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REACTIONS OF ATOMIC MAGNESIUM IN THE BASIC STATE WITH ORGANIC CHLORINE DERIVATIVES AT LOW TEMPERATURES *

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Summary

Low-temperature solid-phase reactions of atomic magnesium in the basic state with a number of aliphatic monochlorine derivatives, chlorobenzene, carbon tetrachloride and 1,2-dichloroethane, have been investigated. The nature of the intermediate particles is discussed, the effect of the phase state of a frozen hydrocarbon on its reactivity examined, and the mechanisms of reactions with the participation of radicals and ion radicals proposed.

The high reactivity of metal atoms at 77 K was first discovered by N.N. Semenov and A.I. Shalnikov in the reaction of cadmium and sulphur [1]. One of the most active metals in the atomic state is magnesium which was used to initiate low-temperature polymerization [2]. Reactions of magnesium with halogen derivatives at low temperatures result in the formation of unsolvated Grignard reagents [3,4]. The object of the work described here was to ascertain the mechanism of the reactions of magnesium atoms in the basic state with organic chlorine derivatives at low temperatures.

Experimental

All experiments were conducted in vacuum. Organic reagents, after drying and purification, were freed of dissolved gases by multiple freezing and gas evacuation with a vacuum of 10^{-4} mm Hg. Samples were prepared by joint condensation of magnesium and a 10—100-fold excess of organic substance onto the surface cooled with liquid nitrogen. A condensation rate of about 10^{16} molecules sec^{-1} cm^{-2} ensured the absence of reactions in the gaseous phase [5]. Throughout the condensation time, varying from 10 minutes to 4 hours, the vacuum maintained in the reactor was 10^{-4} mm Hg. Atomic magnesium was ob-

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* Dedicated to Prof. G.A. Razuvaev on the occasion of his 85th birthday on August 23rd, 1980.

tained by slow evaporation from a quartz crucible at temperatures of 620—670 K.

A schematic diagram of the reactor used to obtain EPR spectra is shown in Fig. 1. The reaction mixture was condensed onto the surface of a thin-walled mobile part of the reactor. The sample was cooled with a flow of nitrogen vapour. After the condensation the mobile part was lowered into the resonator of the EPR spectrometer (Varian E-3). The temperature was maintained with the help of a heater placed in the nitrogen flow. All spectra were recorded at 77 K.

A schematic diagram of the reactor used to record infrared spectra is shown in Fig. 2. The reaction mixture was condensed onto one of the faces of a mirror-smooth copper parallelepiped. After the condensation the parallelepiped was rotated by 180°, and the spectrum was recorded in the reflection mode. The accuracy of the temperature control during the IR and EPR measurements amounted to ±2 K.

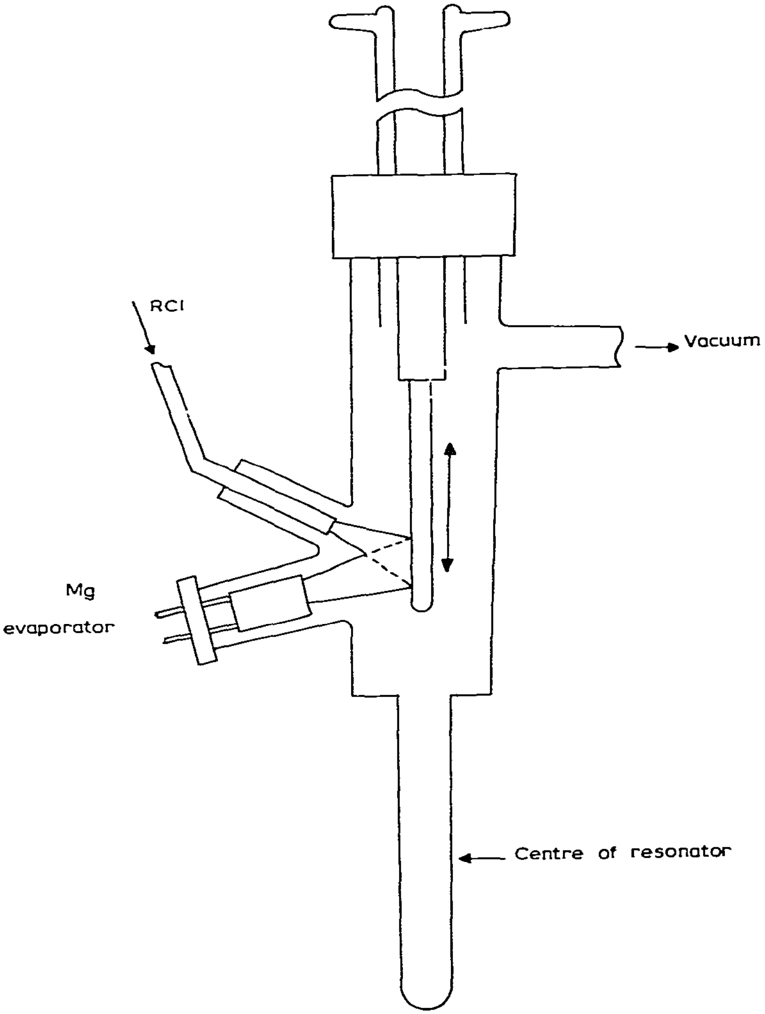


Fig. 1. Reactor for low-temperature EPR spectroscopy.

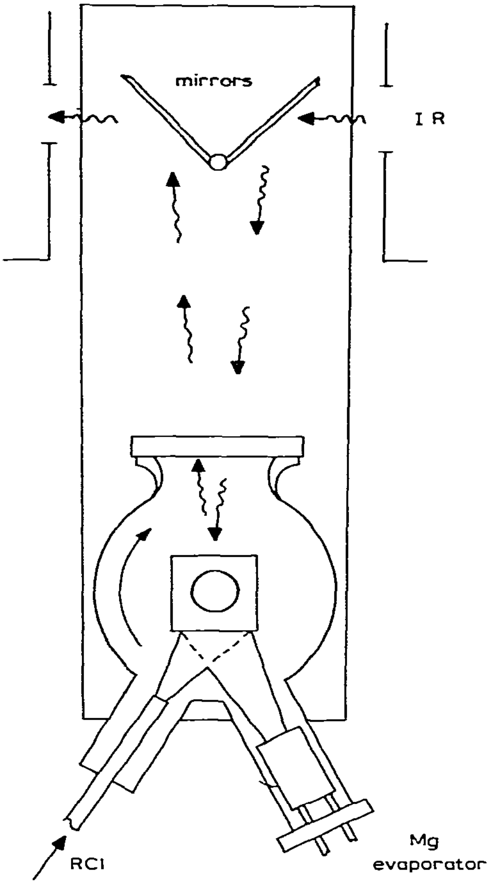


Fig. 2. Reactor for low-temperature IR spectroscopy.

Calorimetric measurements were conducted in a differential microcalorimeter. Each cell contained 40 thermoelectric copper—constantan junctions. The volume of the sample was 0.05 cm^3, the heating rate was 0.6 deg min^{-1} and the sensitivity of the microcalorimeter was 10^{-3} J.

The products of reaction mixture decomposition by water were analyzed using GLC. Decomposition was performed by condensing excess water vapour onto a film of reaction mixture cooled down to 77 K and storing it for 3—5 hours. Control experiments showed that under these conditions atomic magnesium and the products of its interaction with chlorine derivatives react quantitatively with water.

Results and discussion

Our experiments have shown that various organic chlorine derivatives (chloroalkanes, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, 1,2-dichloroethylene, tetrachloroethylene, carbon tetrachloride, chlorobenzene) react with magnesium in the films obtained by joint condensation at temperatures below the melting point of the samples. In the case of monochlorine derivatives the process was observed to be taking place by the disappearance on heating of the initial chestnut colour of the films caused by the presence of metal atoms. Decolouration of the films could indicate that an organomagnesium compound is being formed. To check this assumption the reaction mixtures were decomposed with water after storage at different temperatures. Storage of a 1-chloropentane-magnesium mixture at temperatures below that of the disappearance of colouration results in the formation of a slight amount of pentane, the product of the interaction between the Grignard reagent and water. If before treatment with water the samples are stored at a temperature above that of decolouration the yield of pentane exceeds 90%. The dependence of pentane yield on storage temperature is shown in Fig. 3. It was also observed that 2—3% of decane, the product of the Wurtz reaction, is formed. These data make it possible to unambiguously associate the change in the colouration of the samples with the low-temperature formation of organomagnesium compounds.

The formation of organomagnesium compounds was additionally confirmed with the help of infrared spectroscopy. Valence vibrations of the C—Mg bond in Grignard reagents obtained by conventional methods in solutions of ester and tetrahydrofuran lie in the region of 500—530 cm^{-1} [6]. The spectra of samples obtained by joint condensation of magnesium and chloroalkanes at 77 K do not show any new absorption bands in the 450—600 cm^{-1} region. With an increase in the temperature of films containing, e.g., n-chlorooctane and magnesium an absorption band with a maximum at 560 cm^{-1} is observed to appear, and its intensity increases parallel to the variation of sample colouration. The new absorption band does not belong to unstable intermediate products because it is preserved at 293 K in a solution of the obtained solid compound in the excess of chlorooctane. When the film or the solution is treated with water, the absorption at 560 cm^{-1} irreversibly disappears, and octane is formed. These data make it possible to assign the 560 cm^{-1} band to the C—Mg bond in the organomagnesium compound.

The film obtained by the joint condensation of magnesium with 1,2-dichloroethane is of greyish-brown colour and loses its colouration completely at 170 K. No formation of an organomagnesium compound was observed. The disappearance of colouration is accompanied by a sharp deterioration of the

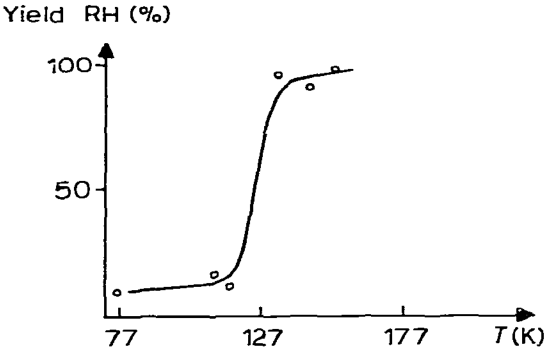


Fig. 3. The yield of n-pentane (with respect to magnesium) vs. temperature.

vacuum, which is associated with the formation of volatile products. Ethylene was identified in the gaseous phase by means of IR spectroscopy and GC.

Joint condensation of magnesium with carbon tetrachloride results in the formation of white films that do not contain any atomic magnesium. The reaction takes place directly at the moment of condensation. This has been additionally proved by the decolouration of the translucent brown film of metallic magnesium on the glass surface when carbon tetrachloride is condensed on it at 77 K. In the infrared spectrum of the reaction mixture after condensation (Fig. 4) intense bands from the stable reaction products, tetrachloroethylene (912 cm^{-1}) and hexachloroethane (683 cm^{-1}), were found [7]. No new bands were detected in the region of organomagnesium compounds absorption in the samples containing an excess of carbon tetrachloride. In the samples containing an excess of magnesium a broad band with a maximum at 565 cm^{-1} appeared. Its intensity was not nearly so high as that of the C—Mg bond vibration band observed in the reaction of magnesium with chloroalkanes. The 565 cm^{-1} band in this case is possibly associated with an absorption of magnesium chloride in a matrix of carbon tetrachloride [8] or with the formation of small amounts of organomagnesium compound. Reaction at 77 K is indicative of a greater, in comparison with chloroalkanes, reactivity of carbon tetrachloride. By contrast, at room temperature chloroalkanes are much more reactive than carbon tetrachloride, which practically does not react with magnesium. It is thus seen that the reactivity of organic chlorine derivatives under the general conditions of obtaining Girgnard reagents and at low temperatures in solid phase is determined by various factors. In low-temperature reactions exothermal phase transitions acquire a great importance. This is most clearly manifested in the case of n-alkyl chlorides. Fast reactions of organomagnesium compound formation (3—5 sec) take place only when glass—crystal type of phase transition is possible in the chlorine derivative. The temperatures of reactions and phase transitions are shown in Table 1.

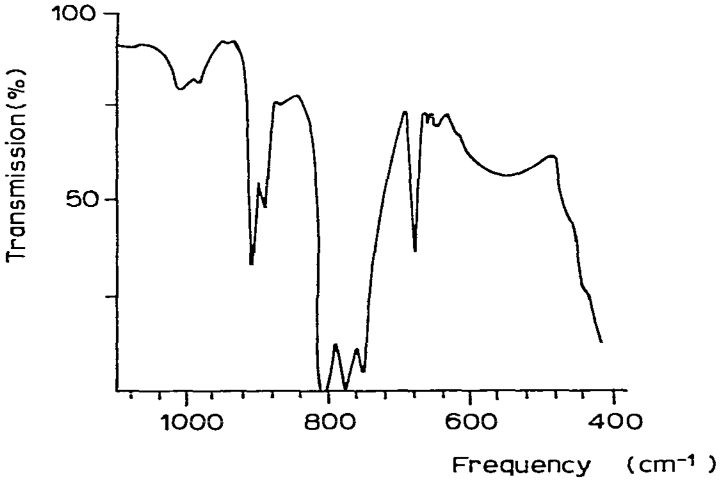


Fig. 4. IR spectrum of CCl_4-magnesium (50 : 1) film at 83 K.

TABLE 1

TEMPERATURES OF REACTIONS AND PHASE TRANSITIONS

Substance	Temperatures (K)			Notes
	phase trans.	melting	fast reaction	
C_4H_9Cl	113	150	115	Fast reaction with a quantitative yield
$C_5H_{11}Cl$	127; 153	174	126	
$C_7H_{15}Cl$	180	203	178	Sharp acceleration of reaction, then slow reaction until melting
$C_8H_{17}Cl$	—	209	—	Slow reaction until melting
C_6H_5Cl	—	228	—	
CH_2ClCH_2Cl	—	238	—	
CCl_4	—	250	—	Reaction in the course of condensation at 77 K

The data presented in Table 1 show that there is a connection between fast reactions and phase transitions in the system, which was previously noted for low-temperature halogenation and hydrohalogenation [9] and solid-phase polymerization [2]. The temperature of the fast reaction coincides with the temperature of phase transition as determined microcalorimetrically. In the case of chlorobenzene, chlorooctane and 1,2-dichloroethane, in which there are no exothermal transitions, the reaction proceeds at a moderate rate over a broad temperature range and terminates at the moment of sample melting. The role of phase transition consists in ensuring the mobility of the reacting particles, necessary for organomagnesium compounds to be formed.

Fast reaction of magnesium with organic chlorine derivatives also occurs at the moment of condensation when a certain critical film thickness is reached. For instance, if in the joint condensation of magnesium with chlorooctane the thickness of the film on the glass surface exceeded 0.2 mm a fast reaction took place. In appearance it is similar to reactions observed at the moment of phase transitions in other chloroalkanes. For 1,2-dichloroethane the critical film thickness is about 10^{-2} mm. A similar phenomenon was observed in the joint condensation of sulphur and cadmium vapour [1]. This is associated with the fact that at the moment of sample preparation the temperature on the surface of relatively thick (10^{-1}—10^{-2} mm) films of organic compounds whose heat conductivity is not high can, because of the heat of condensation, be much higher than 77 K. To explain the observed phenomena one can apply the model proposed for solid-phase hydrobromination of ethylene, which combines the features of chain and thermal processes. In our case, the possibility for chain reactions to be taking place is associated with the formation of free radicals in the system, recorded by the EPR method. Under the conditions of insufficient heat removal at a certain film thickness, individual reaction chains can arise on the surface, accompanied by a thermal wave [9,10]. The thermal wave releases the previously stabilized active particles from the "traps", and this results in the reaction proceeding at a rate close to that of an explosion.

Active particles that have been stabilized in the matrix of the organic chlorine derivative seem to be energetically inequivalent. This is indicated by the shape of the kinetic curves for organomagnesium compound accumulation shown in Fig. 5. It is difficult to measure the reaction kinetics at the moment of phase transition because of the high rate. In the absence of phase transitions the processes taking place have measurable rates and it is possible to conduct kinetic measurements. In mixtures of chlorooctane with magnesium, for example, the C—Mg vibration band manifests itself at about 123 K and smoothly increases with increasing temperature. Termination of heating and storing the sample at constant temperature stops the reaction. Resumption of heating brings about a new increase in the intensity of the C—Mg bond vibration band (see Fig. 5). The stepwise nature of the kinetic curves indicates the inequivalency of the particles reacting in the solid phase [11]. In our case, it can be associated with a certain distribution of magnesium atoms by the nature of their environment in the matrix and the energies at which they leave the "traps" where these atoms have been stabilized.

We have revealed experimentally the formation of free radicals in the course of the interaction of magnesium with chlorine derivatives at 77 K. As an example, Fig. 6 shows the EPR spectrum of the 1-chloropentane-magnesium system. The spectrum is the result of the superposition of a sextet with a distance of 21.5 G between the lines and a half-width of 8.8 G on a singlet with a half-width of 10 G. The ratio of the sextet and the singlet intensities depends on the ratio between the magnesium and the chlorine derivative: with an increase in magnesium fraction the relative intensity of the singlet increases. At 77 K the total yield of paramagnetic particles amounts on the average to 3.5 mol% of the condensed magnesium.

The yield of radical particles depends on the energy of the metal atoms. If before condensation the magnesium vapour is passed through a tungsten helix heated to 1500 K the yield of radicals increases to 6% of the precipitated magnesium. The effect exerted on the magnesium atoms by the high temperature

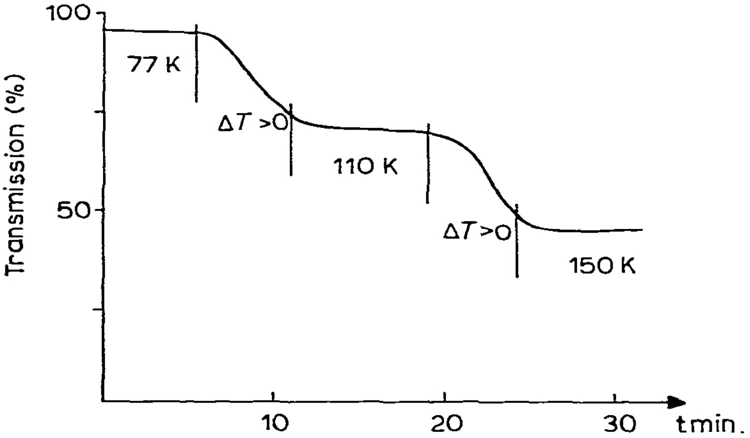


Fig. 5. Variation of 560 cm^{-1} intensity depending on temperature in the 1-chlorooctane-magnesium (25 : 1) system.

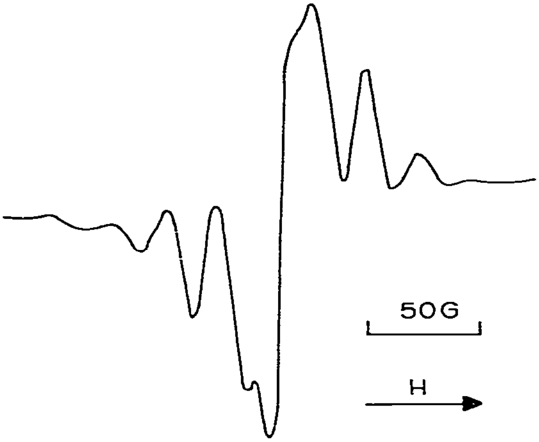


Fig. 6. EPR spectrum of atomic magnesium-1-chloropentane film at 77 K.

and intensive visible and ultraviolet radiation in the zone of the helix can result in some of the atoms passing into the ^3P excited state [4]. The increased yield of paramagnetic particles may be associated with the participation of excited atoms in the reaction.

The concentration of paramagnetic particles in the samples varies in the course of heating. When chloropentane-magnesium and chlorobutane-magnesium mixtures are heated from 77 K to 90—93 K the intensity of the sextet increases by 5—10%. With further heating its intensity slowly decreases. The intensity of the singlet decreases continuously on heating from 77 K to the temperature of phase transition. At the moment of phase transition the sextet disappears irreversibly, and the singlet intensity decreases approximately twofold. The singlet disappears completely at the moment of sample melting. Similar changes were also observed in the spectra of the magnesium-chloroheptane system. In this case, however, the sextet does not disappear completely at the moment of phase transition, and a certain quantity of the corresponding paramagnetic particles remains intact up to the melting. The variation of singlet and sextet intensity described above correlates with the temperature dependence of the organomagnesium compound yield. For chloroheptane the bulk of the organomagnesium compound is formed at the moment of phase transition, but a slow reaction in the solid phase continues up to sample melting. In the case of chlorooctane the intensity of both EPR signals decreases with heating of the sample from 77 K to the melting point, and this is accompanied by C—Mg bond formation. The parallel variation of sextet intensity and organomagnesium compound yield indicates, in our opinion, that radical particles participate in the reaction of Grignard reagents synthesis.

Analysis of EPR spectra in the chloroalkane-magnesium system shows that the sextet belongs to the n-alkyl radical. The assignment is confirmed by comparison with the data published in the literature [12] and with the spectra of radicals obtained by us on irradiation of the corresponding monochloroalkanes with unfiltered ultraviolet light. A precise assignment of the singlet does not at present appears to be possible. In our opinion, it cannot be assigned to the $MgCl^{\bullet}$ particle since the EPR spectrum we obtained when atomic magnesium interacted with chlorine at 77 K (see Fig. 7) differs from the one observed in the reactions of monochloroalkanes (see Fig. 6). One can assume that $MgCl^{\bullet}$ radicals are unstable in the presence of an excess of chlorine derivatives and enter into subsequent reactions. It is possible that the singlet belongs to ion-radical pairs, $[RCl^{-\bullet}\ Mg^{+\bullet}]$. The absence of any connection between singlet intensity and the reaction may indicate that these particles do not play a great role in the interaction of chloroalkanes with magnesium. Based on the totality of the data obtained in this work with the help of EPR and IR spectroscopy and the results of investigating the composition of products it is possible to propose the following mechanism for the reaction of magnesium atoms with aliphatic monochlorine derivatives:

$$Mg + RCl \rightarrow Mg^{+\bullet}RCl^{-\bullet} \rightarrow RMgCl \qquad (1)$$

$$Mg + RCl \rightarrow (R^{\bullet})_{st} + MgCl^{\bullet} \qquad (2)$$

$$MgCl^{\bullet} + RCl \rightarrow MgCl_2 + (R^{\bullet})_{st} \qquad (3)$$

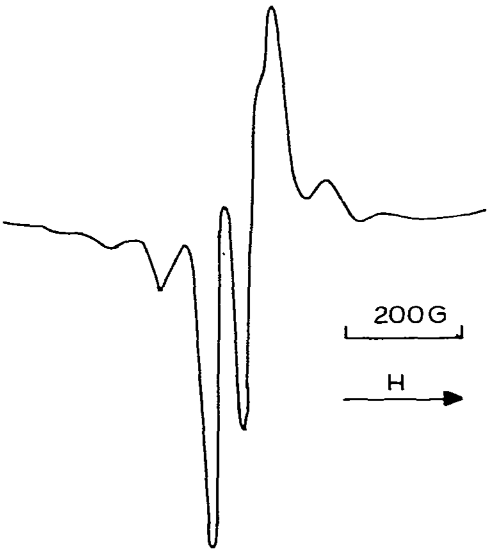
$$(R^{\bullet})_{st} \rightarrow R^{\bullet} \qquad (4)$$

$$R^{\bullet} + Mg \rightarrow RMg^{\bullet} \qquad (5)$$

$$RMg^{\bullet} + RCl \rightarrow RMgCl + R^{\bullet} \qquad (6)$$

$$R^{\bullet} + R^{\bullet} \rightarrow R_2 \qquad (7)$$

This scheme is in agreement with the nature of radicals detected by the EPR spectroscopy. The assumption of a major role played by stabilization processes



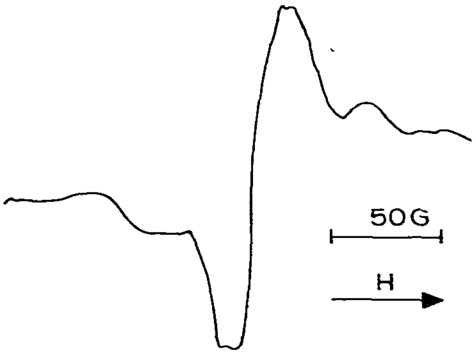


Fig. 7. EPR spectrum of atomic magnesium-chlorine film at 77 K.

Fig. 8. EPR spectrum of atomic magnesium-1,2-dichloroethane film at 77 K.

and by the transition of $(R^{\bullet})_{st}$ radicals to the mobile state is in agreement with the effect exerted on the reaction by phase transitions and the stepwise kinetics of product accumulation.

A possible participation of radicals in Grignard reactions has been repeatedly discussed [13,14] but direct proof of their formation has up to now been absent. The data given in ref. 15 on the chemical polarization of nuclei occurring in the course of reaction are, as it is shown in ref. 16, not conclusive. We have observed alkyl radicals directly by the EPR method.

It is inexpedient to transfer our data onto a liquid phase reaction. In polar media a major role is played by solvation, contributing to the formation of ion and ion radical particles. An important distinction of our experiments from the conventional methods of obtaining Grignard reagents is that at room temperatures compact metal samples are usually used. Paramagnetic particles arising when compact samples and magnesium atoms are used in low temperature reactions will be different. When an excess of chloroalkane is precipitated onto a bright magnesium film, only a weak singlet with the half-width of 10 G is observed. We assigned this signal to an ion-radical pair. The signal is recorded up to the melting point of the samples, and a slow reaction takes place at temperatures above the phase transition point in chloroalkane. The detection of ion radicals in the case of dispersed metal can be also associated with delocalization of the positive charge of magnesium atoms in dimers and polymers. For complete isolation of atoms in the matrix of organic substance it is necessary that the molar excess of the latter should be not less than 1000 : 1. In our work the excess used was of the order of 100 : 1 at which up to 15% of magnesium atoms can be dimerized [17].

Abstraction of the chlorine atom by the magnesium atom (reaction 2) and formation of the hydrocarbon radical seem to depend on the C—Cl bond strength. In chlorobenzene the C—Cl bond is stronger than in chloroalkanes, and phenyl radicals are not formed in the reaction with magnesium. At 77 K and higher temperatures only a singlet is observed whose half-width is 11 G and g factor is 2.0003 ± 0.0010. With heating of the sample the intensity of the signal decreases in the course of reaction. The singlet does not belong to C_6H_5 and MgCl particles, and it can naturally be assigned to the ion-radical pair. The reaction mechanism for chlorobenzene can then be represented as:

$$\mathrm{Mg} + \mathrm{PhCl} \rightarrow \mathrm{Mg}^{+\bullet}\mathrm{PhCl}^{-\bullet} \rightarrow \mathrm{PhMgCl} \tag{8}$$

In polychlorine derivatives, along with the abstraction of one chlorine atom, a simultaneous abstraction of two atoms is also possible. These processes can compete with one another. In the case of 1,2-dichloroethane the product of the reaction is ethylene. Films obtained by cocondensation with magnesium have at 77 K the EPR signal shown in Fig. 8 which differs from the spectrum in the Mg—Cl_2 system. The EPR spectrum can only be due to the chloroethyl radical. This identification is confirmed by the observation in a similar system, that of 1,2-dibromoethane-magnesium, an EPR spectrum coinciding with the known spectrum of the bromoethyl radical in solid phase [18]. For dichloroethane, in our opinion the most probable mechanism is a combination of the chain and one-stage mechanisms:

$$\left\{\begin{array}{ll} Mg + C_2H_4Cl_2 \rightarrow MgCl^{\bullet} + C_2H_4Cl^{\bullet} & (9)\\ MgCl^{\bullet} + C_2H_4Cl_2 \rightarrow MgCl_2 + C_2H_4Cl^{\bullet} & (10)\\ MgCl^{\bullet} + C_2H_4Cl^{\bullet} \rightarrow C_2H_4 + MgCl_2 & (11)\\ C_2H_4Cl^{\bullet} + Mg \rightarrow MgCl^{\bullet} + C_2H_4 & (12) \end{array}\right.$$

$$Mg + C_2H_4Cl_2 \rightarrow C_2H_4 + MgCl_2 \tag{13}$$

The competition between the abstraction of one and two chlorine atoms also takes place in the reaction of magnesium with carbon tetrachloride. The process is facilitated by the relative ease of the C—Cl bond breakage in carbon tetrachloride. It is of interest that, as distinct from monochloroalkanes, superheating of magnesium vapour to 1500 K does not affect the course of the reaction with carbon tetrachloride. From this it follows that the abstraction of chlorine from the CCl_4 molecule by atomic magnesium at 77 K takes place so easily that additional magnesium activation is insignificant.

The abstraction of two chlorine atoms must result in the formation of dichlorocarbene:

$$Mg + CCl_4 \rightarrow CCl_2 + MgCl_2 \tag{14}$$

This reaction is confirmed by the detection of tetrachloroethylene, formed according to the following scheme:

$$CCl_2 + CCl_2 \rightarrow C_2Cl_4 \tag{15}$$

Analysis of infrared spectra of the magnesium-CCl_4 system yielded additional data in favour of the formation of CCl_2. The main lines of CCl_2 absorption in the carbon tetrachloride matrix are not recorded because of the superposition of the intrinsic absorption of the matrix. However, in the spectrum a 658 cm^{-1} band is observed, disappearing at about 113 K. Comparison with the data from literature on the reactions of alkali metals with CCl_4 [19] makes it possible to assign this band to the complex of dichlorocarbene with magnesium chloride.

Formation of hexachloroethane is associated with the participation of trichloromethyl radicals in the process:

$$Mg + CCl_4 \rightarrow CCl_3^{\bullet} + MgCl^{\bullet} \tag{16}$$

$$MgCl^{\bullet} + CCl_4 \rightarrow MgCl_2 + CCl_3 \tag{17}$$

$$2\,CCl_3^{\bullet} \rightarrow C_2Cl_6^{\bullet} \tag{18}$$

$CCl_3^{\bullet}$ radicals have been identified by us from the characteristic 898 cm^{-1} band in the infrared spectrum [7]; the EPR spectrum also coincides with the literature data for the CCl_3 radical [20]. With an increase in temperature a gradual extinction of the radicals takes place. At the same time, in full accordance with the proposed reaction scheme, the intensity of hexachloroethane bands increases in the IR spectrum.

On the whole, it is possible to state that low-temperature reactions of magnesium with organic chlorine derivatives are complex multistage processes. In the case of chloroalkanes a major role in the reaction is played by radicals, for chlorobenzene the participation of ion-radicals can be assumed. In the reactions of polychloro derivatives there is a competition between the processes of abstraction of one or two chlorine atoms. The reactivity and the mechanism of the process are primarily determined by the strength of the C—Cl bond and the presence of phase transitions in the chlorine derivative.

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