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1961

SovietRxiv

Abstract

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CHEMISTRY

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KETONIZATION OF CH_3COOH OVER CdO AND MgO AND THE KINETICS OF THE THERMAL DECOMPOSITION OF $Cd(CH_3COO)_2$ AND $Mg(CH_3COO)_2$

(Presented by Academician A. A. Balandin on 6 IV 1961)

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 CH_3COOH 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 CH_3COOH on the catalyst surface, the ketonization reaction, and desorption of the products into the gas phase.

Table 1

Ketonization of CH_3COOH *over* MgO *and* CdO

For MgO	For MgO	For CdO	For CdO
t, °C	ml CO_2/min	t, °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

CH_3COOH 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 cm^3 of catalyst under conditions of forced zero order of the reaction with respect to CH_3COOH (space velocity $\sim$ 6-8 h^{-1}). Table 1 gives the results of experiments on ketonization of CH_3COOH.

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 $MgAc_2$ and $CdAc_2$ were calculated taking into account the stoichiometry of the equations:

$$Mg(CH_3COO)_2 = MgCO_3 + CH_3COCH_3;$$

$$Cd(CH_3COO)_2 = CdO + CO_2 + CH_3COCH_3.$$

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 $MgAc_2$, 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 $MgAc_2$ and $CdAc_2$

$MgAc_2$	**$MgAc_2$**	**$MgAc_2$**	**$MgAc_2$**	**$CdAc_2$**	**$CdAc_2$**	**$CdAc_2$**	**$CdAc_2$**
t, °C	lg k	n	α	t, °C	lg k	n	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				

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

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

* 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:

$$MeO + 2CH_3COOH \rightarrow Me(CH_3COO)_2 + H_2O;$$

$$Me(CH_3COO)_2 = MeCO_3 \text{ (or } MeO + CO_2) + CH_3COCH_3.$$

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 306–312°, $n \simeq 1$; at 312–323° 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 $MgCO_3 \cdot H_2O$ phase ([6]), and the $MgCO_3 \cdot H_2O$ 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 $5MgO \cdot 4CO_2 \cdot 5H_2O$ 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 $MgCO_3 \cdot H_2O$ and $5MgO \cdot 4CO_2 \cdot 5H_2O$ 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 (306–312°) proceeds up to the formation of $MgCO_3$; decomposition of $MgCO_3$ leads to oxycarbonate, and hydration gives the phase $MgCO_3 \cdot H_2O$. 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 $MgCO_3 \cdot H_2O$, 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 $E_{act} = 39$ 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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Received
5 IV 1961

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Note: Figure translations are in progress. See original paper for figures.