Thermal Decomposition Kinetics of Labile Chromium Complex with Benzoic Acid

M.K.MISHRA* and N.M.MISRA

*Department of Chemistry B.I.T., Sindri, Dhanbad, India
Department of Applied Chemistry ISM, Dhanbad, India
mkmishrabit@gmail.com

Received 6 June 2010; Accepted 2 August 2010

Abstract: Complex $[\text{CrO}_2 (\text{C}_7\text{H}_5\text{O}_2) (\text{C}_2\text{H}_5\text{OH}) (\text{H}_2\text{O})_2]$ was prepared by using benzoic acid. Its spectral characterization was done by using Elemental analysis (C and H), Inductively coupled plasma optical emission spectroscopy (ICP - OES), Ultraviolet - visible (UV-Vis) spectroscopy, Fourier transform infrared (FTIR) spectroscopy and Fast Atomic Bombardment (FAB) Mass spectrometry. Whereas thermal decomposition was investigated by differential scanning calorimetric (DSC). The low value of activation energy of exothermic change indicated lability of complex.

Keywords: Labile, Chromium complexes, Thermal decomposition kinetics, Energetic materials, Benzoic acid

Introduction

Chromium metal has played a prominent role in the development of inorganic chemistry. Chromium trioxide reacts vigorously with organic substances; is widely used as an oxidant in synthetic organic chemistry¹⁻³. Complexation reactions with organic ligands produce coordination compounds / complexes with differing degree of thermodynamic stability and lability⁴⁻⁷. It has been reported that the covalent coordinate bond having energy 20-80 kcal/mol with first row metal ligand bond show high stability and high lability⁸⁻⁹. A rapid reaction rate has been observed between Cr(III)-Schiff's base complexes and nicotinic acid and there are also some other systems such as porphyrin complexes with similar labile kinetic behavior¹⁰⁻¹³. Chromium(III) octahedral complexes are generally inert to the substitution of inner sphere water molecules by other ligands but some report indicate, however, the chromium(III) complexes, Aqua (ethylenediaminetriacetic acid) chromium(III), with one molecule of water and a five coordinate EDTA type ligand shows unexpectedly rapid substitution rates with several anionic ligands. It has been suggested that these reactions are due in part to strain present in the complex¹⁴.

In the present investigation, we have studied on the synthesis and characterization of chromium metal complex using benzoic acid as the ligand. Thermal behavior of this complex has also been investigated to understand the thermodynamic stability and lability of this complex.

Experimental

Benzoic acid (E.Merck), chromic acid CrO_3 (Apex chemicals) and ethyl alcohol (Merck-KgaA) were used as received. The elemental microanalysis of C and H were carried out with a Thomas and Coleman Analyzer-Carlo Erba1106 while the metal content in the complex was determined by Perkin Elmer 5300DV(Duel View), IR spectra was recorded on a perkin-Elmer 1600 series FTIR spectrometer in KBr pellets. The FAB Mass spectrum was recorded on Jeol SX - 102 (FAB) Mass spectrometer. DSC studies was carried out Perkin Elmer's DSC-7, Scan rate: 50 °C.

1.22 g of Benzoic acid was dissolved in 100 mL of ethyl alcohol and 1 g of CrO_3 was dissolved in 40 mL of water. A solution of benzoic acid was slowly added with stirring to a solution of CrO_3 . The resulting solution was refluxed for 30 min. The yellowish-green colored compound formed was separated by filtration. It was washed with 40% ethanol and dried in air. Yield 1.00 g (45%).

Results and Discussion

Elemental (C and H%) and ICP-OES analysis: The chromium-benzoic acid complexes (MRBT1) formed was colored insoluble in water and common organic solvent, but was found to be soluble in DMSO at room temperature. Analytical data found (Calcd.%) for $\text{C}_9\text{H}_{15}\text{CrO}_7$; C,38.74(37.63); H,4.96(5.23); Cr,19.14(18.12)

UV-Visible spectra of complex (Figure 1) shows two bands in the ranges of 470-500 and 525-560 nm which can be assigned respectively to $^4\text{A}_2\text{g} \rightarrow ^4\text{T}_{1\text{g}}$ and $^4\text{A}_2\text{g} \rightarrow ^4\text{T}_{2\text{g}}$ *d-d* transitions of octahedral chromium complexes¹⁵⁻¹⁶.

Electronic spectra

Figure 1. UV-Vis spectrum of MRBT1

The characteristic absorption peak of FTIR (Figure 2) at 1680 cm^{-1} and 1289 cm^{-1} is attributed to C=O of and C-O stretching frequency of carboxyl group of benzoic acid respectively. The broad band 2361 cm^{-1} is due to the hydrogen bonded ν (O-H) stretching vibration. Other vibrational frequency at 1420 cm^{-1} and 1526 cm^{-1} are assigned to ν (C-H) & ν (C=H) of aromatic ring respectively. Appearance of new bands in the region $600\text{--}700\text{ cm}^{-1}$ in the spectra of complex are attributed to ν (Cr-O) as seen in the spectra of metal complexes suggest that the product has been formed. Some weak bending modes are also observed at 1026 cm^{-1} due to (OCO) and 718 cm^{-1} due to (OCO)¹⁷.

The FAB mass spectra

MRBT1: $[\text{CrO}_2 (\text{C}_7\text{H}_5\text{O}_2) (\text{C}_2\text{H}_5\text{OH}) (\text{H}_2\text{O})_2]$. Anal.: found C, 38.74; H, 4.96; Cr, 19.14 Calcd. For $\text{C}_9\text{H}_{15}\text{Cr O}_7$: C, 37.63; H, 5.23; Cr, 18.12. Calculated mol. wt. of the complex: 287; Observed Molecular Ion Peak (m/z): 252. The difference in molecular weight may correspond to the loss of two molecules of water.

The results from FAB Mass spectra as shown in Figure 3, were inferred on the basis as followed by Baranwal *et al*¹⁸ on oxo-bridge multinuclear chromium assemblies like trinuclear complex $[\text{Cr}_3\text{O} (\text{acac})_3 (\text{OCCC}_{15}\text{H}_{31})_3]$ ¹⁸. The FAB mass data of complex MRBT1 are given in Table 1.

Figure 2. FTIR spectrum of the complex

Figure 3. FAB Mass spectrum of the complex

DSC analysis

The values of kinetic parameters - enthalpy (ΔH), activation energy (E_a), $\ln k_0$ and order of reaction (n) were obtained by DSC thermogram for the dehydration and decomposition of the dehydrated complexes. In complex, low value of activation energy of the exothermic change indicated lability of the complex. Comparing kinetic parameters of chromium-benzoic acid complex (decomposition temperature 162-253 °C, activation energy 64.73 kJ/ mole) with the kinetic parameter of some common energetic materials like, match stick

(decomposition temperature 175-280 °C activation energy 25-83 kcal/ mole), ammonium persulphate (decomposition temperature 275-355 °C activation energy 25-83 kcal/mole), Pyrotechnique chocolate bomb (decomposition temperature 645-665 °C, activation energy 75.38 kcal/mole), gun powder (decomposition temperature 280-430 °C, activation energy 24.05 kcal/mole), it could be inferred that the most of the chromium-benzoic acid complex prepared can be considered as energetic materials¹⁹.

Table 1. FAB mass data of complex MRBT1

Peak position	Expected fragmentation species	Calculated mass
252	CrO ₂ (C ₇ H ₅ O ₂) (C ₂ H ₅ OH)	251
216	Cr (C ₇ H ₅ O ₂) (C ₂ H ₅ OH)	219
202	Cr (C ₇ H ₅ O ₂) (C ₂ H ₅ -)	202
178	Cr (C ₇ H ₅ O ₂)	173
120	(C ₇ H ₅ O ₂)	121
105	(COC ₆ H ₅)	105
89	(CC ₆ H ₅)	89
77	(C ₆ H ₅)	77

Conclusion

Chromium complex *i.e.* [CrO₂ (C₇H₅O₂) (C₂H₅OH) (H₂O)₂] was prepared by using benzoic acid. The low value of activation energy of the exothermic change indicated the lability of the complex. Thus the kinetics and lability of the complex could be predicted from the DSC. It was observed that the complexes formed could be used as energetic material.

References

1. Ellis J E, Hentges S G, Kalina D G and Hagen G P, *J Organomet Chem.*, 1975, **97**, 79-93.
2. Rollinson C L, The Chemistry of Chromium, Molybdenum and Tungsten, Pergamon Press, 1973.
3. Wiberg K B, Oxidation by Chromic Acid and Chromyl Compounds, Part 4, Academic Press, New York, 1965.
4. Taube H, *Chem Rev.*, 1952, **50**(1), 59.
5. Lay P A and Levina A, *J Am Chem Soc.*, 1998, **120**, 6704-6714.
6. Templeton D M, Ariese F, Cornelis R, Danielsson, Lars-Goran, Muntau H, Van Leeuwen H P, Ryszard and Lobinski, *Pure Appl Chem.*, 2000, **72**, 1453-1470.
7. Signorella S, Quiros M, Palopoli C, Brondino C, Salas Peregrin J M, Quiros M and Sala L F, *Polyhedron*, 1998, **17**, 2739-2749.
8. Rollinson L, The Chemistry of Chromium, Molybdenum and Tungsten, Pergamon Press, 1973, pp 639-700
9. Goshe A J, Steele Ian M, Ceccarelli C; Rheingold A L and Bosnich B, *PNAS*, 2002, **99**(8), 4823-4829.
10. Ramasami T, Wharton R K and Sykes A G, *Inorg Chem.*, 1975, **14**, 359.
11. Krishnamoorthy C.R and Harris G M, *J Coord Chem.*, 1980, **10**, 55.
12. Anis S S, *Mat Chem Phys.*, 2001, **72**(1), 88-92.
13. Yormah T B R, Fode DV A and Kormoh M K, *AJST*, 2002, **3**(1), 108-112.
14. Gerdorn L E; Baenziger N A and Goff H.M, *Inorg Chem.*, 1981, **20**, 1606-1609.
15. Arenas J F and Marcos J I, *Spectrochim Acta Part A*, 1980, **36**, 1075.
16. Karmoh M K, *Afr J Sci Tech.*, 1995, **B7**(2), 74-76.
17. Bellamy L J, The Infrared Spectrum of Complex Molecules, Third Ed., Chapman and Hall Ltd, London, 1975.
18. Baranwal B P and Fatma T, *J Mol Struct.*, 2005, **750**, 75.
19. Mishra M K, Mishra N M, Singh R K and Mishra R, *J Inst Chemists(India)*, 2005, **77**, 173-177.