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A kinetic investigation of ethyl formate elimination from the $[MgCl_2(HCOOC_2H_5)_2]_n$ adduct using thermoanalytical data

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Abstract

A kinetic investigation of ethyl formate elimination from the polymeric adduct $[M_gCl_2(HCOOC_2H_5)_2]_n$ (V. Di Noto, G. Bandoli, S. Bresadola, R. Zannetti and M. Viviani, submitted to Z. Kristallogr) has been carried out under a rigorously inert atmosphere at reduced pressure by means of thermogravimetric measurements. The elimination appears to occur in two steps which agree well with rate laws of the first and second order of reaction, respectively. The activation energies of these elimination reactions have been also determined and a reaction mechanism is proposed.

INTRODUCTION

Up-to-date heterogeneous Ziegler–Natta catalysts for α-olefin stereospecific polymerization generally consist of titanium(IV) chloride supported on a highly structurally disordered form of $MgCl_2$ [2]. We found that an attractive $MgCl_2$ support can be obtained by thermal elimination at reduced pressure of the coordinated ethyl formate from the polymeric adduct $[MgCl_2(HCOOC_2H_5)_2]_n$ **I** [1].

We report here the results of a kinetic study of the elimination reaction of the coordinated base from the adduct **I**, carried out by thermogravimetric techniques. The kinetic parameters could be evaluated by using the standard TG curve fitting methods [3]; however the results so obtained may be affected by heat and mass transfer phenomena and by the experimental conditions [4,5]. Therefore, in order to obtain reliable kinetic results, we used thermogravimetry as an analytical technique for the measurement of

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the weight loss occurring in the course of the isothermal elimination of ethyl formate from the adduct, care being taken to identify effects due to the overlap of possible consecutive elimination steps. For this purpose it is of fundamental importance to determine the exact weight loss occurring in any elimination step; we have shown that correct kinetic parameters are obtained by measuring for any step a fraction of the total weight loss in place of the total loss.

The obtained results indicate that the isothermal elimination of ethyl formate from the adduct I occurs in two steps, and following the above reported procedure the reaction orders and the activation energy of the two steps have been determined.

EXPERIMENTAL

α-$MgCl_2$ of reagent grade was supplied by Himont Italia S.p.A.; ethyl formate (Aldrich A.C.S. reagent) was further purified and dried by standard methods prior to use.

The thermogravimetric measurements were carried out with a Perkin–Elmer TGS-2 thermobalance operating under a rigorous nitrogen atmosphere inside a Braun MB-150 I/II dry box. The TG data were collected and processed in a dynamic nitrogen flow of 50 ml min^{-1} and with a heating rate of 20 °C min^{-1} by a Perkin–Elmer 3700 Data Station operating in PETOS rev.D, using TADSOFT to read and BASIC rev.A to process the acquired data.

Preparation of the adduct

Dried and oxygen free ethyl formate (250 ml) was added to 22.07 g of α-$MgCl_2$ in a flask equipped with a reflux condenser under a rigorous nitrogen atmosphere at room temperature. The slurry so obtained was heated to the boiling point and vigorously stirred and boiled for 2 h. In the meantime, the magnesium chloride dissolved, yielding a colourless solution. This solution was then filtered and, after slow cooling at room temperature, very fine, unstable and colourless crystals of I were formed in the dark.

X-ray diffraction (XRD) analysis shows that these crystals consist of doubly chlorine bridged chain polymers, as depicted in Fig. 1, in which each magnesium atom is octahedrally coordinated by four chlorine atoms and by the carbonyl oxygens of two $HCOOC_2H_5$ moieties. Among the chains only weak Van der Waals interactions arise.

Elimination of ethyl formate from the adduct

The elimination of ethyl formate from the polymeric adduct was followed isothermically at ten different temperatures (40, 60, 80, 100, 120, 140, 160,

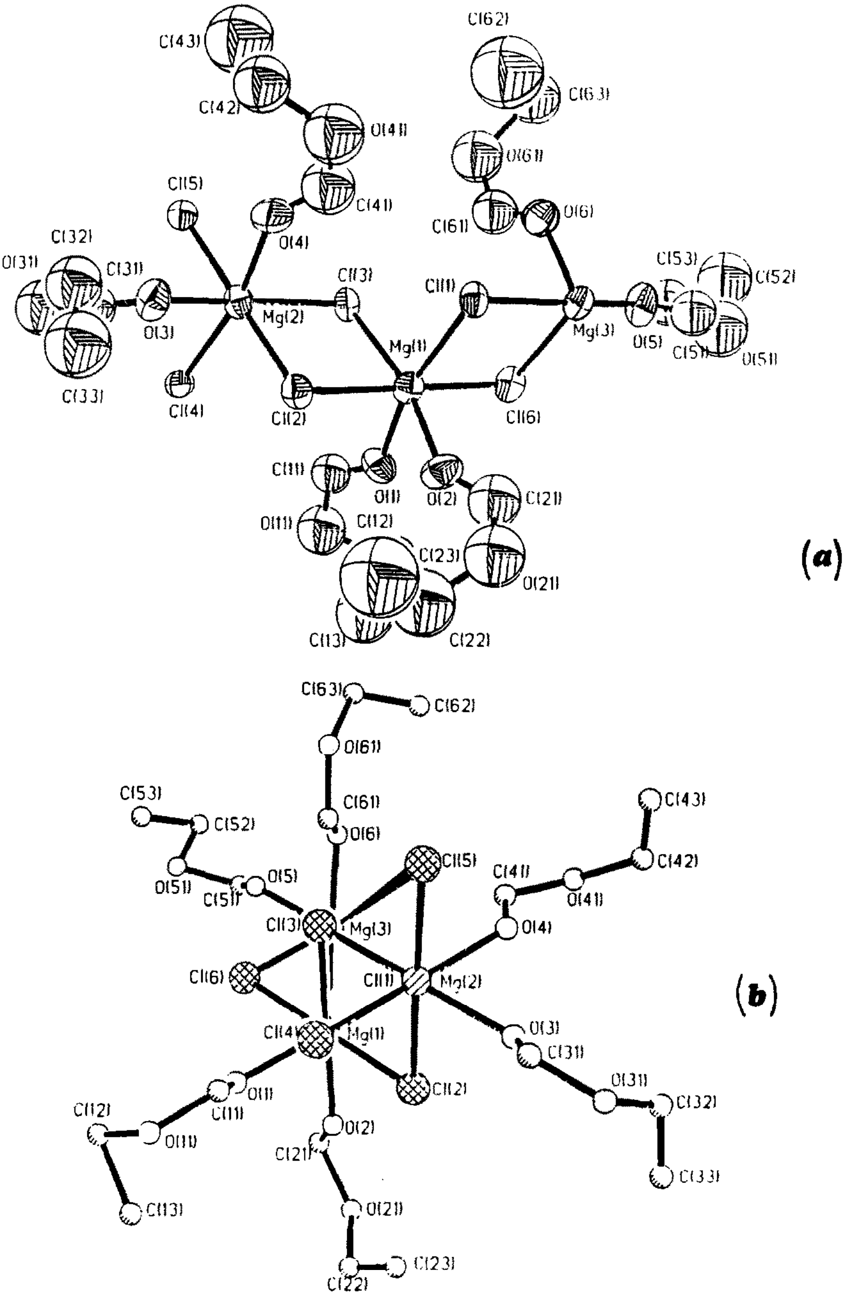

Fig. 1. (a) Perspective view of the asymmetric part of the $[MgCl_2(HCOOC_2H_5)_2]_n$ polymeric adduct; (b) view of the chains along the 001 direction.

180, 200 and 220 ° C) under a rigorously inert atmosphere at 10^{-1} atm. Each run was performed with efficient stirring so as to avoid any transfer resistance with respect to intraparticle phenomena; moreover, the solid was finely powdered so as to reduce the intrusion of any interparticle transfer

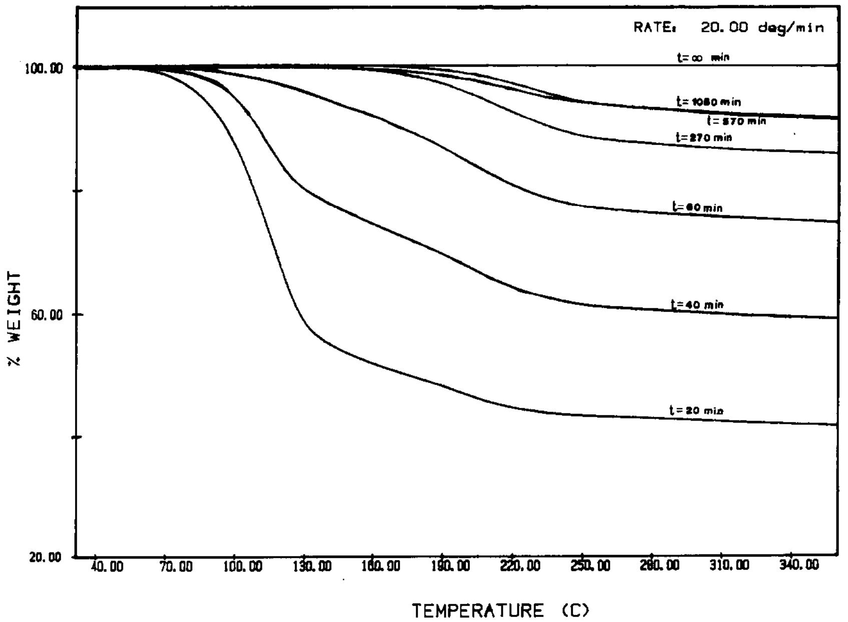

Fig. 2. TG measurements of the elimination reaction performed at 140 °C of ethyl formate from the $[MgCl_2(HCOOC_2H_5)_2]_n$ adduct, **I**, at different times (min) under a pressure of 10^{-1} atm.

resistance. Both these experimental precautions, together with the relatively high decomposition pressure (i.e. a low elimination rate), guarantee that the kinetic evolution of the system is determined by the decomposition only. The residual amount of ethyl formate contained in the samples, corresponding to the same isothermal treatment at different times, was measured by the TG technique. As an illustration, the recorded TG curves of the samples obtained by isothermal treatment of **I** at 140 °C for different times are shown in Fig. 2.

DATA ANALYSIS

Measurement methods

The DTG curve of Fig. 3, which is an example of the experimental run at 180 °C, shows that the kinetic evolution of base elimination is the result of more than one step; moreover, the overlapping effect between the end of the first elimination reaction and the beginning of the second, Fig. 3, is qualitatively evident. In order to avoid errors in the kinetic parameter determinations due to this overlapping effect of the consecutive reactions, we adopted the measurement method detailed below, which allowed us to obtain reliable results.

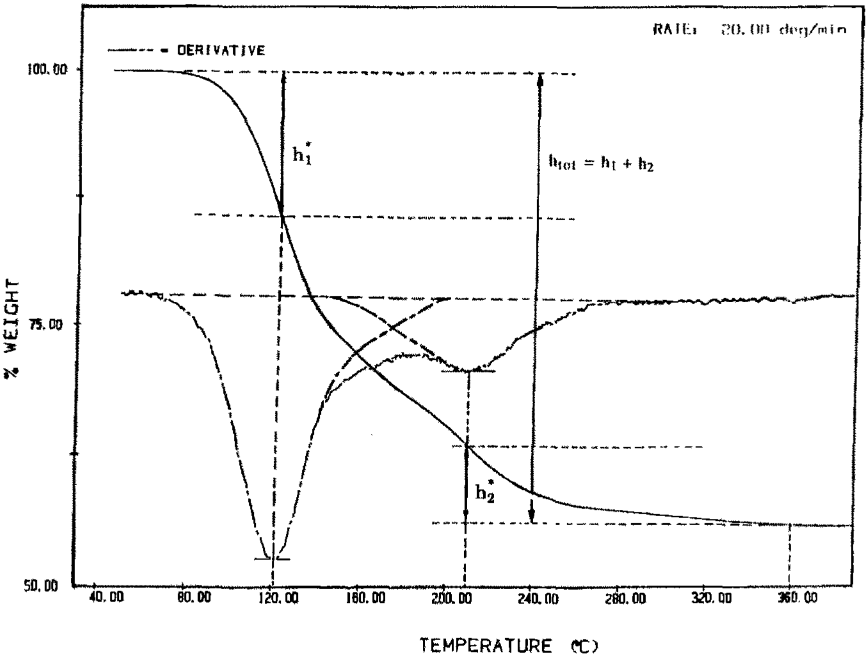

Fig. 3. Representative TG and DTG curves of a sample of the run at 180 °C; h_{tot} is the overall normalized weight loss of ethyl formate from the sample ($h_{tot} = h_1 + h_2$).

In the particular case under examination (two steps), there is overlap between the end of the first elimination step and the beginning of the second. Focusing on the minimum of the DTG curve, a normalized weight fraction $h_1^\star$ can be measured which is not affected by the weight loss of the next step. This fraction is defined by the equation

$$h_1^\star = d_1 h_1 = d_1 \frac{(W_0 - W_1)}{W_0} \tag{1}$$

where h_1 indicates the total normalized weight lost in the course of the first step of the elimination reaction, W_0 the initial weight of the sample, W_1 the weight at the end of the first step of the elimination and $0 < d_1 < 1$. The particular value of d_1 is determined by the occurrence of the first minimum of the DTG curve, as shown in Fig. 3. This approach allows us (i) to fix an absolute reference point in the weight–temperature plane where we can evaluate $h_1^\star$ in a reliable way (independent of the particular experimental conditions) and (ii) to avoid any superposition with the next weight loss step. In the same way, so as to avoid any interaction with the former step, it is possible to define the normalized weight fraction, $h_2^\star$ relative to the second step

$$h_2^\star = d_2 h_2 = d_2 \frac{(W_1 - W_2)}{W_0} \tag{2}$$

with $0 < d_2 < 1$ in dependence on the second minimum of the DTG curve. It is worthwhile to note that the main advantage of this procedure is the reproducibility in terms of the fraction d_i which, as will be verified later, remains practically constant for all examined runs.

Kinetic rate expressions

If we assume that the generic *i*-th decomposition step follows a simple first or second order rate expression, the following time evolutions of the weight loss are readily obtained

$$\ln(h_i) = \ln(h_i^0) - k_{1,i}t \tag{3}$$

$$\frac{1}{h_i} = \frac{1}{h_i^0} + k_{2,i}t \tag{4}$$

where $k_{1,i}$ and $k_{2,i}$ are the rate constants for the first and second order decomposition rate, respectively, and h_i^0 indicates the initial value of the normalized weight.

According to eqns. (1) and (2), and assuming constant d_i, these relationships can be rewritten in terms of the normalized weight loss fraction, $h_i^\star$, as follows

$$\ln(h_i^\star) = \ln(h_i^{\star,0}) - k_{1,i}t \tag{5}$$

$$\frac{1}{h_i^\star} = \frac{1}{h_i^{\star,0}} + k'_{2,i}t \tag{6}$$

where $k'_{2,i} = k_{2,i}/d_i$ and $h_i^{\star,0}$ indicates the normalized weight fraction at $t = 0$.

The Arrhenius equations for the rate constants relating to eqns. (5) and (6) are, respectively

$$\ln(k_{1,i}) = \ln(A_{1,i}) - \left(\frac{E_{1,i}}{R}\right)\left(\frac{1}{T}\right) \tag{7}$$

$$\ln(k'_{2,i}) = \ln\left(\frac{A_{2,i}}{d_i}\right) - \left(\frac{E_{2,i}}{R}\right)\left(\frac{1}{T}\right) \tag{8}$$

where A indicates the preexponential factor, E is the activation energy, R is the gas constant and T is the absolute temperature.

The same kinetic expressions for the weight loss previously considered for each reaction step [eqns. (3) and (4)] can be adopted with reference to the overall weight loss; in this case, the corresponding rate constant will be indicated by $k_{1,\text{tot}}$ and $k_{2,\text{tot}}$ for a first or second order reaction, respectively.

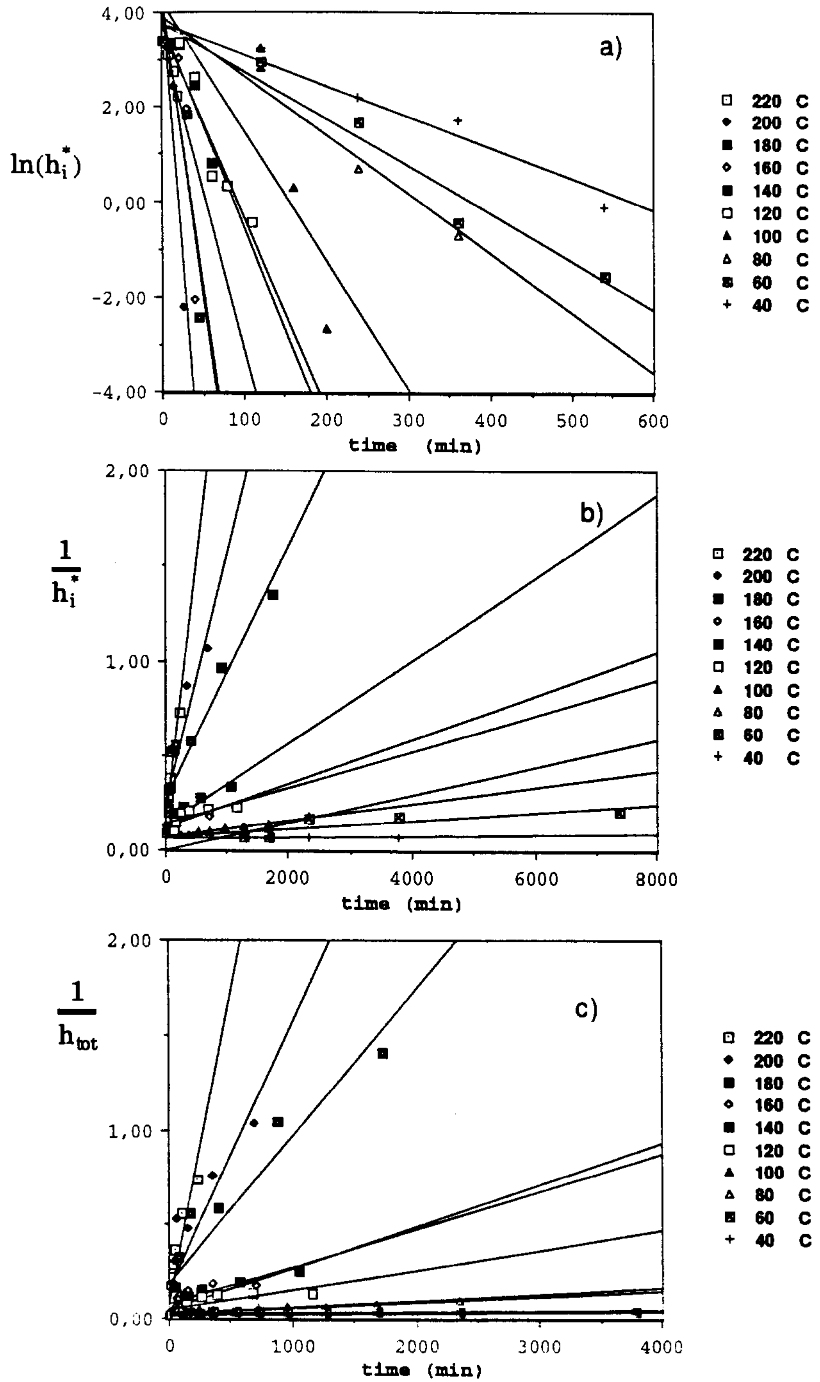

Fig. 4. Time evolutions of the normalized weight loss: (a) normalized weight loss fraction of the first step; (b) normalized weight loss fraction of the second step; (c) overall normalized weight loss.

RESULTS AND DISCUSSION

By using the method described above, ethyl formate elimination from the adduct **I** appears to occur in two steps which follow different kinetic laws. In fact, while the first step takes place according to a first order reaction law [Fig. 4(a)] both the second step and the overall weight loss obey a kinetic law

TABLE 1

Linear interpolation parameters of eqns. (5) and (6), respectively, obtained by the least squares method: (a) first step; (b) second step; (c) total reaction

(a)

T (K)	$\ln(h_1^{*,0})$	$\ln(k_{1,1})$	R
313.15	4.2 ±0.3	−4.86619 ±0.00009	−0.988
333.15	4.2 ±0.6	−4.5015 ±0.0002	−0.979
353.15	5.0 ±0.7	−4.1031 ±0.0004	−0.987
373.15	11.1 ±0.5	−2.6796 ±0.0001	−0.999
393.15	4.0 ±0.6	−3.119 ±0.002	−0.949
413.15	4.7 ±0.5	−2.774 ±0.002	−0.982
433.15	8.6 ±2.6	−1.3679 ±0.03	−0.949
453.15	6.7 ±1.7	−1.65 ±0.01	−0.964
473.15	5.6 ±1.2	−1.25 ±0.02	−0.931

(b)

T (K)	$\ln(1/h_2^{*,0})$	$\ln(k'_{2,2})$	R
313.15	0.060 ±0.005	−12.4473300 ±7E−7	0.920
333.15	0.070 ±0.034	−10.733120 ±3.3E−6	0.828
353.15	0.0017 ±0.018	−9.518472 ±1.3E−6	0.991
373.15	0.070 ±0.0026	−10.018480 ±1E−7	0.991
393.15	0.139 ±0.025	−9.25525 ±1.88E−5	0.748
413.15	0.133 ±0.019	−8.432234 ±7.7E−6	0.922
433.15	0.116 ±0.013	−9.05639 ±1.51E−5	0.779
453.15	0.270 ±0.064	−7.30950 ±1.1E−5	0.962
473.15	0.249 ±0.050	−6.63741 ±2.7E−5	0.935
493.15	0.162 ±0.035	−5.9093 ±5.9E−5	0.932

(c)

T (K)	$\ln(1/h_{tot}^{0})$	$\ln(k_{2,tot})$	R
313.15	0.024 ±0.002	−12.3810400 ±3.5E−7	0.774
333.15	0.031 ±0.0028	−12.311480 ±6.9E−7	0.670
353.15	0.027 ±0.0049	−10.425220 ±6.3E−7	0.933
373.15	0.031 ±0.0036	−10.294490 ±6.1E−7	0.935
393.15	0.049 ±0.013	−9.149642 ±8.0E−6	0.790
413.15	0.054 ±0.016	−8.428358 ±7.0E−6	0.904
433.15	0.075 ±0.020	−8.51518 ±1.6E−5	0.723
453.15	0.193 ±0.077	−7.16329 ±3E−5	0.945
473.15	0.154 ±0.052	−6.56685 ±3E−5	0.910
493.15	0.093 ±0.043	−5.72765 ±9E−5	0.896

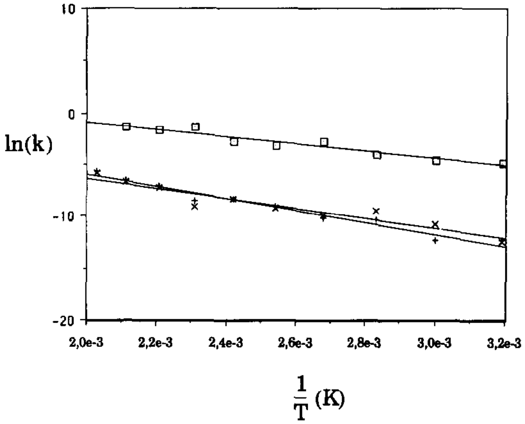

Fig. 5. Arrhenius plots obtained using the least squares method relative to the first (□), second (×) and overall (+) elimination reaction; correlation coefficient values: $R_1 = 0.960$; $R_2 = 0.953$; $R_{tot} = 0.983$, respectively.

TABLE 2

Activation energies (kJ mol^{-1}) and correlation coefficents for the first and second step and the overall elimination reaction obtained by the least squares method

Elimination reaction	E (kJ mol^{-1})	R
First step	29.4 ± 3.2	0.960
Second step	39.8 ± 4.4	0.953
Overall reaction	47.7 ± 3.1	0.983

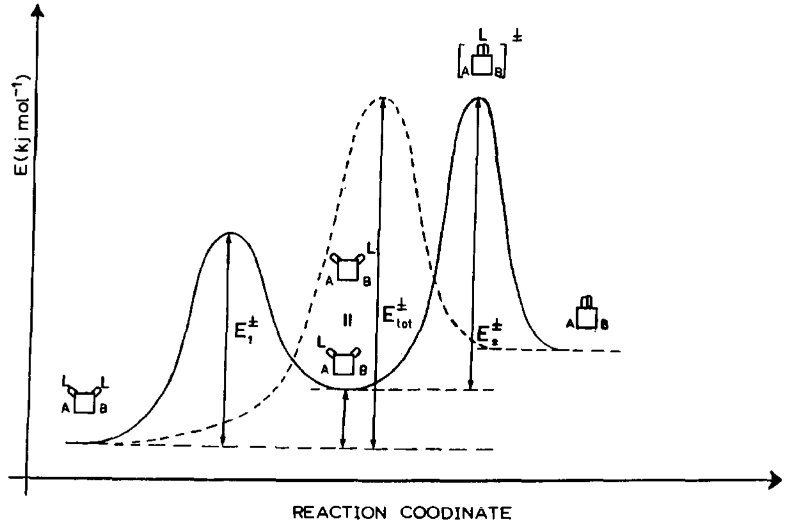

Fig. 6. Schematic diagram illustrating the energy variation along the reaction coordinate for the elimination reaction of ethyl formate from the $[MgCl_2(HCOOC_2H_5)_2]_n$ adduct.

of the second order [Fig. 4(b) and 4(c)]. In Table 1 the absolute temperature of each isotherm, the intercepts, the logarithms of the slopes and the correlation coefficents relating to the graphs of Figs. 4(a), (b) and (c) are summarized. The linear interpolations were obtained by the least squares method [6].

The Arrhenius plots are shown in Fig. 5, while the activation energies are reported in Table 2. The observed linearity of the Arrhenius plots substantiates the accuracy of the analytical procedure and, in particular, the reliability of the assumption that the parameter d_i is constant.

As the same order of rate law and activation energy value characterize both the overall elimination and the second step of the reaction, the latter is the rate determining step of the elimination process. The activation energies found are in agreement with the observed high instability and with the crystallographic disorder of the $[MgCl_2(HCOOC_2H_5)]_n$ adduct [1].

Suggested reaction mechanism

The crystalline $[MgCl_2(HCOOC_2H_5)]_n$ adduct **I** (Fig. 1) consists of double bridged chlorine chains of $MgCl_2$. Moreover, each magnesium atom, in order to attain hexacoordination, is weakly bound to two ethyl formate molecules, which are easily removed by a two step process. Figure 6 shows a schematic diagram illustrating the energy variation along the reaction coordinate for this elimination reaction. On the basis of the obtained kinetic data, the following scheme for the mechanism of the elimination reaction occurring in the solid state can be suggested

$$S_AS_BL_2 \rightarrow S_AL + S_B + L \tag{9}$$

$$S_AL + S_B \rightleftarrows [(S_AS_B)L]^{\neq} \rightarrow S_AS_B + L \tag{10}$$

where $S_AS_BL_2$ and S_AL are the di- and mono-coordinated sites on the magnesium atoms, respectively, S_B is an empty site and S_AS_B are the sites of the doubly uncoordinated Mg. $[(S_AS_B)L]^{\neq}$ represents the activated complex in which one ethyl formate molecule, L, is shared between the two coordination sites available on the same Mg atom. The second order of reaction found for the step (10) agrees with the suggestion that, in the activated complex $[(S_AS_B)L]^{\neq}$ one formate molecule is rapidly shared between the two coordination sites resident on the same magnesium atom.

CONCLUSIONS

The thermal elimination of the coordinated ethyl formate moieties from the polymeric adduct **I** occurs via two consecutive steps, giving very highly disordered $MgCl_2$ covalently bonded chains in which a great number of uncoordinated Mg atoms possess empty sites. These sites can be titanated by treatment with $TiCl_4$. The $MgCl_2$ so obtained then behaves as an effective support for Ziegler–Natta α-olefin polymerization catalysts [7]. The measured low values of the activation energy of the elimination reactions are consistent with the great thermal motion and considerable degree of disorder shown by the ethyl formate moieties in the crystals of the adduct I. Finally, it can be stated that the TG method devised by us for the measurements of the kinetic parameters appears to be very powerful, yielding reliable results unaffected by the instrumental and transport phenomena usually encountered in the standard TG curve fitting technique [4,5].

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