are also consistent with a diradical intermediate. Here $\Delta V^{\ddagger} = -20.0$ cc./mole, compared with -31.6 cc./mole for the over-all change in volume. Again the difference appears too large for a cyclic transition state. At present no data are available to identify the transition state structures in reactions involving strong dienophiles such as maleic anhydride. Here preliminary experiments indicate that such measurements will be difficult because of the great ease with which such systems undergo copolymerization at high pressures.

NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI, AND THE WESTINGHOUSE RESEARCH LABORATORIES]

The Constitution of the Grignard Reagent

BY RAYMOND E. DESSY AND GEORGE S. HANDLER

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The magnesium metal plating out at the cathode in the electrolysis of the Grignard reagent prepared by mixing diethylmagnesium with magnesium bromide labeled with radioactive magnesium contains no significant activity. This is further evidence in support of the concept that a solution of ethyl Grignard contains two types of magnesium. It indicates that the positive discharging species contains, as its basic unit, the RMg^+ ion. The equilibria $(C_6H_5)_2Mg{\cdot}MgBr_2 \rightleftarrows (C_6H_5)_2Mg + MgBr_2 \rightleftarrows 2C_6H_5MgBr$ have also been investigated employing labeled magnesium. The results indicate that phenyl Grignard is better represented by a complex $(C_6H_5)_2Mg{\cdot}MgBr_2$ than by C_6H_5MgBr. The effect of trace impurities on the exchange reaction is discussed.

The equilibria $Et_2Mg{\cdot}MgBr_2 \rightleftarrows Et_2Mg + MgBr_2 \rightleftarrows 2EtMgBr$ have been investigated[1] by employing magnesium bromide labeled with radioactive magnesium. Only a small amount of exchange was noted between Et_2Mg and $MgBr_2$ in ether solution over a 36-hour period. These results, in conjunction with the fact[2] that the same species seem to be present in a solution of Et_2Mg and $MgBr_2$ as are present in ethyl Grignard prepared in the normal manner indicated that the ethyl Grignard is better represented by a complex $Et_2Mg{\cdot}MgBr_2$ than by EtMgBr.

In his comprehensive study on the electrolysis of Grignard reagents Evans[3] showed that in the electrolysis of *n*-butylmagnesium bromide in ether solution in addition to magnesium metal plating out at the cathode, there was a net migration of magnesium to the anode compartment, thus indicating that magnesium is present in the anion, as well as the cation. The results with ethylmagnesium bromide indicated a similar dichotomy, but the results were not as clean because of the difficulty in maintaining a true middle compartment during the electrolysis. From this, and a vast amount of other data, Evans arrived at a simplified picture of the Grignard reagent and its electrolysis

$$R_2Mg + MgX_2 \rightleftarrows 2RMgX \qquad (1)$$

$$RMgX \rightleftarrows R^{\ominus} + MgX^{\oplus} \qquad (2a)$$

$$R_2Mg \rightleftarrows R^{\ominus} + MgR^{\oplus} \qquad (2b)$$

$$R^{\ominus} + R_2Mg \rightleftarrows R_3Mg^{\ominus} \qquad (2c)$$

$$R \quad + MgX_2 \rightleftarrows RMgX_2^{\ominus} \qquad (2d)$$

$$MgX_2 \rightleftarrows X^{\ominus} + MgX^{\oplus} \qquad (2e)$$

$$X^{\ominus} + R_2Mg \rightleftarrows R_2MgX^{\ominus} \qquad (2f)$$

$$X^{\ominus} + MgX_2 \rightleftarrows MgX_3^{\ominus} \qquad (2g)$$

$$\text{cathode} \begin{cases} 2RMg^{\oplus} + 2e \longrightarrow Mg + R_2Mg & (3a) \\ 2MgX^{\oplus} + 2e \longrightarrow Mg + MgX_2 & (3b) \end{cases}$$

$$\text{anode} \begin{cases} R_3Mg^{\ominus} \longrightarrow R\cdot + R_2Mg + e & (4a) \\ R_2MgX^{\ominus} \longrightarrow R\cdot + RMgX + e & (4b) \\ RMgX_2^{\ominus} \longrightarrow R\cdot + MgX_2 + e & (4c) \end{cases}$$

In view of the fact that previous work indicated that equation 1 does not apply, and that ionization 2a may therefore be ignored, it was felt that an investigation of the electrolysis of a mixture of Et_2Mg and $MgBr_2$ would prove of value, since it would distinguish processes 3a and 3b, and therefore offer evidence, indirectly, for one of the ionization steps shown in equations 2a-f.

In addition it was felt that an investigation of the equilibria

$$(C_6H_5)_2Mg{\cdot}MgBr_2 \rightleftarrows (C_6H_5)_2Mg + MgBr_2 \rightleftarrows 2C_6H_5MgBr$$

would also be of value, since aromatic Grignard reagents differ markedly from aliphatic Grignard reagents in reactivity, and appear to be colloidal in nature.

Experimental

Diethylmagnesium.—The diethylmagnesium in ether was prepared by the action of dioxane on an ether solution of ethylmagnesium bromide,[4] with subsequent removal of the solvent, baking at 150° (0.25 mm.) for 3 hours, and dissolution in ether. It contained less than 1 mole % of halogen.

Diphenylmagnesium.—The diphenylmagnesium in ether was prepared in the same manner as the diethylmagnesium except that the final baking temperature was raised to 190° for 5 minutes at the end of the baking period. It contained less than 2 mole % of halogen.

Mg^{28}-Labeled Magnesium Bromide.—Mg^{28} was prepared by a spallation reaction involving proton irradiation of a single crystal of potassium chloride at a radius equivalent to 350 Mev. for one hour in the synchrocyclotron of the Carnegie Institute of Technology. The isolation of the Mg^{28} and the preparation of labeled $MgBr_2$ by reaction of labeled Mg with Br_2 in ether was as previously described.[1] The lower phase of the two phase system, containing 485 mg. $MgBr_2$/ml., was used. It is important to note that the

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[1] R. E. Dessy, G. S. Handler, J. H. Wotiz, and C. A. Hollingsworth, THIS JOURNAL, **79**, 3476 (1957).

[2] R. E. Dessy, J. H. Wotiz and C. A. Hollingsworth, *ibid.*, **79**, 358 (1957).

[3] W. V. Evans and R. Pearson, *ibid.*, **64**, 2865 (1942).

[4] J. H. Wotiz, C. A. Hollingsworth and R. E. Dessy, *ibid.*, **78**, 1221 (1956).

TABLE I

ELECTROLYSIS OF [$Et_2Mg + MgBr_2$]

	Milliequivalents of material in cell[a]							Meq. gained or lost		
	Initial			Final						
Compartment	Cathode	Middle	Anode	Plate	Cathode	Middle	Anode	Cathode	Middle	Anode
Species										
Et	3.0	4.0	3.0		0.8	4.4	4.4	−2.2	+0.4	+1.4
Br	3.0	4.0	3.0		2.6	4.1	3.3	−0.4	+ .1	+0.3
Mg	6.0	8.0	6.0	0.4	3.4	8.5	7.7	−2.6	+ .5	+1.7
Specific activity[b]	357	357	357	44	255	218	565			

[a] The values obtained agree well with those obtained in dry runs. [b] Counts/min./mg. Mg, corrected to the same time of counting.

labeled Mg metal was sublimed immediately prior to its reaction with bromine in most runs. In one run this was deliberately diluted with "Grignard grade" magnesium and used without further purification.

Mg^{25}-Labeled Magnesium Bromide.—Mg^{25} (93.1% enriched) was purchased from the Stable Isotopes Division, Oak Ridge National Laboratory. This was diluted with Mallinckrodt "Grignard grade" Mg metal of normal isotopic composition and allowed to react with Br_2 in dry ether. The lower phase of the two phase system, containing 485 mg. of $MgBr_2$/ml., was used.

Spectrographic analysis of the Mg^{25} sample indicated that it contained these impurities: Ca, 0.1%; Mo, Si, Na, 0.01%; Cu, Fe 0.005%. The Grignard grade Mg turnings used to dilute it was found to contain less than 0.05% Fe, 0.03% Mn, and less than 0.002% Si and Al as the major impurities.

Electrolysis Cell and Power Supply.—The electrolysis cell was a linear three-compartment cell having a total volume of 10.0 ml. including the stopcock bores between compartments. The middle compartment had a volume of 4.0 ml., and the cathode and anode compartments a volume of 3.0 ml. each. The electrodes were bright platinum, 0.80 cm.^{2} in area. The cell was operated vertically, with the cathode at the top. Stopcocks leading from each compartment permitted sampling *via* hypodermic syringes. The cathode was attached to a standard-taper joint to permit easy access.

The power supply was a well filtered line operated rectifier capable of delivering a constant voltage from 0–165 volts.

Electrolysis.—The concentrated magnesium bromide solution and the concentrated diethylmagnesium solution were added to a sufficient volume of ether to yield a solution 0.5 molar in each (1.0 molar in magnesium). The cell was filled, and electrolysis allowed to proceed undisturbed for about 36 hours. In all of the dry and tracer runs made, the initial current was about 0.7 ma. at 160 volts. This dropped rapidly as electrolysis proceeded, so that at the end of about 12 hours a current of only 0.2 ma. could be supported. In general about 35 coulombs were passed through the cell.

At the end of this period, the compartments were isolated from each other, the samples were withdrawn for analysis. The middle and anode compartments were assayed for equivalents of Et by hydrolysis and titration with standard HCl, NaOH solutions using phenolphthalein as an indicator. They were analyzed for equivalents of Br by potentiometric titration with $AgNO_3$. Because of the slow plate the magnesium on the cathode tended to "feather," and sampling of the cathode compartment in most of the dry and tracer runs proved impossible because of the danger of breaking off of the plate. However, the concentrations in the cathode compartment may be calculated by difference.

The magnesium on the cathode was a gray collection of small, light single crystals. It was washed *in situ* with ether five times and dried under vacuum without heat.

The weights collected indicated current efficiencies of 95% or better. Both Mg^{28} and Mg^{25} were used as tracers.

Exchange Reactions.—The exchange of magnesium between $(C_6H_5)_2Mg$ or Et_2Mg and $MgBr_2$ in ether was investigated, the latter as a control on the electrolysis reaction. The solutions were prepared as described for the electrolysis experiment. They were permitted to stand for 36 hours, and then 1.5 mole equivalents of 1,4-dioxane was added slowly over a 15-minute period, with constant agitation. The suspension was agitated slowly for 15 minutes and then centrifuged at 2000 r.p.m. for 5 minutes. The supernatant solution was analyzed for R and X as described in the electrolysis experiment. Both Mg^{28} and Mg^{25} were used as tracers.

Sampling, Counting and Assaying. Mg^{28}.—A sample of each of the compartments in the electrolysis cell, as well as the supernatant liquid from the dioxane precipitate of the exchange runs, was air hydrolyzed, treated with concentrated hydrobromic acid, and dried on glass planchets. A similar planchet was prepared from the original magnesium bromide solution. All of the samples were infinitely thick.

The Mg metal on the cathode was treated with dilute hydrobromic acid, and dried on a glass planchet. It was of finite thickness.

A Packard-Flo-Window proportional counter was used.

A plot of log (activity) *versus* time indicated a high radiochemical purity and a $t_{0.5}$ of 21.25 hr. The reported $t_{0.5}$ of Mg^{28} is 21.25 hr.[5]

Mg^{25}.—A sample of each of the compartments in the electrolysis cell as well as the supernatant liquid from the dioxane precipitation of the exchange runs and the original $MgBr_2$ solution were air hydrolyzed, treated with NH_4OH, and ashed to MgO at 1000°. The Mg metal on the cathode was submitted as such.

The analysis for the Mg^{24}/Mg^{25} ratios were done by the Y-12 mass spectrometer laboratory of the Oak Ridge National Laboratory.

Methods and Results

Radioactive magnesium (Mg^{28}, $t_{0.5} = 21.25$ hr.) was prepared by a spallation reaction involving proton irradiation of potassium chloride. The magnesium, diluted with carrier was separated as the oxinate, and ignited to the oxide. The latter was converted to magnesium chloride, and exchanged with elemental magnesium at 800°. The resulting labeled metal was sublimed, and then treated with bromine in dry ether to yield magnesium bromide.

Equimolar amounts of this magnesium bromide and diethylmagnesium (prepared from ordinary magnesium) were dissolved in ether so as to give a solution 1.0 *M* in magnesium. This was electrolyzed in a three compartment Hittorf-type cell operated vertically with the cathode at the top at a current density of from 1.0 to 0.1 ma./cm.^{2} until about 2% of the total magnesium content had plated out at the cathode (36 hours). Evans[3] has shown that the products of the electrolysis of ethyl Grignard are magnesium at the cathode, and ethane, ethene and hydrogen at the anode. Each compartment of the cell was analyzed for equivalents of Et and Br. The equivs. Et + equivs. Br = equivs. Mg. A sample of each compartment was also withdrawn and its specific activity determined. The specific activity of the magnesium plating out at the cathode was also determined. The results obtained are shown in Table I.

The tagged magnesium bromide also was mixed with equimolar amounts of diethylmagnesium and diphenylmagnesium in ether, and the mixtures permitted to set during the electrolysis. At the end of this time an excess of dioxane was added so as to precipitate the elements of magnesium bromide, leaving Et_2Mg or $(C_6H_5)_2Mg$ in the supernatant liquid. The specific activity of the magnesium in an aliquot of the supernatant fluid was determined, and compared with the specific activity of the magnesium bromide used to prepare the solution. The results are shown in Table II.

When these same experiments were performed using Mg^{25} purchased from the Oak Ridge National Laboratory as a tracer, diluting it with "Grignard grade" magnesium,

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[5] G. Friedlander and J. W. Kennedy, "Nuclear and Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1955.

TABLE II

RADIOACTIVITY EXCHANGE BETWEEN Mg^*Br_2 AND Et_2Mg AND $(C_6H_5)_2Mg$

System	Specific activity,[a] c./min.-mg. Mg Mg*Br	Specific activity,[a] c./min.-mg. Mg R_2Mg	Contact time, hr.	Activity ratio	Migration, %
$Et_2Mg + Mg^*Br_2$	715	32	36	22/1	4.5
$(C_6H_5)_2Mg + Mg^*Br_2$	715	53	36	14/1	7.0

[a] Corrected to the same time of counting.

complete exchange between the Mg^*Br_2 and R_2Mg was noted in all cases. This exchange is not due to impurities in the "Grignard grade" magnesium used for dilution since deliberate dilution of the tagged magnesium in one of the Mg^{28} runs with the same "Grignard grade" magnesium did not affect the final results. The impurity that caused the exchange apparently lies in the Mg^{25} metal supplied by the Stable Isotopes Division. No attempt was made to find whether one of the major impurities, Ca, Mo, Si, Na or Cu was the agent responsible, since trace impurities of other elements may have been responsible.

Discussion

Fundamentally, the present work indicates that "ethylmagnesium bromide" and probably "phenylmagnesium bromide" contain two different types of magnesium. This is evident from the exchange reactions. The comparison of the Mg^{28} and Mg^{25} runs indicates that when sufficient impurities are present the Mg of the two species exchanges. These impurities are apparently not present in "Grignard grade" magnesium, and we may therefore conclude that the Grignard reagent prepared in the normal manner from RX and Mg also contains two types of Mg, and therefore might be best represented as $R_2Mg \cdot MgX_2$.

The mass balance in the electrolysis cell supports the findings of Evans for the butylmagnesium bromide system. Although the middle compartment is not too good it is much better than Evans, and the general result indicates that for ethyl Grignard: 1. The net migration of magnesium to the anode indicates it is present in the anion as well as the cation. 2. The cathode compartment appears to lose Et in preference to Br, while the anode compartment appears to gain Et in preference to Br. 3. The large amount of material transported in comparison to the amount of Mg plated out indicates that the ions are actually large aggregates, probably involving 2 or 3 molecules.

The radioactivity balance in the cell indicates even more surprising features: 1. The magnesium which plates out at the cathode has its origin in the Et_2Mg. 2. The largest portion of the magnesium which migrates to the anode compartment has its origin in the $MgBr_2$. 3. The gain of activity in the anode compartment is at the expense of both the middle and cathode compartments.

The results indicate that process 3b cannot be responsible for the cathodic discharge, and that therefore ionization 2e is not involved. The discharge does arise from a process similar to 3a, which is related to ionization 2b, regardless of what associations take place after this step. The basic ion is therefore $RMg^{\oplus}$.

The negative ion is not as easy to unravel. It is hoped that work on the conductivity of mixtures of Et_2Mg and $MgBr_2$ now in process will shed some light on the problem of the origin and structure of the negative ion.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Organic Peroxides. XXI. A Study of the Decomposition of 2,5-Dimethyl-3-hexyn-2,5-Dihydroperoxide[1]

BY NICHOLAS A. MILAS AND JOHN T. NOLAN, JR.[2]

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The thermal, ferrous ion-catalyzed and acid-catalyzed decomposition of 2,5-dimethyl-3-hexyn-2,5-dihydroperoxide has been studied, and in every case an attempt has been made to isolate and identify all the products formed. Tentative-mechanisms have been proposed to account for the products formed in the various decompositions.

The thermal, ferrous ion-catalyzed and acid-catalyzed decomposition of alkyl hydroperoxides containing a single tertiary hydroperoxy group is well known.[3a-d] However, the decomposition of hydroperoxides containing two tertiary hydroperoxy groups separated by an acetylenic linkage[4] is not known. One may raise two questions regarding the decomposition of these peroxides. Would the two hydroperoxy groups decompose simultaneously or consecutively? If free radicals or ions are formed during the decomposition would they react with the acetylenic linkage or would they decompose to form other products? In the hope of contributing to an answer of these questions a study of the decomposition of 2,5-dimethyl-3-hexyn-2,5-dihydroperoxide was undertaken and the results will be described in the present communication.

Thermal Decomposition.—When 2,5-dimethyl-3-hexyn-2,5-dihydroperoxide was heated above its melting point it was found to decompose explo-

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[1] Paper XX, THIS JOURNAL, **77**, 2536 (1955).

[2] From the Ph.D. Thesis of John T. Nolan, Jr., M.I.T., May, 1955.

[3] (a) N. A. Milas and D. M. Surgenor, THIS JOURNAL, **68**, 205 (1946); (b) M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, **16**, 106, 113 (1951); (c) R. J. Orr and H. L. Williams, *Can. J. Chem.*, **30**, 985 (1952); (d) W. S. Wise and G. H. Twigg, *J. Chem. Soc.*, 2172 (1953).

[4] N. A. Milas and O. L. Mageli, THIS JOURNAL, **74**, 1471 (1952).