Interaction of Methyl Orange with TBC.

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Abstract:
Methyl Orange is a Nitrogen containing Organic acid. It was treated with TBC and complexation was observed interesting results were obtained. The solid products were analysed in different physical parameters.

(Key Words: Methyl Orange, Oxidation, Complexation.)

Introduction:

TBC (Tertbutyl chromate) is oxidizing agent for oxidation of Organic substrates. In this work Methyl Orange is oxidized by TBC in different molar ratios. Four different products were prepared with product code MTR 1,MTR 2, MTR 3 and MTR 4, in the ratio of 1:0.5, 1:1, 1:1.5 and 1:2 respectively. All products were characterized on the basis of elemental analysis, I.R.Spectral studies and thermal analysis.

Chemicals Used:

Methyl Orange, Chromium Trioxide, Tertiary Butyl Alcohol, Acetone, etc. (The chemicals used were of A.R.grade)

Experimental procedure :

Oxidation of methyl orange with TBC was carried out in substrate : oxidant 1:0.5, 1:1, 1:1.5 and 1:2molar ratios.

The desired strength of the oxidant was achieved by taking 0.01 mole of the substrate and 0.5g, 1g, 1.5gand 2g of CrO_3 in TBA (Tert butyl alcohol) respectively.

The substrate was mixed with minimum volume of distilled water (E-Merk). Solid CrO_3 was added with constant and vigorous stirring. Precaution was taken to avoid reaction being violent at the time of mixing the reagent. The solution of the substrate and the oxidant where mixed with constant and vigorous stirringfor about 1.5 hour at 75^0C (No reaction was initiated at room temperature). The mixture wat left overnightfor complete reaction. The product where collected as sample MTR1, MTR2, MTR3 and MTR4.

(in substrate : oxidant 1:0.5, 1:1, 1:1.5 and 1:2 molar ratio respectively.)

The solid obtained was then powdered in mortar and pestle. Successive washings with distilled water. Ethanol, dioxin and finally with acetone removed soluble impurities. The light brown complex obtained wasinsoluble in water and acetone. The product was dried and collected in an air tight bottle.

FTIR Analysis of Products :

The FTIR curves of MTR1, MTR2, MTR3 and MTR4 contain almost all the peak which are expected for their formulation. The FTIR band assigned for various groups are listed below.

MTR1	MTR2	MTR3	MTR4	Band Assignment	References
1033.85	1033.85	1033.85	1033.85	V_a(S = 0)	5a
1600.92	1602.85	1593.20	1595.13	-N = N-	5b
1384.89	1390.68	1384.89	1384.89	C – N	5c
1193.94	1193.94	1186.22	1186.22	N-CH_3 (Symmetric)	5d
1120.64	1120.64	1120.64	1186.22	N-CH_3 (Bending)	5e
3294.42	32803.92	3329.14	3332.99	Co-ordinated H_2O	5f
570.93	572.86	563.21	565.14	V (Cr-N)	5g
433.98	507.28	532.35	430.13	V(Cr-O)	5h

Thermal Analysis of MTR1 :

The complex having empirical formula $Cr_5C_{15}H_{38}N_3SO_{45}$ (MTR1) shows endothermic loss up to temperature 113.36^{0}C. This loss is anticipated due to loss of hydrated water (H_2O) molecule with mass loss 89.071 (theoretical loss 90.075). In the temperature range 113.36^{0}C – 239.43^{0}C. There is expected loss of $3CO_2$ with mass loss 133.607 (theoretical 132.027).

Code	Temperature(^{0}C)	% mass left in experiment	Weight left Experimental (Theoretical)	Empirical Formula Predicted	Loss in Formula wt. Experimental (Theoretical)	Cumulative %Loss in Formula wt. Experimental (Theoretical)	Group loss (Theoretical)
MTR1	R.T.			$Cr_5C_{15}H_{38}N_3SO_{45}$			
	Upto 113.36^{0}C			$Cr_5C_{15}H_{28}N_3SO_{42}$			
		93	1183.376 (1182.372)		89.071 (90.075)	7% (7.079%)	5 H_2O
	Upto 239.43^{0}C			$Cr_5C_{12}H_{28}N_3SO_{34}$			
		82.5	1149.769 (1051.349)		133.607 (132.027)	17.5% (17.376%)	$3CO_2$

Table : Thermal Analysis of MTR1

Proposed Empirical formulation of MTR1 is $Cr_5C_{15}H_{38}N_3SO_{45}$ and the sequence of thermal degradation may be interpreted as follows

$Cr_5C_{15}H_{38}N_3SO_{45}$ ⟶ $Cr_5C_{15}H_{28}N_3SO_{42}$ ⟶ $Cr_5C_{12}H_{28}N_3SO_{34}$

Thermal Analysis of MTR2 :

The complex having empirical formula $Cr_5C_{15}H_{41}N_3SO_{44}$ (MTR2) shows endothermic loss up to temperature 120.96^{0}C. This loss is anticipated due to loss of hydrated water (H_2O) molecule with mass loss 144.839 (theoretical loss 144.120). In the temperature range 120.96^{0}C – 223.35^{0}C. There is expected loss of 2 CO_2, with mass loss 88.163 (theoretical 88.018).

Code	Temperature (^{0}C)	% mass left in experiment	Weight left Experimental (Theoretical)	Formula Predicted	Loss in Formula wt. Experimental (Theoretical)	Cumulative % Loss in Formula wt. Experimental (Theoretical)	Group loss (Theoretical)
MTR2	R.T.			$Cr_5C_{15}H_{41}N_3SO_{44}$			
	Upto 120.96^{0}C	88.5	1114.630 (1115.349)	$Cr_5C_{15}H_{25}N_3SO_{36}$	144.839 (144.120)	11.5% (11.443%)	8H_2O
	Upto 233.35^{0}C	81.5	1026.467 (1026.349)	$Cr_5C_{13}H_{25}N_3SO_{32}$	88.163 (88.081)	18.5% (18.489%)	2 CO2

Table : Thermal Analysis of MTR2

Proposed Empirical formulation of MCR2 is $Cr_5C_{15}H_{41}N_3SO_{44}$ and the sequence of thermaldegradation may be interpreted as follows

$Cr_5C_{15}H_{41}N_3SO_{44}$ ⟶ $Cr_5C_{15}H_{25}N_3SO_{36}$ ⟶ $Cr_5C_{13}H_{25}N_3SO_{32}$

Thermal Analysis of MTR3 :

The complex having empirical formula $Cr_4C_{13}H_{37}N_3SO_{39}$ (MTR3) shows endothermic loss up to temperature 117.54^{0}C. This loss is anticipated due to loss of hydrated water (H_2O) molecule with mass loss 109.043 (theoretical loss 104.090). In the temperature range 117.54^{0}C – 232.28^{0}C. There is expected loss of CO_2 with mass loss 87.954 (theoretical 88.018).

Further in the temperature range 232.28^{0}C – 755.37^{0}C there is expected loss of SO_2 and N_2 withmass loss of 288.851 (theoretical 286.229).

Code	Temperature (^{0}C)	% mass left in experiment	Weight left Experimental (Theoretical)	Empirical Formula Predicted	Loss in Formula wt. Experimental (Theoretical)	Cumulative % Loss in Formula wt. Experimental (Theoretical)	Group loss (Theoretical)
MTR3	R.T. Upto 117.54^{0}C	90	989.485 (991.338)	$Cr_4C_{13}H_{37}N_3SO_{39}$ $Cr_4C_{13}H_{25}N_3SO_{33}$	109.943 (108.090)	10% (9.831%)	$6H_2O$
	Upto 232.28^{0}C	82	901.531 (901.467)	$Cr_4C_{11}H_{25}N_3SO_{29}$	87.954 (88.018)	18% (18.006%)	CO_2
	Upto 755.37^{0}C	56	615.680 (615.302)	$Cr_4C_{11}H_5O_{17}$	285.851 (286.229)	44% (44.304%)	SO_2,N_2 , ½ N_2,$10H_2O$

Table : Thermal Analysis of MTR3

Proposed Empirical formulation of MTR3 is $Cr_4C_{13}H_{37}N_3SO_{39}$ and the sequence of thermaldegradation may be interpreted as follows

$Cr_4C_{13}H_{37}N_3SO_{39}$ ⟶ $Cr_4C_{13}H_{25}N_3SO_{33}$ ⟶ $Cr_4C_{11}H_{25}N_3SO_{29}$ ⟶ $Cr_4C_{11}H_5O_{17}$

Thermal Analysis of MTR4 :

The complex having empirical formula $Cr_4C_{14}H_{44}N_3SO_{45}$ (MTR4) shows endothermic loss up to temperature 116.34^{0}C. This loss is anticipated due to loss of hydrated water (H_2O) molecule with mass loss 133.593 (theoretical loss 135.113). In the temperature range 116. 34^{0}C – 233.44^{0}C. There is expected loss of CO_2 with mass loss 88.050 (theoretical 88.018).

Further in the temperature range 233.44^{0}C – 765.48^{0}C there is expected loss of SO_2 and N_2 13.5H_2O with mass loss of 349.164 (theoretical 349.282).

Code	Temperature (^{0}C)	% mass left in experiment	Weight left Experimental (Theoretical)	Empirical Formula Predicted	Loss in Formula wt. Experimental (Theoretical)	Cumulative % Loss in Formula wt. Experimental (Theoretical)	Group loss (Theoretical)
MTR 4	R.T. Upto 116.34^{0}C	89	1080.889 (1079.369)	$Cr_4C_{14}H_{44}N_3SO_{45}$ ↓ $Cr_4C_{14}H_{29}N_3SO_{37.5}$	133.593 (135.113)	11% (11.125%)	7.5H_2O
	Upto 233.44^{0}C	81.75	992.839 (992.871)	↓ $Cr_4C_{12}H_{29}N_3SO_{33.5}$	88.050 (88.018)	18.25% (18.247)	$2CO_2$
	Upto 765.48^{0}C	53	643.675 (643.557)	↓ $Cr_4C_{12}H_2O_{20}$	349.164 (349.282)	47% (47.010)	SO_2 , N_2 ½ N_2, 13.5H_2O

Table : Thermal Analysis of MTR4

Proposed Empirical formulation of MCR4 is $Cr_4C_{14}H_{44}N_3SO_{45}$ and the sequence of thermaldegradation may be interpreted as follows.

$$Cr_4C_{14}H_{44}N_3SO_{45} \longrightarrow Cr_4C_{14}H_{29}N_3SO_{37.5} \longrightarrow Cr_4C_{12}H_{29}N_3SO_{33.5} \longrightarrow Cr_4C_{12}H_2O_{20}$$

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