Interaction of Methyl Orange with Chromium Trioxide

Anil Kumar Pandey
Department of Chemistry, J.N College, Dhurwa, Ranchi, Jharkhand
Email: pandeyanil08@gmail.com

Abstract:

Methyl Orange is a Nitrogen containing Organic acid. It was treated with Chromium Trioxide and some interesting results were obtained. The solid products were analysed in different physical parameters.

Key Words: Methyl Orange, Oxidation, Complexation.

Introduction:

Chromium Trioxide is very common oxidizing agent used for Oxidation of Organic substrates. In this work Methyl Orange is oxidized by Chromium Trioxide in different molar ratios. Four different products were prepared with product code MCR 1, MCR 2, MCR 3 and MCR 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 CrO_3 was carried out in substrate: oxidant 1:0.5, 1:1, 1:1.5 and 1:2 molar ratios.
The desired strength of the oxidant was achieved by taking 0.01 mole of the substrate and 0.5g, 1g, 1.5g and 2g of CrO_3 in minimum volume of water 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 violet at the time of mixing the reagent. The solution of the substrate and the oxidant where mixed with constant and vigorous stirring for about 1.5 hour at 75^0C (No reaction was initiated at room temperature). The mixture wat left overnight for complete reaction. The product was collected as sample MCR1, MCR2, MCR3 and MCR4. (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 was insoluble in water and acetone. The product was dried and collected in an air tight bottle.

FTIR Analysis of Products:

The FTIR curves of MCR1, MCR2, MCR3 and MCR4 contain almost all the peak which are expected for their formulation. The FTIR band assigned for various groups are listed below.

MCR1	MCR2	MCR3	MCR4	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 MCR1:

The complex having empirical formula $Cr_5C_{16}H_35N_3SO_{35}$ (MCR1) shows endothermic loss up to temperature 106.08^{0}C. This loss is anticipated due to loss of hydrated water (H_2O) molecule with mass loss 99.490 (theoretical loss 99.083). In the temperature range 106.08^{0}C – 358.54^{0}C. There is expected loss of SO_2, CO_2 and ½ N_2 with mass loss 165.818 (theoretical 166.083).

Further in the temperature range 358.54^{0}C – 458.08^{0}C there is expected loss of N_2 and CO_2 with mass loss 71.854 (theoretical 72.023).

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)
MCR 1	R.T.			$Cr_5C_{16}H_{35}N_3SO_{35}$ ↓			
	Upto 106.08^{0}C	91	1005.958 (1006.365)	$Cr_5C_{16}H_{24}N_3SO_{29.5}$ ↓	99.490 (99.083)	09% (08.63%)	5.5 H_2O
	Upto 358.54^{0}C	76	840.140 (839.875)	$Cr_5C_{15}H_{24}N_2SO_{29.5}$ ↓	165.818 (166.083)	24.000% (24.024%)	SO_2, CO_2 ½ N_2
	Upto 458.08^{0}C	69.5	768.286 (768.117)	$Cr_5C_{14}H_{24}O_{27.5}$ ↓	71.854 (72.023)	31.500% (30.515%)	N_2, CO_2

Table: Thermal Analysis of MCR1

Proposed Empirical formulation of MCR1 is $Cr_5C_{16}H_{35}N_3SO_{35}$ and the sequence of thermal degradation may be interpreted as follows

$$[Cr_5C_{16}H_{35}N_3SO_{35}] \xrightarrow{\text{Upto } 106.08^0C} [Cr_5C_{16}H_{24}N_3SO_{29.5}]$$

$$\xrightarrow{\text{Upto } 358.54^0C} [Cr_5C_{15}H_{24}N_2SO_{29.5}] \xrightarrow{\text{Above } 458.08^0C} [Cr_5C_{14}H_{24}O_{27.5}]$$

Thermal Analysis of MCR2:

The complex having empirical formula $CrC_6H_{14}5NSO_9$ (MCR2) shows endothermic loss up to temperature 104.86^{0}C. This loss is anticipated due to loss of hydrated water (H_2O) molecule with mass loss 19.693 (theoretical loss 18.015). In the temperature range 104. 86^{0}C – 333.68^{0}C. There is expected loss of ½ SO_2, and ½ N_2 with mass loss 45.951 (theoretical 46.036).

Further in the temperature range 333.68^{0}C – 520.90^{0}C there is expected loss of 2.5 H_2O with mass loss of 45.951 (theoretical 45.038).

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)
MCR 2	R.T. Upto 104.86^{0}C	94	308.528 (310.206)	$CrC_6H_{14}NSO_9$ ↓ $CrC_6H_{12}NSO_8$	19.693 (18.015)	06% (05.489%)	H_2O
	Upto 333.68^{0}C	80	262.577 (262.492)	↓ $CrC_6H_{12}O_7$	45.951 (46.036)	20% (20.026%)	½ SO_2 ½ N_2
	Upto 520.90^{0}C	66	216.626 (217.539)	↓ $CrC_6H_7O_{4.5}$	45.951 (45.038)	34% (33.722%)	2.5 H_2O

Table: Thermal Analysis of MCR2

Proposed Empirical formulation of MCR2 is $CrC_6H_{14}NSO_9$ and the sequence of thermal degradation may be interpreted as follows

$$[CrC_6H_{14}NSO_9] \xrightarrow{\text{Upto } 104.86^0\text{C}} [CrC_6H_{12}NSO_8]$$

$$\xrightarrow{\text{Upto } 333.68^0\text{C}} [CrC_6H_{12}O_7] \xrightarrow{\text{Above } 520.99^0\text{C}} [CrC_6H_7O_{4.5}]$$

Thermal Analysis of MCR3:

The complex having empirical formula $Cr_{10}C_{19}H_{72}N_3SO_{68}$ (MCR3) shows endothermic loss up to temperature 94.20^{0}C. This loss is anticipated due to loss of hydrated water (H_2O) molecule with mass loss 89.221 (theoretical loss 90.075). In the temperature range 94. 42^{0}C – 212.13^{0}C. There is expected loss of $2CO_2$ and O_2 with mass loss 118.961 (theoretical 120.016).

Further in the temperature range 212.13^{0}C – 364.37^{0}C there is expected loss of SO_2 and N_2 with mass loss of 109.048 (theoretical 109.078).

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)
MCR 3	R.T.			$Cr_{10}C_{19}H_{72}N_3SO$ ↓			
	Upto 94.20^{0}C	95.5	1893.465 (1892.611)	$Cr_{10}C_{19}H_{62}N_3SO$ ↓	89.221 (90.075)	4.5% (4.543%)	$5H_2O$
	Upto 212.13^{0}C	89.5	1774.504 (1773.449)	$Cr_{10}C_{17}H_{62}N_3SO$ ↓	118.961 (120.016)	10.5% (10.553%)	$2\ CO_2$ & O_2
	Upto 364.37^{0}C	84	1665.456 (1665.426)	$Cr_{10}C_{17}H_{61}NO_{56}$ ↓	109.048 (109.078)	16% (16.002%)	SO_2 & N_2
	Upto 469.60^{0}C	81	1605.976 (1605.448)	$Cr_{10}C_{16}H_{61}NO_{53}$	59.480 (60.008)	19% (19.027%)	CO_2, ½ O_2

Table: Thermal Analysis of MCR3

Proposed Empirical formulation of MCR3 is $Cr_{10}C_{19}H_{72}SO_{68}$ and the sequence of thermal degradation may be interpreted as follows

$$[Cr_{10}C_{19}H_{72}N_3SO_{68}] \xrightarrow{\text{Upto } 94.20^0\text{C}} [Cr_{10}C_{19}H_{62}N_3SO_{63}]$$

$$\xrightarrow{\text{Upto } 212.13^0\text{C}} [Cr_{10}C_{17}H_{62}N_3SO_{57}] \xrightarrow{\text{Upto } 364.37^0\text{C}} [Cr_{10}C_{17}H_{61}NO_{56}]$$

$$\xrightarrow{\text{Upto } 469.60^0\text{C}} [Cr_{10}C_{16}H_{61}NO_{53}]$$

Thermal Analysis of MCR4:

The complex having empirical formula $Cr_{10}C_{19}H_{66}N_3SO_{68}$ (MCR4) shows endothermic loss up to temperature 111.62^{0}C. This loss is anticipated due to loss of hydrated water (H_2O) molecule with mass loss 217.431 (theoretical loss 216.180). In the temperature range 111. 62^{0}C – 206.39^{0}C. There is expected loss of $5CO_2$ with mass loss 217.431 (theoretical 220.045).

Further in the temperature range 206.39^{0}C – 345.87^{0}C there is expected loss of SO_2 and N_2 ½ N_2 and $3CO_2$ with mass loss of 237.197 (theoretical 238.106).

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)
MCR 4	R.T.			$Cr_{10}C_{19}H_{66}N_3SO$ ↓			
	Upto 111.62^{0}C	89	1759.213 (1760.464)	$Cr_{10}C_{19}H_{42}N_3SO$ ↓	217.431 (216.180)	11% (10.937%)	$12H_2O$
	Upto 206.39^{0}C	78	1541.782 (1539.168)	$Cr_{10}C_{14}H_{42}N_3SO$ ↓	217. 431 (220.045)	22% (22.132%)	$5CO_2$
	Upto 345.87^{0}C	66	1304.585 (1303.673)	$Cr_{10}C_{11}H_{42}O_{38}$ ↓	237.197 (238.160)	34% (34.046%)	SO_2 , N_2 ½ N_2,
	Upto 475.52^{0}C	61.5	1215.636 (1216.567)	$Cr_{10}C_9H_{42}O_{34}$	88.949 (88.018)	38.5% (38.452%)	$3CO_2$ $2CO_2$

Table: Thermal Analysis of MCR4

Proposed Empirical formulation of MCR4 is $Cr_{10}C_{19}H_{66}N_3SO_{68}$ and the sequence of thermal degradation may be interpreted as follows.

$$[Cr_{10}C_{19}H_{66}N_3SO_{68}] \xrightarrow{\text{Upto } 111.62^0\text{C}} [Cr_{10}C_{19}H_{42}N_3SO_{56}]$$

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