*Studies on the Thermal Decomposition of Cellulose Nitrate by Means of the Recording Thermal Balance**

By Takehiro ABE, Shōtaro TOBISAWA and Yōkan NOMURA

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The products afforded by the thermal decomposition of cellulose nitrate have been investigated by many workers, recently by Wolfrom et al.[1-4] and by others[5,6]. The reaction of thermal decomposition has also been pursued by Will[7,8] and others[9,10] by means of measuring the gases evolved. However, no precise investigation by measuring the decomposition losses in weight has been made, because it is very difficult to measure the losses in weight successively with precision owing to the slow thermal decomposition.

In the present paper, therefore, we have, by means of a recording thermal balance with a high sensitivity, tried to follow the decomposition reaction of cellulose nitrate by raising the temperatures stepwise, after preheating at a low temperature below the decomposition point, or after keeping in reduced pressure.

Experimental

Cellulose nitrate was prepared by immersion of absorbent cotton (5 g.) into a mixed acid (303 cc.) of sulfuric acid (sp. gr.: 1.84, 171 cc.) and nitric acid (sp. gr.: 1.50, 110 cc.) at about 20°C for two hours. The product was washed thoroughly, and boiled with distilled water many times until a litmus paper did not show any trace of acidity on the wet cellulose nitrate. After being squeezed out, the cellulose nitrate was dried under vacuum for a day and kept in a desiccator. The cellulose nitrate contains 10.6% of nitrogen.

A recording magnetic balance devised by Hirone, Maeda and Tsuya[11] was used as our thermal balance without magnetic field. This balance, plotting automatically the loss in weight

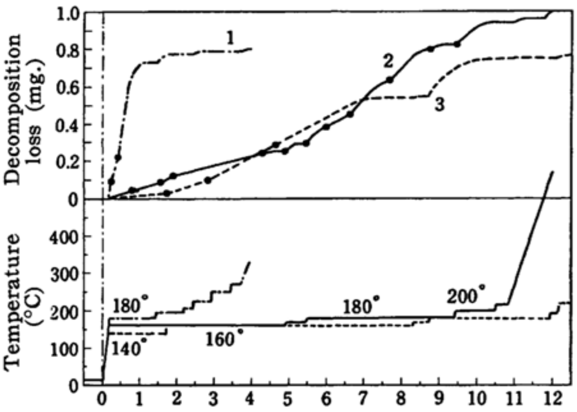

Fig. 1. Thermal decompositions by raising temperatures stepwise.

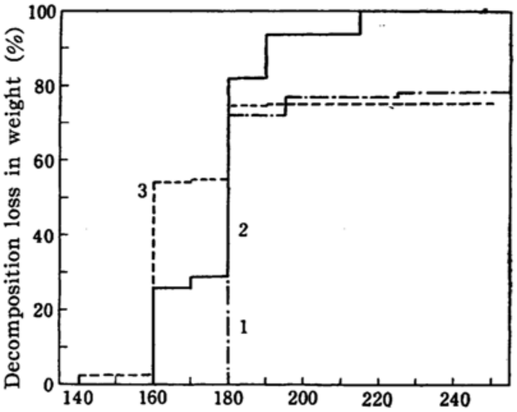

Fig. 2. Relation between the temperature and the decomposition loss in Fig. 1.

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1) M. L. Wolfrom et al., *J. Am. Chem. Soc.*, **77**, 6573 (1955).
2) M. L. Wolfrom et al., ibid., **78**, 4695 (1956).
3) M. L. Wolfrom, A. Chaney and P. McWain, ibid., **80**, 946 (1958).
4) F. Shafizadeh and M. L. Wolfrom, ibid., **80**, 1675 (1958).
5) R. W. Phillips, C. A. Orlick and R. Steinberger, *J. Phys. Chem.*, **59**, 1034 (1955).
6) G. Gelernter, L. C. Browing, S. R. Harris and G. M. Mason, ibid., **60**, 1260 (1956).
7) W. Will, *Fahresbericht der Centralstelle für wissenschaftlich-technische Untersuchungen*, **2** (1900).
8) W. Will, ibid., **3** (1900).
9) T. Hikita, *J. Ind. Explosives Soc., Japan*, **8**, 11 (1947).
10) E. K. Rideal and A. J. B. Robertson, "Third Symposium on Combustion and Flame", Reinhold, Baltimore (1949).
11) T. Hirone, S. Maeda and N. Tsuya, *Rev. Sci. Instr.*, **25**, 516 (1954).

vs. temperature curves of substances, was modulated to be able to indicate distinct differences of 0.02 mg. on a recorded chart. All samples in weight 1.0 mg. were packed in small quartz baskets and thermally decomposed under the pressure of about 50 mmHg, which was necessary for our present instrument.

Results and Discussion

Thermal decomposition by raising temperatures stepwise (Fig. 1).—The cellulose nitrate was decomposed at a constant temperature, and then at a higher temperature after a loss in weight stopped at the former temperature. Temperature was raised in this way. It is remarkable that several breaking points appear on each decomposition curve at constant temperatures. In Fig. 2 it is shown that a greater part of the cellulose nitrate decomposes at 160 and 180°C.

Thermal decomposition at constant temperature (Fig. 3).—As a matter of course, the higher the reaction temperature, the faster becomes the decomposition rate with an increase in the decomposition loss in weight. There appears no breaking point on the decomposition curve at 190°C.

The modes of decomposition at 140 and 150°C, giving only several per cent losses in weight, are different from those above 160°C. The loss in weight below 150°C is, therefore, is not considered to be due to the decomposition of cellulose nitrate itself, but is probably due to the volatilization of absorbed water, as mentioned below. Consequently, the decomposition temperature of the cellulose nitrate may be at about 160°C.

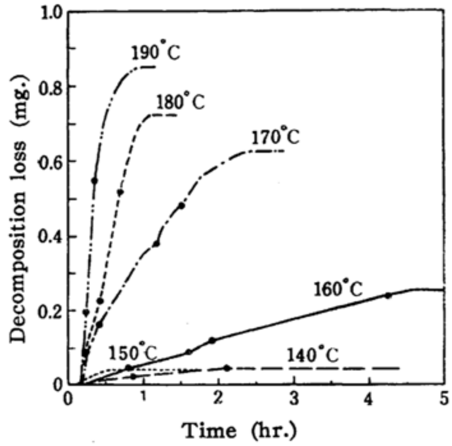

Fig. 3. Thermal decompositions at constant temperatures.

Thermal decomposition after preheating at low temperatures below the decomposition point.—a) In Fig. 4 it is shown that the thermal decomposition at 160°C after preheating at 140 or 150°C for an hour and a half gives a greater loss in weight than that without preheating.

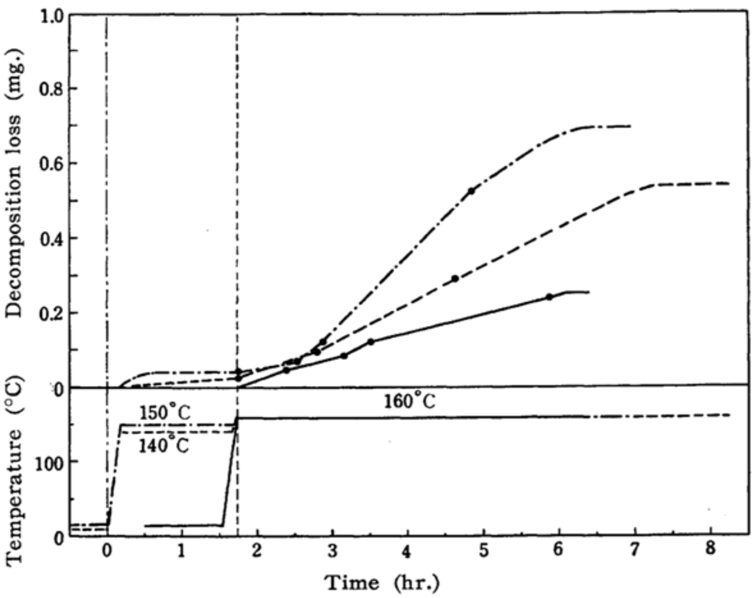

Fig. 4. Thermal decomposition after preheating.
——: not preheated.
------ and —·—: preheated at 140 and 150°C, respectively.

The sample preheated at 150°C decomposes more than that preheated at 140°C.

b) As shown in Fig. 5, the decomposition rate after preheating at 140°C for a long time is slower than that preheated at the same temperature for a short time. Both decompositions give about the same loss in weight.

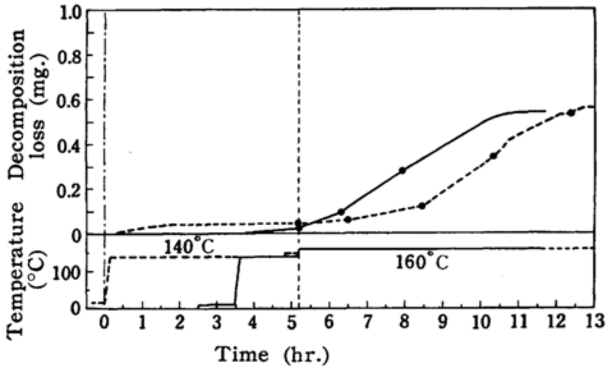

Fig. 5. Thermal decomposition after preheating at 140°C.
——: for a long time.
------: for a short time.

From the above results it is known that a thermal decomposition after preheating at a temperature slightly below the decomposition point for an hour or so results in greater decomposition loss in

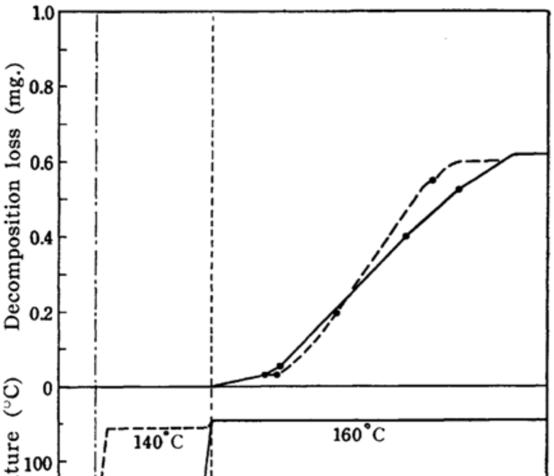

Fig. 6. Thermal decomposition after keeping under a reduced pressure and preheating.
——: not preheated.
------: preheated at 140°C.

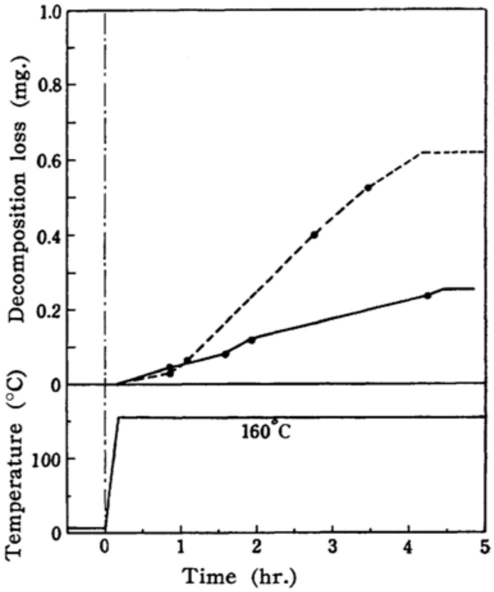

Fig. 7. Thermal decompositions after keeping under a reduced pressure.
——: without this procedure.
------: with this procedure.

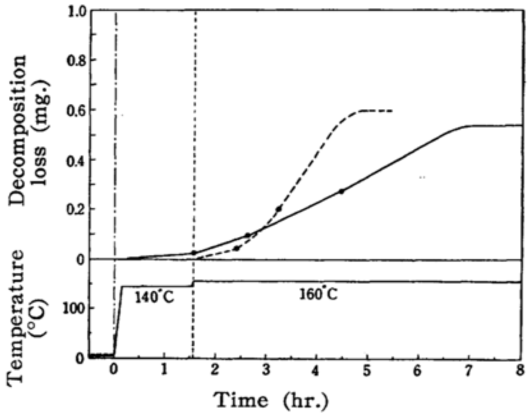

Fig. 8. Thermal decomposition after keeping under a reduced pressure and at 140°C.
——: only preheated.
------: low pressure and preheating.

weight than that without preheating.

Thermal decomposition after keeping a reduced pressure. — After being kept previously under reduced pressure of about 10^{-2} mmHg for four hours in the apparatus, the samples were decomposed under the same condition as measured before.

a) As seen in Fig. 6, the sample kept previously under a reduced pressure of 10^{-2} mmHg and preheated, decomposes rather faster than that kept only under a reduced pressure although both samples yield about the same loss in weight.

Heating the sample at 150°C results in no loss in weight, although the samples, which are not kept previously under a pressure of 10^{-2} mmHg, give several per cent loss in weight, as indicated in Figs. 1, 3, 4 and 5. These loss in weight below 150°C seems to be probably due to the volatilizations of water absorbed strongly by the cellulose nitrate in the air, since they can not be observed by keeping the samples previously under a pressure of 10^{-2} mmHg.

b) It is found from Fig. 7 that the sample kept previously in the reduced pressure yields a greater decomposition loss than that without any treatment.

c) As shown in Fig. 8, the decomposition of the sample kept previously under a reduced pressure and at 140°C, proceeds faster than that of the sample only preheated although there is no great difference between the decomposition losses of the two samples.

Summary

(1) The cellulose nitrate containing 10.6% of nitrogen decomposes above about 160°C. There appear distinct breaking points on the decomposition curves at constant temperatures slightly above the decomposition point. The higher the constant temperature of reaction, the greater becomes the decomposition loss in weight.

(2) The thermal decomposition after preheating at a temperature slightly below the decomposition point for an hour or so gives a greater loss of decomposition than that without preheating.

(3) The cellulose nitrate kept previously under a reduced pressure of about 10^{-2} mmHg yields a greater decomposition loss in weight than that without any treatment.

Department of Chemistry
Defense Academy
Yokosuka, Kanagawa