

NOTE

Thermal Decomposition of Barium Nitrate in Presence of Certain Metal Oxides

BABU I. MALIAKKAL* and T. D. RADHAKRISHNAN NAIR†

Department of Chemistry, St. Joseph's College, Devagiri, Calicut-673 008, India

Thermal decomposition of barium nitrate in presence of several metal oxides has been studied by thermogravimetry. Kinetic parameters are determined by the Freeman-Carroll and Horowitz-Metzger methods. The behaviour of different oxides has been found to be different and quite specific.

Key Words: Thermogravimetry, Kinetic parameters, Barium nitrate, Metal oxides.

Thermogravimetric studies on decomposition of barium nitrate in presence of several metal oxides have been carried out. In dynamic nitrogen atmosphere, at a heating rate of 20°C/min, the decomposition of barium nitrate takes place in a single stage following first order kinetics¹. The final residue is that of barium oxide.

Barium nitrate as well as the metal oxides have been sieved to particle size range of 53–63 microns and the oxides preheated at 473 K for 1 h and kept in desiccators before mixing. Barium nitrate and each of the metal oxides have been mixed in the ratio 4 : 1 by mass. All samples (10 mg each) have been analyzed by thermogravimetry on a Perkin-Elmer thermal analyzer model TGS 2 at a heating rate of 20 K under a dynamic nitrogen atmosphere. The results are summarized in Table-1. The kinetic study was carried out by the Freeman-Carroll² and the Horowitz-Metzger methods³.

All the samples gave single stage TG curve for mass loss. The procedural decomposition temperature (T_d) remained close to 823 K for most of the samples but in some cases such as Cr_2O_3 this is only 733 K and this is likely due to compound formation. In a few cases the final temperature (T_f) is almost unaltered, but in some cases it is lowered by 100 K. The variation in peak temperature (T_s) is more marked. The reduction in T_s is 47 K for TiO_2 and 130 K for Cr_2O_3 , but for ZnO it increases by 60 K. Such variation should be interpreted in terms of various mechanisms of solid-state decomposition reaction.

†Department of Chemistry, University of Calicut, Thenjipalam, Calicut-673 635, India.

TABLE-1
EFFECT OF METAL OXIDES ON THE THERMAL DECOMPOSITION OF BARIUM NITRATE MIXTURES CONTAINING 80% BARIUM NITRATE AND 20% METAL OXIDE BY MASS (4 : 1) KINETIC PARAMETERS DETERMINED BY THE FREEMAN-CARROLL AND HOROWITZ-METZGER METHODS

Metal oxide	T _i	T _s	T _f	Freeman-Carroll methods			Horowitz-Metzger methods		
				E	Z	dS	E	Z	dS
				kJ/mol	s ⁻¹	J K ⁻¹ mol ⁻¹	kJ/mol	s ⁻¹	J K ⁻¹ mol ⁻¹
Without metal oxide	823	978	1068	143.26	2.4 × 10 ⁵	-151.47	163.82	3.8 × 10 ⁶	-128.67
Al ₂ O ₃	823	1003	1048	185.75	3.1 × 10 ⁷	-111.47	217.81	1.9 × 10 ⁹	-77.30
CuO	813	948	1068	136.68	1.1 × 10 ⁵	-157.93	149.63	1.1 × 10 ⁶	-138.34
Cr ₂ O ₃	733	848	953	237.22	3.6 × 10 ¹²	-13.23	263.92	2.6 × 10 ¹⁴	22.55
Fe ₂ O ₃	773	918	953	192.66	1.1 × 10 ⁹	-80.96	208.88	7.6 × 10 ⁹	-65.06
MnO ₂	793	958	993	172.86	3.5 × 10 ⁷	-110.01	189.02	1.6 × 10 ⁸	-97.10
TiO ₂	823	931	953	303.39	1.0 × 10 ¹⁵	33.00	334.86	9.5 × 10 ¹⁶	70.65
ZnO	818	1038	1053	132.45	3.1 × 10 ⁴	-169.04	185.17	1.4 × 10 ⁷	-118.27

The kinetic parameters determined in each case are comparable with those already reported⁴. CuO lowered the activation energy, but with Cr₂O₃ and TiO₂ it increased markedly. The latter could be due to occurrence of chemical reactions. However, in all the cases, the order of the reaction was found to be unity.

The wide variation in kinetic parameters recorded would suggest that the behaviour of metal oxides in the thermal decomposition of barium nitrate is different and quite specific.

Ettarh and Galwey⁵ have pointed out that as nitrate anion breakdown is endothermic, the catalytic promotion of metal oxides would be relatively small. Further, as melting of barium nitrate (m.p. 865 K) must be considered to occur in almost all samples, the effect of these oxides would be limited, unless a chemical reaction is involved. The maximum change in kinetic parameters was obtained with TiO₂ and this could only be explained assuming a tendency for compound formation. No definite conclusions could be arrived at from the present study. However, it can be stated that the stability of the nitrate ion, melting of barium nitrate prior to its decomposition and tendency for compound formation are some of the factors determining the reactivity, in addition to the catalytic effect of the metal oxides. Another important aspect is the possibility of change in mechanism of the thermal decomposition of solid/liquid in presence of these metal oxides.

REFERENCES

1. B.I. Maliakkal, Ph.D. Thesis, University of Calicut, Calicut (1997).
2. E.S. Freemann and B. Carroll, *J. Phy. Chem.*, **62**, 94 (1958).
3. H.H. Horowitz and G. Metzger, *Anal. Chem.*, **35**, 1464 (1963).
4. B.I. Maliakkal and T.D.R. Nair, *Asian J. Chem.*, **15**, 1859 (2003).
5. C. Ettarh and A.K. Galwey, *Thermochim. Acta*, **261**, 125 (1995).