Identification of intermediates in the reaction of 2-thenyl halides with magnesium

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The reaction of 2-thenyl chloride with magnesium was shown by the ESR method to proceed *via* the intermediate formation of radicals and radical ion pairs, whereas similar reactions of 2-thenyl bromide and iodide occur through the formation of free radicals only.

Key words: 2-thenyl halides, magnesium, radicals, radical ions.

The capture of radical species in a solution by radical traps¹⁻³ does not allow reliable detection and identification of intermediates in the Grignard reaction on the magnesium surface to be performed. The results obtained by the ESR method are the most convincing proof that paramagnetic species participate in the reaction. However, despite the high stability, the 2-thenyl radical virtually cannot be observed, under the steadystate conditions, by the ESR method.⁴ In several works.5-7 the authors have found by the ESR method for the low-temperature reaction of magnesium with halohydrocarbons in the solid state that radical ion pairs $\overline{RX^-...Mg_n^+}$ are formed along with radical species of the R* type, and the ratio between these intermediates depends on the energy of carbon--halogen bond cleavage in the starting halide.

In this work, the intermediates of reactions of three 2-thenyl halides with magnesium were studied by the ESR method in the matrix of the corresponding 2-thenyl halide at 77 K; the latter was obtained by a previously published procedure.^{5,6} Our study showed that the ESR spectrum of the cocondensate of magnesium with 2-thenyl bromide at 77 K is a multiplet with a full width of ~55 G and a g factor of ~2.002. The parameters of the ESR spectrum (a/G) and published data⁴ for the spectrum of the 2-thenyl radical are presented below.

g Factor	а ^н сн ₂	a3 ^H	a_4^{H}	а ₅ н	Refs.
2.002±0.001	13.8±0.5	7.90±0.5	1.60 ± 0.5	7.90±0.5	This
-	13.68±0.5	7.87±0.5	1.62±0.5	7.87±0.5	work Ref. 4

A comparison shows that the ESR spectrum of the cocondensates of magnesium with 2-thenyl bromide coincides with that of the 2-thenyl radical.

The spectrum of the magnesium cocondensate with 2-thenyl iodide is poorly resolved and represents a multiplet with a full width of \sim 55 G and g factor of \sim 2.002.

The poor resolution of the spectrum is due to the superposition of signals from several paramagnetic species that formed by the partial decomposition of 2-thenyl iodide under the experimental conditions.

The ESR spectrum of the magnesium cocondensate with 2-thenyl chloride contains two types of signals: a multiplet similar to that in the spectrum of magnesium cocondensate with 2-thenyl bromide; and a multiplet is superimposed on a singlet with a half-width of 9 ± 2 G. The singlet in the spectrum of the magnesium cocondensate with 2-thenyl chloride can belong to the radical MgCl or the radical ion pair $RCl^{-}...Mg_n^{+}$. The study of the spectra of the magnesium cocondensates with 2-thenyl chloride at 77 K at different RX/Mg ratios showed that an increase in this ratio from 50 to 100 resulted in a 40% decrease in the intensity of the signal of the radical ion pair, and the yield of the recombination product, 2,2'-dithenyl, increased twofold after the sample became defrosted to 298 K (Table 1). When the magnesium cocondensate with 2-thenyl chloride was irradiated at 77 K with the nonfiltered UV light of a DRSh-250 lamp, the singlet instantly disappeared, and the intensity of the multiplet proportionally increased. It would be difficult to explain these facts if the signal belonged to the 'MgCl radical. Since the signal of this radical cannot be detected under the experimental conditions due to the large width and low intensity (as compared to the spectrum of the 2-thenyl radical),⁶ we may conclude that the singlet with a half-width of 9 ± 2 G corresponds to the radical ion pair RCI⁻...Mg_n⁺, and the absence of the hyperfine structure is related to exchange processes.6-8

An increase in the temperature of the cryosynthesis of magnesium-2-thenyl halides results in a gradual decrease in the intensity of the ESR signals. In the case of the 2-thenyl chloride-magnesium system, the signal of the radical ion pair (singlet) decreases more rapidly than

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RX	RX : Mg	T ^a	Yield [*] (mol.%)			Mg : RH	Mg : H ₂	n ^c
		/K	R-R	R-H	H ₂			
	50	160	7.0	68.0	13	1.16	6	1.16
, y CH₂CI	50	298	12.1	57.4		1.00		1.00
	100	160	15.3	56.0	4	1.07	14	1.07
	100	298	23.0	47.3		1.00		1.00
	50	160	12.0	58.2	2	1.03	30	1.03
, CH₂Br	50	298	16.6	52.0		1.00		1.00
	100	160	20.0	50.8	-	1.00		1.00
	100	298	26.0	42.1		1.00	-	1.00
	50	160	32.3	36.0	-	1.00	-	1.00
< ^с у—Сн₂і	50	298	42.0	22.8	-	1.00	_	1.00

Table 1. Yield of the reaction products of atomic magnesium with 2-thenyl halides (RX)

^a Ethanolysis temperature.

^b The reaction mixture contained 20-30% polymeric products.

^e The average number of magnesium atoms in the prepared organomagnesium compounds.

that of the 2-thenyl radical and completely disappears at 120 K. This is related to an increase in the recombination and decomposition rates of the radical ion pairs $\overline{RCI^-...Mg_n^+}$ on the surface-bound radicals R⁺ and 'MgCl. The paramagnetic species disappear when the samples melt. The obtained results indicate that both the radical ion pairs $\overline{RCI^-...Mg_n^+}$ and free radicals R⁺ can be intermediates in the formation of the Grignard compounds of the 2-thenyl series.

It has been shown⁵ for the reactions of butyl and phenyl halides with magnesium that the nature of intermediates depends on the energy of the carbon—halogen bond. Only radical species were formed when bromides and iodides were used (the cleavage energies ranged from 226 to 298 kJ mol⁻¹), and for chlorides and flourides (the cleavage energy from 340 to 490 kJ mol⁻¹), the formation of radical ion pairs was observed.

In our case, the radicals are intermediates in the reactions of 2-thenyl bromide and iodide with magnesium, and both paramagnetic species (viz., radicals and radical ion pairs) are formed in the case of 2-thenyl chloride. According to the ESR data, the total fraction of paramagnetic species in the samples at 77 K amounts to 14, 30, and 9% of the amount of the precipitated magnesium atoms and depends on the energy of the carbon--halogen bond in the starting 2-thenyl halide. A high number of the paramagnetic species observed in the cocondensation of 2-thenyl iodide with magnesium is related to the partial decomposition of 2-thenyl iodide under the cryosynthesis conditions. The total fraction of the paramagnetic species formed by the decomposition of 2-thenyl iodide on the heated glass walls of the ESR tube, under the cryosynthesis conditions (without magnesium), was 12%. After defrosting the reaction system contained H1, 12, polymeric products of decomposition. 2,2'-dithenyl (2%), and 2-methylthiophene (0.7%). The detection of the paramagnetic species by the ESR method

indicates that, under the cryosynthesis conditions, 2-thenyl iodide decomposes by the radical mechanism.

It is known that the carbon—halogen bond in allyl, 2-thenyl, and benzyl halides is less stable than those in other halohydrocarbons, and the energy of the cleavage of this bond in benzyl chloride (285 kJ mol⁻¹) is close to those in alkyl(aryl) bromides.⁹ It follows from this that if the direction of the reaction of 2-thenyl halides with magnesium is determined by the energy of the carbon—halogen bond only, radical intermediates R⁺ would exclusively form in the case of 2-thenyl chloride.

The detection of radical ion pairs $RX^-...Mg_n^+$ along with radical intermediates R^+ suggests that the stabilization of the radical ion pair by the magnesium surface is another factor that determines the reaction route.

When an excess of 2-thenyl halide is condensed on the compact magnesium film, losses of SHF power in the sample increase due to an increase in the electroconductivity, which results in a considerable worsening of the resolution of the ESR spectra. Paramagnetic species that appeared in the 2-thenyl halide-atomic magnesium systems do not differ from those formed when the compact magnesium film is formed. The ESR spectra observed during the condensation of 2-thenyl bromide or iodide on the compact magnesium film at 77 K are similar to that of the magnesium cocondensate with 2-thenyl bromide, but have a lower intensity and worse resolution. For the 2-thenyl chloride-compact magnesium system, the ESR spectrum is similar to the low-intensity spectrum of the magnesium cocondensate with 2-thenyl chloride when the ratio of singlet : triplet of quartets increases 2-3-fold, which is most likely the result of a higher stabilization of the radical ion pair due to the charge distribution over the whole group of magnesium atoms.

Both mono- and polymagnesium organic compounds can be formed by the decomposition of the radical ion

pair $RX^{-}...Mg_n^+$, and the reaction route also depends on the energy of the carbon-halogen bond in the starting halide.^{7,10} The composition of the organomagnesium compounds was determined by the ratio of the amounts of magnesium, 2-methylthiophene, and dihydrogen in the ethanolysis products before and after defrosting of the samples. The low melting point of ethanol (160 K) made it possible to detect the reaction products both before (160 K) and after (298 K) defrosting of the sample and to observe unstable at 298 K polymagnesium organic compounds whose ethanolysis proceeds via the equation

$$\begin{array}{c} \swarrow \\ S \end{array} \xrightarrow{} CH_2Mg_nCl + (2n-1) EtOH \\ \hline \\ \hline \\ S \end{array} \xrightarrow{} Me + (n-1) Mg(OEt)_2 + \\ + (n-1) H_2 + EtOMgCl \end{array}$$

The available data (see Table 1) indicate that each organomagnesium compound obtained by the cocondensation of magnesium with 2-thenyl bromide or iodide contains only one magnesium atom. This differs from the published data 10-13 about the insertion of di- or trinucelar magnesium clusters at the carbon-halogen bond of methyl and phenyl halides and can be explained by a very low energy of the carbon-halogen bond^{7,8,13} in 2-thenyl halides; because of these bond energies, radical ion pairs $RX^{-}...Mg_{n}^{+}$ are not formed. In the case of 2-thenyl chloride, dihydrogen was observed in the ethanolysis products at 160 K (conversion of magnesium 100%).

Therefore, polymagnesium-2-thenyl chlorides form due to the recombination of the radical ion pairs $RX^{-}...Mg_{n}^{+}$ rather than by the successive insertion of magnesium atoms at the C-X bond. A minor amount (<15%) of the cluster structures and their disappearance after ethanolysis at 298 K can be easily explained: polymagnesium-2-thenyl chlorides can decompose already at 77 K to form magnesium in the reaction

$$C_{S}$$
 - CH₂Mg_nCl - C_{S} - CH₂MgCl + Mg_{n-1}

and/or rapidly react with an excess of 2-thenyl chloride to form the Grignard reagent



The 1.5-1.7-fold increase in the content of 2,2'-dithenyl in the reaction products with the temperature increase from 160 to 298 K (see Table 1) is related to both the disappearance of the cluster structures by the equation

$$\begin{array}{c} \swarrow \\ S \end{array} - CH_2Mg_nCl + \\ \swarrow \\ S \end{array} - CH_2CH_2CH_2CH_2Cl - \\ + MgCl_2 + Mg_{n-1} \end{array}$$

and an increase in the rates of the Würtz reaction and recombination of free 2-thenyl radicals. The last two reactions determine the 1.3-1.4-fold increase in the content of 2,2'-dithenyl with an increase in the temperature of the ethanolysis of the magnesium cocondensates with 2-thenvI bromide from 160 to 298 K, where polymagnesium organic compounds are not formed (see Table 1).

The amount of the synthesized hydride complexes was estimated by the condensation of CCl₄ on the sample surface at 77 K. After treatment with ethanol and defrosting, the amount of chloroform was determined by GLC.¹³ The reaction of CCl₄ with the organomagnesium compounds obtained in the magnesium cocondensate with 2-thenyl chloride affords chloroform (0.16%). The reaction products of CCl4 with the organomagnesium compounds synthesized in the magnesium cocondensates with 2-thenyl bromide or iodide contain <0.001% chloroform.

Based on the obtained data, we may conclude that the reaction of 2-thenyl halides with magnesium proceeds predominantly at the C-X bond, and the low energies of this bond cleavage prevent the insertion of magnesium at the C-H bond, and magnesium-2-thenyl hydrides are virtually not formed.

The detection and identification of the reaction intermediates on the magnesium surface and a correlation between them suggest a presumable scheme of the lowtemperature reaction of magnesium with 2-thenyl halides (Scheme 1).

Scheme 1



R - 2-thenyl; X = Cl, Br, I; n = 1-3

Despite the fact that this scheme ignores the formation and reactions of compounds with the C--Mg_n-H bonds, which were observed in minor amounts, and the isomerization and behavior of the radical and radical ion pairs during their recombination.^{14,15} it well agrees with the scheme of the formation of the "classical" Grignard reagent via the radical and radical ion route¹⁶ and shows the dependence of the direction of the reaction on the energy of carbon-halogen bond cleavage in the starting 2-thenyl halide.

Experimental

ESR spectra were recorded on a Rubin radiospectrometer in the film of magnesium cocondensates with a 50-100-fold excess of 2-thenyl halides at 77 K by the known procedure.^{5,6}

The reaction products were analyzed by GLC, GC, and ion chromatography, and the conditions of analysis have been described previously.⁷

2-Chloromethylthiophene (2-thenyl chloride) was synthesized by the treatment of thiophene with HCl and formaldehyde by the previously published procedure.¹⁷ The yield was 40%, b.p. 80-81 °C (18 Torr) (cf. Ref. 17; b.p. 80-81 °C (18 Torr)). 2-Bromomethylthiophene (2-thenyl bromide) was synthesized by the reaction of 2-methylthiophene and N-bromosuccinimide in the presence of benzoyl peroxide by the known procedure.¹⁸ The yield was 65%, b.p. 34-36 °C (0.25 Torr) (cf. Ref. 18; b.p. 34-36 °C (0.3 Torr)). 2-lodomethylthiophene (2-thenyl ordide) was synthesized¹⁹ by the reaction of 2-thenyl chloride and sodium iodide in acetone in a yield of ~100%. After the separation of NaCl and evaporation of acetone, the obtained 2-thenyl iodide was used without pre-distillation.

Cryosynthesis of the organomagnesium compounds was performed in a vacuum installation.⁷ The samples were prepared by the cocondensation of magnesium and a 50–100-fold excess of 2-thenyl halide on the reaction surface cooled by liquid nitrogen (77 K) with continuous evacuation (10^{-4} Torr). Magnesium was evaporated from a quartz crucible at 640–670 K. 2-Thenyl halides were evaporated at 0–35 °C. The time of the cocondensation of the reactants was 2 h. The cocondensates are chestnut-colored films that are discolored at the melting temperature of the hydrocarbon.

To perform the reaction with CCl_4 , an excess of CCl_4 was condensed on the prepared sample of the organomagnesium compound. The reaction mixture was left in an evacuated reactor for 1 h at 77 K and then decomposed with ethanol. The decomposition was carried out by the condensation of an excess of ethanol on the film of the reaction mixture at 77 K and warming of the obtained condensate film to the complete discoloration and melting (160 K). The time of ethanolysis at 160 K was 30 min. The reaction products were determined in the liquid and gas phases after the decomposition of the reaction mixture with ethanol.

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