Thermal Decomposition of Irradiated Lead Bromate

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Thermal decomposition of lead bromate has been studied in the temperature range 170-190°C. The decomposition curves proceed through (i) short induction period, (ii) acceleratory and (iii) decay stages. Both acceleratory and decay stages follow Prout-Tomkins equation. Irradiation enhances decomposition rate. The activation energies are not affected significantly by irradiation. Post irradiation annealing tends to restore the decomposition characteristics of unirradiated sample.

T he study of damage induced by Co$^{60}$ $\gamma$-rays in alkaline earth bromates was reported by Chase and Boyd. The thermal decomposition of lead bromate had been studied by Rammelsberg but no analysis of kinetic aspects has been made. The present work deals with kinetics of isothermal decomposition of lead bromate in vacuo and the effect of thermal annealing of irradiated salt on its subsequent decomposition behaviour.

Materials and Methods

Lead bromate was synthesised by the reaction of a solution of potassium bromate (GR) with a solution of lead nitrate (AR). The crystalline lead bromate was powdered, dried over phosphorus pentoxide and dehydrated at 105°C till a constant weight was obtained. The composition of anhydrous salt was confirmed by usual analysis. The anhydrous salt was preserved over phosphorus pentoxide.

Irradiation — Samples sealed in glass ampoules in vacuo were irradiated with Co$^{60}$ $\gamma$-rays of doses between 1 and 20 Mrad at a dose rate of 0.37 Mrad/hr. The irradiated samples were also preserved over P$_2$O$_5$ before thermal decomposition studies.

The damage product BrO$_2^-$ was estimated by direct micropotentiometric titration using saturated calomel as reference electrode.

The thermal decomposition of both the irradiated and unirradiated samples was studied with about 45 mg of bromate accurately weighed, distributed flat in a Y-shaped reaction vessel, preheated to desired temperature in the range 170-90°C. The temperature was controlled within ± 1°C. The decomposition was followed by measuring total gas pressure developed during decomposition with apiezon-oil manometer.

Results and Discussion

Lead bromate prepared is white, needle shaped crystals which are monohydrated. The hydrated crystals get dehydrated at about 95°C and decomposition starts at 165°C in vacuo.

The results of isothermal decomposition of unirradiated lead bromate at different temperatures between 170° and 190°C are presented in Fig. 1 and those of $\gamma$-irradiated samples of 2 Mrad and 10 Mrad in
Figs 2 and 3 respectively. The pressure-time (p-t) plots are sigmoid with short induction period. The decomposition proceeds through (i) short induction period, (ii) acceleratory stage followed by (iii) decay stage. The induction period decreases with rise of temperature and increase of irradiation dose.

Acceleratory and decay stages follow Prout-Tompkins' equation:

\[ \log \left( \frac{p}{p_0} \right) = kt + c \quad \cdots (1) \]

with different reaction constants \( k_1 \) and \( k_2 \) for the acceleratory and decay stages respectively. The effect of temperature is to increase decomposition rate. The activation energies \( E_1 \) for acceleratory and \( E_2 \) for decay stages are calculated from the linear Arrhenius plots and given in Table 1. The estimated accuracy of the data is \( \pm 1.5 \) kcal.

It is evident from Table 1 that \( E_1 \) and \( E_2 \) are not appreciably affected by irradiation and therefore it appears that the same processes govern the decomposition reaction of both unirradiated and irradiated samples.

The effect of \( \gamma \) irradiation on isothermal decomposition of lead bromate is illustrated in Fig. 4. An increase in the irradiation dose progressively enhances the decomposition rate, the general shape of (p-t) curve is however unaffected. The increase in \( k_1 \) and \( k_2 \) is not linear with respect to chemical damage induced in the samples. The data are summarized in Table 2.

### Table 1 — Activation Energies

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E_1 ) kcal/mol</th>
<th>( E_2 ) kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirradiated</td>
<td>34.6</td>
<td>32.3</td>
</tr>
<tr>
<td>2 Mrad</td>
<td>34.7</td>
<td>35.4</td>
</tr>
<tr>
<td>10 Mrad</td>
<td>33.8</td>
<td>34.6</td>
</tr>
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</table>

The rate of chemical damage increases almost linearly with irradiation dose.

The effect of partial pre-annealing of the chemical damage on the subsequent thermal decomposition of the sample irradiated with 20 Mrad at 170\(^°\) is graphically shown in Fig. 5. The decomposition characteristics of the irradiated sample tends to restore to that of unirradiated sample upon thermal annealing. Values of \( k_1 \) and \( k_2 \) corresponding to different amounts of annealing are given in Table 3.

### Table 2 — Reaction Constants for Different \( \gamma \)-Irradiation Doses

<table>
<thead>
<tr>
<th>Dose, (Mrad)</th>
<th>( \text{BrO}_3^- ) ppm</th>
<th>( 10^2 k_1 ) (min(^{-1}))</th>
<th>( 10^2 k_2 ) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>—</td>
<td>1.14</td>
<td>0.71</td>
</tr>
<tr>
<td>1</td>
<td>437.9</td>
<td>1.60</td>
<td>1.34</td>
</tr>
<tr>
<td>2</td>
<td>1567.0</td>
<td>2.00</td>
<td>1.48</td>
</tr>
<tr>
<td>10</td>
<td>4004.0</td>
<td>2.75</td>
<td>2.19</td>
</tr>
<tr>
<td>20</td>
<td>7048.0</td>
<td>5.42</td>
<td>3.19</td>
</tr>
</tbody>
</table>
It appears from Table 3 that initially, values of rate constants $k_1$ and $k_2$ decrease almost linearly with increasing fraction of chemical damage annealed and tend to become constant at higher values of $f$.

**Mechanism of irradiation enhancement of thermal decomposition** — Of the three mechanisms by which $\gamma$-rays interact with matter, viz. the photoelectric effect, the Compton effect and pair production, the Compton effect has the largest cross-section for Co$^{60}$ $\gamma$-rays except in the case of materials of very high atomic numbers, where some photoelectric emission and pair production also occur. It has been shown that the Compton electrons generated by 1 MeV $\gamma$-rays are capable of producing atomic displacements in very light elements, but this capacity decreases sharply with increasing atomic weight, becoming zero at atomic weight $\sim 125$ (ref. 7). The atomic weight of lead is 208. Therefore the possibility of atomic displacement by Compton electrons is nil. The production of displacements by photoelectric recoil is also not significant in this case (atomic number 82), since photoelectric absorption for 1.17 and 1.33 MeV $\gamma$-rays (obtained from Co$^{60}$) is small and every photoelectric absorption does not displace the atom because of the distribution of emitted electrons with respect to incoming $\gamma$-ray$^5$. In pair production, recoil energies above the displacement threshold may be imparted only in light elements. Thus, it appears that displacement of lead is unimportant for $\gamma$-ray energies employed in the present study. The production of anion displacement by the Verley$^6$ mechanism of multiple ionization of the ion is unlikely in the case of polyatomic anions like bromate ion, because when the ion loses two or more electrons the species formed (BrO$_2^-$, BrO$_3^-$ etc.) are highly unstable and breakup spontaneously rather than under displacement as a whole.

Howard et al. (see ref. 9) have suggested a few modifications in the mechanism of atomic displacement, which are also not important in the case of polyatomic ion (like bromate ion). The Seitz$^7$ mechanism is also incapable of producing displacement of compound anions because the release of excitation energy at lattice irregularities is used up preferentially in producing bond rupture rather than in the production of anion vacancies. Co$^{60}$ $\gamma$-irradiation produces excitation and ionization of compound anion (BrO$_5^-$). The excitation and ionization of the anion, however, cause chemical damage in the crystal matrix. The presence of damaged species in the crystal matrix will result in a steady accumulation of strain. At temperature sufficient to produce decomposition this strain may induce rupture in the crystals. The nuclei present before or formed during irradiation grow accordingly and the observed enhancement of decomposition rate follows.

Since decomposition of solids occurs through the formation of nuclei and not through activated complex, in the opinion of present authors $E_1$ and $E_2$ may be called as nucleation energies instead of so called activation energies.

**Acknowledgement**

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**References**

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