removal of two molecules of water. Therefore, the endothermic peak at 150° in DTA curve is due to the loss of two molecules of water thereby giving anhydrous sodium tungstate. The TG curve neither indicates the possibility of formation of any intermediate during dehydration nor exhibits any significant weight-change in the temperature range 220-750°. Hence, the endothermic changes at 600° and 700° are due to some processes which do not accompany any weight change.

The pure sample exhibits IR bands at 930 and 800 cm⁻¹ which may be assigned to the 2W-O of normal tungstates. The other bands appearing at 3300-1600 cm⁻¹ region are due to symmetric and antisymmetric O-H and 3H-O-H of lattice water. The tungstate appears to be completely dehydrated at 250° as indicated by the absence of characteristic bands due to water molecules. Therefore, the endothermic change at 150° is clearly due to dehydration. The significant observation at and after 250° is that the band at 800 cm⁻¹ shifts to 830 cm⁻¹ with enhanced intensity followed by the disappearance of the 930 cm⁻¹ band. Thus, the strong band of ST 250 (sodium tungstate calcined at 250°) sample at 800 cm⁻¹ may be expected to be coupled with frequency, characteristic of water. As the IR bands of the samples ST 660 and ST 710 are almost the same as those of ST 250, it can be suggested that the endothermic changes after 250° are not due to decomposition of the tungstate rather due to phase changes. The last endothermic peak at 700° is, however, due to melting.

The pure sample exhibits a well defined XRD pattern with characteristic lines at d = 6.95, 4.9, 3.5, 3.3, 3.17, 2.98, 2.17, 2.12 Å, etc. The d-values of the samples ST 250, ST 660 and ST 710 are compared excellently with those reported in the ASTM Card No. 1-011 for the standard patterns of sodium orthotungstate(VI) dihydrate it is seen that the sample is pure Na₂W₃O₁₁. XRD patterns of the catalyst are little changed at and after 250° with the registration of strong lines at d = 5.25, 3.21, 3.16, 2.75 Å, etc. The d-values of the ST 250, ST 660 and ST 710 samples compare excellently with those reported in the ASTM Card No. 5-0247 for Na₂W₃O₁₁ (d = 5.19, 3.18, 2.72 Å, etc.), indicating that the endothermic change at 150° is due to dehydration and those after 250° are due to crystal transformation. Earlier workers also found sodium tungstate to undergo the following phase changes at the temperature region 431-700°:

\[ \delta-\text{Na}_2\text{W}_3\text{O}_{11} \rightarrow \gamma-\text{Na}_2\text{W}_3\text{O}_{11} \rightarrow \delta-\text{Na}_2\text{W}_3\text{O}_{11} \]

The present studies, however, reveal that sodium tungstate does not undergo any phase change in the temperature range 431-570°. The temperature range at which phase changes take place, seems to be 570-700°. Magnetic measurements indicate that the pure sodium tungstate as well as its thermal transition products are diamagnetic. Surface acidity measurements reveal that this tungstate does not have surface acidic sites at any stage of thermal treatment. This study also rules out the possibility of the decomposition reaction Na₂W₃O₁₁→Na₂O+3WO₃ till the melting of the tungstate as WO₃ is known to have a good number of surface acidic sites.

**References**


**Thermal Decomposition of Gamma-irradiated Barium Bromate**

S. D. BHATTACHARYYA & S. R. MOHANTY

Nuclear Chemistry Laboratory, Utkal University
Bhubaneswar 751004

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The effect of gamma-irradiation of barium bromate is to shorten the induction period and increase the rates of its decomposition in the linear, acceleratory, and decay stages. The activation energy of the linear reaction decreases under irradiation and that of the acceleratory stage increases whereas the activation energy of the decay stage remains unaffected.

DUKE and Shute found that the decomposition of potassium bromate catalysed by bromide ion in fused alkali nitrates was first order with respect to both bromate and bromide. Jach has shown that whereas the isothermal decomposition of sodium bromate followed a contracting envelope formula that of potassium bromate occurred according to a first order rate law. Both these substances undergo fusion when sufficient bromide accumulates during the course of the decomposition because of which a discontinuity occurs in the Arrhenius plots. The discontinuity is removed by Y-irradiation in the case of potassium bromate. The present work deals with the influence of irradiation on the isothermal decomposition of barium bromate which takes place throughout in the solid condition.

AR grade barium bromate, dried at 170°, was irradiated in sealed glass ampoules with 60Co Y-rays to various doses up to 420 Mrad at room tem-
perature. Portions of the unirradiated (normal) bromate as well as of irradiated samples were decomposed at temperatures in the range 290-315° and the decomposition followed at each temperature by measuring the pressure of oxygen developed at different times \( t \) of heating. The decomposition apparatus and the procedure employed have already been described\(^4,6\). For each run, the final pressure upon complete decomposition was determined and the fraction decomposed \( \alpha \) for different times of heating was calculated.

The \( \alpha \)-characteristics for normal barium bromate and for the sample irradiated to 100 Mrad are shown in Fig. 1. The decomposition of the normal substance is characterized by (i) initial rapid gas evolution up to \( \alpha \approx 0.06 \); (ii) a short induction period noticeable only at the lower temperatures; (iii) a linear reaction extending up to \( \alpha \approx 0.2 \); and (iv) an accelerating followed by a decay stage as is characteristic of autocatalytic decompositions. Pre-irradiation abolishes induction and shortens the linear stage (Figs. 1 and 2). It, however, enhances the rate of decomposition in proportion to the dose.

The linear stage (iii),

\[
\alpha = k_1 t + C_1 \quad \ldots (1)
\]

for the normal substance is shown in Fig. 3 (inset). The duration of the linear stage decreases with increase in temperature, viz. from 80 min at 295° to 35 min at 315°. Analysis of the data in stage (iv) according to the Prout-Tompkins relationship

\[
\log [\alpha/(1-\alpha)] = k_{2,3} t + C_{2,3} \quad \ldots (2)
\]

is represented in Fig. 3; the rate constant \( k \) has two values \( k_2 \) and \( k_3 \) for the accelerating and the decay stages respectively. The equation holds for almost the whole of the sigmoid region, \( 0.15 < \alpha < 0.95 \).

The rate constants \( k_1, k_2, \) and \( k_3 \) increase with increase in temperature and the plots of \( \log k \) against \( 1/T \) are linear. The activation energies \( E_1, E_2, \) and \( E_3 \) in kJ (± 5) mole\(^{-1} \) for the linear, accelerating, and deceleratory stages respectively are given below:

<table>
<thead>
<tr>
<th>Substance</th>
<th>( E_1 )</th>
<th>( E_2 )</th>
<th>( E_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>167</td>
<td>195</td>
<td>188</td>
</tr>
<tr>
<td>100 Mrad</td>
<td>153</td>
<td>196</td>
<td>184</td>
</tr>
<tr>
<td>420 Mrad</td>
<td>136</td>
<td>210</td>
<td>185</td>
</tr>
</tbody>
</table>

It is seen that whereas the energy of activation \( E_1 \) for the linear reaction decreases substantially under irradiation, the decrease being higher at higher doses, the activation energy \( E_2 \) for the accelerating reaction increases but slightly at the highest irradiation dose employed. The activation energy \( E_3 \) for the deceleratory reaction is, on the other hand, unaffected by irradiation.

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References