the reactions of magnesium with organic halides, suggest that radicals and ion-radicals are the most probable intermediates formed in the process. The mechanism of the reaction seems to be dependent on the nature of the halogen derivative, namely on the carbon–halogen bond strength. An increase in the carbon–halogen bond strength promotes an ion-radical mechanism for formation of the unsolvated Grignard reagent. It must be borne in mind that the electron affinity of aromatic halides is much higher than that of alkyl halides, which also facilitates formation of ion-radical pairs through transfer of an electron from magnesium to an organic molecule.

The chromatographic data presented reveals that aggregation of metallic atoms strongly affects the nature of intermediates formed in the reaction of magnesium with organic halides. An increase in the degree of aggregation of magnesium favors the formation of ion-radical pairs. The EPR data also supports this observation. In the EPR spectra of magnesium condensed with fluorooctane and chlorobutane the relative intensity of the singlet assigned to an ion-radical pair increases with increasing magnesium content in the system. Therefore, in order to suppress the side Würtz reaction in the low-temperature formation of the Grignard reagent, the magnesium content in the system should be increased slightly, since a too large a degree of aggregation leaves a certain amount of magnesium unreacted.

The data obtained in the present work suggests a general scheme of formation of the unsolvated Grignard reagents, as was previously proposed for chloroalkanes [5]:



The modern concept of the "classical" formation of a Grignard reagent in ether solvents also involves radical and ion-radical mechanisms [10]. The concept is based on the indirect studies of the intermediate nature. Besides, the organic halide-metallic magnesium-ether systems, being heterogeneous, are very difficult to study. In such a system the ether is not merely a solvent and its involvement is not completely clear. To elucidate the mechanism of the formation of the Grignard reagent it is important first of all to determine which active intermediates are generated in the first stage of the reaction. This information can be obtained by studying the mechanisms of the low-temperature reactions of atomic magnesium with organic halides in the absence of an ether solvent. The investigation reported here demonstrates that the mechanisms of the reactions conducted under various conditions and in the presence and absence of a solvent are very similar. In the absence of a solvent and at low temperatures magnesium becomes very active and reacts with organic polychlorine [4] and fluorine [3] derivatives.

The formation of the Grignard reagent during joint condensation of magnesium with organic halides at low temperatures allows comparison under similar conditions of the reaction mechanisms of magnesium with all halides including fluorobenzene, and reveals the crucial influence of the carbon–halogen bond strength in the initial compound on the competitive reactions via radical and ion-radical mechanisms.

References

1 P.S. Skell and J.E. Girard, J. Amer. Chem. Soc., 94 (1972) 5518.

2 J.E. Girard, Ph.D. Thesis, Pennsylvania State University, University Park, Pa., 1971.
3 G.B. Sergeev, V.V. Smirnov and F.Z. Badaev, J. Organometal. Chem., 224 (1982) C29.
4 G.B. Sergeev, V.V. Smirnov and V.V. Zagorsky, J. Organometal. Chem., 201 (1980) 9.
5 G.B. Sergeev, V.V. Smirnov and V.V. Zagorsky, Vestnik Moskovskogo Universiteta, seriya khimicheskaya, 21 (1980) 257.
6 Energii razryva khimicheskikh svyazey. Potentzialy ionizatzii i srodstvo k elektronu. Pod redaktziey Kondratieva V.N.: Nauka, 1974.
7 V.A. Tolkachev, I.I. Chkheidze and N.Ya. Buben, Zhurnal structurnoi khimii, 3 (1962) 709.
8 J.E. Bennet, B. Mile and A. Thomas, Proc. Roy. Soc., A293 (1966) 246.
9 P.B. Ayscough and C. Thomson, Trans. Faraday Soc., 58 (1962) 1477.
10 H.M. Walborsky and M.S. Aronoff, J. Organometal. Chem., 51 (1973) 31.