Journal of Thermal Analysis, Vol. 36 (1990) 55-60

THERMAL DECOMPOSITION OF THE ADDITION COMPOUND OF MELAMINE WITH HYDROGEN PEROXIDE

T. Nagaishi, M. Matsumoto and *S. Yoshigana*

DEPARTMENT OF INDUSTRIAL CHEMISTRY, KYUSHU SANGYO UNIVERSITY, 2-3-1 MATSUKA-DAI, HIGASHI-KU, FUKUOKA, JAPAN

(Received March 10, 1989)

The thermal decomposition of the addition compound of melamine with hydrogen peroxide was studied by means of DTA, TG, X-ray diffraction analysis, chemical analysis of hydrogen peroxide, and gas chromatography. The decomposition occurs at 110 °C to produce oxygen and water vapor. Melamine is not oxidized by oxygen or hydrogen peroxide in the decomposition. The decomposition kinetics obeys the first-order reaction rate law and the rate constant was measured to be $4.3x10^7 \exp\{-70.4(kJ/mol)/RT\}$. The addition compound of melamine seems to be more stable than that of urea against heat.

Organic addition compounds with hydrogen peroxide were prepared first by Tanatar [1]. Compounds are formed for example, with urea, urethane, succinimide and erythritol. Krepelka and Buksa [2] also prepared addition compounds of hydrogen peroxide with hexamethylene tetramine, diacetylhydrazine, quininesulfate and aminoacetic acid. Of these compounds, the addition compound of urea with hydrogen peroxide is well known and important in industry [3]. The thermal decomposition of this substance was reported earlier [4].

Melamine, which is widely used as a fire retarder in polymers, also forms an addition compound with hydrogen peroxide. The thermal behaviour of melamine was recently discussed by Costa and Camino [5]. The aim of the present report is to clarify the thermal decomposition of the addition compound of melamine with hydrogen peroxide by means of DTA, TG, X-ray diffraction, gas chromatography and chemical analysis of hydrogen peroxide.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

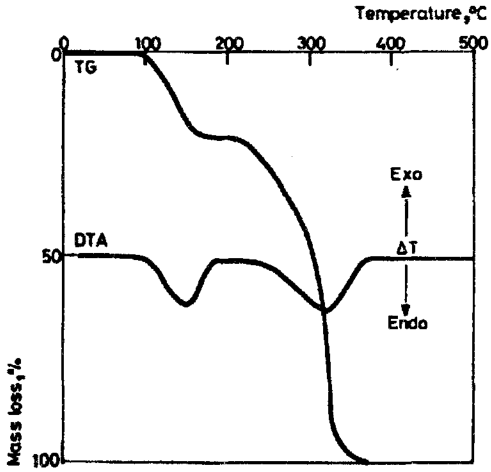

Fig. 1 DTA and TG curves of the addition compound of melamine with hydrogen peroxide in air

Experimental

Material used in the experiment

The addition compound of melamine with hydrogen peroxide was provided by courtesy of Nippon Peroxide Co. Ltd. The chemical analysis of hydrogen peroxide showed that the sample contained 1 mol hydrogen peroxide per mol of melamine. The chemical formula is therefore $C_3N_3(NH_2)_3.H_2O_2$.The sample consists of white and rather hygroscopic crystals.

Thermal analysis and kinetic measurements

Thermal analysis was carried out by the methods described earlier [4, 6]. For the kinetic measurements, two methods were employed under isothermal conditions in the temperature range 140 to 200°, to observe the effects of the gaseous products and the heat of reaction on the decomposition.

One method is a static one to measure the rate of disappearance of hydrogen peroxide, and the other is a flow method [6] to measure the evolution of oxygen by gas chromatography in a helium gas flow.

Results and discussion

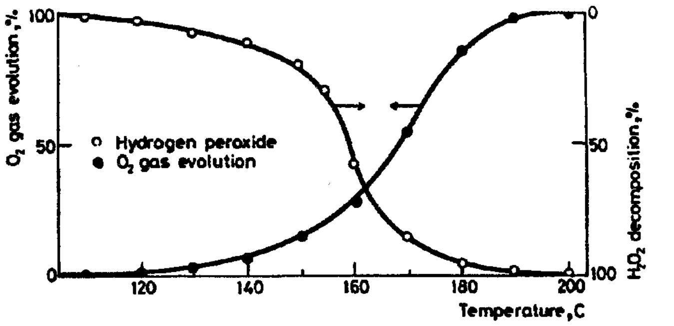

Fig.2 Oxygen gas evolution curve from gas chromatography, and decomposition curve of hydrogen peroxide in the addition compound of melamine at elevated temperatures

Thermal analysis

The DTA and TG curves of the material in air are shown in Fig. 1. The curves revealed that two-step endothermic reactions occur, one of which begins at 100° and the other at 220°. In the first reaction, the weight loss is measured to be 20%; in the second reaction, it becomes between 220 and 370°. From X-ray diffraction analysis (not reported here), the solid product at 200° was identified as melamine.

The results of chemical analysis of hydrogen peroxide, and of oxygen gas evolution by gas chromatography at elevated temperatures, are shown in Fig. 2.

As hydrogen peroxide decomposes, the oxygen gas evolution becomes larger. It is concluded from Figs 1 and 2 that the first reaction is the decomposition of melamine with hydrogen peroxide to melamine, oxygen and water (gas). The overall reaction in the first step is as follows:

$$C_3H_6N_6.H_2O_2 \Rightarrow C_3H_6N_6 + H_2O_{(g)} + 1/2O_2 \qquad (1)$$

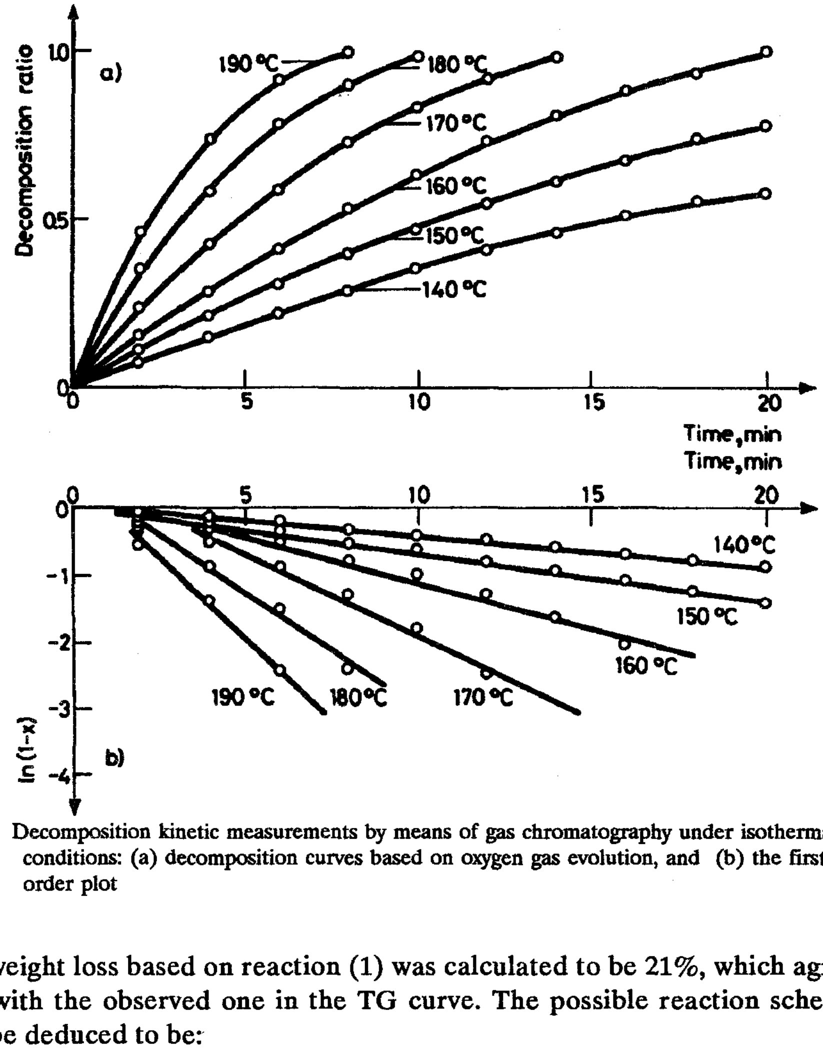

Fig.3 Decomposition kinetic measurements by means of gas chromatography under isothermal conditions: (a) decomposition curves based on oxygen gas evolution, and (b) the first order plot

The weight loss based on reaction (1) was calculated to be 21%, which agree well with the observed one in the TG curve. The possible reaction scheme may be deduced to be:

$$C_3H_6N_6.H_2O_2 \Rightarrow C_3H_6N_6 + H_2O_{2(l)} \quad (2)$$

$$H_2O_{2(l)} \Rightarrow H_2O_{(g)} + 1/2O_2 \quad (3)$$

These two reactions may occur simultaneously and the heat of reaction of (2) endothermic may be greater than that of (3) (exothermic), from which the overall reaction of (1) becomes endothermic, corresponding to the DTA curve.

The second reaction, at 220°, is the sublimation, melting and decomposition of melamine [5]. The detailed mechanism of melamine decomposition has been discussed in the literature [5].

It is to be noted that hydrogen peroxide did not oxidize melamine in its decomposition. The same result was obtained for the addition compound of urea with hydrogen peroxide. The addition compound of melamine seems to be more stable than that of urea, which decomposed at 80°.

Kinetic measurements

Isothermal decomposition curves in the temperature range 140 to 190° were obtained from the measurement of oxygen gas involved, by means of gas chromatography, as shown in Fig. 3(a).

It is suggested from Fig. 3(b) that the decomposition seems to obey the first-order reaction rate law.

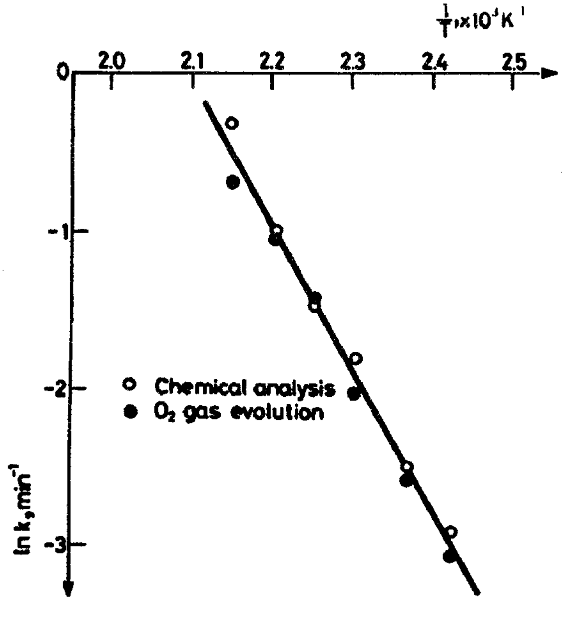

Fig.4 Arrhenius plot

The decomposition rate was also measured from the chemical analysis of hydrogen peroxide in the same temperature range. The first-order reaction rate law again fitted well. The results are illustrated in Fig. 4. The rate constant of the decomposition of the material is $4.3 \times 10^7 \exp\{-70.4(\mathrm{kJ/mol})/RT\}$. It is clear that neither the gaseous products nor the heat of reaction has an effect on the decomposition, for the kinetic measurements gave the same result in the two methods.

The rate constant of the thermal decomposition of the addition compound of urea has been reported to be $8.6 \times 10^8 \exp\{-61.5(\mathrm{kJ/mol})/RT\}$ [4]. This suggests that the addition compound of melamine is more stable than that of urea against heat, which is consistent with the thermal analysis, as mentioned above.

Conclusions

The addition compound of melamine with hydrogen peroxide decomposes at 110° to produce oxygen and water (vapor). The rate of decomposition obeys the first-order reaction rate law, and the rate constant was observed to be $4.3 \times 10^7 \exp\{-70.4(\mathrm{kJ/mol})/RT\}$. The addition compound of melamine seems to be more stable than that of urea against heat.

References

1 S. Tanatar, J. Russ. Phys-chem. Ges., 40 (1908) 376.
2 J. Krepelka and R. Buska, Chem. Ztrbl.,(1938) 1583.
3 W. Machu, Das Wasserstoffperoxyd und die Perverbindungen, Springer Verlag, 1951, p.336. Chemistry and Chemical Industry (in Japanese), 37 (1984) 417.
4 T. Nagaishi, M. Matsumoto and S. Yoshinaga, Bulletin of the Faculty of Engineering, Kyushu Sangyo University (in Japanese), 23 (1986) 39.
5 L. Costa and G. Camino, J. Thermal Anal., 34 (1988) 423.
6 T.Nagaishi, M. Kaneda, M. Matsumoto and S. Yoshinaga, ibid, 18 (1980) 501.

Zusammenfassung - Mittels DTA-, TG- und Röntgendiffraktionsanalyse, chemischer Analyse von Wasserstoffperoxid und Gaschromatografie wurde die thermische Zersetzung der Additionsverbindung von Melamin mit Wasserstoffperoxid untersucht. Die Zersetzung verluft bei 110°C und liefert Sauerstoff und Wasserdampf. Melamin wird während der Zersetzung weder von Sauerstoff noch von Wasserstoffperoxid oxydiert. Die Zersetzung kann kinetisch mit dem Geschwindigkeitsgesetz für die erste Reaktionsordnung mit einer Geschwindigkeitskonstanten von $4.3 \times 10^7 \exp\{-70.4(\mathrm{kJ/mol})/RT\}$ beschrieben werden. Die Additionsverbindung von Melamin scheint wärmebeständiger als die von Harnstoff zu sein.