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Abstract

Full Text

CHEMISTRY

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KETONIZATION OF CH₃COOH OVER CdO AND MgO AND THE KINETICS OF THE THERMAL DECOMPOSITION OF Cd(CH₃COO)₂ AND Mg(CH₃COO)₂

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Ketonization of acids in the vapor phase over various catalysts is closely connected with the processes of decomposition of salts of the corresponding acids in the solid or liquid (melt) phase. Depending on the nature of the catalyst, the process may proceed either in the bulk of the catalyst or on its surface. Accordingly, the regularities of ketonization will be different. In the first case, the process will consist of the reaction of vaporous CH₃COOH with the solid phase of the catalyst and of a topochemical decomposition process with formation of solid and gaseous products (there may be several such processes). In the second case, the process will consist of adsorption of CH₃COOH on the catalyst surface, the ketonization reaction, and desorption of the products into the gas phase.

Table 1

Ketonization of CH₃COOH over MgO and CdO

For MgO		For CdO	
<i>t</i> , °C	ml CO ₂ /min	<i>t</i> , °C	ml CO ₂ /min
324	2.0	259	0.66
326	2.6	270	1.7
328	4.7	272	2.0
329	5.3	277	3.1
332	7.0	280	4.0
336	9.1	286	6.5
337	10.3		
338	10.0		
341	10.6		
342	11.8		

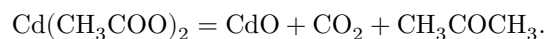
In the present work we have studied in detail both the ketonization of

CH₃COOH over oxides of Cd and Mg and the thermal decomposition of acetates of Cd and Mg. The methods for preparing the catalysts, carrying out experiments on thermal decomposition of acetates and ketonization, and X-ray phase analysis of the catalysts and solid decomposition products are described in (1,2). Ketonization experiments were carried out with 1 cm³ of catalyst under conditions of forced zero order of the reaction with respect to CH₃COOH (space velocity ~ 6-8 h⁻¹). Table 1 gives the results of experiments on ketonization of CH₃COOH.

The E_{act} values calculated from these data are, for CdO, 51 kcal/mol, and for MgO (see Fig. 1), 114 (324-332°) and 39 (332-342°) kcal/mol.

The change in E_{act} in the case of MgO is not connected with diffusion complications, as was shown by specially designed experiments.

The thermogravimetrically measured kinetics of decomposition of MgAc₂ and CdAc₂ were calculated taking into account the stoichiometry of the equations:



The mathematical treatment of the kinetic data was carried out according to the Erofeev equation (3)

$$\alpha = 1 - e^{-k\tau^n}.$$

The data obtained are presented in Table 2 (in the case of MgAc₂, the numerals I and II denote the first and second periods of the reaction).

In which phase—liquid or solid—does the decomposition of Cd and Mg acetates occur? Visual observations did not show a transition of the solid phase

Table 2

Thermal decomposition of MgAc₂ and CdAc₂

MgAc ₂	MgAc ₂	MgAc ₂	MgAc ₂	CdAc ₂	CdAc ₂	CdAc ₂	CdAc ₂
<i>t</i> , °C	lg <i>k</i>	<i>n</i>	α	<i>t</i> , °C	lg <i>k</i>	<i>n</i>	α
306	3.09	1.04	up to 0.49	230	4.55	1.29	0.05– 0.58
309	3.33	0.975	up to 0.39	232	4.73	1.28	0.18– 0.76
312	3.41	0.975	up to 0.48	239	3.00	1.23	0.10– 0.72

MgAc_2	MgAc_2	MgAc_2	MgAc_2	CdAc_2	CdAc_2	CdAc_2	CdAc_2
313 (I)	3.41	1.23	up to 0.20	240	3.01	1.22	0.03– 0.70
(II)	2.36	0.63	0.20– 0.39	244	3.14	1.22	0.03– 0.78
317 (I)	2.03	1.18	up to 0.26	247	3.39	1.14	0.10– 0.66
(II)	2.73	0.54	0.26– 0.40	255	3.70	1.98	0.08– 0.61
318 (I)	3.94	1.14	up to 0.20	257	2.04	1.74	0.06– 0.68
(II)	2.71	0.53	0.20– 0.39	259	3.88	1.77	0.11– 0.62
321 (I)	3.71	2.04	up to 0.17	263	3.91	1.77	0.08– 0.51
(II)	1.06	0.44	0.17– 0.50	264	2.06	1.65	0.14– 0.57
321 (I)	3.79	1.83	up to 0.25	268	2.16	1.69	0.08– 0.63
(II)	2.90	0.62	0.25– 0.60	275	2.32	1.60	0.05– 0.58
321 (I)	3.56	1.93	up to 0.22				
(II)	2.90	0.54	0.22– 0.47				
323 (I)	3.96	1.71	up to 0.26				
(II)	1.16	0.40	0.26– 0.39				

$$E_{\text{act}}^* = 120 \text{ kcal/mol (306—318}^\circ\text{)}$$

$$E_{\text{act}} = 52 \text{ kcal/mol (230—275}^\circ\text{)}$$

* In the presence of two reaction periods, the figures referring to the first period were used to determine E_{act} .

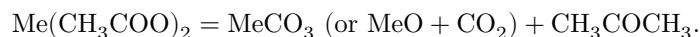
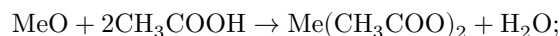
into the liquid phase. However, the value of n increases sharply precisely near the melting temperature. By analogy with the decomposition of potassium perchlorate (⁴), one might suppose that, as the solid reaction product appears, the melting temperature of the mixture decreases, the reaction passes into the melt, and the reaction rate will increase; at the end of the reaction, when the mass solidifies, the reaction rate will decrease. However, in the case of CdAc_2 this is

Fig. 1

Figure 1: Fig. 1

not observed, while in the case of MgAc_2 the increase in k in the second period of the reaction is associated with a change in the decomposition mechanism.

In addition, a single Arrhenius dependence is observed over the entire temperature range, and in the case of CdAc_2 and MgAc_2 the induction period is absent, which would be impossible if the reaction passed from the solid phase into the liquid phase and back. Consequently, the reaction proceeds predominantly in the solid phase. Comparison of the E_{act} values of the processes shows that the ketonization of CH_3COOH over the oxide and the decomposition of the corresponding acetate are characterized by one and the same energy barrier. The Arrhenius plot for the decomposition of cadmium acetate is presented in Fig. 2. X-ray phase analysis of the spent catalysts (an acetate phase was found) and the impossibility of carrying out the ketonization reaction of CH_3COOH below the decomposition temperatures of the corresponding acetates^(1,2) indicate the following staged character of the process:



The limiting stage of the process is not the formation but the decomposition of the acetate. The value of n in the Erofeev equation makes it possible to decide in which region—kinetic ($n > 1$) or diffusion ($n < 1$)—the decomposition reaction of the acetate⁽⁵⁾, and consequently also the ketonization process of CH_3COOH , proceeds. Decomposition of CdAc_2

Fig. 1

is characterized by $n > 1$, i.e., the overall rate of the process is determined by the chemical reaction. The situation is more complex in the decomposition of MgAc_2 . At $306\text{--}312^\circ$, $n \simeq 1$; at $312\text{--}323^\circ$ in the first period of the reaction $n > 1$, while in the second period $n < 1$; consequently, in the first period the reaction proceeds in the kinetic region, and in the second period in the diffusion region. The change in n from 0.63 to 0.43 with increasing temperature indicates an increasing degree of immersion of the process into the diffusion region⁽⁵⁾. Decomposition of the acetate may lead either to the carbonate or to the oxide and CO_2 . To choose between these two paths, we subjected CdCO_3 to decomposition and established that the rate of decomposition of the carbonate is many times lower than the rate of decomposition of CdAc_2 .

Fig. 2

Fig. 2

Figure 2: Fig. 2

It appeared that CdCO_3 cannot be an intermediate product of the decomposition of CdAc_2 , especially since at $t = 255^\circ$ the X-ray patterns of the solid decomposition products contained no lines of the carbonate phase. However, at $t < 255^\circ$, when the reaction rate is small, we were able to detect lines corresponding to CdCO_3 . These lines were also detected in the case when the decomposition of CdAc_2 was carried out not in air, but in a stream of N_2 . Thus, the primary product of decomposition of CdAc_2 is amorphous CdCO_3 , which decomposes into CdO and CO_2 . The absence of a crystalline lattice facilitates decomposition. At low temperatures the rate of decomposition of amorphous CdCO_3 apparently becomes commensurate with the rate of its crystallization.

The nature of the decomposition of MgAc_2 , as shown by the kinetic data and by X-ray phase-analysis data, is complex, which is connected with the ability of MgO to form basic carbonates of various composition ⁽⁶⁾. Comparison of X-ray patterns of MgO catalysts and of the decomposition products of MgAc_2 shows: a) an independent MgO phase is absent in the decomposition products of MgAc_2 and is present in MgO catalysts; b) in both types of X-ray patterns there is a $\text{MgCO}_3 \cdot \text{H}_2\text{O}$ phase ⁽⁶⁾, and the $\text{MgCO}_3 \cdot \text{H}_2\text{O}$ phase is absent; c) the MgAc_2 phase is X-ray-amorphous in the decomposition products of MgAc_2 and crystalline in MgO catalysts after operation; crystallization is apparently a consequence of the presence of water released during the ketonization of CH_3COOH over MgO ; d) during decomposition of MgAc_2 a solid solution of MgO and $5\text{MgO} \cdot 4\text{CO}_2 \cdot 5\text{H}_2\text{O}$ is formed (X-ray pattern of MgAc_2 after 7.5, 11, 15, and 20 h of heating at 306°); e) at the beginning of decomposition of MgAc_2 (312° , $\alpha = 0.1$) the phases $\text{MgCO}_3 \cdot \text{H}_2\text{O}$ and $5\text{MgO} \cdot 4\text{CO}_2 \cdot 5\text{H}_2\text{O}$ are formed; f) in addition to those indicated, some other carbonate phases are also present, found as well in specially prepared magnesium carbonate; the latter was obtained by heating the basic carbonate at 220° in a stream of CO_2 .

Thus, decomposition of MgAc_2 at low temperatures ($306\text{--}312^\circ$) proceeds up to the formation of MgCO_3 ; decomposition of MgCO_3 leads to oxycarbonate, and hydration gives the phase $\text{MgCO}_3 \cdot \text{H}_2\text{O}$. In accordance with what has been said, one kinetic constant is observed throughout the entire process. Since $n \simeq 1$, the topochemical decomposition process imitates monomolecular reactions. At $t > 313^\circ$, in the first period of decomposition magnesium carbonate is formed, which in the second period of decomposition undergoes various transformations. Decomposition of MgAc_2 to MgCO_3 proceeds in the kinetic region, while decomposition of MgCO_3 proceeds in the diffusion region.

Let us briefly discuss the transformation of the carbonate phase as a stage in the process of acetate decomposition. Judging from the literature data ⁽⁶⁾, decomposition of magnesium carbonate, promoted by water vapor, proceeds in the same temperature range as the decomposition of MgAc_2 . Decomposition

of MgCO_3 begins in air at 315° , i.e., precisely at the temperature at which decomposition of MgAc_2 passes through two decomposition periods (Table 2). In air, MgCO_3 can

to hydrate to $\text{MgCO}_3 \cdot \text{H}_2\text{O}$, which decomposes at lower temperatures and at a higher rate into magnesium oxycarbonate. Water vapor promotes the decomposition, hydration, and recrystallization of the preparation. Depending on the temperature, the rate-limiting stage may be either the decomposition of MgAc_2 to MgCO_3 , or the decomposition of MgCO_3 . The decomposition of MgCO_3 is apparently characterized by $E_{\text{act}} = 39$ kcal/mol, which agrees well with the E_{act} for the decomposition of MgCO_3 in vacuum (⁷). Thus, the primary products of the decomposition of MgAc_2 and CdAc_2 are carbonates, not oxides. Depending on the temperature, the carbonate subsequently decomposes more or less rapidly.

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