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Note

THERMAL DECOMPOSITION OF STRONTIUM NITRATE DOPED WITH STRONTIUM NITRITE AT MILLIMOLAR CONCENTRATIONS

S.M.K. NAIR and C. JAMES

Department of Chemistry, University of Calicut, Kerala 673 635 (India)

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The effect of γ-irradiation on the kinetics of thermal decomposition of strontium nitrate has been investigated by the gas evolution method [1] and also by dynamic thermogravimetry [2,3]. It has been observed that irradiation lowers the activation energy of the decomposition process. It has been suggested that the NO_2^- formed under irradiation catalyses the decomposition of strontium nitrate and, in consequence, the activation energy is lowered. Further evidence is now provided for the catalytic action of NO_2^- by studies on thermal decomposition of strontium nitrate doped with strontium nitrite at millimolar concentrations.

EXPERIMENTAL

GR grade strontium nitrate (Merck, 7872) in the form of fine powder (200–240 mesh), which was dried and stored in vacuo over P_2O_5, was used for the thermal studies.

Crystals of strontium nitrate doped with NO_2^- in the mole fraction range 10^{-4} to 10^{-1} were prepared by the slow crystallization of solutions containing calculated amounts of strontium nitrate and strontium nitrite. Crystals of strontium nitrite were prepared by a method similar to that of Thiel and Stoll [4] for the preparation of lead nitrite, by the reaction between strontium chloride and silver nitrite in equivalent proportions in the presence of a little water. The filtered solution of strontium nitrite, which was free from silver and chloride ions, was concentrated under reduced pressure. The crystals of strontium nitrite were separated under suction, washed five times with small amounts of cold water and dried in vacuo over P_2O_5. The concentration of NO_2^- in the doped samples was determined spectrophotometrically by the method of Shinn [5] as modified by Kershaw and Chamberlin [6]. The structure of the doped crystals was examined, but no changes in the position or the intensities of the lines in the X-ray powder diffraction photographs could be detected for the impurity levels used in these investigations. The

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doped crystals in the 200–240 mesh range were used for the decomposition studies.

The mass loss of samples of untreated and doped strontium nitrate in air was measured on a Stanton automatically recording thermobalance (HT-SM). The heating rate was 6° min^{-1} and chart speed was 13.5 cm h^{-1}. Measurements were also made in argon flowing at about 100 ml min^{-1}. The samples were taken in tall, narrow silica crucibles to avoid loss by spattering. In all experiments 100 mg of the sample was used. The recorded total mass loss in all cases was 51 ± 1 mg for 100 mg of sample. The mass of the material left behind after decomposition agreed with the instrument reading.

RESULTS AND DISCUSSION

The recorded TG traces were redrawn as mass versus temperature (TG) curves and are presented in Fig. 1. All TG curves are of the same pattern. In the doped samples the decomposition proceeds faster (curves 2–5). Replacement of air by argon had no effect on the decomposition as shown by the TG curves. These curves are not included in Fig. 1. Three non-isothermal runs were taken for each sample and the mass loss–temperature relationship was found to be in good agreement in the three runs.

The TG curves obtained under conditions of non-isothermal decomposition were used to evaluate the kinetic parameters using the Coats–Redfern [7] and Horowitz–Metzger [8] methods. The method of calculation in each case has already been reported [3].

Order of the reaction

The order of the reaction was determined as described earlier [3] by the use of the Coats–Redfern equation [7] from plots of

$$\log\left[-\log(1-\alpha)/T^2\right] \text{ versus } 1/T \text{ for } n=1 \qquad (1)$$

and

$$\log\left[1-(1-\alpha)^{1-n}/T^2(1-n)\right] \text{ versus } 1/T \text{ for } n \neq 1 \qquad (2)$$

where α is the fraction decomposed, n the order of the reaction and T the temperature (K). The application of eqns. (1) and (2) to our data on strontium nitrate by the least-squares linear regression method revealed that the best correlation is obtained (0.998–0.999) with eqn. (1) and, hence, the order of the reaction is 1 in both the untreated and doped samples. The energy of activation (E) and frequency factor (Z) were calculated from the slopes and intercepts, respectively, of the plots. The entropy of activation (ΔS) was calculated as shown previously [3]. The values of E, Z and ΔS obtained are given in Table 1.

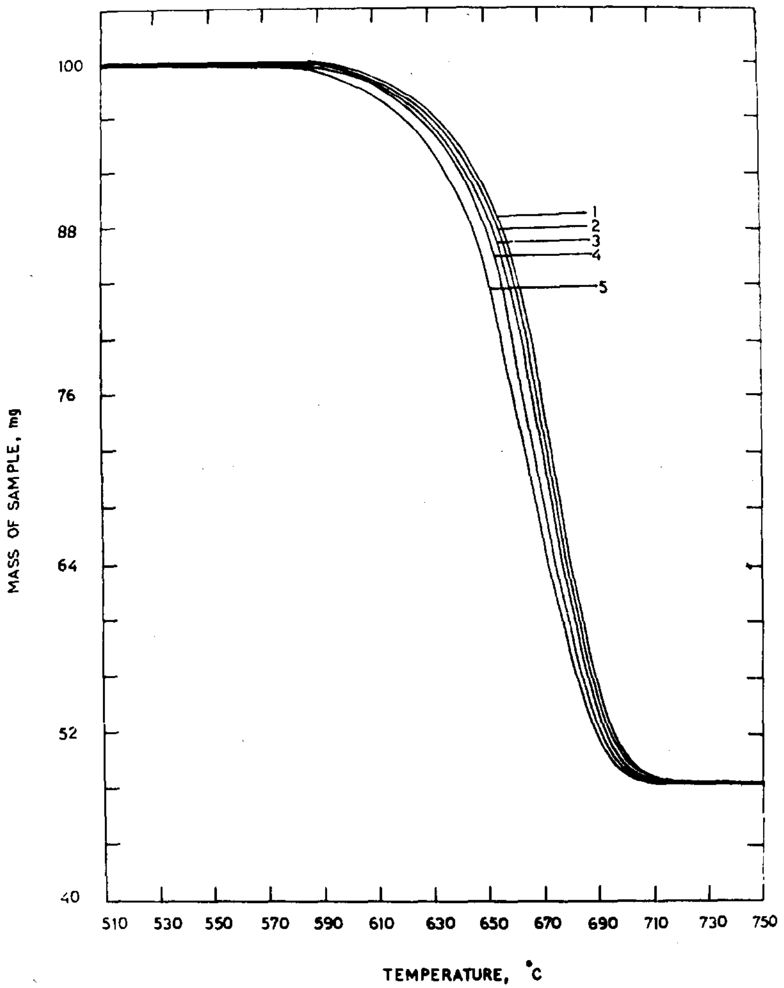

Fig. 1. TG curves of strontium nitrate: (1) untreated; (2) doped with 10^{-4} M NO_2^-; (3) doped 10^{-3} M; (4) doped 10^{-2} M; (5) doped 10^{-1} M.

The Horowitz–Metzger method

The present data were analysed using the Horowitz–Metzger equation [8] as modified by Dharwadkar and Karkhanavala [9] in the form

$$\ln\left[\ln(1-\alpha)^{-1}\right] = 100E\theta/RT_i^2(T_f - T_i) + C \qquad (3)$$

where R = gas constant, T_i = temperature of the inception of the reaction, T_f = temperature of the completion of the reaction, T_s = temperature at the inflection point of the thermogram, θ = difference between T_s and the temperature under consideration, and C = constant. A plot of the left-hand side of eqn. (4) versus θ was linear as required by the theory and E was

TABLE 1

Thermal decomposition data and kinetic parameters calculated using the Coats–Redfern (CR) and Horowitz–Metzger (HM) equations

Sample: $Sr(NO_3)_2$ doped with NO_2^- of molar concentration		T_i (°C)	T_f (°C)	T_s (°C)	E (kJ mol^{-1})		Z (s^{-1})		ΔS (J K^{-1} mol^{-1})	
					CR	HM	CR	HM	CR	HM
1	0 (untreated)	590	700	688	400.8 (0.9998)	405.4 (0.9992)	3.59×10^{21}	3.5×10^{21}	158.1	157.7
2	10^{-4}	590	702	685	391.8 (0.9996)	404.1 (0.9995)	1.21×10^{21}	3.4×10^{21}	148.9	157.7
3	10^{-3}	600	710	679	391.9 (0.9980)	401.7 (0.9975)	1.33×10^{21}	3.5×10^{21}	149.8	157.7
4	10^{-2}	590	700	670	382.5 (0.9993)	387.6 (0.9985)	4.34×10^{20}	9.3×10^{20}	140.6	146.8
5	10^{-1}	590	700	667	360.6 (0.9998)	366.2 (0.9990)	3.09×10^{19}	6.7×10^{19}	118.8	125.1

calculated from the slope. The pre-exponential factor (Z) and ΔS were calculated as previously described [3]. The results of the analysis are given in Table 1.

The slopes and intercepts of all the plots obtained by the two methods given above were calculated by the least-squares linear regression method. The correlation coefficients (r) were in the range 0.997–0.999. These values are given in parentheses in Table 1. The E and Z values obtained by the two methods show that the general agreement between these methods is good, within about 5%.

The value of E for the decomposition of untreated strontium nitrate obtained in the present studies (Table 1) agrees well with that obtained in the previous investigations [3]. The activation energy decreases only to a small extent with increasing concentration of the dopant (NO_2^-). That the change in E is small suggests that the same chemical process governs the decomposition of the untreated and doped samples. Doping has no influence on T_i and T_f, but T_s is lowered from 688 to 667°C as the concentration of the dopant increases from 10^{-4} to 10^{-1} M. Doping also lowers ΔS by 25% in the case of strontium nitrate doped with 10^{-1} M NO_2^-. The decrease in the entropy of activation suggests that the decomposition is catalysed in the doped samples.

Figure 1 shows that the decomposition proceeds faster in the case of the doped samples. This is due to the catalysing action of NO_2^- which may be explained as follows: NO_2^- may act as an electron donor and attract oxygen atoms from the neighbouring nitrate ion. The resulting nitrate ion being oxygen deficient, may attract oxygen atoms from the neighbouring nitrate ions. In this manner the reaction may proceed through the melt and a stream of oxygen would flow from the interior to the surface along a line of NO_2^- ions.

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