CHEMISTRY OF METAL PICRAMATES—PART II

(COPPER AND SILVER)

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Copper and silver picramates have been prepared and their compositions have been established by micro-analysis. This has been further confirmed by conductometric and potentiometric methods. I.R. Studies of metal picramates show $-H_2N->M$ coordination where M is copper and silver. Various explosive properties of these picramates have also been studied.

The practical utility of metal picramates as primary explosives may be of great interest in the technology of explosives chiefly because of the ease of their preparation and increased sensitivity towards heat and shock as compared to metal picrates[1,2]. Glowiak[1] has studied the explosive properties of lead picramates[1]. However no detailed information is available on other metal picramates. It is only recently that the chemistry and explosive properties of ferrous, cobalt and nickel picramates have been intensively studied[2]. The object of the present investigation is to extend this work to picramates of copper and silver.

MATERIALS AND METHODS

All the chemicals used were obtained from B.D.H. and were of A.R. grade. The methods used for conductometric, potentiometric and I.R. studies have been described earlier[2].

Preparation of Metal Picramate

Copper and silver nitrate solutions were added to a solution of sodium picramate. The maximum precipitation would occur when the two components A and B are in stoichiometric ratio.

$$xA + yB = A_x\ B_y \text{ (Precipitate)}$$

At the first instance, it would appear that metal picramate is precipitated when the product of metal ion concentration and picramate ion concentration exceeds the solubility product of metal picramate. However, this view is not correct since I.R. studies indicated that metal picramates are complex compounds. The products were filtered, washed with water and finally with alcohol. The samples were dried in desiccator to constant weight and analysed for their constituents.

COMPOSITION OF PICRAMATES

Micro-analysis

The composition of metal picramates was determined by micro-analysis, results of which are given in Table 1.

TABLE 1

COMPOSITION OF COPPER AND SILVER PICRAMATES DETERMINED BY MICRO-ANALYSIS

Formula		Metal %	C %	H %	N %	H_2O %
$Cu\,[C_6H_2\,(NO_2)_2\,(NH_2)\,O]_2 . H_2O$	Cald.	13·31	30·15	1·67	17·59	3·77
	Found	13·10	30·16	1·70	17·62	4·0
$Ag\,[C_6H_2\,(NO_2)_2\,(NH_2)\,O]$	Cald.	35·27	23·54	1·31	14·06	—
	Found	34·20	23·58	1·31	14·10	—

The following physico-chemical studies were conducted to establish the composition of these complexes :

Conductometric Studies

The monovariation method[3] has been employed in the present study and the results so obtained are represented in Fig. 1 and Fig. 2.

Fig. 1 represents the plot of specific conductance against the volume of sodium picramate solution (0·02 M) added. It is evident from the lower part of the curve (Fig. 1) that conductivity remained almost constant upto the addition of two moles of sodium picramate solution per mole of copper sulphate solution.

This was due to the formation of undissociated copper picramate

$$Cu^{++} + 2\,[\,C_6H_2\,(\,NO_2)_2\,(NH_2)\,O\,]^- = Cu\,[\,C_6H_2\,(NO_2)_2\,(NH_2)\,O\,]_2\,.$$

The conductivity suddenly increased after the addition of two moles of sodium picramate solution as is evident from the upper part of the curve (Fig. 1) indicating that the reaction was complete when two moles of sodium picramate solution per mole of copper sulphate solution were added. This clearly shows that in this system the complex is formed at the ratio of 1 : 2 of metal and ligand respectively.

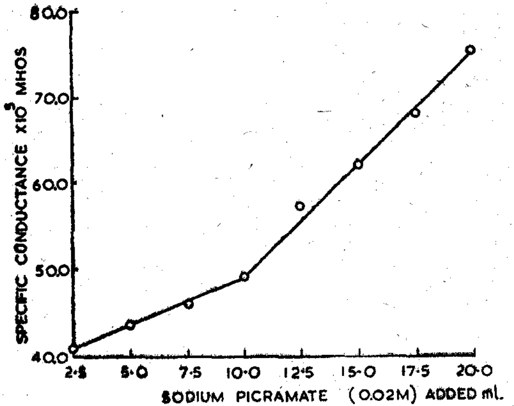

Fig. 1—Copper sulphate-sodium picramate system (initial conc. of metal salt solution = 0·02M; initial conc. of sodium picramate solution = 0·02M; volume of copper sulphate solution = 5 ml. and total volume = 50 ml.).

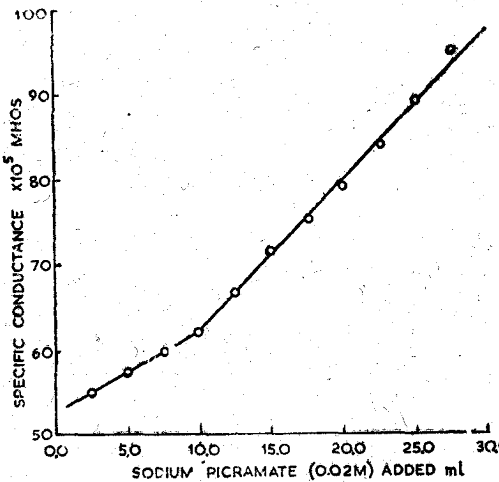

Fig. 2—Silver nitrate-sodium picramate system (initial conc. of $AgNO_3$ sol. = 0·02M; initial conc. of sodium picramate sol. = 0 02M; volume of $AgNO_3$ sol. = 10 ml. and total volume = 50 ml.).

Similarly from Fig. 2, it may be concluded that in silver nitrate-sodium picramate system the complex is formed in the ratio of 1 : 1 of metal and ligand respectively.

Potentiometric Studies

The results of potentiometric studies are represented graphically in Fig. 3 and Fig. 4.

In Fig. 3 the four curves from bottom represent the potentiometric titrations of the solutions containing copper sulphate and sodium picramate in the molar ratios of 1 : 0, 1 : 1, 1 : 2 and 1 : 3 respectively (copper picramate is precipitated in last three solutions and the amount of precipitate depends upon the availability of Cu^{++} ions and $[C_6H_2(NO_2)_2(NH_2)O]^-$ ions) with sodium hydroxide solution. The examination of the bottom curve shows that two moles of sodium hydroxide are needed for the complete precipitation of Cu^{++} ions as copper hydroxide whereas in the curve second from bottom only one equivalent of alkali is needed for the complete precipitation. This shows that half of the Cu^{++} ions present in solution have been bonded with the ligand and only half of the Cu^{++} ions are free to react with one equivalent of alkali. The sharp rise in *p*H with the addition of alkali as seen in the curve third from bottom shows the absence of free Cu^{++} ions in the solution, i.e. whole of the Cu^{++} ions have been attached with the ligand. The top curve is quite similar to the curve third from bottom but is at higher *p*H due to excess of sodium picramate. These observations clearly indicate the formation of 1 : 2 complex in copper picramate system

In Fig. 4 the four curves from bottom represent the potentiometric titrations of silver nitrate-sodium picramate in the molar ratios of 1 : 0, 1 : 1, 1 : 2 and 0 : 1 respectively with sodium hydroxide. On the basis of the discussion similar to above, it may be concluded that in silver nitrate-sodium picramate system the complex is formed at the ratio of 1 : 1 of metal and ligand respectively.

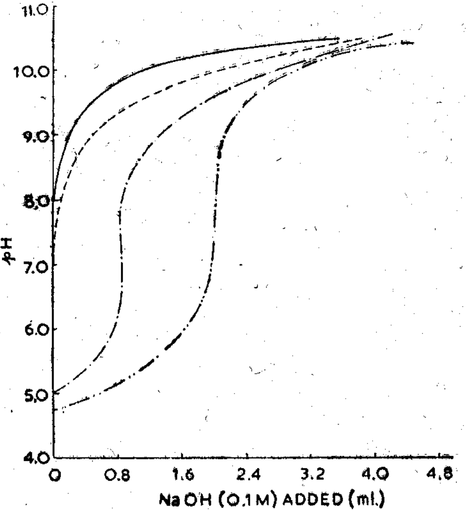

Fig. 3—Electrometric titrations of (–··–) 20 ml. 0·005*M* $CuSO_4$ + 30 ml. H_2O (—·—) 20 ml., 0·005*M* $CuSO_4$ + 5 ml. 0·02*M* sodium picramate + 25ml. H_2O (– – – –) 20ml. 0·005*M* $CuSO_4$ + 10 ml. 0·02*M* sodium picramate + 20 ml. H_2O and (—) 20 ml. 0·005*M* $CuSO_4$ + 15 ml. 0·02*M* sodium picramate + 15 ml. H_2O.

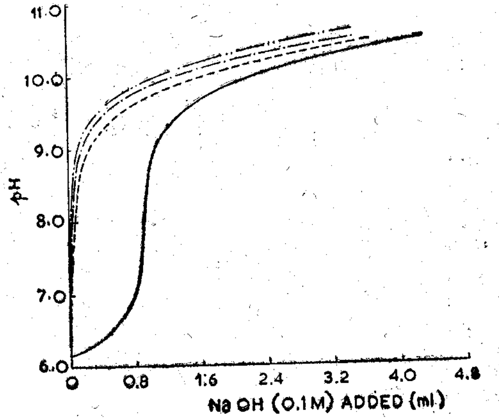

Fig. 4—Electrometric titrations of (—) 20 ml. 0·005*M* $AgNO_3$ + 30 ml. H_2O (– – – –) 20 ml. 0·005*M* $AgNO_3$ + 5 ml. 0·02*M* sodium picramate + 25 ml. H_2O (—·—) 20 ml. 0·005*M* $AgNO_3$ + 10 ml. 0·02*M* sodium picramate + 20 ml. H_2O and (–··–) 20 ml. 0·005*M* sodium picramate + 30 ml. H_2O.

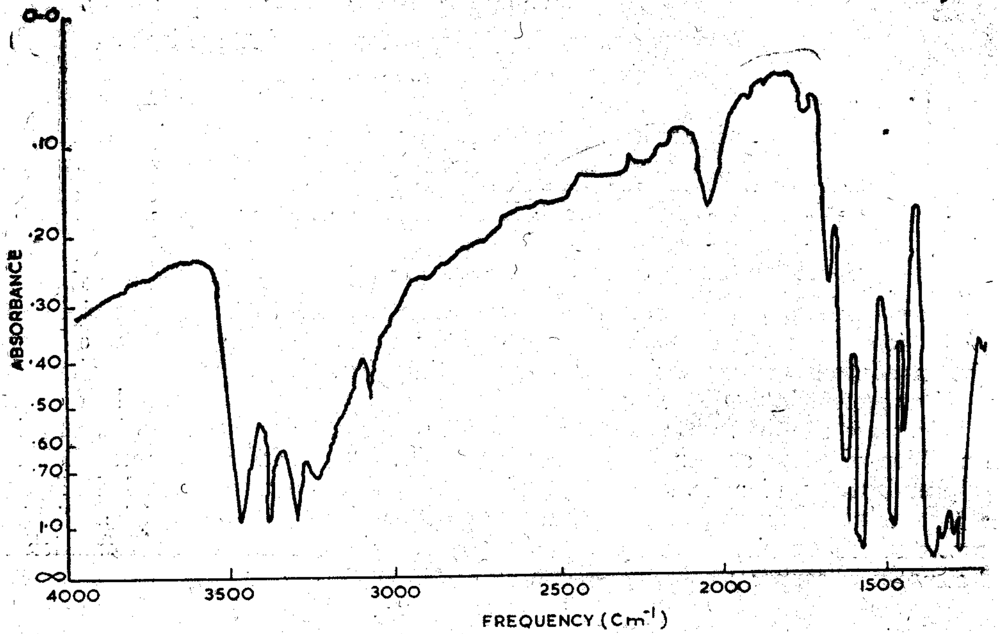

Fig. 5(*a*)—I.R. spectra of sodium picramate in potassium bromide.

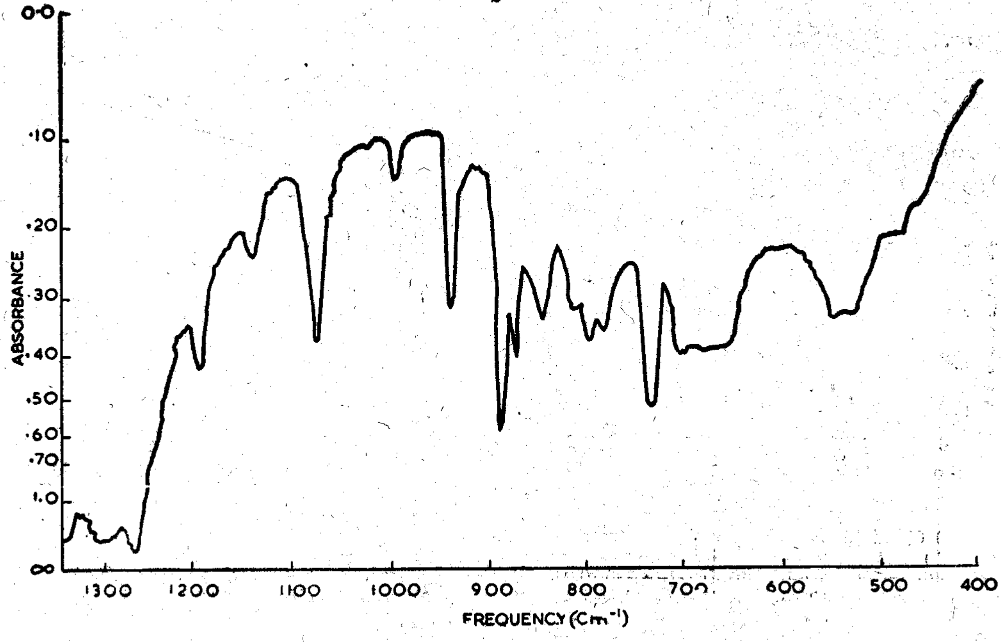

Fig. 5(*b*)—I.R. Spectra of sodium picramate in potassium bromide.

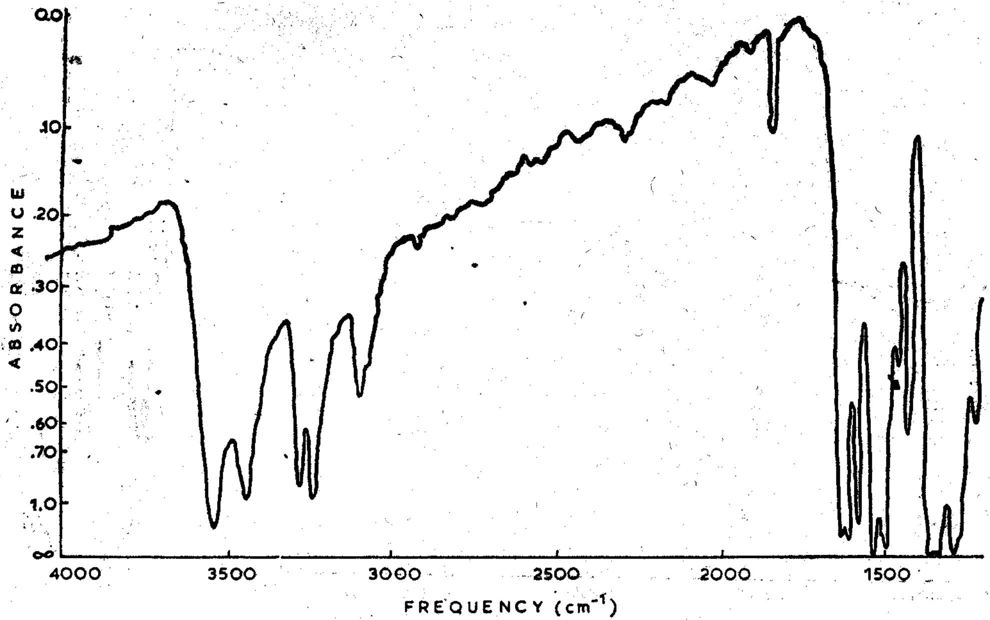

Fig. 6(*a*)—I.R. spectra of copper picramate in potassium bromide.

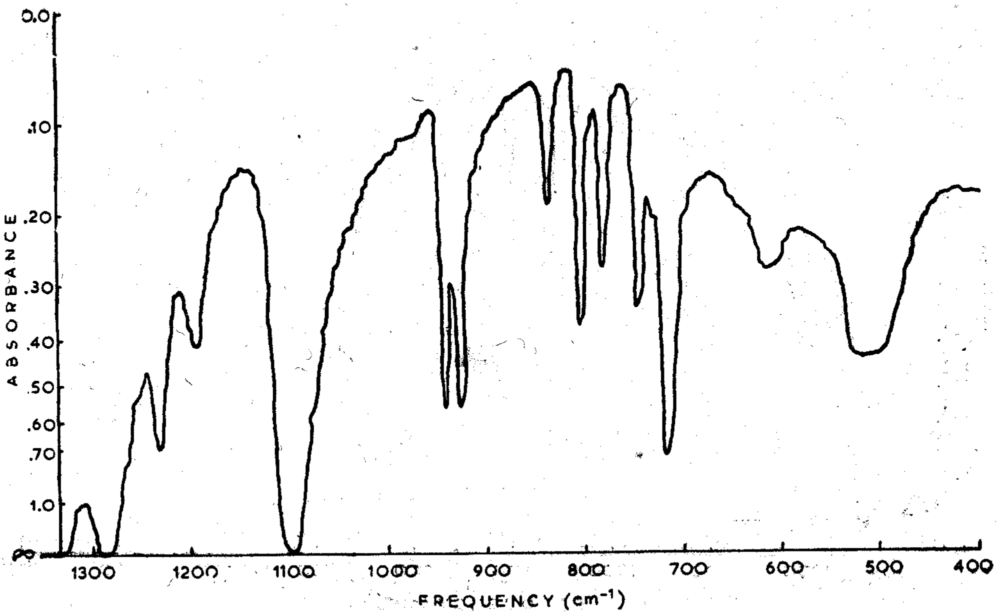

Fig. 6(*b*)—I.R. spectra of copper picramate in potassium bromide

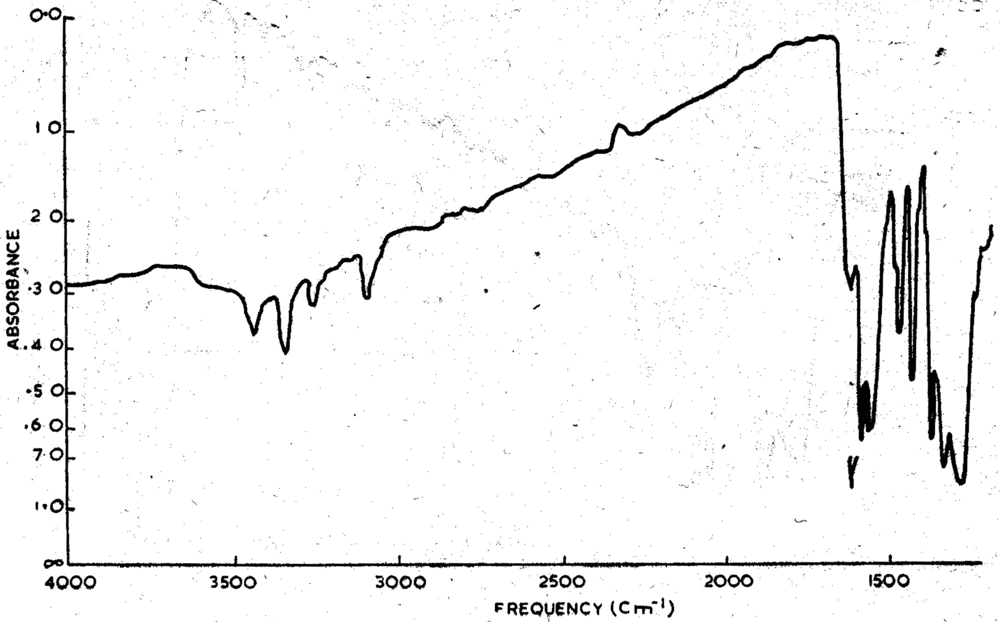

Fig. 7(*a*)—I.R. spectra of silver picramate in potassium bromide.

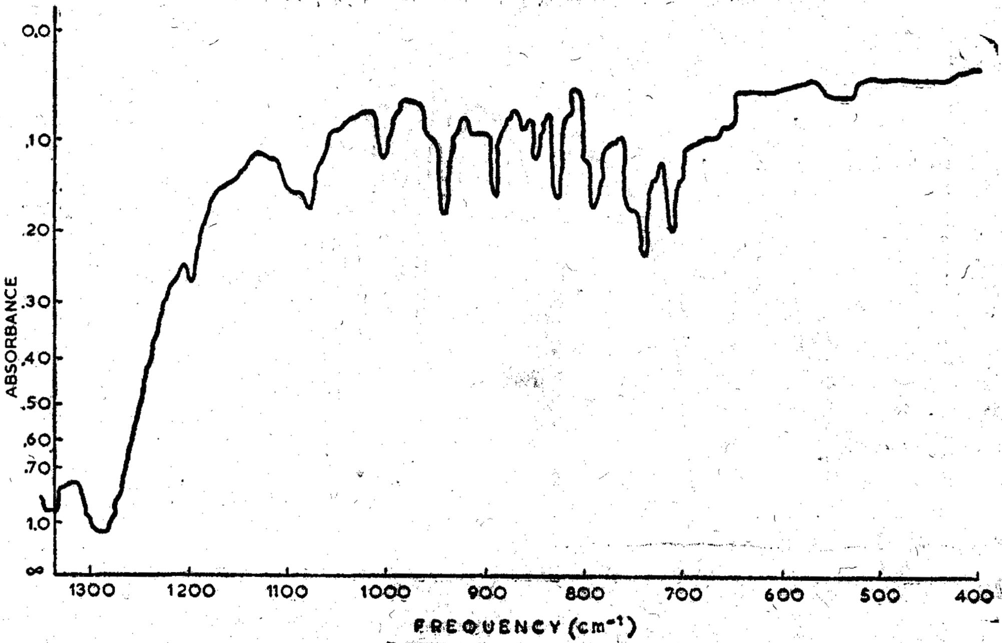

Fig. 7(*b*)—I.R. spectra of silver picramate in potassium bromide.

TABLE 2

VALUES OF EXPLOSION DELAY AND TEMPERATURE

Compound	Explosion delay at 320°C (sec.)	Explosion temperature for explosion delay of 10 sec. (°C)
Copper picramate	23·5±0·4	375·0±2
Silver picramate	13·2±0·4	342·0±2

TABLE 3

VARIATION OF EXPLOSION DELAY WITH TEMPERATURE

Temperature	Explosion delay	
(°C)	Copper picramate (sec.)	Silver picramate (sec.)
280	42·6	20·7
290	36·0	—
300	30·7	16·2
310	26·4	—
320	23·5	13·2
330	19·0	—
340	17·0	10·8

Structural Studies

The results of micro-analysis, conductometric and potentiometric studies suggest the formula

$$[\,C_6H_2\ (NO_2)_2\ (NH_2)\ O\,]_x\ .\ \ M$$

where $x = 1$ for Ag and 2 for Cu

and M is Cu or Ag.

INFRA-RED SPECTRA STUDIES

The I.R. spectra are given in Fig. 5 to 7. The absorption associated with the -NH degenerate deformation mode[4] is expected to appear near 1600 cm.$^{-1}$ but is greatly masked by the strong absorption due to -NO_2 groups in the same region. The -NH rocking and twisting modes[4] appear as doublets at 870-885 cm.$^{-1}$ in sodium picramate (Fig. 5*a,b*) are shifted to 930-940 cm.$^{-1}$ in copper picramate (Fig. 6*a,b*) and appear as a single peak at 940 cm.$^{-1}$ in silver picramate (Fig. 7*a,b*) which clearly indicate the presence of $N \rightarrow M$ coordination.

The above conclusion is also supported by the shift of -NH asymmetric stretching vibration frequency to 3280 cm.$^{-1}$ and 3340 cm.$^{-1}$ in copper and silver picramates respectively (Fig. 6*a,b* and 7*a,b*) as compared to 3400 cm.$^{-1}$ in the spectrum of sodium picramate[5,6] (Fig. 5*a,b*).

EXPLOSIVE PROPERTIES

The compounds used for the measurement of explosive properties were dried at 100°C for two to three hours.

Explosion Delay and Temperature

Explosion delay and temperature were measured by the methods described earlier[2] and the results so obtained are given in Table 2.

Table 4

Values of E and B for different compounds

Compound	Activation energy (E) (K cal. mole^{-1})	Constant (B)
Copper picramate	10·3	14·4
Silver picramate	7·3	9·7

Thermal Sensitivity

Values D_E of explosion delay at various temperatures are given in Table 3. The curves representing the relationship.

$$\log D_E = \frac{E}{4 \cdot 57T} + B$$

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, are shown in Fig. 8. From the slopes of these curves which are almost rectilinear, values of activation energies have been estimated[7] and are given in Table 4.

Thermogravimetric Analysis

This was done by the method described earlier[2]. The results are plotted in Fig. 9.

From the results it is evident that mixture of silver and silver oxide is obtained at 420°C but copper oxide is not obtained as copper picramate explodes at 280°C. This is so because the decomposition of silver picramate starts at a comparatively lower temperature whereas that of copper picramate starts at a higher temperature.

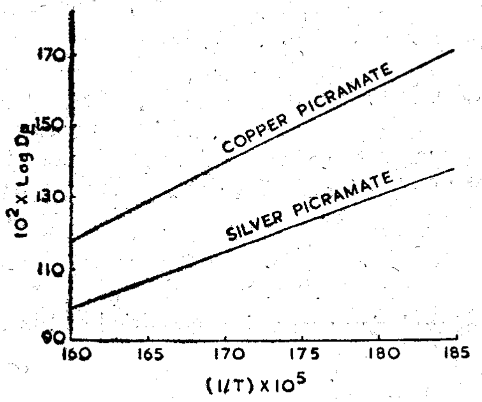

Fig. 8—Variation of log D_E with reciprocal of absolute temperature.

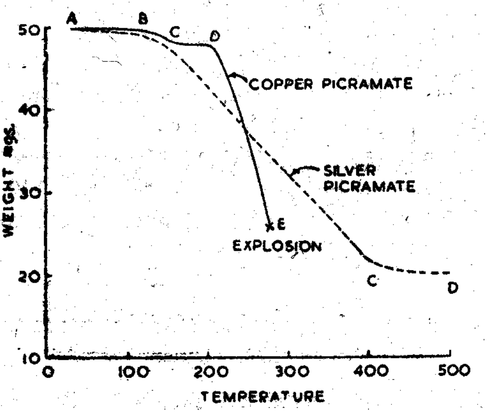

Fig. 9—Thermogravimetric analysis of Cu(II) and Ag(I) picramates.

Details of thermograms of *Cu*(II) and *Ag*(I) Picramates (Fig. 9) are given below :

Copper Picramate Curve

A-B	Desiccator-120°C	No decomposition of *Cu* (picramate)$_2H_2O$.
B-C	120-160°C	Loss in weight due to removal of 1 H_2O.
C-D	160-210°C	Constant weight of *Cu* (picramate)$_2$.
D-E	210-260°C	Loss in weight due to decomposition of *Cu* (picramate)$_2$.
	280°C	Explodes in 5 minutes.

The colour of copper picramate changes to light black at 220°C and dark black at 230°C.

Silver Picramate Curve

A-B	Desiccator-120°C	Loss in weight due to slight decomposition of *Ag* picramate.
B-C	120-420°C	Loss in weight due to decomposition of *Ag* picramate.
C-D	420-500°C	Constant weight of mixture of ($Ag+Ag_2O$).
	160°C	The solid melts.

The colour of silver picramate changes to black at 140°C and blackish white at 420°C.

The results of thermogravimetric analysis suggest that copper picramate is thermally more stable than silver picramate which is also supported by the data of explosion delay, explosion temperature and activation energy etc. The possible explanation for this decrease in thermal stability from copper to silver picramate may be due to the increase in *-O-M*-bond distance in this order.

Explosion Pressure

Pressure of gases developed on explosion is an important factor because it serves as a measure of the capacity of an explosive to do work, although the character of the work

TABLE 5

EXPLOSION PRESSURE FOR DIFFERENT COMPOUNDS

DENSITY OF MERCURY (d)=13·595 gm/cc. : GRAVITATIONAL ACCELERATION (g) = 980·665 cm/sec.^{2}

Compound	Height (H) (cm.)	Explosion pressure* (Bath temp. 350±2°C) (dynes/cm.$^2\times10^4$)
Copper picramate	7·148	9·530
Silver picramate	4·918	6·557

*The explosion pressure was obtained by taking 10·0 mg. of the explosive material.

TABLE 6

HEIGHTS AND IMPACT ENERGIES FOR 50% IGNITIONS

WEIGHT OF THE HAMMER = 2 kg. : WEIGHT OF THE CHARGE = 20 mg.

Compound	Height (H) (cm.)	Impact energy $K_p m$
Copper picramate	32·8	0·656
Silver picramate	16·6	0·332

is determined by the rate at which the pressure is built up and it was measured by the method outlined earlier[8]. The results of explosion pressure given in Table 5 indicate that pressure exerted during the explosion of copper picramate is more than that of silver picramate.

Impact Sensitivity

The information obtained by the data of impact sensitivity is considered most valuable as it gives assurance of safety in manufacture, handling and transportation.

The impact sensitivity of the picramates was determined on a machine slightly modified in design to one used by Taylor & Weale[9].

The test consists of dropping a hammer of definite weight from a known height on to a weighed quantity of the samples kept in between the surfaces of two stainless steel Hoffman rollers which are kept in position by the steel collar. At each height, 20 trials were carried out and numbers of ignitions recorded.

Curves showing the percentage of ignitions out of 20 trials at various heights are shown in Fig. 10. The critical heights which bring about 50% ignitions in copper and silver picramates and impact energies[10] for the same are given in Table 6.

These results show that silver picramate is more sensitive towards impact than copper picramate.

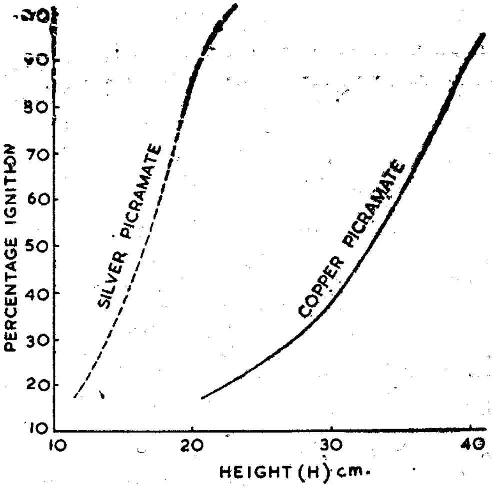

Fig. 10—Impact sensitivity of Cu(II) and Ag(I) picramates.

Gas Analysis

The explosion of samples were carried out at 300°C in vacuum and the products were analysed for hydrogen, nitrogen, carbon monoxide, carbon dioxide, nitric oxide and nitrogen dioxide. The gases were also analysed on a mass spectrometer. The errors of these estimations are approximately ± 5 per cent.

The volume (in litres) of gases evolved during explosion of 1 kg. explosive, measured at NTP, is called specific or normal volume[11] (V_0). The results given in Table 7 show that the value of specific volume comes to be 346·23 cc. and 142·72 cc. for copper and silver picramates respectively.

TABLE 7

GAS ANALYSIS DATA OF THE GASEOUS PRODUCTS PRODUCED DURING EXPLOSION OF THESE METAL PICRAMATES

Gas	Volume of gas at NTP per gm.	
	Copper picramate (cc.)	Silver picramate (cc.)
CO	100·30	4·10
N_2	20·0	41·72
CO_2	162·10	82·00
NO	63·83	13·90
NO_2	—	1·0

On the basis of gas analysis data, the explosive decomposition of copper and silver picramates may be represented by the equations.

$$[C_6H_2\,(NO_2)_2\,(NH_2)\,O]_2\cdot Cu = 57.44\,CO + 11.49\,N_2 + 146.13\,CO_2 + 38.06\,NO + 79.54\,CuO + C$$

$$[C_6H_2\,(NO_2)_2\,(NH_2)\,O]\,Ag = 1.53\,CO + 15.90\,N_2 + 5.81\,NO + 49.24\,CO_2 + 0.61\,NO_2 + 115.87\,Ag_2O + C$$

(When 1 gm. mole of the compound is exploded the amount of different gases (gm.) liberated are given in above equations.)

However when explosion takes place, the decomposition products are more complicated than mentioned above.

ACKNOWLEDGEMENTS

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