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A NON-ISOTHERMAL KINETIC STUDY OF THE THERMAL DECOMPOSITION OF MAGNESIUM ALKOXIDES AND AMIDES

E.C. ASHBY and G. FRED WILLARD

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332 (U.S.A.)

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Summary

The thermal decomposition of alkoxides and amides of magnesium have been studied by vacuum TGA under both isothermal and non-isothermal conditions. These compounds were found to follow a unimolecular decay law, which in integrated form is $-\ln(1-\alpha) = kt$, where α is the fraction of material reacted, and k is the Arrhenius rate constant. The rate-controlling process is random nucleation, one nucleus on each particle. Energies of activation calculated by isothermal and non-isothermal methods agree to within ±20%.

Introduction

We recently reported on the thermal decomposition of alkoxides [1] and amides [2] of magnesium. These reagents are prepared by the reaction of a suitable dialkyl- or diarylmagnesium compound with an alcohol or secondary amine as illustrated in eqs 1 and 2. Then in a second step the alkoxide or amide


(1)

$$Ph_2Mg + HN\text{-}i\text{-}Pr_2 \longrightarrow PhMgN\text{-}i\text{-}Pr_2 + PhH \qquad (2)$$

is thermally decomposed to give an olefinin and a hydrocarbon (eqs 3 and 4).


(3)

$$PhMgN\text{-}i\text{-}Pr_2 \xrightarrow{\Delta} PhH + CH_3CH{=}CH_2 + (MgN\text{-}i\text{-}Pr)_x \qquad (4)$$

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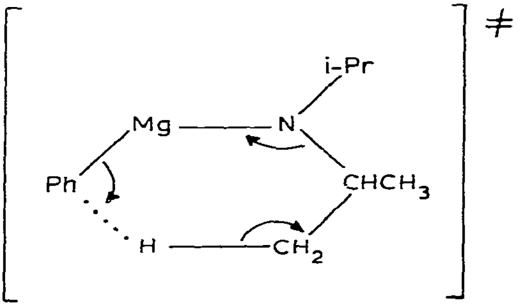
The by-product in the decomposition of the alkoxides is magnesium oxide, and the by-products from the amides are substituted magnazines [3]. The thermal decomposition of diisopropylamino(phenyl)magnesium involves a cyclic, six center transition state (A). An incipient phenyl carbanion abstracts a β-hydrogen to give benzene, propene, and a residue of empirical formula $(\mathrm{MgN\text{-}i\text{-}Pr})_x$. The reaction has been shown [2] to be first-order and occurs in a *syn*-stereochemical fashion.



(A)

Energies of activation (E_a) and Arrhenius preexponential factors (A) were calculated from isothermal kinetic studies at three different temperatures for each of the alkoxides or amides. However, this procedure is tedious and requires a relatively large amount of material. The accuracy of the results could be questionable since the sample undergoes considerable reaction in being raised to the required temperature.

In order to determine the accuracy of the isothermal kinetic data and to better understand the mechanism of the thermal decomposition of magnesium alkoxides and amides in the solid state, a non-isothermal kinetic study of these decomposition reactions was undertaken. We now wish to report our results.

Experimental

Apparatus

All operations were performed under a nitrogen atmosphere using either a nitrogen-filled glove box equipped with a special recirculating system to remove oxygen and moisture [4] or on the bench using Schlenk tube technique [5]. Glassware was flash flamed and flushed with nitrogen prior to use. DTA-TGA analyses were performed using a Mettler Thermoanalyzer II equipped to operate under vacuum [6]. Powdered alkoxide or amide samples were loaded into a cylindrical aluminium crucible with a fritted disk and cap (preheated to 250°C and cooled to room temperature) in the glove box using a vibrator to ensure uniform particle size. Samples were transferred to the DTA-TGA instrument under nitrogen and were heated at 4°C per minute at 10^{-6} mmHg from 25 to 450°C at a six inches per hour chart speed.

Analyses

The alkoxides and amides were hydrolyzed by methanol on a standard vacuum line equipped with a Toepler pump [5]. Methane was determined by gas evolution. Benzene, toluene, and the amine or alcohol hydrolysis products were determined by GLPC on an F & M Model 720 gas chromatograph. Magnesium was determined by EDTA titration at pH 10 using Eriochrome Black T as the indicator.

Materials

Diethyl ether (Fisher Anhydrous Reagent Grade) was distilled from $LiAlH_4$, and benzene (Fisher Certified Reagent Grade) was distilled from $NaAlH_4$ (Ventron) prior to use. Dimethylmercury, diphenylmercury, and dibenzylmercury were obtained commercially (Orgmet). The corresponding dialkyl- or diarylmagnesium compounds were prepared by reaction of the appropriate mercury compound with magnesium metal (Ventron chips) by known methods [7]. Standard solutions were prepared and analyzed.

All alcohols and amines were commercially available and were dried and distilled prior to use. The exceptions were *erythro*- and *threo*-1,2-diphenyl-1-propanol. These compounds were prepared by the method of Cram [8].

General preparation of alkoxides and amides

The general method for the preparation of the starting materials is illustrated for diisopropylamino(phenyl)magnesium.

A dry, weighed 100-ml flask is fitted with a rubber septum cap, purged with dry nitrogen and fitted with a needle connected to a nitrogen bubbler. A measured quantity of diisopropylamine is added to the flask via syringe and the flask reweighed (0.402 g, 3.98 mmol). The flask is cooled to −78°C, and the calculated amount of diphenylmagnesium diethyl ether solution (4.00 mmol) is added via syringe. The flask is warmed to 25°C and a solid forms with corresponding formation of benzene. The septum is replaced with a three-way stopcock, and the solvent is distilled under vacuum. The solid diisopropylamino(phenyl)magnesium is transferred to the glove box for further manipulation and analysis. Ratio of magnesium/benzene/diisopropylamine/diethyl ether = 1.00/1.03/0.93/0.89.

Results and discussion

Constant temperature kinetics were conducted on several alkoxides and amides of magnesium via thermogravimetric analysis (TGA). First-order rate constants were determined by following the loss in weight of a tared sample of the alkoxide or amide due to the formation of volatile reaction products. A linear least squares plot of the natural logarithm of mol alkoxide or amide versus time in minutes gave first-order rate constants. The frequency factor (A) and experimental activation energy (E_a) were calculated from the Arrhenius equation $k = A_e^{-E_a/RT}$ with the aid of a least squares plot of log k versus $1/T$, where T is absolute temperature. The energies of activation were obtained by use of the equation $E_a = -2.303\ R\ x$ slope, and the frequency factors were calculated from the Arrhenius equation where the intercept = log A. Having calculated the E_a and A values for a given compound, we could then calculate an entropy of activation ($\Delta S^{\mp}$) at a specific temperature using the equation of O'Connor and Nace [9], $\Delta S^{\pm} = 2.303\ R \log (A) - 2.303\ R \log\ Ke\frac{k'T}{h}$, where

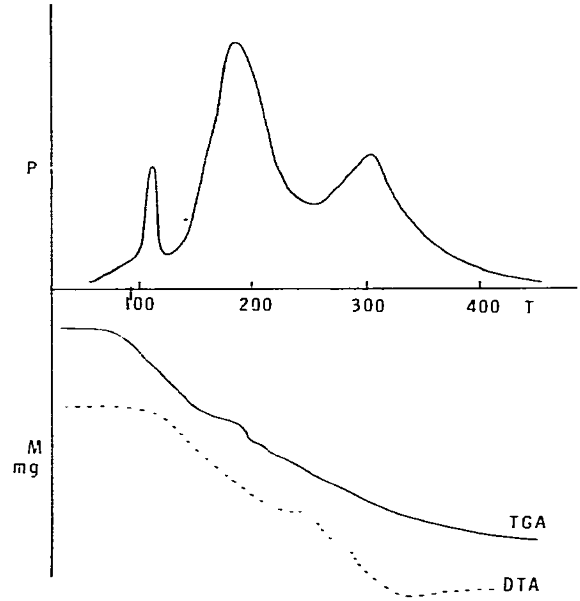


Fig. 1. Vacuum DTA-TGA on PhMgN-i-Pr_2 · 0.89 Et_2O.

k′ is the Boltzman constant, *h* is Planck's constant, and *K* is the transmission coefficient which is assumed to be unity.

Several methods exist for studying the kinetics of thermal decomposition reactions by dynamic thermogravimetry [10]. The methods of Freeman and Carroll [11] and Coats and Redfern [12] were applied to the thermal decomposition of the magnesium alkoxides and amides studied here. However, the correlations were very poor leading to a large scattering of data points. A better fit of the experimental data was obtained by the method of Achar [13]. This

TABLE 1

ACTIVATION PARAMETERS FOR ALKOXIDES AND AMIDES

Compound	E_a (kcal/mole) at		A (sec^{-1}) at	
	Constant *T*	Variable *T*	Constant *T*	Variable *T*
threo-$PhCH_3CHCHPhOMgCH_3$ · 0.50 Et_2O	19.4	26.7	1.15×10^4	9.52×10^6
erythro-$PhCH_3CHCHPhOMgCH_3$ · 0.50 Et_2O	15.5	9.2	1.26×10^3	8.8
CH_3MgO-c-C_6H_{11}	14.6	13.7	1.29×10^2	5.95×10^{-4}
PhMgO-i-Pr · 0.16 Et_2O	11.8	12.7	3.3	52
$PhCH_2MgO$-i-Pr · 0.56 Et_2O	24.7	28.6	2.83×10^6	2.91×10^8
$CH_3MgNCH_3MgN(c\text{-}C_6H_{11})_2$	18.1	8.3	2.55×10^4	9.9×10^{-1}
$PhMgN(c\text{-}C_6H_{11})_2$ · 0.94 PhH	4.1	9.2	2.96×10^{-3}	1.1
CH_3MgN-i-Pr_2	39.4	23.2	8.35×10^{19}	2.10×10^{10}
PhMgN-i-Pr_2 · 0.89 Et_2O	14.7	9.3	86	3.3
$PhCH_2Mg$-i-Pr_2 · 1.17 Et_2O	11.7	9.2	3.10×10^2	60
CH_3MgS-n-Bu	13.2	18.7	4.5×10^1	1.11×10^5

method applies to all reaction mechanisms, provided that the correct mechanism is known.

The Achar method is based on the equation $\ln \frac{1}{f(\alpha)} \cdot \frac{d\alpha}{dT} = \ln(A/B) - \frac{E_a}{RT}$, where R is the gas constant, α is the fraction of sample reacted in time t, and B is the heating rate. When the left-hand side of the equation is plotted against $1/T$, a straight line is obtained from which E_a and A can be determined. The energy of activation is calculated from the equation $E_a = -R \times$ slope, and A (the Arrhenius preexponential factor) is calculated from the equation $\ln(A/B) =$ intercept. The form of $f(\alpha)$ depends on the nature of the reaction and must be determined prior to the application of the Achar equation.

Application of the procedure of Satava [14] led to the determination of the correct form of $f(\alpha)$. The most commonly used mechanisms were considered, and the experimental data gave the best straight line, as determined by the correlation coefficient (R) from a linear least squares plot of $\log g(\alpha)$ versus $1/T$, for the equation $-\ln(1-\alpha) - kt$. Therefore, the form of $f(\alpha) = (1-\alpha)$, and the revised Achar equation becomes $\ln \frac{1}{1-\alpha} \cdot \frac{d\alpha}{dT} = \ln(A/B) - \frac{E_a}{RT}$

A typical DTA-TGA curve is illustrated in Fig. 1 for diisopropylamino(phenyl)-magnesium. Coordinated solvent (diethyl ether) was lost first and then the main decomposition occurs in one step with no apparent intermediate. Data for the Achar equation were obtained from the steep portion of the curve.

Isothermal and non-isothermal calculations of E_a and A are summarized in Table 1. The average agreement between the E_a values calculated by the two methods was ±20%. Only two compounds, dicyclohexylamino(methyl)-magnesium and dicyclohexylamino(phenyl)magnesium, lie significantly outside of this range (±38%). The best estimate of the "true" E_a is probably the average number obtained by the two methods. As expected, the agreement between the A values is not as good since a small fluctuation in slope can cause a large change in the intercept.

Several interesting observations can be made employing the data in Table 1. For example, *erythro*-1,2-diphenyl-1-propylanilino(methyl)magnesium has a lower E_a than the corresponding *threo* isomer. This observation reflects the greater steric hindrance involved in eclipsing two phenyl groups in the transition state leading to *cis*-1,2-diphenylpropene from the *threo* isomer compared to the steric hindrance involved in eclipsing a methyl and a phenyl group in the transition state leading to *trans*-1,2-diphenylpropene from the *erythro* isomer. A comparison of phenylmagnesium isopropoxide and benzylmagnesium isopropoxide indicates that the phenyl compound has a lower E_a. However, the opposite trend is observed when the diisopropylaminomagnesium amides are considered. The order of increasing E_a is $PhCH_2 < Ph < CH_3$. This apparent conflict in trends can be explained in terms of a variable Ei mechanism as proposed previously [1]. In the case of the alkoxides the transition state exhibits some carbanion character at C_β and magnesium—aryl cleavage is advanced. Therefore, phenylmagnesium isopropoxide has a lower E_a than the benzyl compound since phenyl carbanion is more reactive than benzyl carbanion. On the other hand, the magnesium amides decompose via a more synchronous transition state. The observed order of increasing E_a's ($PhCH_2 < Ph < CH_3$) indicates that the most stable incipient carbanion is responsible for the lowest E_a. The decomposition reaction was also applied to a representative mercaptan. The E_a calculated for n-butylthio(methyl)magnesium is the same as that for the alkoxides and amides. The rather small values for the Arrhenius factors (A) results in large negative entropies of activation ($\Delta S^{\neq}$) for the alkoxides and amides of magnesium. These entropies of activation fall in the range −32 to −73 e.u. at 200°C. The only exception is diisopropylamino(methyl)magnesium which gave a positive $\Delta S^{\neq}$ (+30 e.u.).

Isothermal kinetic data usually does not give information concerning the detailed mechanism of decomposition in the solid phase. Several possible rate-determining phenomena include diffusion of gaseous products from the surface of the material, growth of product-reactant interfaces, and random nucleation. Therefore, the non-isothermal kinetic study was conducted.

The results of the non-isothermal kinetic study gave more information concerning the mechanism of the thermal decomposition of the alkoxides and amides of magnesium. The integrated equation for f(α) indicated that the rate-controlling process is random nucleation; one nucleus on each particle [14]. That is, reactions of each individual crystal result from the formation of a single nucleus on the surface of that particular particle. Thus, the decomposition rate is controlled by the nucleation process. Since each individual particle in the assemblage may be nucleated with equal probability, the rate of decomposition obeys first-order kinetics [15].

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