

# EXPLOSIVE PROPERTIES OF CHROMIUM (III) AND MANGANESE (II) PICRAMATES

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Explosive properties of chromium (III) and Manganese (II) picramates have been studied and discussed in this paper.

Metal picramates have been of more interest than the picrates due to their ease of preparation and increased sensitivity towards heat and shocks<sup>1</sup>. Recently Agrawal and Agrawal<sup>2-5</sup> have prepared some transition metal picramates and investigated their stereochemistry from infrared and magnetic susceptibility measurements. They have also investigated the explosive properties of these metal picramates. Also, Aggarwal and Singh<sup>6</sup> have prepared picramates of chromium (III) and manganese (II) but have only investigated their stereochemistry from infrared, electronic spectra and magnetic susceptibility measurements. However, since, the explosive properties may throw some direct utility of the picramates as a primary explosive. A detailed study of the explosive properties have been carried out.

## EXPERIMENTAL

### *Explosive Properties.*

The compounds used for the measurements of explosive properties were dried at 100-115°C for 2-3 hours.

*Explosion delay and temperature* : Explosion delay and explosion temperature were measured by the method described earlier<sup>2-5</sup> and results so obtained are given in Table 1. The explosion delay ( $D_E$ ) is related to the energy of activation ( $E$ ) by the following expression<sup>7</sup>  $D_E = Ae^{E/RT}$ , where  $R$  is the gas constant  $T$  is the temperature of bath in degrees  $K$  and constant  $B = \log A$ .

*Thermal sensitivity* : Values of explosion delay ( $D_E$ ) are given in Table 1. The curves representing the relationship<sup>7</sup>.

$$\log D_E = \frac{E}{4.57T} + B$$

where  $E$  is the activation energy of the physico-chemical process controlling explosion delay,  $B$  is a constant and  $T$  is the absolute temperature of the bath in which experiment is carried out are shown in Fig. 1. From the slopes of these curves which are almost rectilinear, values of activation energies<sup>7</sup> have been estimated and are given in Table 1.

*Explosion pressure* : During the explosion, the pressure developed due to the formation of gases is an important factor because it serves as a measure of the capacity of an explosion to do work, although the character of the work is determined by the rate at which the pressure is built up and it was measured by a method similar to that employed by Yoffe<sup>8</sup> for studying the thermal decomposition of azides. The apparatus we used was slightly modified from the one used by Yoffe<sup>8</sup>. Instead of silicon oil, potassium hydrogen sulphate was used in the bath in which explosion is carried out. The results so obtained are given in the Table 2.

## RESULTS AND DISCUSSION

From these results it may be concluded that  $Cr$  (III) picramate is thermally more stable than the  $Mn$ (II) picramate, possibly due to the fact that oxygen-metal bond distance is lesser in  $Cr$  (III) picramate than  $Mn$  (II) picramate. Picramates are thermally less stable than picrates which support the observation made by Glowiak<sup>9</sup>. Ionization potential and ionic radii of  $Cr$  (III) and  $Mn$  (II) are:  $Cr$  (III) 31.7 e.v., 0.65Å<sup>o</sup>;  $Mn$  (II) 15.770 e.v., 0.80Å<sup>o</sup>.

\*Deceased.

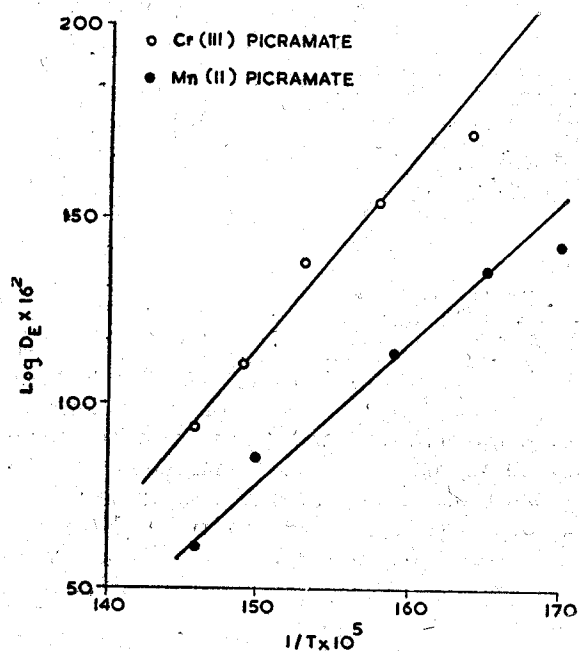


Fig. 1.—Variation of  $\log D_E$  with reciprocal of absolute temperature

TABLE 1  
EXPLOSION DELAY, TEMPERATURE, ACTIVATION ENERGY AND CONSTANT P FOR PICRAMATES

Compound	Explosion delay at $320 \pm 2^\circ\text{C}$ (sec)	Explosion temp. for explosion delay of 10 sec ( $^\circ\text{C}$ )	Activation energy (E) K. cal/mole	Constant B
Chromium Picramate	7.2	$4.2 \cdot 20 \pm 2$	20.0220	6.19758
Manganese Picramate	3.6	$368.00 \pm 2$	17.1775	3.61724

TABLE 2  
EXPLOSION PRESSURE FOR DIFFERENT COMPOUNDS  
Density of Mercury = 13.595 g/ml.

Gravitation acceleration ( $g$ ) = 980.665 cm/sec<sup>2</sup>

Compound	Height (H) (cm)	Explosion pressure† (bath temp. $350 \pm 2^\circ\text{C}$ ) (dynes/cm <sup>2</sup> × 10 <sup>4</sup> )
Chromium Picramate	8.798	11.7296
Manganese Picramate	10.001	13.3334

†Explosion pressure was obtained by taking 16 mg of the explosive materials.

Thermal stability decreases from *Cr* (III) to *Mn* (II) picramates which is supported by the data of explosion delay, explosion temperature, activation energy etc. It may, therefore, be concluded that thermal stability increases as the ionic radii decrease or ionization potential increases. This has also been established by Evans<sup>10</sup> and Deb<sup>11</sup> in the case of inorganic azides and cyanamides respectively.

On the basis of bond dissociation energies<sup>12,13</sup> of different linkages present in the metal picramates, it may be suggested that initial stage in the explosion reaction is the breaking of the *N-O* linkages<sup>14, 15</sup>. This then enables oxygen which was linked wholly to nitrogen, to be consumed for the complete oxidation of carbon and hydrogen obtained from ring rupture and thus produces a large amount of heat.

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