Solid State Oscillatory Reaction. I. Thermal Decomposition Studies of $[Co(NH_3)_6]Br_3$ and $CoBr_2 \cdot 2H_2O$

Murlidhar D. Patil, Gopal N. Natu, and Shantaram B. Kulkarni*
Department of Chemistry, University of Poona, Pune 411007, India

(Received May 9, 1991)

Thermogravimetric analysis, TGA, of cobalt(II)bromide, $[Co(NH_3)_6]Br_3$ —henceforth referred to by the short-name HCBR— was carried out using a wide diameter short one and a narrow diameter long sample cups. In the former type of cup the TGA trace was similar to that reported one. However, when the latter cup was used, the TGA showed oscillations in the % weight-loss. Cobalt(II)bromide, $CoBr_2$, is formed as an intermediate product in the thermal decomposition of HCBR. The oscillatory nature of weight-loss curve was studied for both HCBR and $CoBr_2$.

The oscillatory behavior in the present system has been confirmed on the basis of the following experiments:

(a) Dynamic TGA and differential thermal analysis, DTA, of HCBR and $CoBr_2 \cdot 2H_2O$.
(b) Isothermal TGA by weight-loss method for HCBR and $CoBr_2$.
(c) Thermal decomposition studies, in closed system, of (i) $CoBr_2$ and of (ii) CoO in a mixture of O_2 and Br_2 gases, and of a mixture of (iii) Co_3O_4 and $CoBr_2$ in dry nitrogen.

The oscillations in the composition of the solid residue were attributed to the formation of CoOBr as an intermediate. Final product of thermal decomposition of $CoBr_2$ in air is Co_3O_4. Hence it is possible to imagine that the point of CoOBr formation makes branching off point. This sets the reaction to oscillate in the composition domain. Therefore, it was thought that Edelstein mechanism would be operative in this reaction. Alternately, the population growth model may also be used to explain this observation. Formation of CoOBr was thought to be the weight-loss step, i.e. decrease in the 'population' of $CoBr_2$, while the formation of $CoBr_2$ was the weight-gain step, i.e. increase in the 'population' of $CoBr_2$ under the proposed reaction, $CoBr_2 + 1/2O_2 \rightleftarrows CoOBr$. The purpose of this article is, therefore, to present the interesting facts of this reaction before the readers, and not to ascribe any particular model for its explanation.

The TGA of HCBR was similar to the reported[1—3] one in the temperature range 210—250 °C, when the sample container quartz cup had dimensions 8 mm (id)×10 mm (h). However, the TGA of the samples in the sample cup of dimensions 4 mm (id)×40 mm (h) showed oscillations in composition in the temperature range of about 500 to 650 °C. The final product of decomposition beyond 700 °C was Co_3O_4.

Oscillatory chemical reactions are common in nature and are best described[4] as periodic rise and fall in one of the properties of a substance such as concentration, position and so on. Laboratory reports of such phenomena, date back to 1905 when Liesgang[5] observed spatial periodicities during the formation of Ag_2CrO_4. These types of temporal and spatial periodicities were observed by many experimentalists and were attributed in those times, to heterogeneities, dust particles etc. At this stage Belousove[6] and Zhabotinsky,[7] (BZ) first offered an accessible, reproducible system to demonstrate and study chemical oscillations.

The probability of spatial and temporal oscillations for systems away from equilibrium have been predicted on theoretical ground in seventies and mid eighty.[8,9] A chemical reaction can be 'closed' or 'open' reactor type. In the former system no matter is gained or lost while the latter system permits the flow of matter in and out of the system. The open system allows for the continuous and convenient changes of composition. Thus experimenter can measure concentration of different reactant and product species. Mathematical models have been proposed by Lotka[10] and Edelstein[11] and others.[12] Apart from mathematical analysis of few differential rate equations, the important point is that suitable plots of concentrations from which time has been eliminated should show closed segments (Lotka Mechanism) or a sudden branching or discontinuity (Edelstein Mechanism).

Therefore, the purpose of this study is to investigate, on the basis of variety of experimental observations, the prevalence of oscillatory behavior in this solid state decomposition reaction. So far there are few reports[13,14] on solid state oscillatory reactions, even though lot of work is known on the reactions showing oscillatory behavior in solution. One of the first solid state oscillatory reactions reported is that between calcium oxide and quartz.[13]

Experimental

Materials: All the chemicals used were BDH (Reagent Grade) unless otherwise stated and were used without further purification. Hexaammine-cobalt(III)bromide, HCBR, was prepared[15] and recrystallized using reported method. It was ground in an agate pestle and mortar, sieved through +200 −250 mesh sieve, and stored in ground glass bottle in a desiccator over potassium hydroxide.

Cobalt(II)bromide Dihydrate: Pure cobalt(II)bromide hexahydrate was prepared by the literature method.[16] The powdered hexahydrate was desiccated over sodium hydroxide for three days, then it was meshed as for HCBR and preserved over anhydrous calcium chloride.

Both the compounds were analysed by reported method.[17] Cobalt(II)oxide was prepared[16] by thermal decomposition of freshly prepared cobalt(II)carbonate at 400 °C under pure, dry nitrogen, and was analysed by standard method.[18]

The thermobalance used in the present work was constructed in this laboratory. It consisted of (i) a chainomatic balance (Keroy, India) of 0.1 mg. accuracy, (ii) 800 watts, silica tube furnace (25cm (l)×3cm (id)), (iii) a pyrometer upto 1000 °C (Electroflow) of 10 °C accuracy, (iv) a temperature controller (Type 8 D-1 p, 8 amp, Automatic Electric), (v) a cylindrical sample cup made of quartz.

The following specifications of the samples were used for dynamic TGA experiments:

Sample size, 70 ± 2 mg
Particle size, +200, −250 mesh
Rate of heating, 2 to 3 $°C\ min^{-1}$
Temperature range of study, RT to 700 °C
Thermocouple, chromel–alumel (24 gauge)
Narrow diameter tube, 4 mm (id)×40 mm (h)
Wide diameter tube, 8 mm (id)×10 mm (h)
Atmosphere, static air, unless otherwise stated.

The air buoyancy effect of the furnace on sample cup determined in the temperature range ambient to 700 °C, at a heating rate of 3 °C min^{-1} showed that there was no weight change in this temperature range. The standardization of TGA instrument using standard recystallized samples[17,19,20] of $CuSO_4\cdot 5H_2O$ and $CaC_2O_4\cdot H_2O$ showed that the weight losses and the nature of weight-loss curves were in excellent agreement with those reported in the literature.

DTA studies were carried out on the locally fabricated instrument in porcelain cups, with MgO as a reference material. Temperature range scanned was between ambient to 700 °C with a differential sensitivity of ±0.005 °C. The instrument constant was calculated using the method described in the standard text.[19,21] Sample characteristics were same as those for dynamic TGA, except, that the amount of sample was in the range of 100 to 200 mg. DTA was studied in duplicate for each sample.

The reactions between (i) $CoBr_2$ and O_2+Br_2 mixture, (ii) CoO and O_2+Br_2 mixture, and (iii) Co_3O_4 and $CoBr_2$ under dry nitrogen were followed by estimating cobalt using nitroso-R- salt[22] on Unicam SP 600 spectrometer.

Results and Discussion

Dynamic TGA of hexaammine cobalt(III)bromide, HCBR in the temperature range ambient to 535 °C using wide diameter, low height sample cup is similar to that reported. It exhibited three distinct loss-steps as under:

(I) 210—310 °C (per cent weight-loss ca. 34; residue $CoBr_2+1/2\ NH_4Br$),

(ii) 355—435 °C (per cent weight-loss ca. 12; residue, $CoBr_2$), and

(iii) 485—535 °C (per cent weight-loss ca. 33; residue, Co_3O_4).

Since $CoBr_2$ is formed as an intermediate which is responsible for the oscillatory behavior (vide infra), in the decomposition of HCBR, TGA of pure $CoBr_2\cdot 2H_2O$ was also studied in the temperature range ambient to 500 °C. The TGA of $CoBr_2\cdot 2H_2O$ showed two step decomposition as under:

(i) 110—160 °C (per cent weight-loss ca. 14, residue, anhydrous $CoBr_2$) and

(ii) 350—500 °C (per cent weight-loss ca. 54; residue, Co_3O_4).

TGA of $CoBr_2\cdot 2H_2O$ showed a low temperature shift i.e. it started decomposing at about 350 °C instead of 485 °C giving Co_3O_4 than that for HCBR because anhydrous $CoBr_2$ is stable in the temperature range 160—350 °C. The evolution of bromine gas from the residue of both HCBR and $CoBr_2\cdot 2H_2O$ was confirmed from its extraction in the absorption tube filled with a solution of potassium iodide (10 per cent aqueous) followed by volumetric determination of liberated iodine with standard sodium thiosulphate.

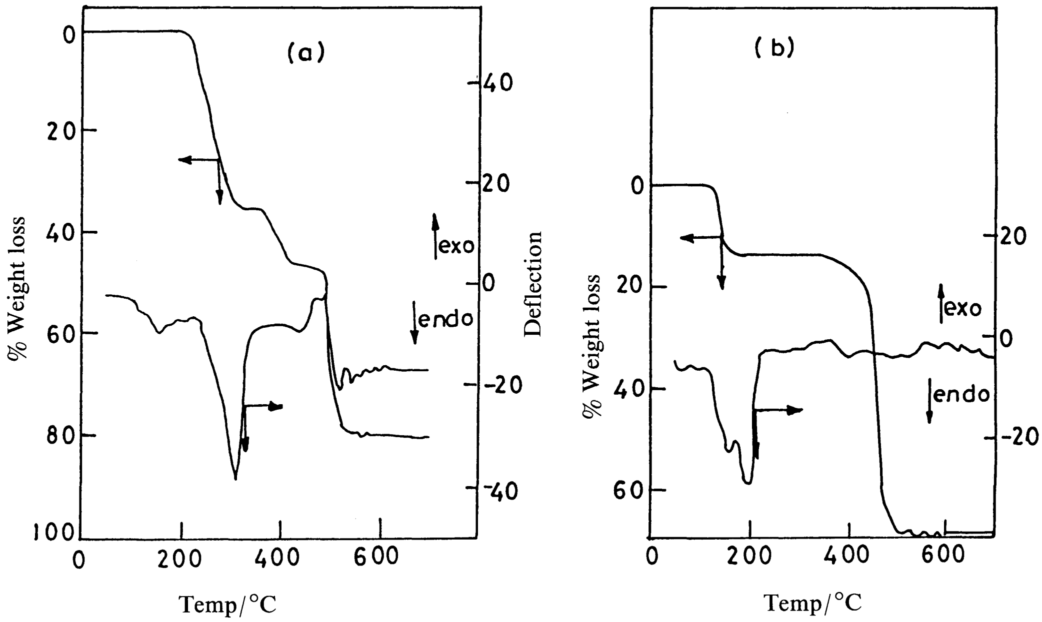

Fig. 1. Dynamic TGA and DTA of $[Co(NH_3)_6]Br_3$ (a) and $CoBr_2\cdot 2H_2O$ (b).

$$\begin{array}{l} CoBr_2 + 1/2\, O_2 \rightarrow CoO + Br_2 \\ \qquad\qquad\qquad\quad \downarrow +2KI \\ \qquad\qquad\qquad\quad 2KBr + I_2 \end{array}$$

The observed weight-losses upto 80% in case of HCBR and upto 54% in case of $CoBr_2 \cdot 2H_2O$ could be explained on the basis of reported[23,24] chemical reactions for these compounds.

However, when a flat, wide diameter sample holder was replaced by a narrow diameter long tube, the dynamic TGA of HCBR showed a periodic rise and fall in the weight-loss curve, i.e. oscillatory weight-loss-gain behavior beyond 520 °C until about 650 °C. A similar behavior was observed in the dynamic TGA of $CoBr_2 \cdot 2H_2O$ beyond 500 °C and up to 600 °C (Fig. 1).

This curious wavy nature in the dynamic TGA of both compounds was confirmed by repeating the experiments three times. Further, the observed wavy nature is beyond the experimental error since the accuracy of the thermobalance is 0.1 mg (ca. 0.15%, with a sample of about 20 mg).

In order to find another independent evidence for oscillations dynamic DTA of HCBR was also studied (Fig. 1). Beyond 500 °C the DTA trace, too, showed oscillations to an amplitude (ΔT) of 0.1 °C. Again DTA of $CoBr_2 \cdot 2H_2O$ supported this behavior (Fig. 1.). Further, the oscillatory behavior observed in dynamic DTA for both compounds is beyond the experimental error since the sensitivity of the differential potentiometer is ± 0.0001 mV (ca. 0.02 °C). Preliminary calculations on the composition of the residue from HCBR have shown steady state components, Co_3O_4 and CoOBr with approximate weight-fractions, (α), of 0.95 and 0.05 respectively. The composition of the residue at the mean of trough and crest resolves to 0.97 and 0.03 weight fractions of Co_3O_4 and CoOBr respectively from the TGA residue of $CoBr_2 \cdot 2H_2O$. Table 1 contains the percent weight-loss-gain data within the periodic region of dynamic TGA-DTA curves for HCBR and $CoBr_2 \cdot 2H_2O$.

Table 1. Data on Periodic Weight-Loss-Gain Region from TGA-DTA

Compound					
$CoBr_2 \cdot 2H_2O$			$[Co(NH_3)_6]Br_3$		
Temp/°C	% Loss	T[a]	Temp/°C	% Loss	T[a]
480	67.0	−3.0	520	79.0	−22
490	68.0	−4.0	530	80.0	−16
500	69.0	−3.0	540	79.0	−20
510	67.5	−3.0	550	80.5	−18
520	69.0	−3.0	560	80.0	−18
530	68.5	−3.0	570	79.5	−17
540	67.5	−2.0	580	80.5	−18
550	69.0	−1.0	590	79.0	−17
560	68.0	−1.0	600	80.0	−18
570	68.5	−1.5	610	80.5	−16
580	69.0	−2.0	620	80.0	−17
590	68.5	−1.0			
600	69.0	−1.0			

a) In terms of galvanometer deflection.

The findings on the basis of dynamic TGA-DTA studies could be summarized as under:

(i) there is initial normal weight-loss behavior until the formation of $Co_3O_4 + Br_2$,

(ii) the reversibility appears to begin with the reaction of Co_3O_4 with bromine gas, and

(ii) bromine gas forms a distinct layer on the residue, Co_3O_4 such that a condition of ambient atmosphere with poor oxygen content is reached around the residue.

Owing to the increased height of the sample tube (40 mm) the upper end of the tube could be cooler than the bottom end. The evolved bromine gas cools down at the upper end. The heavy bromine starts descending

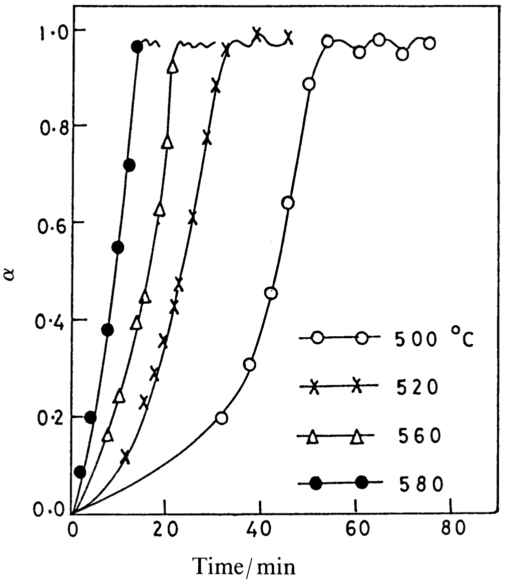

Fig. 2(a). Isothermal TGA of $[Co(NH_3)_6]Br_3$.

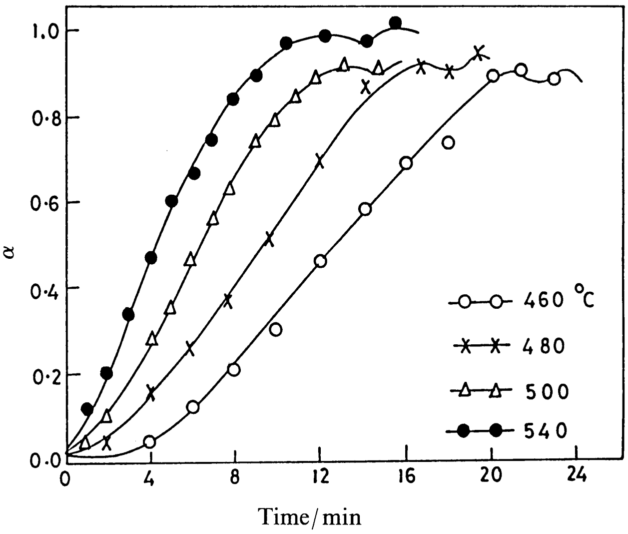

Fig. 2(b). Isothermal TGA of $CoBr_2 \cdot 2H_2O$

the bottom of the sample tube just like the convention currents. Due to this a critical equilibrium ($O_2(g)+Br_2(g)$) is reached which sets in oscillations in chemical composition. Further isothermal TGA by weight-loss method for both HCBR and $CoBr_2 \cdot 2H_2O$ also indicates the oscillatory behavior in α vs. time plots (Figs. 2 (a) and (b)). The wavy part, at the lasting periods in isothermal TGA, appears after a smooth decomposition until α (fraction of $CoBr_2$ decomposed) of about 0.95. This wavy nature sustained for quite a long time. This, also, was a novel observation in this work; which emphasized in our mind of the oscillatory reaction. The onset of oscillation could thus, be at a point when Co_3O_4 formation is nearing to completion.

The oscillatory behavior observed in the dynamic TGA-DTA of HCBR and $CoBr_2 \cdot 2H_2O$ and in the isothermal TGA by weight-loss method for both HCBR and $CoBr_2 \cdot 2H_2O$ leads one to speculate a following sequence of chemical reactions:

$$CoBr_2 + 1/2\,O_2 \rightarrow CoO + Br_2 \tag{1}$$

$$CoO + Br_2 \rightleftarrows CoOBr + 1/2\,Br_2 \tag{2}$$

$$CoO + 1/6\,O_2 \rightleftarrows 1/3\,Co_3O_4 \tag{3}$$

$$Co_3O_4 + Br_2 \rightarrow CoBr_2 + Co_2O_3 + 1/2\,O_2 \tag{4}$$

$$CoO + Co_2O_3 \rightarrow Co_3O_4 \tag{5}$$

$$CoOBr + 1/6\,O_2 \rightarrow 1/3\,Co_3O_4 + 1/2\,Br_2 \tag{6}$$

Further it was thought that the above speculative reaction sequence could be operative during the conversion of $CoBr_2$ into Co_3O_4. Hence an intensive series of experiments were designed using a closed system containing O_2 and Br_2 gases in definite proportions. The fractions of residual $CoBr_2$, CoO, and Co_3O_4 were experimentally determined. All the fractions were expressed as weight fractions of cobalt. Figures 3 (a) and (b) represent respectively reaction between $CoBr_2$ and O_2+Br_2 mixture and that between CoO and the mixture of O_2+Br_2 studied at 600 °C. A close examination of Fig. 3 (a) clearly indicates that:

(i) there is almost quantitative conversion (>99%) of $CoBr_2$ into CoO and a sudden change in this trend beyond 50 per cent v/v of Br_2,

(ii) reconversion into $CoBr_2$ is observed until 70 per cent v/v of Br_2 in the gaseous mixture and a break appears at this stage wherein a decrease in $CoBr_2$ fraction sustains up to 80 per cent v/v of Br_2, and

(iii) later there is a reversal of equilibrium from $CoO \rightarrow CoBr_2$ as shown below,

$$CoBr_2 + 1/2\,O_2 \underset{>80\%\ v/v\ Br_2}{\overset{<50\%\ v/v\ Br_2}{\rightleftarrows}} CoO + Br_2$$

The above reaction sequence could be explained on the basis of the difference in the densities of bromine and air at 600 °C; the density of bromine is higher by about 20% than that of oxygen. Hence it is difficult for bromine to diffuse away from the reaction site. The layer of bromine gas thus formed above the reacting substance prohibits free access of oxygen to undecomposed $CoBr_2$. The CoO formed on the surface of solid could be considered to be reacting with bromine giving CoOBr and/or $CoBr_2$. Such a formation is plausible since $Co(II) \rightarrow Co(III)$ conversion is fairly easy under oxidizing atmosphere of bromine.

The reaction between CoO and bromine should have yielded $CoBr_2$ to a sufficient extent if CoO would have been formed extensively from a single reaction, $CoBr_2 + 1/2\,O_2 \rightleftarrows CoO + Br_2$.

However in spite of a large excess of bromine (>40% v/v bromine) $CoBr_2$ formed is meager. This is shown in Fig. 3 (b) which indicates fraction of $CoBr_2$ formed due to reaction between CoO and mixture of O_2+Br_2. This is indirectly indicating the formation of CoOBr as an intermediate and/or catalytic species in the oscillatory process. Here CoOBr is called as catalyst only on the basis of its property of reformation during the reaction. Also, it is called as an intermediate because CoOBr is not a starting compound but is produced due

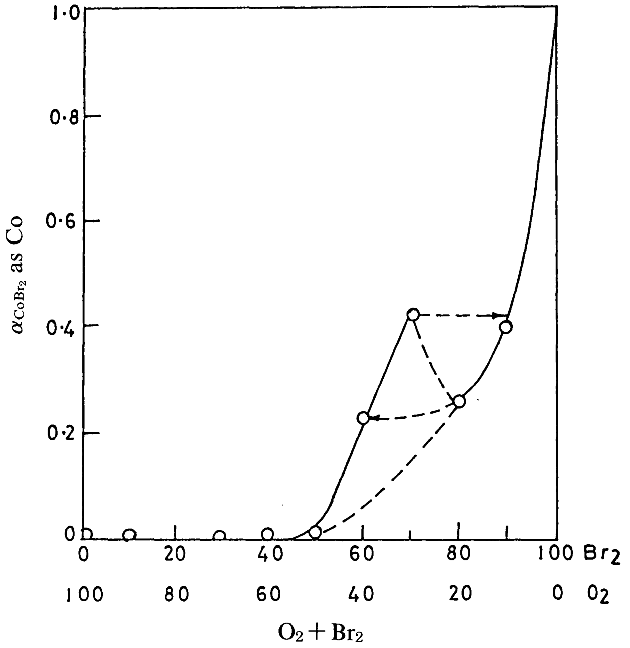

Fig. 3(a). Reaction of $CoBr_2$ in O_2+Br_2 mixture in a closed system.

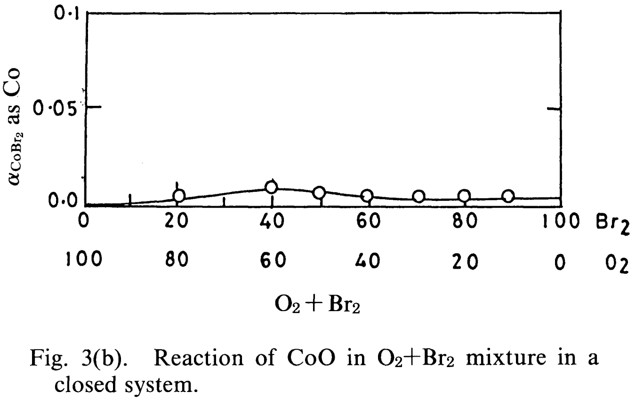

Fig. 3(b). Reaction of CoO in O_2+Br_2 mixture in a closed system.

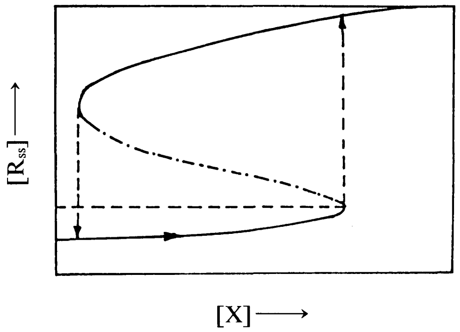

Fig. 3. (c). Schematic plot for Edelstein mechanism for oscillatory reactions.

to a solid (CoO)-gas (Br_2) reaction. CoOBr cannot be extracted in acetone while $CoBr_2$ could be completely extracted in it. These experimental evidences aptly support the oscillatory behavior. The mechanism of the oscillatory reaction observed in the present work (Fig. 3 (a)) closely resembles the Edelstein branching mechanism.[11)]

Figure 3 (b) clearly shows that the formation of $CoBr_2$ is in trace amounts. Thermodynamic consideration of oscillatory reaction needs that such a reaction must be far from equilibrium. In the present system, therefore, we cannot consider Co_3O_4 or CoO as the final products because then, the reaction would be very close to equilibrium. Instead, $CoO+Co_3O_4$ formed from $CoBr_2$ be considered as the reactants and $CoBr_2$ be imagined as the product. Under this situation the transitory existence (temporal existence) is capable of branching into several side reactions,

$$CoOBr + 1/2\ Br_2 \rightarrow CoO + Br_2 \qquad (7)$$

$$CoOBr + 1/2\ Br_2 \rightarrow CoBr_2 + 1/2\ O_2 \qquad (8)$$

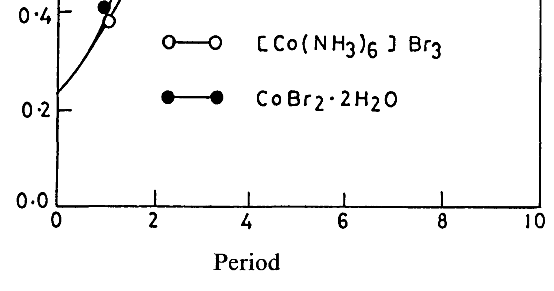

Fig. 4. Simulation of oscillations by population growth model.

$$CoOBr + 1/6\ O_2 \rightarrow 1/3\ Co_3O_4 + 1/2\ Br_2 \qquad (9)$$

This reveals the presence of multiple steady states at a given instant. Thus autocatalysis and the multiple steady states which are prerequisites of Edelstein mechanism seem to be operating in the present reaction.

The Population Growth Model: Another simple model known as population growth model has also been applied to the present system. Oscillating decomposition reaction is described[14,25)] by a series of partial differential equations. However, this simple model does not precisely simulate the oscillatory region but presents an idea that the temporal oscillations could be traced based on the preliminary hypothesis of the formation of a single species, CoOBr, as a catalytic substance. The kinetic factors of other reaction sequences in the entire process are mingled into the constants A, B, C, and /or D to simulate the oscillatory region. The data regarding the simulation of oscillations using population growth model are presented in Tables 2 (a) and (b), Fig. 4. The agreement between the observed and computed data is surprisingly satisfactory. The other models for solid state oscillatory reactions are found to be spe-

Table 2(a). Parameters to Fit Oscillation Using Population Growth Model

Compound	Temp/°C	Time for setting oscillation/min	A
$[Co(NH_3)_6]Br_3$	500	57	0.82
	520	33	0.91
	560	21	1.00
	580	16	1.10
$CoBr_2\cdot 2H_2O$	460	20	0.88
	480	26	0.94
	500	13	0.96
	540	10	1.00

Assumption $A/B=B/C=C/D=$mean value; where A, B, C, D are empirical constants.

$A=0.82$, $B=0.041$, $C=0.00205$, $D=0.0001025$ for HCBR at 500 °C.

$A=0.96$, $B=0.046$, $C=0.0022$, $D=0.000104$ for $CoBr_2\cdot 2H_2O$ at 500 °C.

Table 2(b). Assumed Amount of Co_3O_4 in the Beginning=5 mg i.e. α=Fraction of $CoBr_2$ Reacted=0.227, Temp=500 °C

Compound					
$[Co(NH_3)_6]Br_3$			$CoBr_2\cdot 2H_2O$		
Period	mg of Co_3O_4	α	Period	mg of Co_3O_4	α
0	5	0.227	0	5	0.227
1	8.27	0.375	1	8.86	0.403
2	12.93	0.587	2	14.66	0.670
3	18.23	0.829	3	20.98	0.950
4	20.65	0.939	4	21.02	0.960
5	19.50	0.886	5	20.90	0.950
6	20.27	0.922	6	21.02	0.900
7	19.80	0.900			
8	20.11	0.914			
9	19.92	0.906			

cific[13,16] for the system under consideration.

The sequence of reactions responsible for oscillations include reactions of Co_3O_4 with bromine and/or $CoBr_2$. It was thought that the reaction producing CoO would be,

$$CoBr_2 + Co_3O_4 \rightarrow 4CoO + Br_2$$

For confirming whether such a reaction is possible a series of experiments were conducted at 600 °C between Co_3O_4 and $CoBr_2$ under dry nitrogen atmosphere (Fig. 5). This figure is self-explainatory in that the amount of CoO formed goes on increasing with a break in the time interval between 40 and 60 minutes. A similar break is observed in the fraction of Co_3O_4 formed. However, there is no such a break in the fraction of $CoBr_2$ which shows a normal first order decrease. This figure again supports the nonmonotonous behavior which exists between CoO and Co_3O_4 through some kind of intermediate with bromine gas. This again suggests that the final product in this oscillatory reaction should be assumed to be $CoBr_2$ and not Co_3O_4. Co_3O_4 reacts with $CoBr_2$ as well as with bromine producing CoOBr and/or CoO which supports the sequence of reactions proposed to explain the oscillatory behavior. The decay curves of Co_3O_4 and of $CoBr_2$ appear to merge with that of CoO at a fraction, α=0.167 in terms of cobalt. This merging takes place on the abscissa scale of about 180 min. This is the period where oscillations start dying out. Again this experiment supported the TGA/DTA results discussed earlier and the break in the α-time plots shown in Figs. 3 (a) and (b) indicating branching mechanism as suggested by Edelstein.

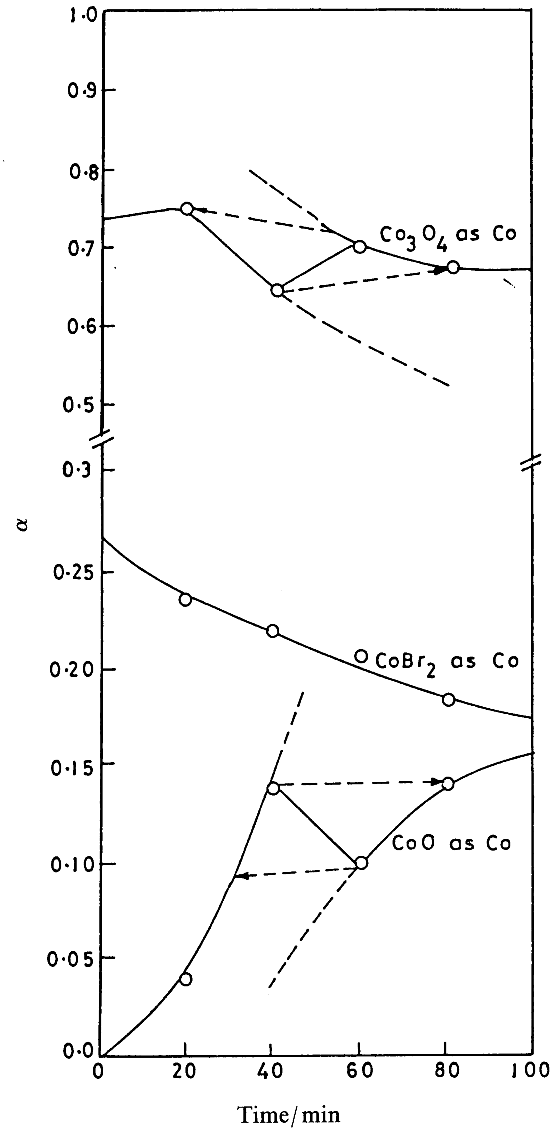

Fig. 5. Reaction of Co_3O_4 and $CoBr_2$ in N_2 atmosphere 600 °C

The authors are thankful to the Head of the Department of Chemistry, University of Poona, for the facilities and encouragement given during the work. One of the authors (MDP) is thankful to UGC, New Delhi, for the financial assistance extended, under Faculty Improvement Program, during the course of this work.

References

1) W. W. Wendlandt and J. P. Smith, "The Thermal Properties of Transition Metal Ammine Complexes," Elsevier, Amsterdam (1967).

2) E. L. Simmons and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, **28**, 2437 (1966).

3) W. W. Wendlandt, *Thermochim. Acta*, **37**, 89 (1980).

4) I. R. Epstein and K. Kustin, *Struct. Bonding* (*Berlin*), **56**, 1 (1984).

5) R. E. Liesegang, *Z. Phys. Chem.*, **52**, 183 (1905).

6) B. P. Belousove, "Sb. Ref. Radiots. Med. (1958)," Megdiz, Moscow (1959), p. 145.

7) A. M. Zhabotinsky, *Dokl. Acad. Nauk SSSR*, **157**, 392 (1964).

8) A. G. Nicolis and Prigogine, "Self-Organisation in Nonequilibrium System," John-Wiley, New York (1977).

9) G. A. Neece and B. Widom, *Annu. Rev. Phys. Chem.*, **20**, 167 (1969).

10) A. Lotka, *J. Am. Chem. Soc.*, **42**, 1595 (1920).

11) B. B. Edelstein, *J. Theor. Biol.*, **29**, 57 (1970).

12) C. G.Tukoudis, L. D. Schmidt, and R. Aris, *Surf. Sci.*, **10**, 325 (1981).

13) V. Jesnek, *Thermochim. Acta*, **85**, 91 (1983), and references therein.

14) H. Strobel, *Thermochim. Acta*, **102**, 29 (1986).

15) W. C. Fernelius, "Inorganic Synthesis," McGraw-Hill, New York (1946), Vol. 2.

16) G. Brauer, "Handbook of Preparative Inorganic Chemistry," 2nd ed, Academic Press, New York (1965), Vol. II.

17) J. Basset, R. C. Denny, and G. H. Jaffery, "Vogel's Text Book of Quantitative Inorganic Analysis," 4th ed, ELBS (1978).

18) R. S. Young, "Chemical Phase Analysis," Charles Griffin and Co., Ltd. (1974).

19) A. Blazek, "Thermal Analysis," Van Nostrand-Reinhold, New York (1972).

20) C. Duval, "Inorganic Thermogravimetric Analysis,"

2nd ed, Elsevier, Amsterdam (1963).

21) C. H. Bamford and C. F. H. Tipper, "Comprehensive Chemical Kinetics," Elsevier, Amsterdam (1980), Vol. 22.

22) F. D. Snell, C. T. Snell, and C. A. Snell, "Colourimetric Methods of Analysis," D. Van Nostrand, New York (1959), Vol. IIA.

23) S. Onodera, *Bull. Chem. Soc. Jpn.*, **50**, 123 (1972).

24) K. Miyokawa, N. Abe, and I. Masuda, *Bull. Chem. Soc. Jpn.*, **55**, 3647 (1982).

25) C. Kusniowski, "Fun Mathematics," Cambridge Univ. Press, Cambridge (1984).