APPENDIX

Submitted by Shri M. Satapathy on the thesis entitled
'A COMPARATIVE STUDY OF THE INFLUENCE OF DOPING AND IRRADIATION ON THE THERMAL DECOMPOSITION OF BARIUM BROMATE.'

1. The contribution of the worker in the present investigation over that of the work of E.G. Prout is as below:

The present investigation has got significant contribution to the chemistry of thermal decomposition study and the findings are completely new in comparison to the work of previous worker. Prout's work deals with the Effect of Irradiation on the Thermal Decomposition of Potassium Permanganate suggesting that irradiation either with thermal neutron, γ-rays, electrons or protons prior to decomposition shortens the induction period and the shortening is related to prior dose as

\[ I = C_1 - C_2 \log I \]

Induction period = (constant)1 - (constant)glog(Irrad. Dose).

But the present study reveals the role of doping as well as γ-irradiation on the thermal decomposition of barium bromate. The data show that decomposition occurs in different stages: (i) initial rapid gas evolution, (ii) a short induction period, (iii) a slow linear reaction followed by sigmoidal regimes consisting of (iv) acceleratory and (v) decay stages.

**Initial gas Evolution:**

The initial gas evolution is not affected by doping or the temperature of decomposition but is increased by irradiation in
case of both pure as well as doped crystals.

**Induction period:**

Considering the data below at 553 K for the induction period (min.):

<table>
<thead>
<tr>
<th></th>
<th>Unirradiated</th>
<th>100 Mrad</th>
<th>400 Mrad</th>
<th>Unirradiated</th>
<th>100 Mrad</th>
<th>400 Mrad</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ba(BrO$_3$)$_2$</strong></td>
<td>54.00</td>
<td>18.00</td>
<td>11.00</td>
<td>22.00</td>
<td>9.00</td>
<td>5.00</td>
</tr>
</tbody>
</table>

It is seen that both irradiation as well as doping shortens induction period, the effect being more prominent in the case of the former.

**Linear Stage:**

The duration of the linear stage for a given temperature is shorter for the doped than for the pure sample and the kinetics at the former stage is given as

$$\alpha = k_1 t + C_1$$

The velocity constant $k_1$ of the linear stage at a given temperature is enhanced on doping. It also increases on irradiation. For both the pure and the doped crystals, the effect being slowing down at higher doses.

**Sigmoidal Regime:**

The data for the sigmoidal regime analyse according to the Prout-Tompkin's equation as well as the contracting square formula. The effect of doping is to enhance the velocity constants of both the Prout-Tompkins and the contracting square formula at a given temperature:
It would appear that the effect of irradiation is more pronounced for the doped than for the pure crystals especially in the decay stage.
In the present appendix all the comments and suggestions made by the external examiner have been taken care of.

1. P-V: Decomposition of barium bromate occurs in five different stages and Induction period is one of the stages. The energy required to carry out the reaction at that period is known as activation energy for the induction period.

Next line: Although, doping does not affect the activation energy of the induction period, it affects the other stages of the decomposition process.

2. P-VI: As suggested by the examiner, $X_{2}^{2-}$ is mended as $X_{2}^{E-}$.

3. P-3: 'C' is the velocity of the incident particle.

4. P-6: Pair production:

In pair production process, there is complete absorption of a photon of energy greater than 1.02 MeV in the neighbourhood of an atomic nucleus forming two particles viz., electron and positron. The particles are emitted in opposite directions with an energy of 0.51 MeV each, so the incident energy of the Y-ray must be at least twice the value for the two particles to be formed. The kinetic energy and the energies of the incident quantum are related as follows:

$$E_{0} = E_{g} + E_{p} + 1.02 \text{ MeV} \ldots \ldots \ldots (1)$$

where $E_{0}$ is the energy content of the radiation, $E_{g}$ and $E_{p}$ are the kinetic energies of the electron and the positron respectively. The observed maximum energy of the positron by a given radiation is independent of the nature of the absorber suggesting that pair production does not take place:
inside the nucleus and it is an extranuclear phenomenon occurring in the Coulomb field outside the nucleus. Thus the target atom is internally bombarded by these fairly energetic electrons due to which the changes that are observed in the target materials by exposure to electromagnetic radiations are almost exclusively due to the secondary electrons.

5. P-7: Varley reported that upon exposure to ionizing radiation an anion may be stripped off its electrons and may become positively charged. This positively charged unstable species is an unfavourable position being surrounded by positive ions and eject itself to an interstitial position.

6. P-11: The equation governing the nucleation process in unimolecular decomposition can be represented\(^2,3\) as

\[
dN/dt = k_1 N_0 \exp(-k_1 t) \quad \ldots (2.2)
\]

where 'N' is the number of nuclei present at time 't' and 'N_0' is the potential nucleus forming sites and \(k_1\) is the probability of occurrence of the decomposition. For the process, in which \(\exp(-k_1 t)\) is approximately unity, nucleation follows a linear law

\[
dN/dt \simeq k_1 N_0 \quad \ldots (2.3)
\]

However, for processes having very large values of \(k_1\) the nucleation is instantaneous and is given by the relation

\[
N = N_0 \quad \ldots (2.4)
\]
At time $t = Y$, nuclei begin to grow after attaining a critical size that has been mentioned as $t = Y$. The size of the nucleus at the beginning of the growth at any time $t = Y$ is given by the general expression:

$$ V(t, y) = \int_{Y}^{t} R(X) \, dx $$

where $R$ is a function of growth rate, $V$; appropriate size parameter of the nucleus, $Y$ is the time at the commencement of the nucleation growth and $t$ being the time at attainment of the maximum growth at a particular stage.

7. P-12: Topochemistry deals with the physico-chemical reactions taking place in the crystal lattice in the solid state.

8. P-14: Equations (2.16) and (2.17) (2.16 repeated in the thesis) represent the power law and contracting envelope equation respectively. The power law is represented by $\alpha = B t^n$ where $\alpha$ is the fraction decomposed and $B$ is a constant. It is known that $\alpha = (kt)^n = k^n t^n = B \cdot t^n$ when $k^n = B$, a constant, $k$ is the rate constant, $n$ is a factor which depends upon the number of successive stages required for the formation of a stable nucleus.

In the present context, the meaning of density and availability is same.

9. P-16: Duke and Shute found that the decomposition of potassium bromate catalysed by the bromide ion in fused alkali nitrate matrices was first order with respect to bromate as well as bromide.

10. P-18: The thermal decomposition of potassium bromate has been studied at atmospheric pressure, 380-404°C, with special
regard to the effects of solid products of the reaction end of copper(II) oxide. The decomposition of the pure substance is an autocatalytic reaction, while by adding potassium bromide the rate is shifted towards the initial stage of the decomposition. The decomposition rate is enhanced by the addition of potassium bromide and the catalytic effect is proved to be a first order process. The value of the activation energy is decreased using greater amount of the catalyst.

Duke and Lawrence have reported the catalytic effect of alkali metal nitrates on alkali metal bromates where melting point is much above 300°C (except lithium bromate). Dilute solution of these bromates in fused alkali nitrates are stable below 300°C but decomposes at higher temperature. The melting point data are given in the thesis.

\[
\begin{align*}
Zn^{2+} & < Ni^{2+} < Cu^{2+} < Co^{2+} \\
1 : 1 & : 50 : 800
\end{align*}
\]

The numbers indicated above represent the proportion of the rate constants.

A favourable thermodynamic energy relationship should be there between the metal ion and its oxide.

Even though the following catalysts, Pb^{2+}, Cd^{2+} and Hg^{2+} are treated with alkali bromates in fused alkali nitrates, the bromate complexes are not formed.

Slight change in activation energy is observed by the action of ultraviolet light.

As the rate determining step of the reaction, postulated by mechanism (1) is an initial electron transfer process, it is suggested that decomposition as well as interaction
of the radicals proceed at a much faster rate.

13. P-22: \[ \text{NH}_2\text{BrO}_3 + \text{HNO}_3 \rightarrow \text{NH}_2\text{NO}_3 + \text{HBrO}_3 \] .... (14)

HBrO₃ (Bromic acid) decomposes as suggested in the thesis.

14. P-24: The changes produced in the decomposition characteristics are due to the formation of additional nucleus forming sites which sensitize the reactivity of the crystals.

Irradiation dose prior to thermal treatment is referred as pre-irradiation dose.

15. P-24,25,26: Nucleus Growth During Irradiation:

The progress of the reaction occurring in the induction period, either during heating or exposure to radiation is known as 'induction period variable', 'n' which increases from an initial value 'n₀' to a final value 'nₑ'. 'n', refers to a physical quantity and is the size or extent of the decomposition nuclei. It is a function of \( \frac{t}{\dot{\phi}} \), where 't' is the time for which the material has been exposed to irradiation and \( \dot{\phi} \) is the total irradiation dose, given by \( \dot{\phi} = t\phi \).

\( \phi \) represent the rate of irradiation dose (Mrad).

'j' is the factor relating \( dn/dt \) to the dose rate and/or irradiation time for nuclei growth during irradiation, i.e., \( n(t) \) will be the function of \( j\phi t = j\dot{\phi} \). Though 'j' could be a function of one or more variables, in the present treatment 'j' is constant.

'g' is the rate of growth of the decomposition nuclei according to the exponential law.
Linear Radiation-Induced Nuclei Growth during Irradiation:

The differential equation for the linear growth is given by
\[ \frac{dn}{dt} = j \phi \quad \ldots \quad (1) \]
and the average size of the decomposition nuclei at time 't', after the radiation has commenced is expressed as
\[ n = n_0 + j \phi t \quad \ldots \quad (2) \]

But when the total radiation time is 't', the average size of the nuclei is expressed by
\[ n = n_0 + j \phi \quad \ldots \quad (3) \]

Induction Period vs. Total Dose Equations:

Considering linear and exponential equations for nucleus growth during irradiation as well as heating, the relationship between the induction period \( I \) and the total irradiation dose \( \phi \) is given as
\[ I = C_1 - C_2 \log \phi \quad \ldots \quad (3.1) \]

where \( C_1 \) and \( C_2 \) are constants.

The nucleus growth during heating is
\[ \frac{dn}{dt} = gn \quad \ldots \quad (3.2) \]
and the solution of this is
\[ \ln n = gt + C' \quad \ldots \quad (3.3) \]
where \( C' \) is a constant and is to be evaluated in two specific cases: by applying this equation to (a) unirradiated materials and (b) materials subjected to irradiation prior to any thermal treatment. In case of (a), by putting \( n = n_0 \) at \( t = 0 \) in eqn. (3.3),
\[ n = n_0 e^{gt} \quad \ldots \quad (3.4) \]
represents the nucleus growth of the unirradiated material during heating. In the second case, when the radiation-induced nucleus growth is linear, the equation

$$ n = n_0 + j \phi $$

specifies the size of the nucleus as heating is commenced.

In order to evaluate the constant in equation (3.3), applying (3.5),

$$ n = (n_0 + j \phi )e^{gt} $$

After irradiation, the average nucleus size will increase from

$$ n_0 + j \phi $$

to

$$ n_c $$

while the sample is heated for a time $$ t = 1 $$.

Putting $$ n = n_c $$ in eq. (3.6)

$$ n_c = (n_0 + j \phi )e^{gI} $$

It can be written as

$$ \ln n_c = \ln (n_0 + j \phi ) + gI $$

or

$$ gI = - \ln \left( \frac{n_0}{n_c} + \frac{j}{n_c \phi} \right) $$

Since $$ n_c >> n_0 $$ (approximation used) and $$ j \phi /n_c = j \phi t/n_c $$

approaches unity for sufficiently large doses

$$ \frac{n_0}{n_c} + j/n_c \phi \approx j/n_c \phi $$

and

$$ I = \frac{1}{g} \left( \ln \frac{n_c}{j} - \ln \phi \right) $$

By putting $$ C_1 = \frac{1}{g} \ln \left( \frac{n_c}{j} \right) $$

and $$ C_2 = \frac{1}{g} $$, eq. (3.11) is converted to

$$ I = C_1 - C_2 \ln \phi $$
A metal atom cluster may be defined as a group of two or more metal atoms in which there are substantial direct bonds between the metal atoms.

The contracting Cube equation\(^9\) is expressed as

\[
1 - (1 - \alpha) = kt
\]

which can be applied for the kinetics of a reaction proceeding through comparable contraction of a sphere. In this case the kinetics is known as contracting sphere kinetics.

Galwey and Jacobs carried out thermal decomposition study on ammonium perchlorate and evaluated \(\alpha\) vs. \(t\) curves using the contracting cube formula.

The effect of irradiation on the thermal decomposition of uranyl oxalate is given by the equation

\[
\Delta - \Delta_0 = k(t - t_0)^2 \quad \ldots (3.16)
\]

where \(\Delta - \Delta_0\) is the difference in the curves for the irradiated and the unirradiated samples at time \(t\) and \(t_0\) respectively. \(\Delta\) is the curve for the irradiated sample at time \(t\) and \(\Delta_0\) is the curve for the unirradiated sample at \(t_0\).

When a solid substance is subjected to irradiation, the resultant effect depends upon the nature of the solid as well as the nature and energy of the incident radiation such as charged particles (electrons, protons, \(\alpha\)-particles etc.), photons (X-ray and Y-ray) and neutrons. Significant changes occur in the physical and chemical properties of the solids. The primary effects are excitation, ionization, displacement of atoms from the normal lattice sites and transmutation of nuclei, whereas the secondary interactions
constitute the reactions of the ions, excited species, radicals etc. to produce the final products.

20. P-37: The chemical changes, produced during irradiation are expressed in terms of 'G' value i.e. the number of molecules formed or decomposed or reacted per 100 eV of energy absorbed, which depends upon the linear energy transfer, free space in the lattice, temperature, degree of dispersion of the crystals, the donor-acceptor properties of the impurities present etc. Considering the work of Andersen et al.\textsuperscript{15}, Holzer et al.\textsuperscript{16} have suggested that $O_2^-$ species is paramagnetic in nature and may be detected by esr spectroscopy even when present in ppm concentration, but its presence in irradiated bromates have not been confirmed.

21. P-38: Though number of species are generated when alkali metal and alkaline earth metal perchlorates are exposed to $\gamma$-rays considering the 'G' values of the species, \textsuperscript{\textit{generated}}, $G(CIO_3^-) = 8.4$. $CLO_3^-$ is the primary radiolytic product and this idea has been supported by the work of Das and Mohanty\textsuperscript{17} in this laboratory working on barium perchlorate.

22. P-41: When permanganates, oxalates, bromates etc. are subjected to irradiation prior to thermal decomposition, the rate of decomposition is enhanced, the effect being higher with higher irradiation dose.

23. P-43: In order to get the $P_f$ value, the substance was heated up to $400^\circ C$ and then it was cooled down up to the temperature of the experiment, for each run.

24. P-45: When barium bromate is exposed to $\gamma$-irradiation the major radiolytic products are $Br^-$, $BrO^-$ and $BrO_2^-$. 
On keeping the irradiated crystals at room temperature for a longer period, the colour of the crystals are faded slightly which may be ascribed to annealing of damaged fragments, taking place at room temperature. When the concentrations of the radiolytic fragments are measured at different time intervals (days), small decrease in the concentration is observed suggesting that a fraction of the damage entities undergoes slow recovery. Definite conclusions have been derived by considering the present data in the light of the works carried out in this laboratory and in other laboratories.

25. P-46: On dissolving the irradiated salt in water evolution of oxygen was detected by alkaline solution of potassium pyrogallate. Previous workers have carried out mass spectrometric study of the gaseous product and have reported it to be oxygen.

26. P-49: At a particular temperature the effect of doping is to enhance the velocity constants of the acceleratory ($k_2$) as well as decay stage ($k_3$) of the decomposition process for which Prout-Tompkins relation (Eqn. 4) has been applied.

27. P-52: Values of the velocity constant ($k_9$) of the decay stage of the decomposition process for which contracting square relation (Eqn. 9) has been applied are shown in Table Y.

28. P-54: As the data obtained for the initial gas evolution at 568 K and 583 K are almost same, few points are not shown in Fig. 1 for those temperatures.

29. P-31: The rate of decomposition is enhanced by irradiation and increases with increasing radiation dose.
30. P-84: By usual chemical analysis, it is found that the evolved gas is gaseous oxygen only (discussed in point 25).

31. P-85: Such idea has been reported by many workers²,³.

32. P-86: The induction period for irradiated barium bromate at 568 K are respectively 7 min. (100 Mrad) and 5 min. (400 Mrad.), confirmed from both experimental as well as theoretical study.

33. P-96: Data in p. 96 (thesis) represent the energy of activation for pure as well as doped (Al³⁺) barium bromate.

34. P-106: Data in Table IX (thesis) represent the ranges of applicability of linear equation in minutes.

35. P-115: At a given temperature, velocity constants of the acceleratory (k₂) and decay (k₃) stages, for which Prout-Tompkin's relation has been valid are enhanced on doping.

The energy of activation for the acceleratory (185 kJ) and the decay (173 kJ) stages of the decomposition process is not affected by doping.

36. P-118: At a given temperature, doping enhances the velocity constants of the acceleratory (k₆) and the decay (k₇) stages of the decomposition process, for which Avrami-Erofeev equation has been applied.

37. P-118: The activation energy (186 kJ) obtained for the reaction taking place at the acceleratory stage of the decomposition process, by using Power law is almost same for the pure as well as doped materials.
37. P-148: The velocity constants of the reactions at the acceleratory and decay stages of the decomposition process for which Avrami-Erofeev equation is applied are enhanced by irradiation.

38. P-149: The velocity constants of the reaction taking place in the decay stage, for which constructing square formula is applied is enhanced upon irradiation in case of both pure as well as doped substances.

39. P-169: In the linear stage and in the induction period the following data are obtained:

<table>
<thead>
<tr>
<th>Energy (kJ/mol) of activation for the reaction taking place in the induction period</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ba(BrO$_3$)$_2$</strong></td>
</tr>
<tr>
<td>Unirrad.</td>
</tr>
<tr>
<td>151.00</td>
</tr>
</tbody>
</table>

The data suggest that the energy of activation for the reaction taking place in the induction period is not affected either by the doping or irradiation.

<table>
<thead>
<tr>
<th>Activation energy (kJ/mol) for the reaction taking place in the linear stage</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ba(BrO$_3$)$_2$</strong></td>
</tr>
<tr>
<td>Unirrad.</td>
</tr>
<tr>
<td>154.00</td>
</tr>
</tbody>
</table>

The data show that the activation energy of the reaction taking place in the linear stage is not affected by doping but decreases by irradiation, the effect being more pronounced with doped material than the pure crystals.
REFERENCES


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APPENDIX


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