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SOME DATA ON THE KINETICS OF THE THERMAL DECOMPOSITION OF ALKALINE-EARTH METAL ACETATES

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The study of the kinetics of the thermal decomposition of salts of carboxylic acids is of interest because knowledge of it may help to establish the role of the formation and decomposition of these compounds in the vapor-phase catalytic ketonization of acids, used as a method for obtaining ketones, especially unsymmetrical ones. An example of such kinetics may be the decomposition of acetates. According to Squibb (1) and Ipatiev (2), the vapor-phase ketonization of acetic acid may proceed with the intermediate formation of acetates and their subsequent decomposition into the metal carbonate and acetone. The same conclusion follows from the work of Nefedov et al. (3); however, other views on the course of this reaction have also been expressed (4-7).

A study of the kinetics of decomposition of the acetates of Mg, Ca, Sr, and Ba appeared advisable in connection with the observation of a rare case of formation of a bulk phase of an intermediate compound—an acetate—during the catalytic ketonization of CH_3COOH over Ca and Ba carbonates in a certain temperature interval, made on the basis of X-ray data in work (8). In the present work we intended to determine the initial decomposition temperatures, as well as the values of the reaction-rate constants and activation energies, in order subsequently to compare them with the corresponding values for catalytic ketonization.

The rate of a chemical reaction cannot be predicted on the basis of the change in free energy; however, for reactions of the same type, characterized by one and the same activated complex, there is a definite relationship between the kinetic and thermodynamic characteristics of reactions (9). Changes in free energy in the process of decomposition of acetates

$$\mathrm{Me(CH_3COO)_2 = MeCO_3 + CH_3COCH_3}$$

for different cations and process conditions were calculated by the Temkin-Shvartsman method (10)

Fig. 1. Course of the change in the free energy of the decomposition reaction of acetates of Ca (a), Sr (b), and Ba (c) with temperature

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Fig. 2. Thermogravimetric curves for the decomposition of acetates of Mg (a), Sr (b), and Ca (c)

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$$\Delta F_T^0 = \Delta H_{298}^0 - T\Delta S_{298}^0 - T\left(M_0\Delta a + M_1\Delta b + M_2\Delta c + M_{-2}\Delta c'\right),$$

where the values ΔH_{298}^0 and S_{298}^0 were taken from Rossini' s handbook of thermodynamic properties, as well as from several other sources, and the missing values of the absolute entropies for the acetates of Mg, Ca, Sr, and Ba were calculated by approximate methods using the formulas of Eastman (11) and Wenner (12). The course of the changes in free energy with temperature is presented in Fig. 1, showing that the corresponding equilibrium yields vary in the sequence $\mathrm{BaAc_2} > \mathrm{SrAc_2} > \mathrm{CaAc_2}$ at 350–480° and $\mathrm{CaAc_2} > \mathrm{SrAc_2} > \mathrm{BaAc_2}$ at 480–550°. Below 350°, ΔF becomes positive, the equilibrium constant is very small, and in the case of Ca, Sr, and Ba acetates represents the lower temperature of their decomposition. Similar calculations for Mg acetate showed that the reaction according to the above scheme does not proceed. Indeed, in this case, calc—

proceeds with the formation of the oxide, as was shown by X-ray structural analysis.

We studied the decomposition of the acetates by the thermogravimetric method in a vertical tubular electric furnace with a Chromel-Copel thermocouple in the reaction zone; a quartz cup, or one made of Pyrex, containing the substance was suspended directly on a torsion balance. The weighed portions were about 1 mm; the temperature rise up to the temperature at which the reaction began was carried out at a rate of 1 deg/min. The thermogravimetric curves in Fig. 2 show that the decomposition of $\mathrm{MgAc_2}$ begins at 300°, $\mathrm{CaAc_2}$ at about 370°, and $\mathrm{SrAc_2}$ at about 400°, i.e., at somewhat lower temperatures than had been determined by Křenig (13). Repetition of the experiments with previously dehydrated acetates gave the same results.

Fig. 1. Course of the change in the free energy of the decomposition reaction of acetates of Ca (*a*), Sr (*b*), and Ba (*c*) with temperature

Fig. 2. Thermogravimetric curves for the decomposition of acetates of Mg (*a*), Sr (*b*), and Ca (*c*)

Fig. 3. Kinetic curves of the decomposition of calcium acetates under various conditions at 385-435°. a —in the coordinates of the monomolecular equation; b —in the coordinates of Erofeev’ s topokinetic equation. 1 —in Pyrex, 2 —in quartz, 3 —in the presence of Al_2O_3

Figure 3: Fig. 3. Kinetic curves of the decomposition of calcium acetates under various conditions at 385-435°. a —in the coordinates of the monomolecular equation; b —in the coordinates of Erofeev’ s topokinetic equation. 1 —in Pyrex, 2 —in quartz, 3 —in the presence of Al_2O_3

In carrying out the experiments, the following complications in the course of the process were observed, to which none of the investigators had paid attention: 1) the temperature regime of the process proves to be nonstationary, and 2) in the presence of atmospheric oxygen some chemical changes take place. Indeed, upon reaching the initial decomposition temperature, the weighed sample heats up spontaneously, and its temperature, for example in the case of $CaAc_2$, rises by 70°, after which it again falls to the furnace temperature. Special experiments with a thermocouple placed inside the substance found that, with a total duration of decomposition of 10 min, such a maximum temperature rise occurs after 5 min. Further, visual observations of the reaction showed that the substance, white at the beginning of the reaction, becomes carbon-coated. If the reaction is interrupted by removing the weighed sample from the furnace, the sample retains a dark color. X-ray examination established that at this stage the mass consists of $CaAc_2$ with an admixture of a small amount of $CaCO_3$.

If the reaction is carried to completion, then the carbonaceous deposit, which is the result of a side reaction, disappears, apparently as a result of oxidation. The same picture was observed in experiments in a stream of N_2 or CO_2 containing O_2 on the order of 1%, and was absent in experiments in a sealed tube with preliminary purging with nitrogen containing no O_2 impurity.

The kinetic curves constructed for the decomposition of $CaAc_2$ from the data we obtained in the interval 385—435° are shown in Fig. 3*a*. They show that the monomolecular decomposition reaction of this compound does not fit within the framework of classical concepts. Only in the middle part do the curves obey the first-order equation. The rate of decomposition strongly

depends on the material of the vessel walls: in a Pyrex dish it is greater than in a quartz one. When the sample of $CaAc_2$ is decreased from 1.7 to 0.6 mM, the reaction rate decreases. In Pyrex, the initially rapid reaction slows down and then accelerates again. When Al_2O_3 is added, heat removal is improved (the reaction is strongly exothermic) and the curves straighten. The activation energy, calculated from the rectilinear middle portions of the curves in Fig. 3a, is 90 kcal/mole. Taking into account the anomalies described above, we come to the conclusion that the kinetic curves presented by Rideau ([14]) (as well as the curves in Fig. 3a) are in fact pseudokinetic and cannot serve as evidence in favor of the radical mechanism of acetate decomposition proposed by him.

Fig. 3. Kinetic curves of the decomposition of calcium acetates under various conditions at 385–435°. *a* —in the coordinates of the monomolecular equation; *b* —in the coordinates of Erofeev’ s topokinetic equation. 1 —in Pyrex, 2 —in quartz, 3 —in the presence of Al_2O_3.

Much more rigorous results are given by calculation according to Erofeev’ s topokinetic equation (^{15})

$$\alpha = 1 - e^{-kt^n}$$

in its logarithmic form (see Fig. 3b). It describes up to 100% decomposition in experiments carried out in a Pyrex dish, from 30–40 to 80–90% in experiments carried out in a quartz dish, and from 50 to 100% in experiments with additions of Al_2O_3; the acceleration of the reaction in the initial stage is probably due to self-crushing of the substance.

The exponent n is close to unity (0.813-1.26). Thus, decomposition of Ca acetate proceeds by growth of flat reaction nuclei (^{16}). $\lg k$ decreases appreciably when the vessel material is changed—for quartz it is smaller than for Pyrex. Dilution of the substance with an inert carrier (Al_2O_3) decreases $\lg k$ only insignificantly. With an increase in the sample of substance from 0.57 to 1.14 and 1.7 mM, $\lg k$ increases, while n decreases somewhat. The decrease in n indicates an increase in the thermodynamic stability of the initial centers. Calculation of the activation energy gives values considerably more reasonable than calculation by the classical first-order equation. Thus E_{act}, calculated from the graph in the coordinates $\lg k - \frac{1}{T^\circ K}$, is 24 kcal/mole for experiments in a quartz dish (sample 1.7 mmole), 29.6 kcal/mole for a Pyrex dish (sample 1.14 mmole), and 38 kcal/mole in the case of the addition of 100 mg Al_2O_3 (sample 1.14 mmole).

The classical equation of a monomolecular reaction describes the kinetics of the acetate decomposition process considerably worse in all cases, except

experiments with the addition of an inert substance (Al_2O_3). Obviously, in this case the catalytic action of the solid reaction product is suppressed by Al_2O_3.

In conclusion, we note that additional experiments showed that irradiation of the sample during the reaction with ultraviolet light does not change the kinetics of the process.

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