

SYNTHESIS AND CHARACTERIZATION OF TETRAPHENYLPHOSPHONIUM HALOCHROMATES

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Abstract

Ion-associated halochromates (*halo*=F, Cl, Br) from tetraphenylphosphonium cation (Ph_4P^+) are synthesized by stepwise solvent extraction technique and characterized based on XRD, spectral and thermal studies. The $\text{Ph}_4\text{P}^+\text{CrO}_3\text{Br}^-$ crystal is tetragonal with $a=b=12.368$ and $c=7.511$ Å. Thermal stabilities of these complexes are found to be decreasing in the order of $\text{Ph}_4\text{P}^+\text{CrO}_3\text{F}^- > \text{Ph}_4\text{P}^+\text{CrO}_3\text{Cl}^- > \text{Ph}_4\text{P}^+\text{CrO}_3\text{Br}^-$.

Keywords: complexes, ion-associated halochromates, tetraphenylphosphonium halochromates

Introduction

One of the major interests in chromium(VI) chemistry is the synthesis of new Cr(VI) compounds for effective and selective oxidations of alcohols to carbonyl compounds, under mild conditions [1]. In view of the increasing importance of pyridinium halochromates (*halo*=F, Cl, Br) in organic synthesis as potential oxidizing agents [2], an attempt has been made to extend the study to ion associated halochromates with tetraphenylphosphonium cation. This onium ion, as frequently termed, has a single positive charge and is of analytical interest as a better precipitant and extractant [3–5]. Diemann and Muller [6] synthesized stable tetraphenylphosphonium fluoro and chlorochromate complexes by an indirect procedure through the synthesis of KCrO_3X ($X=\text{F}, \text{Cl}$) in presence of 1:1 acidity. On the other hand, Koniger-Ahlborn and Muller [7] reported the synthesis of analogous iodochromate which is stable only at -45°C . In the present study, synthesis of these onium halochromates (*halo*=F, Cl, Br) by a direct procedure and at low acidity (0.1 mol/l), and their characterization by powder X-ray diffraction pattern, spectral and thermal data are discussed.

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Experimental

All the chemicals used were of AnalaR grade. Hexane and dichloromethane were distilled before use. Tetraphenylphosphonium bromide (Fluka) was converted into the corresponding hydroxide by continuous stirring of its aqueous solution with Ag_2O for 24 h. The solution was then filtered and made 0.1 mol/l acidic with HF, HCl or HBr according to the requirement.

Synthesis

Anhydrous CrO_3 dried over P_2O_5 (1 g, 0.01 mol) in 0.1 mol/l HCl (10 ml) was added slowly to tetraphenylphosphonium hydroxide solution (10 ml, 0.01 mol) previously made 0.1 mol/l acidic with HCl. The yellow precipitate so formed was extracted into dichloromethane by stepwise extraction method till the organic layer became colorless. The chlorochromate complex was then crystallized from the organic extract by adding hexane. The yellow crystals were filtered through sintered glass filters, washed with hexane and dried in vacuo. (Yield=92%)

Corresponding fluoro-, bromo- and iodochromate complexes were synthesized in the similar fashion only by varying the halo acid. However, the analogous iodochromate complex decomposes soon after its formation.

C and H analyses were done by Carlo-Erba EA 1108 Elemental Analyzer. For Cr(VI) estimation, 0.1 g of the complex was dissolved in 0.1 mol/l NaOH solution. 0.05 g of LiClO_4 was added to the solution and boiled for five minutes to precipitate tetraphenylphosphonium cation as its perchlorate derivative. Cr(VI) was estimated by titrating against standard thiosulphate solution using starch indicator [8]. Chloride and bromide were estimated by Volhard titration procedure [8]. Fluoride was estimated by lead chlorofluoride procedure [8].

Instrumental

Conductivity measurements were done in methanol at room temperature by Conductivity meter NCM 705.

X-ray diffraction data were collected on a Philips PW 1710 Diffractometer Control equipped with Philips PW 1830 X-ray generator using $\text{CuK}\alpha$ radiation and graphite monochromatic filter. Crystals were scanned with a scanning rate of 1 degree per minute. The structure was solved by using a fully automatic program written in ALGOL 60 for finding the unit cell from powder data based upon the algorithm of Visser [9].

Absorption spectra of these complexes in dichloromethane (10^{-3} M) were recorded on a Varian DMS 100S UV-Vis spectrophotometer. Infrared spectra were recorded on a Zasco Fourier Transform IR spectrometer model 5300, using KBr pellets in the range $4000\text{--}400\text{ cm}^{-1}$. Thermal studies on these complexes in static

air were carried out by Shimadzu DT-40 Thermal Analyzer, which records the thermogravimetric (TG) and differential thermal analysis (DTA) curves simultaneously. As the complexes splutter on heating, a 1:1 homogeneous mixture of these complexes with $\alpha\text{-Al}_2\text{O}_3$ as diluent was prepared for thermal studies. $\alpha\text{-Al}_2\text{O}_3$ was also used as the DTA reference material. Samples were heated upto 1000°C at a linear heating rate of $10^\circ\text{C min}^{-1}$.

Results and discussion

These complexes are soluble in common organic solvents e.g., dichloromethane, chloroform, acetone, ethanol, dimethyl sulphoxide, but, insoluble in water. For prolonged storing, the complexes should be kept in dark colored bottles. Analytical data and conductivity values are presented in Table I.

Table I Analytical and physical data of tetraphenylphosphonium halochromate complexes

Complex	Elemental analysis ^a				Conductivity/ $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$
	%C	%H	%Cr	%X ^b	
$\text{Ph}_4\text{P}^+\text{CrO}_3\text{F}^-$	61.28	4.30	11.06	4.05	111
	(62.38)	(4.40)	(11.34)	(4.14)	
$\text{Ph}_4\text{P}^+\text{CrO}_3\text{Cl}^-$	61.03	4.10	10.59	7.25	122
	(60.65)	(4.24)	(10.95)	(7.46)	
$\text{Ph}_4\text{P}^+\text{CrO}_3\text{Br}^-$	54.05	3.95	9.79	15.10	128
	(55.46)	(3.88)	(10.01)	(15.18)	

^a calculated values are in parentheses

^b X=F, Cl or Br

Crystal data and parameters of tetraphenylphosphonium fluorochromate and tetraphenylphosphonium chlorochromate have been reported by Diemann *et al.* [6]. Crystal data and parameters of tetraphenylphosphonium bromochromate are presented in Table 2. Like the fluoro- and chlorochromate complexes, the bromochromate complex has also been observed to possess the tetragonal crystal structure. As expected, a significant increase in the unit cell volume with the increase in ionic size of halide ions has been noticed.

Halochromates typically display two distinct bands in their near ultraviolet and visible spectra. A weak band due to $t_1 \rightarrow e$ transition at 450 nm ($\epsilon=160\text{--}180 \text{ l mol}^{-1} \text{ cm}^{-1}$) and a very strong band around 350 nm ($\epsilon=1200\text{--}1400 \text{ l mol}^{-1} \text{ cm}^{-1}$) due to oxygen to chromium charge transfer i.e. $2p\pi(\text{O}) \rightarrow d(\text{Cr})$ transition are the characteristic absorptions of the complexes. The spectra also exhibits a partially resolved vibrational progression due to excitation of the symmetric stretching mode in the CrO_3 group ($0 \rightarrow n$). Variations of the ligand on CrO_3X^- ion are known to cause small shift in the charge transfer absorption band [10, 11]. A good elec-

Table 2 Crystal data of $\text{Ph}_4\text{P}^+\text{CrO}_3\text{Br}^-$ complex

	$d/\text{\AA}$	Int.	h	k	l
formula $(\text{C}_6\text{H}_5)_4\text{PCrO}_3\text{Br}$	7.31	6	0	0	1
formula weight 519.31	6.73	8	1	0	1
space group I-4 (82)	6.16	50	2	0	0
lattice type tetragonal	4.41	100	2	1	1
$a, \text{\AA}=12.3685$	4.11	75	3	0	0
$b, \text{\AA}=$	3.90	30	3	1	0
$c, \text{\AA}=7.5114$	3.79	14	2	2	1
$V, (\text{\AA})^3=1149.09$	3.68	15	0	0	2
$Z=2$	3.58	30	1	0	2
$d_{\text{calc.}} \text{ g cm}^{-3}=1.5004$	3.10	20	2	1	2
$\mu (\text{CuK}\alpha) \text{ cm}^{-1}=74.124$	3.00	21	4	1	0
$\lambda, \text{CuK}\alpha \text{ \AA}=1.54186$	2.76	22	4	2	0
temperature=25°C	2.60	10	4	2	1
data collection	2.60	10	4	2	1
angle $2\theta, \text{deg}=4-60$	2.36	14	4	0	2
	2.25	20	4	2	2

tron acceptor, e.g. F^- might decrease the electron density around chromium, thereby facilitating the charge transfer from oxygen and therefore decreases the molar extinction coefficient (ϵ) value for this band. As the electron accepting capacities of halides are in the decreasing order $\text{F} > \text{Cl} > \text{Br}$, the ϵ values for the corresponding oxygen to chromium charge transfer absorption band are in the order $\text{F} < \text{Cl} < \text{Br}$.

Electrical conductivities of these complexes in methanol indicate the complexes to be 1:1 electrolyte and CrO_3X^- in ionic form. A comparison of the IR spectra of these complexes with the corresponding KCrO_3X salts ($\text{X}=\text{F}, \text{Cl}$ and Br) led to the conclusion that the ion CrO_3X^- belongs to the XYZ_3 type molecule with C_{3v} symmetry [12]. For a five atomic molecule of this symmetry group, six fundamental vibrations are expected. The assignments of fundamental vibrations in these complexes are made in analogy with those reported for related compounds [13, 14]. Cr–F stretching vibration frequency (ν_1) is fixed at 637 cm^{-1} , and that of Cr–Cl at 430 cm^{-1} . The symmetric stretch of X–Z bond has a lower frequency than the asymmetric stretch. Comparison with the related molecules made the assignment of symmetric stretch frequency (ν_2) and asymmetric stretch frequency (ν_4) at 905 and 950 cm^{-1} respectively. The deformation mode frequency (ν_3), bending mode frequency of ZXY (ν_5) and ZXZ bond (ν_6) and Cr–Br stretching frequency could not be assigned because of the instrumental limits, as all these peaks occur below 350 cm^{-1} .

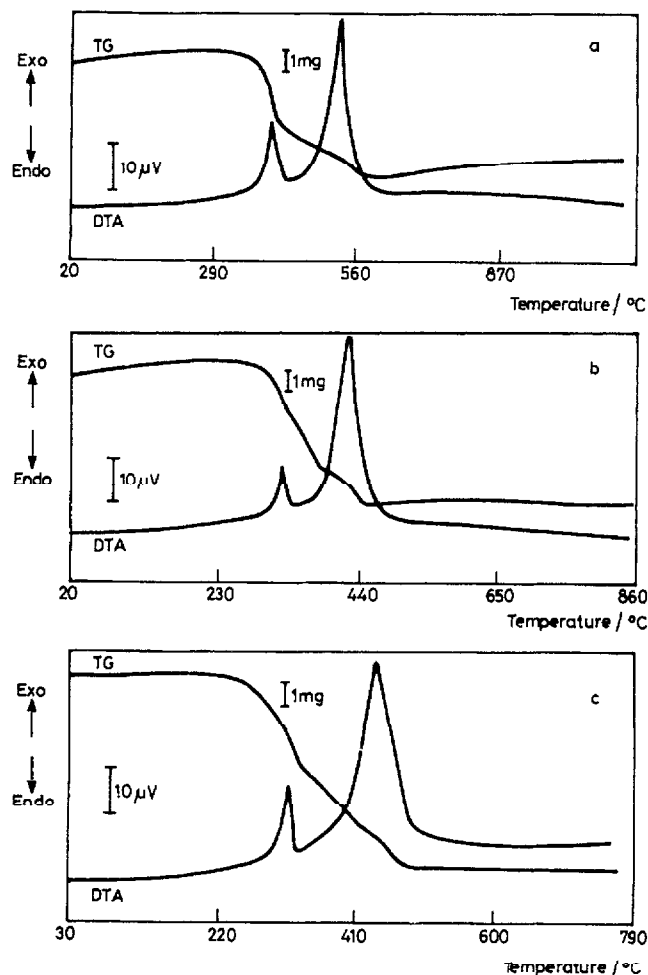


Fig. 1 Typical simultaneous TG-DTA behaviour of $\text{Ph}_4\text{P}^+\text{CrO}_3\text{X}^-$ complexes in static air, rate of heating = $10^\circ\text{C min}^{-1}$, sample mass = 10 mg. (a) F, (b) Cl, (c) Br

Figure 1 represents the simultaneous TG-DTA curves obtained for these halochromate complexes in static air. The TG and DTA results are presented in Table 3. All these complexes undergo a two-stage decomposition with corresponding mass losses in TG curve. First stage of decomposition involves the reduction of Cr(VI) to Cr(III) and loss of two phenyl halide molecules. Though an endothermic DTA peak is expected for Cr(VI) to Cr(III) reduction step, the simultaneous occurrence of one Ph-P bond rupture predominates over the former reaction step and is responsible for the exothermic DTA peak.

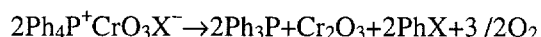
The product after first stage of decomposition was extracted into chloroform for its compositional analysis. However, the total mass was not extractable into

Table 3 TG and DTA data of $\text{Ph}_4\text{P}^+\text{CrO}_3\text{X}^-$ complexes

Complexes	DTA 1st peak		DTA 2nd peak		TG 1st peak	
	decomp. peak temp./°C	peak nature	decomp. peak temp./°C	peak nature	Mass loss% calc./	obs./
$\text{Ph}_4\text{P}^+\text{CrO}_3\text{F}^-$	395	Exo	421	Exo	26.18	26.98
$\text{Ph}_4\text{P}^+\text{CrO}_3\text{Cl}^-$	364	Exo	435	Exo	28.74	28.86
$\text{Ph}_4\text{P}^+\text{CrO}_3\text{Br}^-$	322	Exo	443	Exo	34.84	34.70

chloroform. The quantitative reduction of Cr(VI) to Cr(III) was confirmed by the negative response of diphenylcarbazide test carried out with the extractable and unextractable mass. The extractable mass was crystallised from chloroform and analyzed for carbon and hydrogen contents. The mass contains carbon =81.10% and hydrogen =5.50%. Further, solution IR spectra of the mass (in chloroform) indicated the presence of a sharp band at 1437 cm^{-1} for Ph-P stretching and a weak band at 999 cm^{-1} for Ph-P bending modes of vibration [15]. Brown *et al.* [16] who examined the IR spectra of tertiary phosphine oxide complexes, indicated the presence of a sharp band at 1193 cm^{-1} due to P=O stretching in pure $\text{Ph}_3\text{P}=\text{O}$ molecule. The perfect matching of IR spectra of the mass with that of pure Ph_3P molecule, absence of sharp peak at 1193 cm^{-1} and carbon, hydrogen analysis indicated the formed intermediate to be Ph_3P only (calc. C=81.5%, H=5.63%). This is in agreement with the observations made by Nambier and Jain [17] during the thermal decomposition of tetramethyl phosphonium halide. The second step decomposition is due to the oxidation of liberated Ph_3P molecule and therefore responsible for the exothermic DTA peak. The final product had been identified to be Cr_2O_3 by X-ray diffraction study. Similar decomposition scheme has been observed in case of 2, 3, 5-triphenyltetrazolium halochromate complexes studied by the authors [18].

The first stage decomposition for these complexes may be represented as follows



Kinetics of the first step decomposition of these complexes have been studied from TG. The best fitting reaction model for the decomposition step was selected by a statistical analysis of thirty different reaction models. These models pertain to the diffusion control, random nucleation growth, nucleation growth according to power law, phase boundary reaction and chemical reaction mechanism. The decompositions follow diffusion controlled reaction mechanism in contracting volume governed by $g(\alpha) = 1 - (1 - \alpha)^{1/3}$, where α = fraction decomposed at temperature $T^\circ\text{C}$. Activation energy (E) is obtained from the Coats-Redfern plot of $\ln g(\alpha)/T^2$ vs. $1/T$ (Fig. 2). Where $E = \text{Slope} \times R$ ($R = 8.31465\text{ J/mol K}$); pre-exponential factor ($\ln A = \beta E/R$ [exp (Intercept)]; β = rate of heating).

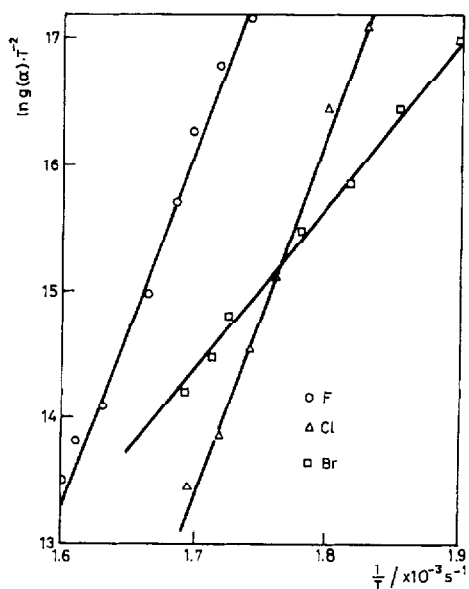


Fig. 2 Coats-Redfern plot for $\text{Ph}_4\text{P}^+\text{CrO}_3\text{X}^-$ complexes. F, Cl, Br

Activation energy values and pre-exponential factors for the first step decomposition are presented in Table 4.

Table 4 Activation energy and other related values for the first step decomposition of $\text{Ph}_4\text{P}^+\text{CrO}_3\text{X}^-$ complexes

Complex	$E/\text{kJ mol}^{-1}$	$\ln A/\text{s}^{-1}$	r
$\text{Ph}_4\text{P}^+\text{CrO}_3\text{F}^-$	224.21	37	0.9980
$\text{Ph}_4\text{P}^+\text{CrO}_3\text{Cl}^-$	217.02	35	0.9868
$\text{Ph}_4\text{P}^+\text{CrO}_3\text{Br}^-$	119.48	15	0.9877

First decomposition peak temperature of complexes decreases with the increase in ionic size and decrease in electronegativity of halide ions. Based on the first peak decomposition temperature and activation energy values, thermal stability of these complexes may be arranged in the decreasing order as $\text{Ph}_4\text{P}^+\text{CrO}_3\text{F}^- > \text{Ph}_4\text{P}^+\text{CrO}_3\text{Cl}^- > \text{Ph}_4\text{P}^+\text{CrO}_3\text{Br}^-$.

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