

## **SYNTHESIS AND CHARACTERISATION OF TETRAPHENYLARSONIUM HALOCHROMATES**

*Usharani Patnaik and J. Muralidhar\**

Regional Research Laboratory, Bhubaneswar-751 013, Orissa, India

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### **Abstract**

Tetraphenylarsonium halochromate (*halo*=fluoro, chloro and bromo) complexes are synthesised and characterised by spectral and thermal studies. The effect of ionic size and electronegativity of halide ions on the infrared spectra, X-ray emission spectra, activation energy of the first decomposition step and thermal stability of the complexes are investigated. The complexes possess tetragonal unit cell with  $a=b=12.93$  Å and  $c=7.68$  Å. These complexes decompose in two exothermic stages. Cleavage of one Ph–As bond to give triphenylarsine and reduction of Cr(VI) to Cr(III) occur simultaneously. First step mass loss corresponds to the loss of two phenyl halide molecules and 3/2 moles of oxygen. The overall kinetics of the first step is described by diffusion controlled reaction mechanism with a function  $g(\alpha)=[1-(1-\alpha)^{1/2}]$ . The second step decomposition is due to the further degradation of triphenylarsine. The final product is Cr<sub>2</sub>O<sub>3</sub>.

**Keywords:** complexes, tetraphenylarsonium halochromates

### **Introduction**

In continuation of the study on thermal decomposition of ion association halochromates such as 2,3,5-triphenyl tetrazolium halochromates in static air [1] and tetraphenyl phosphonium halochromates in static air [2] and in nitrogen atmosphere [3], now we are presenting the thermal decomposition of tetraphenylarsonium halochromates. In this communication, these halochromate complexes are synthesised by a direct and simple procedure and in low acidity (0.6 M) compared to that proposed by Diemann *et al.* [4]. The complexes are then characterised by spectral and thermal studies.

### **Experimental**

All the chemicals used are of AnalaR grade. 5 g of tetraphenylarsonium bromide (Fluka) is converted into its hydroxide by continuous stirring of its aqueous solution

\* Author to whom all correspondence should be addressed.

with silver oxide for 24 h. The solution is then filtered and made 100 ml to give 0.11 M tetraphenylarsonium hydroxide.

### Synthesis of complexes

These halochromate complexes are synthesised by taking 100 ml of 0.01 M  $\text{CrO}_3$  and 8.5 ml of 0.11 M tetraphenylarsonium hydroxide solution, adjusting the net acidity of the solution to 0.6 M with the required halo acid and following the procedure as described for the synthesis of tetraphenylphosphonium halochromates [2].

Tetraphenylarsonium chromate adduct is synthesised by mixing 10 ml of 0.11 M tetraphenylarsonium hydroxide and 20 ml of 1% potassium chromate solution. The formed yellow adduct is then extracted into dichloromethane and isolated as described earlier [2].

Carbon and hydrogen analysis are done by Carlo Erba EA 1108 Elemental Analyser. Chromium and halides are estimated by standard procedures. The compositional analysis of these complexes are presented in Table 1.

**Table 1** Compositional analysis of tetraphenylarsonium halochromates

Complex	C	H	Cr	X	Yield
	%				
$\text{Ph}_4\text{As}^+\text{CrO}_3\text{F}^-$	57.24 (57.38)	3.98 (4.01)	10.30 (10.35)	3.65 (3.78)	97
$\text{Ph}_4\text{As}^+\text{CrO}_3\text{Cl}^-$	55.28 (55.56)	3.72 (3.89)	10.02 (10.02)	6.80 (6.83)	95
$\text{Ph}_4\text{As}^+\text{CrO}_3\text{Br}^-$	51.08 (51.19)	3.55 (3.58)	9.22 (9.23)	14.15 (14.19)	97
$(\text{Ph}_4\text{As})_2\text{CrO}_4$	65.09 (65.31)	4.54 (4.57)	5.86 (5.89)	—	97

Bracketed values are the calculated values  $X=\text{F}$ ,  $\text{Cl}$  or  $\text{Br}$

### Instrumental

Infrared spectra of these halochromate complexes are recorded within  $4000\text{--}200\text{ cm}^{-1}$  on a Perkin Elmer Fourier Transform Infrared spectrometer Model Paragon 500 using potassium bromide pellets.

X-ray emission spectra of these complexes are recorded with a Philips PW 1400 wavelength dispersive X-ray spectrometer. The instrumental parameters are: X-ray tube target, scandium; analysing crystal, Lithium Fluoride (200); detector, flow proportional counter; voltage and current, 50 KV and 60 mA, respectively; medium, vacuum; spectrum order = 1st; emission spectra line,  $\text{CrK}_\alpha$  and  $\text{K}_\beta$ . The spectra are scanned at the step scan of 0.005 degree;  $2\theta$  measurements for 5 s at every step. The powders are pelletized with boric acid as a backing material in a Herzog HTP-40 press operating at 30 ton load pressure. The diameter of the uniformly exposed surface of the pellet is 30 mm.

X-ray diffractograms of the powdered samples are analysed using a Philips automatic powder diffractometer having PW 1830 generator, PW 1820 goniometer and PW 1710 control unit.  $\text{CuK}_\alpha$  radiation is used for the analysis. The diffractograms are taken within 6–70 degrees with a scanning rate of 2 degree per minute.

Thermal studies on these complexes in static air are carried out by Shimadzu DT-40 Thermal Analyser, which records the thermogravimetric (TG) and differential thermal analysis (DTA) curves simultaneously. To avoid the corrosion of sample holders during heating, a 1:1 homogeneous mixture of these complexes with  $\alpha\text{-Al}_2\text{O}_3$  is used for the studies.  $\alpha\text{-Al}_2\text{O}_3$  is also used as the DTA reference material. The complexes are studied upto 1000°C at a linear heating rate of 10°C min<sup>-1</sup>, in static air. Tetraphenylarsonium chlorochromate is studied in nitrogen atmosphere under similar experimental conditions.

## Results and discussion

A comparison of the infrared spectra of these halochromate complexes with those of 2,3,5-triphenyl tetrazolium halochromates [1] and tetraphenylphosphonium halochromates [2] revealed that the halochromate ions of these complexes also belong to  $\text{XYZ}_3$  type and possess  $c_{3n}$  symmetry. Sharp bands at 908 and 951 cm<sup>-1</sup> are assigned to symmetric and antisymmetric stretchings of Cr–O bonds respectively. The stretching frequencies of Cr–F, Cr–Cl and Cr–Br bonds are assigned at 641, 435 and 230 cm<sup>-1</sup> respectively.

Similar to the effects of substitution of halides in place of one oxygen atom of chromate ion, on the infrared spectra of these complexes, shifts in the X-ray emission spectra are also observed. The  $\text{K}_\alpha$  and  $\text{K}_\beta$  spectra of the target chromium atom appear within energy ranges 5433.3–5365.4 and 6010.0–5860.7 eV, respectively. The peak energy values of  $\text{K}_\alpha$  and  $\text{K}_\beta$  spectra and corresponding shifts are presented in Table 2. The substitution of halogen atom in place of one oxygen atom shifts the peak energy of  $\text{CrK}_\alpha$  spectra by 3 eV from that of chromate ion. It has been observed that the peak energy of  $\text{K}_\alpha$  spectra is not changed by the type of halogen. However, the type of halogen has more significant effect on the  $\text{CrK}_\beta$  spectra. The peak energy of  $\text{CrK}_\beta$  spectra shifts upto 2.34 eV on changing the halogen from fluorine to bromine. This change is explained by the decrease in electronegativities of halogens. Similar shifting in peak energy values of the  $\text{K}_\beta$  spectra of target atom with the change in electronegativity of the surrounding atoms has been observed in various calcium compounds by Shuvaev *et al.* [5].

Diemann *et al.* [4] solved the crystal structure of tetraphenylarsonium fluoro and chloro chromates by powder X-ray diffraction studies. They found the crystals to possess tetragonal unit cells. In this communication, crystal structure of tetraphenylarsonium bromochromate is solved by using the X-ray powder diffraction data and the computer package developed and supplied by R. G. Garvey of North Dakota State University, Fargo, USA. The most intense lines with  $d(\text{Å})$  values and crystal parameters for this complex are presented in Table 3. This bromochromate complex is also found to possess tetragonal unit cells.

**Table 2** Peak energy values and peak energy shifts of CrK $_{\alpha}$  and K $_{\beta}$  spectra

Complex	K $_{\alpha}$ peak energy/	Peak energy/	K $_{\beta}$ peak energy/	Peak energy/
	eV			
(Ph $_4$ As) $_2$ CrO $_4$	5404.63	–	5932.81	–
Ph $_4$ As $^+$ CrO $_3$ F $^-$	5401.46	3.17	5933.40	0.59
Ph $_4$ As $^+$ CrO $_3$ Cl $^-$	5401.48	3.15	5934.57	1.76
Ph $_4$ As $^+$ CrO $_3$ Br $^-$	5401.45	3.18	5935.16	2.34

**Table 3** Crystal data of Ph $_4$ As $^+$ CrO $_3$ Br $^-$  complex

Formula	C $_{24}$ H $_{20}$ AsCrO $_3$ Br	$d/A^\circ$	Int	$h$	$k$	$l$
Formula mass/g	563.27	8.670	10		n.i.	
Temperature/ $^\circ$ C	25	6.250	45	2	0	0
$\lambda$ , CuK $_{\alpha}$ , Å	1.54186	6.100	30		n.i.	
Lattice type	tetragonal	4.624	100	2	1	1
$a/\text{Å}$	12.93	4.091	20	3	1	1
$b/\text{Å}$	12.93	3.761	60	3	0	1
$c/\text{Å}$	7.68	3.322	10		n.i.	
$V/\text{Å}^3$	1285.41	3.234	20	4	0	0
$Z$	2	2.781	50	3	1	2
$d_{\text{calc.}}/\text{g cm}^{-3}$	1.455	2.350	20	4	3	1
$d_{\text{obs.}}/\text{g cm}^{-3}$	1.438	2.260	30	5	2	1
$\mu(\text{CuK}_{\alpha})/\text{cm}^{-1}$	76.223	2.151	20	5	3	0

*n.i.*=not indexed

A comparison of the unit cell dimensions of tetraphenylarsonium bromochromate with those of corresponding fluoro and chlorochromates as reported by Diemann *et al.* [4] revealed that the unit cell volume increases with the increase in ionic radii of halides.

Effect of size and electronegativity of halides is also observed in the thermal studies of these complexes. The thermoanalysis data are presented in Table 4. In static air, these complexes decompose with two exothermic changes within the temperature regions 270–370 and 310–455 $^\circ$ C with corresponding mass losses in TG curves. The first mass loss in TG curve corresponds to the loss of two phenyl halide molecules and 3/2 moles of oxygen. The product after first stage of decomposition is extracted into chloroform and the extracted part is tested for Cr(VI) by diphenylcarbazide reagent. Negative response to this test indicated the quantitative reduction of Cr(VI) to Cr(III). The infrared spectra of the chloroform extract exhibited sharp bands at 1435 and 990  $\text{cm}^{-1}$  due to Ph–As stretching and bending modes of vibrations respectively. The disappearance of the strong bands at 885 and 1082  $\text{cm}^{-1}$  in the spectra indicate the absence of As=O bond [6] and quaternary arsonium atom [7] respectively. The carbon and hydrogen analysis of the crystallised mass obtained from chlo-

roform extract indicated the formation of triphenylarsine ( $\text{Ph}_3\text{P}$ ) (obs. C=70.5%, H=4.94%, calc. C=70.2%, H=4.89%). Formation of triphenylarsine during thermal decomposition of tetraphenyl and triphenylmethylarsonium salts is also reported by Loach [8]. Thus the first stage decomposition involves the simultaneous occurrence of the cleavage of one Ph–As bond and reduction of Cr(VI) to Cr(III). An exothermic DTA peak is expected for Ph–As bond cleavage and an endothermic DTA peak is expected for reduction of Cr(VI) to Cr(III). But, the appearance of an exothermic DTA peak in the region 270–370°C corresponding to the first TG loss in all these complexes indicated the predominance of the Ph–As bond cleavage step over the reduction step. To get a better picture on the decomposition scheme, thermal studies on tetraphenylarsonium chlorochromate is carried out in nitrogen atmosphere. Though the first step decomposition starts at a higher temperature than that in static air, the appearance of an exothermic DTA peak in the region 289–342°C even in nitrogen atmosphere strongly supports the fact that Ph–As bond cleavage is predominant over the reduction of Cr(VI) and Cr(III).

**Table 4** Thermoanalysis data on tetraphenylarsonium halochromate complexes. a) DTA data; b) mass losses (%) from TG curves

a) DTA data						
Complex	1st peak decomposition			2nd peak decomposition		
	range/°C	max./°C	type/°C	range/°C	max./°C	type/°C
In static air						
$\text{Ph}_4\text{As}^+\text{CrO}_3\text{F}^-$	284–352	312	exo	352–452	429	exo
$\text{Ph}_4\text{As}^+\text{CrO}_3\text{Cl}^-$	274–349	306	exo	315–434	408	exo
$\text{Ph}_4\text{As}^+\text{CrO}_3\text{Br}^-$	285–371	296	exo	338–453	429	exo
In nitrogen atmosphere						
$\text{Ph}_4\text{As}^+\text{CrO}_3\text{Cl}^-$	289–342	326	exo	362–490	428	exo
b) Mass losses from TG curves						
Complex	1st peak		Total			
	obs./%	calc./%	obs./%	calc./%		
In static air						
$\text{Ph}_4\text{As}^+\text{CrO}_3\text{F}^-$	23.64	23.88	83.94	84.87		
$\text{Ph}_4\text{As}^+\text{CrO}_3\text{Cl}^-$	27.92	26.30	84.35	85.35		
$\text{Ph}_4\text{As}^+\text{CrO}_3\text{Br}$	32.00	32.12	86.23	86.51		
In nitrogen atmosphere						
$\text{Ph}_4\text{As}^+\text{CrO}_3\text{Cl}^-$	26.00	26.30	60.41	85.35		

The second stage decomposition of these complexes in the regions 310–455 in static air and 362–490°C in nitrogen atmosphere are due to the further oxidation of triphenylarsine. The final product in static air is identified to be  $\text{Cr}_2\text{O}_3$  by X-ray diffractometric studies. The total mass loss from TG curve matches well with the calcu-

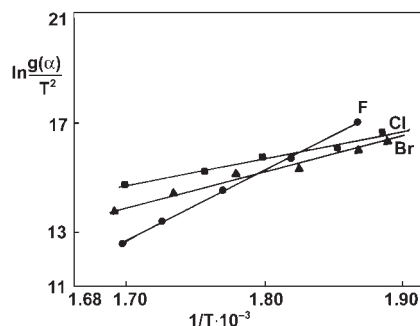


Fig. 1 Coats-Redfern kinetic plots for tetraphenylarsonium halochromates in static air

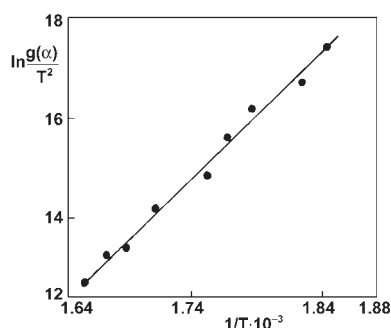


Fig. 2 Coats-Redfern kinetic plots for tetraphenylarsonium halochromates in nitrogen atmosphere

lated values. However, in nitrogen atmosphere, a 25% discrepancy is observed between the observed total mass loss and calculated mass loss values. This is due to the incomplete degradation of the compound in nitrogen atmosphere.

Thus the decomposition of these complexes can be described by the following two stages:

a) In the region 270–370°C



b) In the region 310–455°C



As these type of complexes are used in the oxidation of alcohols [9–11], the ease of removal of chromium from the complex is of major importance. Hence the kinetic studies are limited to the first stage decomposition only. Since it is difficult to distinguish the two overlapping reactions from TG curve, the overall kinetics of this step is studied by using Coats-Redfern equation [12]. The most probable reaction mechanism is identified by applying statistical analysis to thirty different reaction models pertaining to nucleation according to power law, diffusion controlled mechanisms, chemical reactions etc. [13]. The overall reaction in both the atmospheres is found to

proceed through diffusion controlled reaction mechanism in a contracting area with the function  $g(\alpha)=[1-(1-\alpha)^{1/2}]$ . The Coats and Redfern kinetic plots are presented in Figs 1 and 2. The related kinetic parameters such as activation energy ( $E$ ), pre-exponential factors ( $A$ ), entropy of activation  $\Delta S$ , order of reaction ( $n$ ) and correlation coefficient ( $r$ ) are presented in Table 5.

**Table 5** Kinetic parameters for first stage decomposition of tetraphenylarsonium halochromates

Complex	$E/$ kJ mol <sup>-1</sup>	$A/$ s <sup>-1</sup>	$\Delta S/$ J K <sup>-1</sup> mol <sup>-1</sup>	$n$	Range of $\alpha$	$r$
In static air, $g(\alpha)=[1-(1-\alpha)^{1/2}]$						
Ph <sub>4</sub> As <sup>+</sup> CrO <sub>3</sub> F <sup>-</sup>	203.4	2.61·10 <sup>14</sup>	25.46	0.51	0.1–0.9	0.9915
Ph <sub>4</sub> As <sup>+</sup> CrO <sub>3</sub> Cl <sup>-</sup>	163.1	7.93·10 <sup>10</sup>	-41.71	0.55	0.1–0.9	0.9901
Ph <sub>4</sub> As <sup>+</sup> CrO <sub>3</sub> Br	111.4	3.52·10 <sup>5</sup>	-144.12	0.52	0.1–0.9	0.9887
In nitrogen atmosphere, $g(\alpha)=[1-(1-\alpha)^{1/2}]$						
Ph <sub>4</sub> As <sup>+</sup> CrO <sub>3</sub> Cl <sup>-</sup>	198.4	1.73·10 <sup>10</sup>	-35.54	0.55	0.1–0.9	0.9899

The activation energy values are found to decrease with the decrease in electro-negativity and increase in the ionic radii of the halides. Lowering of entropy of activation values from fluorochromate to bromochromate indicated that the activated complexes become more ordered structure than the reactants with the increase in ionic size of the halides and the reaction proceeds at a slower rate than normal which is evident from the pre-exponential factor values [14]. Based on the first decomposition peak temperatures, the relative thermal stability of these halochromate complexes can be arranged as follows:



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