CHEMISTRY OF METAL (BENZYLIDENE) PICRAMATE—PART III BENZYLIDENE PICRAMATES OF ZINC, CADMIUM AND MERCURY

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Benzylidene picrates of zinc, cadmium and mercury have been prepared by treating the corresponding aqueous sulphate and chloride solutions with sodium salt of 4'-dimethylaminobenzylidene-2-hydroxy-3,5-dinitroaniline. A metal : ligand ratio of 1:2 has been established in all these cases. I.R. spectral studies of metal benzylidene picrates show N→M coordination (where M is zinc, cadmium or mercury). Explosive properties of these benzylidene picrates have also been studied and it was found that the thermal stability increases as the atomic radius decreases or ionization potential increases.

A number of explosive properties of metal picrates and picramates have been studied by various workers. Little work, however, seems to have been carried out on benzylidene picrates of metals. The present communication deals with the chemistry and explosive properties of zinc, cadmium and mercury benzylidene picrates.

EXPERIMENTAL

All the chemicals used were of Analar grade (BDH). 4'-Dimethylaminobenzylidene-2-hydroxy-3,5-dinitroaniline was prepared by refluxing picramic acid and p-dimethylamino-benzaldehyde at 100°C in ethanol for 3-4 hours in 1:1 molar ratio. Sodium benzylidene picrate was prepared by suspending a known weight of 4'-dimethylaminobenzylidene-2-hydroxy-3,5-dinitroaniline in water and then treating it with an equivalent amount of sodium bicarbonate. The resulting mixture was digested on water bath to ensure complete reaction. After cooling, the product was filtered and washed with ice-cool water. Red crystals of sodium benzylidene picrate were obtained.

The general method employed for the preparation of metal benzylidene picrate is similar to that employed for metal picrates. The benzylidene picrate in question is simply prepared by adding a solution of an appropriate salt of the metal to a solution of sodium benzylidene picrate. For example, the benzylidene picrates of zinc, cadmium and mercury was precipitated from zinc sulphate, cadmium chloride and mercury chloride respectively. After keeping the reaction mixture overnight, the precipitate was separated by filtration, washed with water and ethanol and dried in a vacuum desiccator to constant weight and analysed for its constituents. This simple procedure was employed in the preparation of all these compounds. Results of microanalyses are listed in Table 1.

Spectrophotometric (visible) measurements were carried out with the help of a Unicam SP 8000 recording Spectrophotometer and a Unicam Spectrophotometer number 23704. (Job's continuous variation method). The pH measurements were carried out with a Leeds and Northrup Co. (Philadelphia, U.S.A.) pH meter. The electrical conductances of the solutions were measured with a Toshniwal's conductivity bridge (type CL01/02). Job's monovariation method was employed to determine the composition of these complexes. I.R. spectra of the complexes were recorded with the help of a Perkin-Elmer Infrared Spectrophotometer model 337 using KBr pellet technique in the range of 400-4000 cm⁻¹. T.G. was carried out on a thermogravimetric analyser supplied by Planning and Development Division, Fertilizer Corporation of India, Sindi Bihar. The magnetic susceptibility measurements were carried out with the help of Gouy's method using a semimicro balance and a field of 1000 gauss at room temperature (303°K).

EXPLOSIVE PROPERTIES

The compounds used for the measurements of explosive properties were dried at 373-383°K for 2-3 hours to constant weight.
The explosive properties like explosion delay, explosion temperature, activation energy and explosion pressure were measured in a manner similar to that reported in an earlier communication.

For measuring explosion delay ($D_E$), approximately 20 milligrams of the prepared compound was taken in a small pyrex tube (diameter 0·96 cm and thickness 0·14 cm) at the room temperature. The tube was then suddenly plunged into a paraffin liquid bath maintained at 595° K. The interval between the time of insertion and the moment of explosion was noted with the help of a stop watch. A mean of three reading was taken as the final reading in each case. Values of $D_E$ re given in Table 2.

To measure explosion temperature ($T_E$), the above experiment was carried out at various temperatures in potassium hydrogen sulphate bath (instead of liquid paraffin) and $D_E$ was plotted against the temperature of the bath. Explosion temperature was read off from this plot as the temperature necessary to cause explosion in exactly 10 seconds. Results are recorded in Table 2.

Thermal sensitivity of an explosive is related to the activation energy controlling $E$

$$\log D_E = \frac{E}{4·57 T} + B$$

($T$ is the absolute temperature of the bath in which the experiment is carried out). Curves obtained by plotting $D_E$ against $1/T$ are given in Fig. 1.

Explosion pressure was measured in a manner similar to that employed by Yoffe for studying thermal decomposition of azides. Instead of silicone oil potassium hydrogen sulphate was used in the bath in which explosion was carried out. The results obtained are listed in Table 4.

RESULTS AND DISCUSSION

Result are recorded in Tables 1—5: Plots of $D_E$ against $1/T$ are given in Fig. 1 (values of $E$ obtained by these straight line curves are given in Table 3).
SRIVASTAVA, et al.: Chemistry of Metal Benzyldiene Picramate

Table 1

Analytical data for metal benzyldiene picramates

<table>
<thead>
<tr>
<th>Complex*</th>
<th>M (%)</th>
<th>N (%)</th>
<th>H₂O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn[O₃C₆H₅(NO₃)₂NO₃N(CH₃)₂(H₂O)]₂</td>
<td>9.0</td>
<td>15.0</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>(8.6)</td>
<td>(14.7)</td>
<td>(4.7)</td>
</tr>
<tr>
<td>Cd[O₃C₆H₅(NO₃)₂NO₃N(CH₃)₂(H₂O)]₂</td>
<td>13.7</td>
<td>13.7</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>(13.9)</td>
<td>(13.9)</td>
<td>(4.5)</td>
</tr>
<tr>
<td>Hg[O₃C₆H₅(NO₃)₂NO₃N(CH₃)₂(H₂O)]₂</td>
<td>22.2</td>
<td>12.7</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>(22.4)</td>
<td>(12.5)</td>
<td>(4.0)</td>
</tr>
</tbody>
</table>

* Satisfactory C, H analyses were obtained for all complexes. Calculated values are given in parentheses.

Table 2

Explosion delay and explosion temperature for the metal benzyldiene picramates

<table>
<thead>
<tr>
<th>Complex</th>
<th>Explosion delay at 698°K (sec.)</th>
<th>Explosion temp. for explosion delay of 10 sec (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn benzylidene picramate</td>
<td>60.3</td>
<td>694±2</td>
</tr>
<tr>
<td>Cadmium benzylidene picramate</td>
<td>35.4</td>
<td>645±2</td>
</tr>
<tr>
<td>Mercury benzylidene picramate</td>
<td>9.1</td>
<td>582±2</td>
</tr>
</tbody>
</table>

Table 3

Values of E for different compounds

<table>
<thead>
<tr>
<th>Complex</th>
<th>Activation energy (KJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn benzylidene picramate</td>
<td>78.50</td>
</tr>
<tr>
<td>Cadmium benzylidene picramate</td>
<td>62.22</td>
</tr>
<tr>
<td>Mercury benzylidene picramate</td>
<td>51.70</td>
</tr>
</tbody>
</table>

Table 4

Explosion pressure for different compounds density of mercury = 13.595 g/ml; gravitational acceleration (g) = 980 - 985 cm Sec²

<table>
<thead>
<tr>
<th>Complex</th>
<th>Height (m)</th>
<th>Explosion pressure* (bath temp. 623±2 K) (nm⁻² × 10⁵)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn benzylidene picramate</td>
<td>0.1050</td>
<td>14.00</td>
</tr>
<tr>
<td>Cadmium benzylidene picramate</td>
<td>0.0890</td>
<td>11.87</td>
</tr>
<tr>
<td>Mercury benzylidene picramate</td>
<td>0.0830</td>
<td>11.06</td>
</tr>
</tbody>
</table>

*The Explosion pressure was obtained by taking 10 mg of the explosive material.

Table 5

Some characteristic absorption frequencies in Schiff base and its metal derivatives

<table>
<thead>
<tr>
<th>Compound</th>
<th>Characteristic absorption frequencies (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Metal-Nitrogen</td>
</tr>
<tr>
<td>p-Dimethylamino benzyldiene picramic acid</td>
<td></td>
</tr>
<tr>
<td>Zn—(II) p-dimethylamino benzyldiene picramate</td>
<td>495</td>
</tr>
<tr>
<td>Cd—(II) p-dimethylamino benzyldiene picramate</td>
<td>478</td>
</tr>
<tr>
<td>Hg—(II) p-dimethylamino benzyldiene picramate</td>
<td>490</td>
</tr>
</tbody>
</table>
In all the cases, the spectrophotometric (visible), potentiometric and conductometric studies and micro-analysis point to the formation of complex in the metal : ligand ratio of 1:2. The general formula may be expressed as

\[ [\text{C}_{13} \text{H}_7 (\text{NO}_2)_3 \text{NO} \cdot \text{N} (\text{CH}_3)_2 \text{H}_2 \text{O}]_2 \text{M} \]

where \( \text{M} \) stands for zinc (II), Cadmium (II) or mercury (II). Table 5 gives some characteristic absorption frequencies in the Schiff base and its metal derivatives in the IR region. Absorption, associated with \(-\text{N}=\text{C}\) deformation mode is expected to appear near 1640 cm\(^{-1}\)\(^{11,12}\) In Schiff base a band appears at 1630 cm\(^{-1}\) while in the metal complexes it is found in the region 1620-1600 cm\(^{-1}\). The lowering in the \(-\text{N}=\text{C}\) frequency in the complexes is due to the coordination of \(-\text{N}=\text{C}\) with the metals \(^{11,13}\). Other bands appear in the region 1600-1300 cm\(^{-1}\) and are due to ring deformation modes. Coordinated water gives bands in the range 880-650 cm\(^{-1}\) \(^{11,14,15}\).

In the Schiff base a band is present near 3475 cm\(^{-1}\). This could be assigned to the phenolic group which normally absorbs in the region 3600-3500 cm\(^{-1}\). The shift in the absorption peak is due to the intramolecular hydrogen bond present between the hydrogen of the phenolic group and the oxygen of the nitro group ortho to each other\(^{12,16,17}\). However, a band in the region 3600-3400 cm\(^{-1}\) could also be due to the presence of water molecules\(^{18}\) and is not influenced by coordination. But, hydrogen-bonding in the complexes is expected to disappear completely due to ionization of the labile hydrogen and coordination of the negative oxygen with the metal concerned. Thus, benzylidene picramic acid has two centres of coordination, viz. the nitrogen of the \(-\text{N}=\text{C}\) group and the oxygen of the phenolic group.

In addition to these frequencies a frequency is observed between 500-300 cm\(^{-1}\). This may be assigned to the metal-nitrogen stretching modes similar to the metal-nitrogen stretching modes in metal glycine complexes assigned by Nakamura\(^{19}\). The metal-oxygen stretching frequency has been reported at 360-260 cm\(^{-1}\)\(^{20,21}\). However, Lane et. al. \(^{22}\) assumed that metal-oxygen vibration appears below 200 cm\(^{-1}\) because metal-oxygen band is highly ionic.

The magnetic susceptibility measurements carried out by us show that these benzylidene picramates are diamagnetic. This is also what we would expect for \(d_{10}\) ions\(^{14}\).

A gravimetric estimation of coordinated water molecules show that two molecules are present in each of these complexes. The fact that a bidentate ligand is involved and two water molecules are coordinated to it points to an octahedral geometry for these complexes which can be represented as shown in Fig. 2.

![Fig. 2—Structural formula of metal (benzylidene) picramates](image)

Fig. 2—Structural formula of metal (benzylidene) picramates (\( \text{M} \) stands for \( \text{Zn} \) (II), \( \text{Cu} \) (II) or \( \text{Hg} \) (II)).

![Fig. 3—Thermogravimetric analysis of metal-benzylidene picramates](image)

Fig. 3—Thermogravimetric analysis of metal-benzylidene picramates (\( A=\text{Zinc benzylidene picramate}, B=\text{Cadmium benzylidene picramate} \& C=\text{Mercury benzylidene picramate} \).
From the T.G. study (Fig. 3) it has been observed that the zinc and cadmium benzylidene picramates explode at 553°K and 513°K respectively while mercury benzylidene picramate does not explode even up to 673°K. As obvious from the T.G. curve in the case of mercury complex, the loss in weight is accompanied by elimination of water molecules. A change in curve between 473-513°K clearly indicates that the complex is decomposed into mercury oxide. After 513°K a nearly constant weight is obtained which indicates that the complex is completely decomposed into mercury oxide between 473-513°K.

On the basis of the above discussion it may be concluded that the zinc benzylidene picramate is thermally more stable than the analogous complexes formed by cadmium and mercury. These conclusions are further supported by the data on explosive properties viz. explosion delay, explosion temperature and activation energy. For example, the explosion temperature, (TE) follows the order: 

\[ \text{TE (Zn complex)} > \text{TE (Cd complex)} > \text{TE (Hg complex)} \]

which is the same as that observed in T.G. Studies. It may be concluded that the thermal stability increases as the ionic radius decreases or ionization potential increases. This has also been established by various other workers 23-25.

On the basis of the value of bond dissociation of different linkages present in the metal benzylidene picramates, it may be suggested that the initial stage in the explosion reaction is the breaking of the N-O linkage 22,23 of the \(-\text{NO}_2\) group directly linked to the benzene nucleus. This then enables the oxygen which was linked wholly to nitrogen to be consumed for the complete oxidation of carbon and hydrogen obtained from the ring rupture and thus produces a huge amount of heat.

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REFERENCES