THERMAL DECOMPOSITION OF THE ADDITION COMPOUND OF POTASSIUM CARBONATE WITH HYDROGEN PEROXIDE

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The kinetics of the thermal decomposition of the addition compound of potassium carbonate with hydrogen peroxide was carried out using a fixed bed flow reactor with gas-chromatography. The experimental results can be best represented over the whole range of the decomposition, by the equation $-\ln(1 - \alpha) = kt$, where α = degree of decomposition, t = time (min.), and k = rate constant (min.$^{-1}$). The activation energy and the pre-exponential factor for $0 < \alpha < 0.8$, are 74.3 kJ/mol and $7.8 \cdot 10^9$, and for the decay period $(0.8 < \alpha < 1.0)$, 77.3 kJ/mol and $1.38 \cdot 10^{10}$, respectively.

There are many addition compounds of carbonates with hydrogen peroxide [1]. Those of sodium or potassium carbonate with hydrogen peroxide are widely used as detergents in industry.

Nevertheless, the thermal analysis of these substances has been little studied, although the thermal decomposition of the addition compound of sodium carbonate with hydrogen peroxide was studied and discussed by this author [2]. In previous papers [2, 3] a fixed bed flow reactor with gas-chromatography was shown to be very useful for the accurate determination of the thermal decomposition process of a solid. This flow method can eliminate the effects of heat of reaction and catalytic action of product gas(es) on thermal decomposition.

This paper discusses the kinetics of the thermal decomposition of the addition compound of potassium carbonate with hydrogen peroxide by means of the DTA, TG, X-ray diffraction analysis, mass-spectrometry and gas-chromatography.

Experimental

Material used in the experiment

The sample was prepared from "Special" grade reagents. The addition compound of potassium carbonate with hydrogen peroxide was synthesized at room temperature [1]. It was crystallized with 150 ml methanol from a solution mixed with 10 ml of 6.5M potassium carbonate solution and 40 ml of 30 wt% hydrogen peroxide. The precipitate was washed with methanol till free from potassium ions, carbonate ions and hydrogen peroxide, and dried at 35° for 24hrs.

Thermal analysis

The fixed bed flow reactor with gas-chromatography (Toyo Instruments Co. Lttd., colum packing material: molecular sieve 5A, carrier gas: Helium) was used to obtain the decomposition curves for the determination of kinetic parameters under isothermal conditions in the temperature range of 65 to 80° and in helium gas flow (flow velocity = 77 ml/min).

A set of runs was devised for powders.

The DTA and TG data for the sample were obtained simultaneously in a Shimazu Thermal Analyzer, DT-2B apparatus under the following conditions: sample weight = 100 mg, heating rate = 10 deg/min, sensitivity of DTA = ± 50 μV, that of TG = 0.33 mg/division, atmosphere = air.

X-ray diffraction analysis was carried out at variable temperatures in air with a $_\Lambda$D-1 apparatus.

Mass spectra were recorded on a Shimazu GC-MS analyzer at variable temperatures under a highly reduced atmosphere.

Results and discussion

DTA and TG curves of $K_2CO_3 \cdot 1/2 \, H_2O \cdot 2 \, H_2O_2$ are shown in Fig. 1.

The curves are characterized by an exothermic peak and sharp weight loss at ca. 70 °C. In the 120—150 °C region, a small broad endothermic rise and similar weight loss occur.

The probable mode of the decomposition of $K_2CO_3 \cdot 1/2 \, H_2O \cdot 2 \, H_2O_2$ would be,

$$K_2CO_3 \cdot 1/2 \, H_2O \cdot 2 \, H_2O_2 = K_2CO_3 \cdot 1/2 \, H_2O + O_2 + 2H_2O \tag{1}$$

$$K_2CO_3 \cdot 1/2 \, H_2O = K_2CO_3 + 1/2 \, H_2O \tag{2}$$
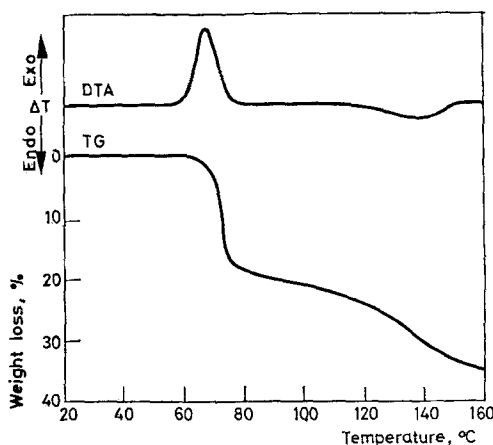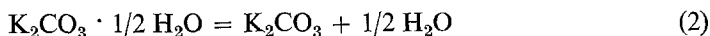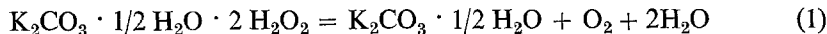
Fig. 1. DTA and TG curves of $K_2CO_3 \cdot 1/2 \, H_2O \cdot 2 \, H_2O_2$

The observed weight losses were 21% at 102° and 35.3% at 200°, which are in close agreement with the calculated ones corresponding to 23.3% for the reaction (1) and to 35.8% for the reaction (1) + (2), respectively.
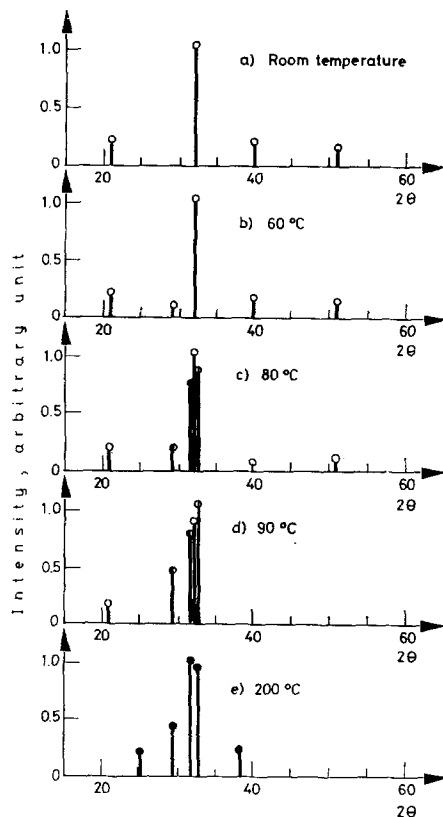

Fig. 2. X-ray diffraction patterns at various temperatures. ○: $K_2CO_3 \cdot 1/2 \ H_2O \cdot 2 \ H_2O_2$; ⊙: $K_2CO_3 \cdot 1/2 \ H_2O$; ●: K_2CO_3

Figure 2 shows X-ray diffraction patterns at various temperatures, which indicate the formation of $K_2CO_3 \cdot 1/2 \ H_2O$ and K_2CO_3, and confirm the above interpretation of the DTA and TG curves.

The mass spectrometer run is presented in Fig. 3.

The data indicate a noticeable shift of the decomposition toward lower temperature probably due to the accuracy with which the temperature in the pyrolyzer is measured. It is, however, important to notice in the mass spectra that hydrogen peroxide molecules were detected in addition to oxygen and water molecules.

It is revealed from the mass spectra result that the reaction (1) can be replaced

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by the following sequence of reactions:

$$K_2CO_3 \cdot 1/2\, H_2O \cdot 2\, H_2O_2 = K_2CO_3 \cdot 1/2\, H_2O + 2\, H_2O_2 \qquad (1a)$$

$$H_2O_2 = H_2O + 1/2\, O_2 \qquad (1b)$$

That the DTA curve has only one exothermic peak at ca. 70° suggests that either the rate of reaction (1a) or that of reaction (1b) is faster than the other.
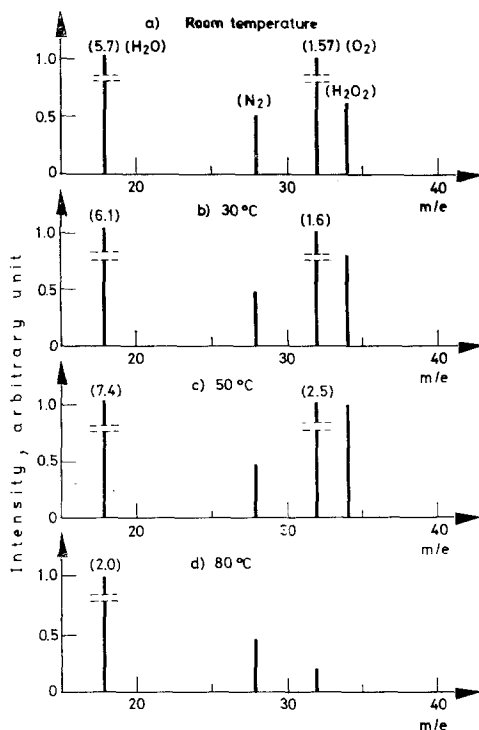

Fig. 3. Mass spectra record at variable temperatures

The rate of O_2 gas evolution, $d(O_2)/dt$ (ml/min) is plotted versus time at various temperatures measured with the fixed bed flow reactor with gas-chromatography (Fig. 4). These curves were integrated graphically to obtain the decomposition curves. The rate of the reaction obeys the first-order equation in the whole range of decomposition,

$$-\ln(1 - \alpha) = kt \qquad (3)$$

The applicability of Eq. (3) is shown in Figs 5 and 6, where $\ln(1 - \alpha)$ is plotted vs. time, t.

For $0 < \alpha < 0.8$, this equation assumes both random nucleation and the reaction ending at different times in different crystals [5].

In the decay period ($0.8 < \alpha < 1.0$), the equation can be derived on the basis that the rate of reaction is simply proportional to the amount of substance un-
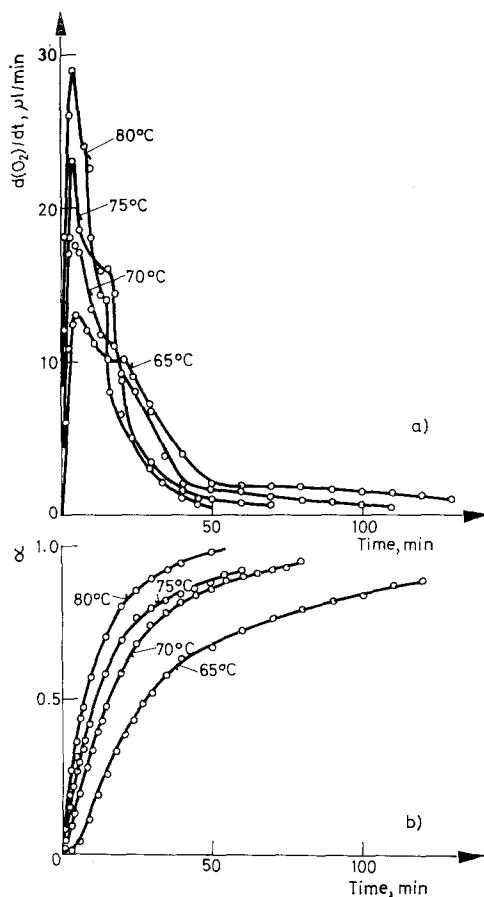

Fig. 4. (a) The rate of O_2 gas evolution vs. time and (b) the decomposition curves

decomposed, if each molecule possesses an equal probability for decomposition [6].

The Arrhenius plots are shown in Fig. 6, from which the activation energy and pre-exponential factor are computed as follows:

$$k = 7.82 \cdot 10^9 \exp\left(-74.3 \; (kJ/mol)/RT\right) \text{ for } 0 < \alpha < 0.8 \text{ and}$$

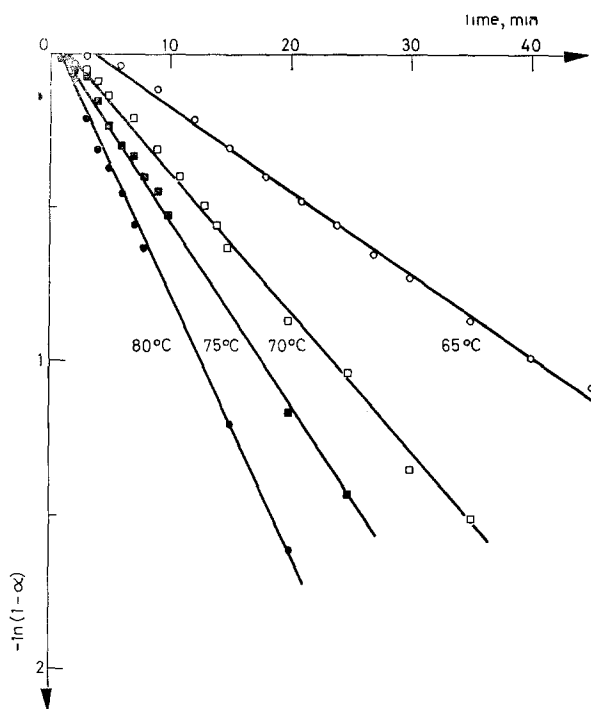$$k = 1.38 \cdot 10^{10} \exp\left(-77.3 \; (kJ/mol)/RT\right) \text{ for } 0.8 < \alpha < 1.0.$$

Fig. 5. The first-order plot for $0 < \alpha < 0.8$
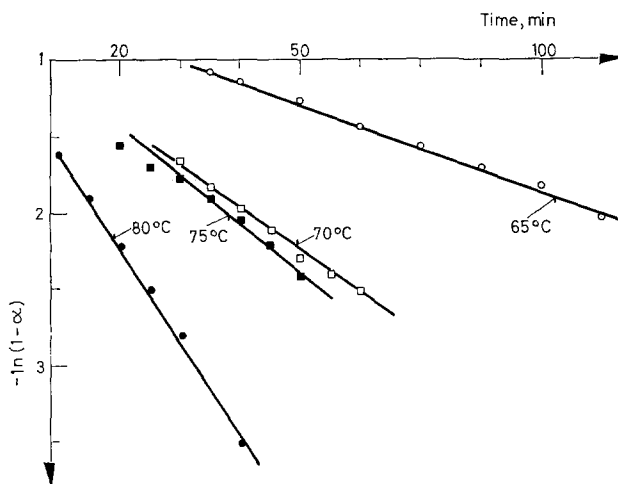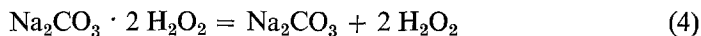
Fig. 6. The first-order plot for $0.8 < \alpha < 1.0$

The reaction scheme of the thermal decomposition of $Na_2CO_3 \cdot 2 H_2O_2$ which is the same as that of potassium, is expressed by the equations:

$$Na_2CO_3 \cdot 2 H_2O_2 = Na_2CO_3 + 2 H_2O_2 \qquad (4)$$

$$H_2O_2 = H_2O + 1/2 O_2 \qquad (1b)$$

The decomposition occurs at higher temperature (at ca. 120°) than $K_2CO_3 \cdot 1/2 H_2O \cdot 2 H_2O_2$.
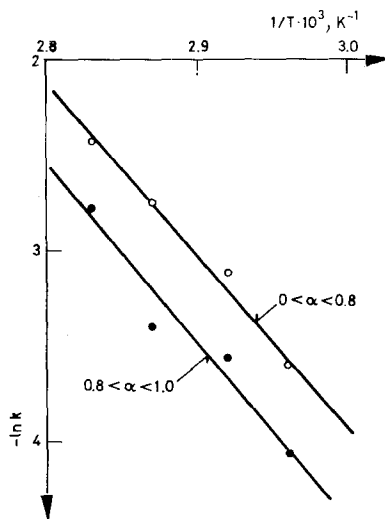

Fig. 7. The Arrhenius plot

The decomposition process of $Na_2CO_3 \cdot 2 H_2O_2$ is described by three stages which are nucleation, growth period of nuclei and the decay period. The kinetic laws obey the first-order equation for the nucleation, the Avrami—Erofeev equation for the growth period and the first-order equation for the decay period.

The activation energies of each process are 154.1, 115.9 and 75.2 kJ/mol, respectively, which is different from the decomposition of $K_2CO_3 \cdot 1/2 H_2O \cdot 2 H_2O_2$ except for the decay period.

It is concluded from the activation energy and the decomposition temperature that the bond strength between carbonate and hydrogen peroxide is larger in $Na_2CO_3 \cdot 2 H_2O_2$ than in $K_2CO_3 \cdot 1/2 H_2O \cdot 2 H_2O_2$, and $K_2CO_3 \cdot 1/2 H_2O \cdot 2 H_2O_2$ is less stable towards heat than $Na_2CO_3 \cdot 2 H_2O_2$.

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RÉSUMÉ — On a étudié, par chromatographie en phase gazeuse, la cinétique de la décomposition thermique du composé d'addition du carbonate de potassium avec de l'eau oxygénée, en se servant d'un réacteur à écoulement, type lit fixe.

Les résultats expérimentaux peuvent être décrits avec un bon ajustement dans tout l'intervalle de décomposition, par l'équation (I) $-\ln(1-\alpha) = kt$; α = degré de décomposition, t = temps (min) et k = constante de vitesse (min^{-1}).

L'énergie d'activation et le facteur préexponentiel sont pour $0 < \alpha < 0.8$, respectivement égaux à 74.3 et 7.8 · 10^9 kJ/mole, et pour la période d'amortissement ($0.8 < \alpha < 1.0$) à 77.3 et 1.38 · 10^{10} kJ/mole.

ZUSAMMENFASSUNG — Die Kinetik der thermischen Zersetzung der Additionsverbindung von Kaliumcarbonat mit Wasserstoffperoxid wurde unter Anwendung eines Fixbett-Durchflußreaktors durch Gaschromatographie untersucht.

Die Versuchsergebnisse können im ganzen Bereich der Zersetzung am besten durch die Gleichung (I) $-\ln(1-\alpha) = kt$ beschrieben werden; α = Zersetzungsgrad, t = Zeit (min) und k = Geschwindigkeitskonstante (min^{-1}).

Die Aktivierungsenergie und der präexponentielle Faktor betragen, für $0 < \alpha < 0.8$, 74.3 kJ/Mol, bzw. 7.8 · 10^9 und für die Periode des Abklingens ($0.8 < \alpha < 1.0$) 77.3 kJ/Mol, bzw. 1.38 · 10^{10}.

Резюме — Исследована кинетика термического разложения продукта присоединения карбоната калия и перекиси водорода, используя упорный реактор для непрерывного процесса совместно с газовым хроматографом. Во всей области разложения экспериментальные результаты наилучше могут быть представлены уравнением $-\ln(1-\alpha) = \kappa t$, где α-степень разложения, t-время (мин.) и κ-константа скорости (мин.$^{-1}$). Энергия активации и предэкспоненциальный фактор для $0 < \alpha < 0.8$, соответственно, равны 74.3 кдж/моль и 7.8 . 10^9, а для периода распада ($0.8 < \alpha < 1.0$) — 77.3 кдж/моль и 1.38 . 10^{10}.