

## **THERMAL DECOMPOSITION OF 2,3,5-TRIPHENYL TETRAZOLIUM HALOCHROMATE COMPLEXES**

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### **Abstract**

Thermal decomposition studies of 2,3,5-triphenyl tetrazolium halochromates have been carried out upto 1000°C at a linear heating rate of 10 deg·min<sup>-1</sup>. The complexes undergo two stage decomposition. First one corresponds to the redox decomposition of the complex along with the loss of a phenyl halide molecule and 3/2 mol of oxygen. While, the second step corresponds to the oxidation of the formazan type structure formed in the first step. The first step decomposition follows diffusion controlled reaction mechanism in a sphere governed by the equation  $g(\alpha) = [1 - (1 - \alpha)^{1/3}]^2$ . Activation energy and pre-exponential factors have been determined by Coats-Redfern model and Dixit-Ray model. Activation energy decreases as the electronegativity of the halide ion decreases.

**Keywords:** complexes

### **Introduction**

Chromate oxidation involves the formation of a substituted chromate ion, CrO<sub>3</sub>L<sup>n-</sup> where the ligand may be organic [1] or inorganic [2]. Halochromates CrO<sub>3</sub>X<sup>-</sup> (X = F, Cl, Br) are mostly used as potentially mild and selective oxidising agents in the conversion of alcohols to their corresponding carbonyl compounds [3]. Chromates or dichromates in halo acids give halochromates [4], which react with onium salts to give ion associated complexes [5]. 2,3,5-triphenyl tetrazolium ion (TPT<sup>+</sup>) reacts with halochromates to give 1:1 ion associated 2,3,5-triphenyl tetrazolium halochromate complexes (TPT<sup>+</sup>CrO<sub>3</sub>X<sup>-</sup>; X = F, Cl, Br). Synthesis of these complexes and their characterization by IR spectra and TG-DTA studies are discussed in this paper.

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## Experimental

2,3,5-triphenyl tetrazolium chloride of Fluka was used without further purification. Anhydrous  $\text{CrO}_3$  (dried over  $\text{P}_2\text{O}_5$ ),  $\text{HCl}$ ,  $\text{HBr}$  and  $\text{HF}$  of AnalaR grade were used. Dichloromethane and hexane were distilled before use.

2,3,5-triphenyl tetrazolium chloride was converted into its hydroxide by stirring the aqueous solution with silver oxide for 24 h, filtered and the filtrate was made upto 250 ml in a volumetric flask by adding distilled water and adjusting the net acidity of the solution upto 0.1 *N* with respect to the corresponding halo acid.

IR studies were carried out on a JASCO FT/IR-5300 instrument. IR spectra were recorded in the 400–4000  $\text{cm}^{-1}$  region using KBr pellets.

Thermal studies were carried out on a Shimadzu thermal analyzer: model DT-40. The instrument records both TG and DTA curves simultaneously.  $\alpha\text{-Al}_2\text{O}_3$  was used as reference. Open alumina crucibles of identical dimensions were used as both sample and reference holders.

### *Synthesis of the complexes*

To  $\text{CrO}_3$  (0.125 g), 0.1 *N*  $\text{HCl}$  (5 mL) was added with constant swirling till a yellow coloured solution of chlorochromate was formed. To it, 2,3,5-triphenyl tetrazolium hydroxide (24.5 mL) was added. The yellow precipitate of 2,3,5-triphenyl tetrazolium chlorochromate so formed was then extracted into dichloromethane by stepwise extraction method till the organic layer became colourless. The complex was recrystallized from the organic extract by adding hexane, filtered and dried under vacuum for 3 h. Corresponding fluoro and bromo complexes were synthesized similarly by using  $\text{HF}$  and  $\text{HBr}$  respectively instead of  $\text{HCl}$ . On analysis, these complexes were found to be of 99.9% purity (Yield = 90%).

## Results and discussion

### *IR studies*

The IR spectra of these three complexes are presented in Fig. 1. A comparison with  $\text{CrO}_3\text{Cl}^-$  in  $\text{KCrO}_3\text{Cl}$  and  $\text{CrO}_3\text{F}^-$  in  $\text{KCrO}_3\text{F}$  led to the conclusion that the vibrational spectra of  $\text{TPT}^+\text{CrO}_3\text{X}^-$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ) are consistent with that reported for  $\text{CrO}_3\text{X}^-$  ion. The molecule belongs to  $\text{C}_{3v}$  symmetry [6]. In  $\text{XYZ}_3$  type molecules, the symmetric stretch of  $\text{X-Z}$  bond occurs at a lower frequency than the antisymmetric stretch [7]. Hence,  $908 \pm 2 \text{ cm}^{-1}$  is assigned to  $\text{Cr-O}$  symmetric stretching frequency, while,  $949 \text{ cm}^{-1}$  to the  $\text{Cr-O}$  antisymmetric stretching. Absorption frequencies at  $640 \text{ cm}^{-1}$ ,  $437 \text{ cm}^{-1}$  are assigned to  $\text{Cr-F}$

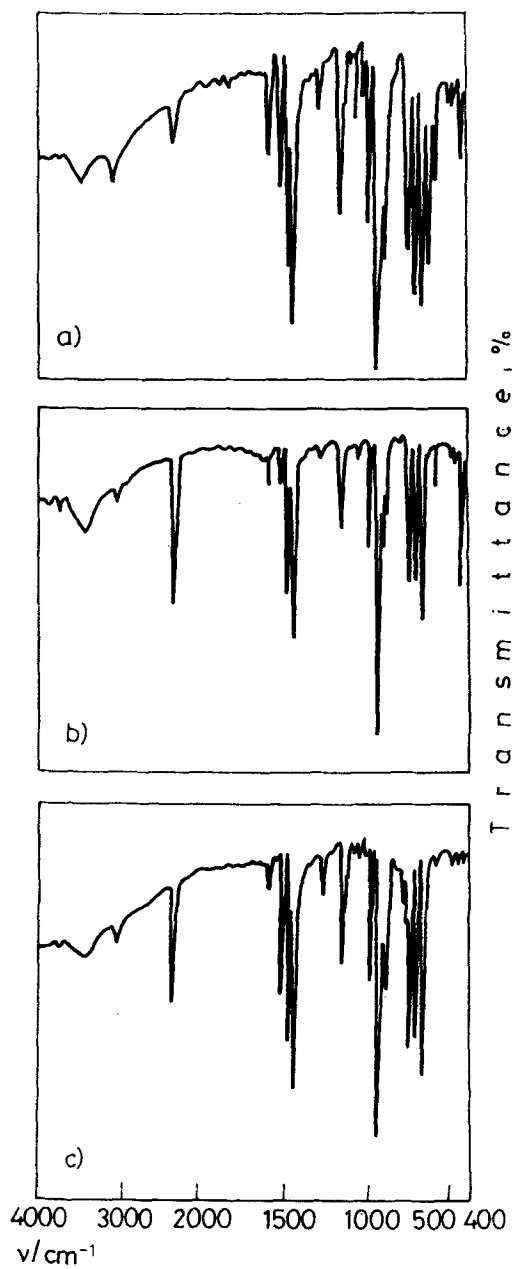


Fig. 1 IR spectra of the  $\text{TPT}^+\text{CrO}_3\text{X}^-$  complexes

and Cr-Cl stretchings, while the expected frequency of Cr-Br at  $237\text{ cm}^{-1}$  could not be observed due to the limitations of the instruments.

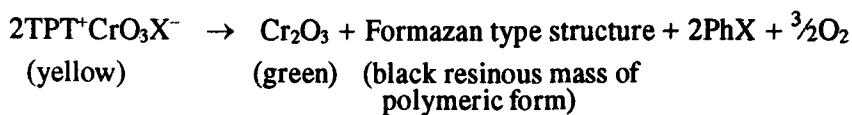
### Thermal studies

Thermal studies of  $\text{TPT}^+\text{CrO}_3\text{X}^-$  complexes were done in static air. As the complexes are sticky on heating, a 1:1 homogeneous mixture of these complexes with  $\alpha\text{-Al}_2\text{O}_3$  were used. Samples were heated upto  $1000^\circ\text{C}$  at a linear heating rate of  $10\text{ deg}\cdot\text{min}^{-1}$ . Figure 2 represents the TG-DTA curves of these halochromate complexes. Both the DTA and TG curves show no change upto  $190^\circ\text{C}$  indicating that the complexes are thermally stable upto that temperature. The DTA curve exhibits two exothermic peaks within the temperature regions  $195\text{--}315^\circ\text{C}$  and  $330\text{--}530^\circ\text{C}$ .

**Table 1** Weight loss values (%) for first step and total decomposition of the  $\text{TPT}^+\text{CrO}_3\text{X}^-$  complexes

Complex name	1st step decomposition		Total weight loss / %	
	Theor. wt. loss / %	TG loss / %	Theor. loss / %	TG loss / %
$\text{TPT}^+\text{CrO}_3\text{F}^-$	28.68	28.50	81.83	81.24
$\text{TPT}^+\text{CrO}_3\text{Cl}^-$	31.38	30.75	82.52	82.49
$\text{TPT}^+\text{CrO}_3\text{Br}^-$	37.74	37.49	84.14	84.73

As all these complexes are used in the oxidation of alcohols, the ease of removal of  $\text{Cr}_2\text{O}_3$  from these complexes is of major importance. Hence the kinetic studies have been limited only to the first step of decomposition. The weight losses indicated by the TG curves in this region correspond to the loss of a phenyl halide molecule and  $\frac{3}{2}$  mol of oxygen (Table 1). After the completion of first peak, the decomposed products were extracted in chloroform. However, the total mass was not extractable. The quantitative reduction is confirmed by the negative response of diphenyl carbazide test carried out with the unextractable mass as well as with the organic extract. IR spectra of the chloroform extracts do not show any peak corresponding to Cr-O or Cr-X bond. Further, the spectra are identical to that obtained from  $\text{TPTCl}$  after heating at the same temperature and both reveal the presence of a formazan type structure [8]. Absorption peaks at  $1380$  and  $1490\text{ cm}^{-1}$  are assigned respectively to the symmetric and antisymmetric vibrations of N=C-N bond. Peak at  $1255\text{ cm}^{-1}$  corresponds to the antisymmetric vibration of N=N-Ph group. Formation of a formazan type structure is further supported by the mass spectra of 2,3,5-triphenyl tetrazolium salts where they undergo thermal decomposition as reported by Horváth and Jerkovich [9]. Based on these observations, the first step decomposition may be represented as follows:



where *PhX* = Phenyl halide

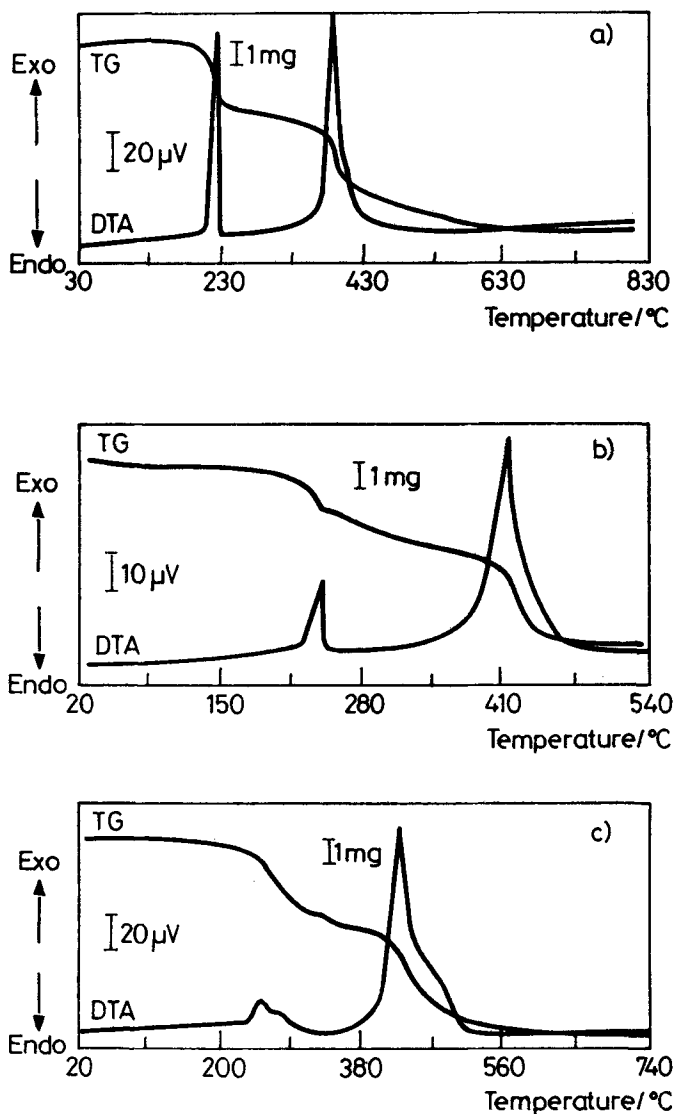


Fig. 2 TG-DTA curves of the  $\text{TPT}^+\text{CrO}_3\text{X}^-$  complexes

As this step involves the reduction of Cr(VI) to Cr(III), an endothermic DTA peak should have been observed. However, the oxidation of TPT to a formazan type structure occurs simultaneously and predominates over the reduction of Cr(VI) to Cr(III) and hence an exothermic DTA peak is observed.

The weight loss in the region 330–550°C of TG is due to the further oxidation of the polymeric formazan type structure. This is responsible for the second large exothermic DTA peak in all the complexes. The final residue after total decomposition of these complexes is Cr<sub>2</sub>O<sub>3</sub>. The total theoretical weight loss was calculated on this basis. The thermoanalytical data on these complexes are presented in Table 1.

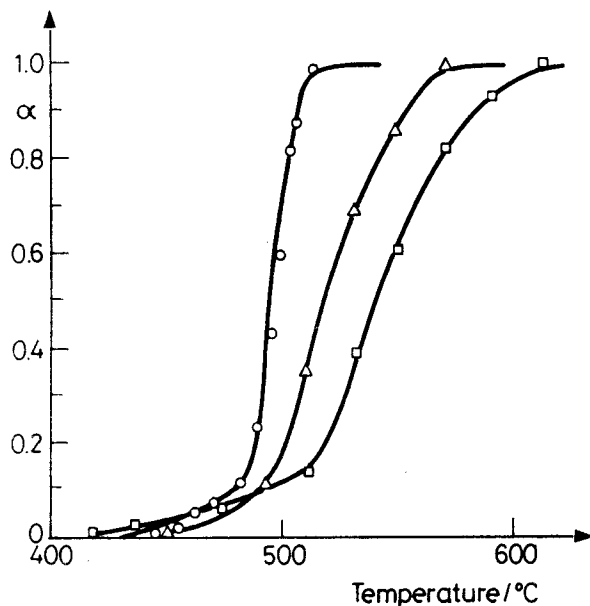
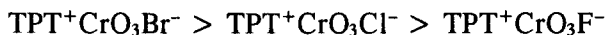


Fig. 3  $\alpha$ -temperature plots for the TPT<sup>+</sup>CrO<sub>3</sub>X<sup>-</sup> complexes

The kinetics of first step solid state decomposition of these complexes have been studied from TG. The  $\alpha$  vs. temp. plots for this step are presented in Fig. 3. The steepness of the curve increases from fluoro complex to chloro and then to bromo complex. Hence, the rate of first step decomposition of these complexes may be arranged in the following order as



To choose the best fitting reaction model for this decomposition step, nine reaction models pertaining to diffusion control, random nucleation growth, nu-

cleation growth according to power law, phase boundary reaction and chemical reaction have been used. The Coats-Redfern plot i.e.

$$\frac{\ln [1 - (1 - \alpha)^{1/3}]^2}{T^2} \text{ vs. } \frac{1}{T}$$

where  $\alpha$  = fraction decomposed at temperature  $T$  (Fig. 4) gives the best fitting straight line with highest square of correlation coefficient ( $r^2$ ) for diffusion controlled reaction mechanism in a sphere.

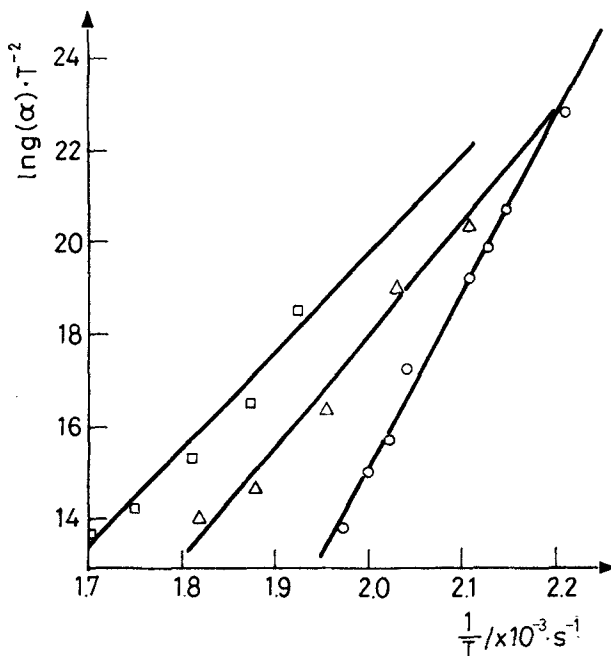


Fig. 4 Coats-Redfern plot for  $\text{TPT}^+\text{CrO}_3\text{X}^-$  complexes

Table 2 Activation energy and other related values for the first step decomposition of the  $\text{TPT}^+\text{CrO}_3\text{X}^-$  complexes

Complex name	$E/ \text{kJ} \cdot \text{mol}^{-1}$ by		$\ln A / \text{s}^{-1}$	$r^2 / \%$	Electroneg. of halogen
	C.-R. method	D.-R. method			
$\text{TPT}^+\text{CrO}_3\text{F}^-$	287.4	295.4	59.87	96.03	3.90
$\text{TPT}^+\text{CrO}_3\text{Cl}^-$	182.2	190.6	31.45	96.23	3.15
$\text{TPT}^+\text{CrO}_3\text{Br}^-$	121.7	130.4	15.96	98.21	2.85

Activation energy values and pre-exponential factors  $\ln A$  ( $A$  in  $\text{sec}^{-1}$ ) for the first step of decomposition calculated by Coats-Redfern [10] and Dixit-Ray methods [11] are presented in Table 2.

## Conclusion

Based on the above observations, it may be concluded that the first step decomposition of these complexes are controlled by the ionic size and electronegativity of the halide ions.

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**Zusammenfassung** — Bei einer linearen Aufheizgeschwindigkeit von  $10 \text{ deg}\cdot\text{min}^{-1}$  wurden bis zu Temperaturen von  $1000^\circ\text{C}$  thermische Zersetzungsstudien an 2,3,5-Triphenyltetrazoliumhalochromaten durchgeführt. Die Komplexe durchlaufen zwei Zersetzungsstufen. Die erste entspricht der Redoxzersetzung des Komplexes unter Verlust eines Phenylhalogenidmoleküles und von  $3/2$  mol Sauerstoff. Der zweite Schritt entspricht der Oxidation der beim ersten Schritt entstandenen Struktur vom Formazan-Typ. Die zum ersten Schritt gehörende Zersetzung verläuft nach einem diffusionskontrollierten Reaktionsmechanismus innerhalb einer Kugel entsprechend der Gleichung  $g(\alpha) = [1 - (1 - \alpha)^{1/3}]^2$ . Die Aktivierungsenergie und die präexponentiellen Faktoren wurden anhand des Coats-Redfern'schen und des Dixit-Ray'schen Modelles bestimmt. Die Aktivierungsenergie sinkt mit steigender Elektronegativität des Halogenidions.