

An experimental evaluation of preparation of stock solutions and isolation of chelates from propyl and butyl alcohol.

Dr. Alka Rani

Associate Professor, Department of Chemistry, Hindu College Moradabad, UP

Abstract:

The paper here describes the source from which materials used in this investigation have been procured. The details of preparation and characterisation of certain starting materials commercially not available to the author are given. A brief description of various physicochemical methods employed for the characterisation and determination of the structure of the synthesized compound is presented as follows.

Keywords: propyl and butyl alcohol, stock solutions, chelates

I. Introduction.

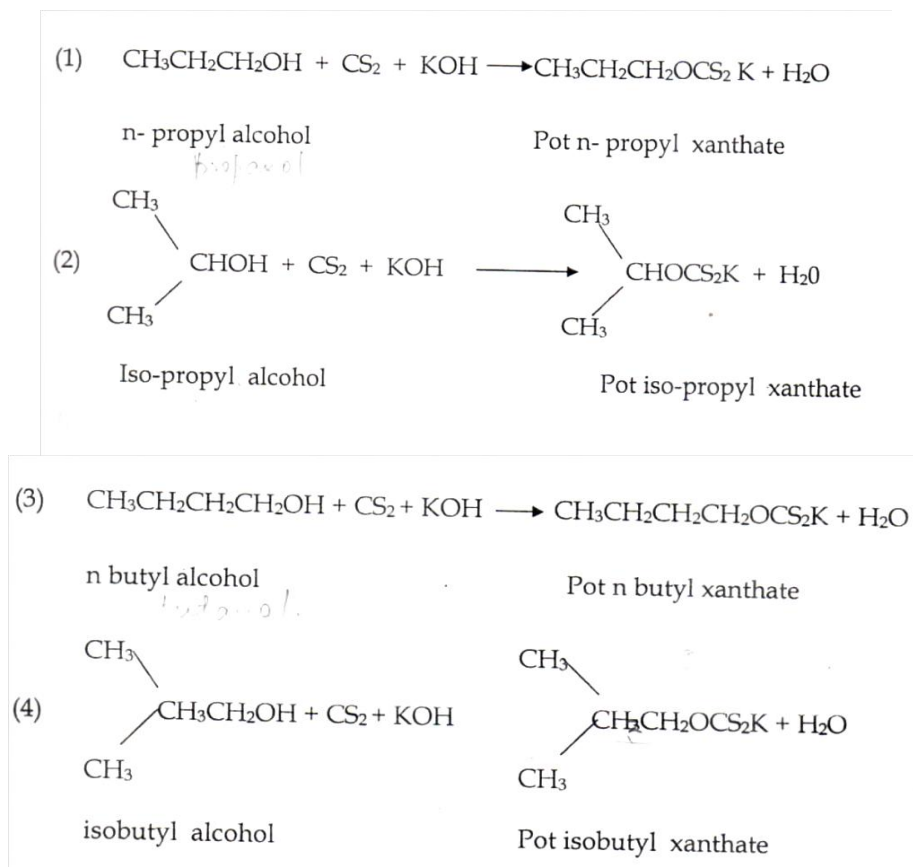
Xanthates are formed by the reaction between metal alkoxide (alkyl hydroxide), carbon disulphide and alcohol. Water is eliminated. Contacting an alkali metal hydroxide with a stoichiometric excess of carbon disulphide and of an aliphatic alcohol having two to six carbon atoms in the molecule, the carbon disulphide and alcohol being in the gas phase and in admixture with an inert gas, at a temperature in the range 50°C. To 120°C., thus bringing about a reaction between the alkali metal hydroxide, carbon disulphide and alcohol to form solid alkali metal xanthate and water vapour, and Separating the gaseous mixture of unreacted carbon disulphide, unreacted alcohol, by-product water vapour and inert gas from the solid alkali metal xanthate. Separating the gaseous mixture of unreacted carbon disulphide, unreacted alcohol, by-product water vapour and inert gas from the solid alkali metal xanthate.



The ratio of alcohol, carbon disulphide and alkali is 1:1:1. This is a nucleophilic addition of alkoxide ion to the CS₂ molecule." A variety of alcohol have been xanthated by the same manner the chemistry of xanthate ligand has been reviewed and studied extensively.

It is convenient to carry out the reaction in a moving bed reactor of inert particles such as glass spheres. the inert gas carrying the carbon disulphide and alcohol reactants being passed through the bed maintained at the desired temperature, while powdered alkali metal hydroxide is added continuously or stepwise to the bed. The unreacted carbon disulphide and unreacted alcohol together with the by-product water are carried in gaseous state from the reactor by the inert gas. It is of advantage to remove the water from the inert gas, add carbon disulphide and alcohol and recycle the gas through the reactor. The alkali metal xanthate remains in the reactor, or may be entrained in the gas stream and separated therefrom by means such as a cyclone. Since alkali metal xanthates are of lower density than corresponding alkali metal hydroxides it is possible to effect a separation of the xanthate product from the unreacted alkali metal hydroxide by entraining only the xanthate in the gas stream issuing from the reactor and then passing the gas stream through a cyclone where the xanthate is deposited.

Xanthates were prepared by dissolving potassium hydroxide in distilled water, adding benzene followed by respective alcohol (n-propanol, iso-propanol, n-butanol, isobutanol) with constant stirring and finally adding carbon disulphide very slowly and maintaining the temp. 40-5°C. (Benzene is toxic so, appropriate precaution is necessary). The molar ratio of KOH, alcohol, and CS₂ was 1+1+1. The solid product was filtered and washed with ether and dried under vacuum. The reaction was as follows:



PREPARATION OF STOCK SOLUTIONS:

- (1) REAGENT SOLUTION: Standard solution of reagents were prepared by dissolving a known weight of reagent in distilled water (.02 M/V) and diluted.
- (2) COPPER SULPHATE SOLUTION: 0.02 M Copper Sulphate (A.R.) was prepared by dissolving appropriate amount in distilled water and standardised.
- (4) COBALT SULPHATE HEPTA HYDRATE SOLUTION: .02 M solution of cobalt sulphate hepta hydrate (B.D.H.) was prepared in distilled water and standardised gravimetrically
- (5) NICKEL SULPHATE SOLUTION: 0.2 M solution of nickel sulphate (A.R) was prepared by dissolving appropriate amount in distilled water and standardised.
- (6) RUTHENIUM TRICHLORIDE SOLUTION: A stock solution of ruthenium trichloride (J.M.) was prepared by dissolving it in 2 ml. conc hydrochloric acid and diluting it to 100 ml. distilled water and standardised."
- (7) RHODIUM TRICHLORIDE SOLUTION: A stock solution of rhodium trichloride (J.M.) was prepared by dissolving it in 2 ml. con. hydrochloric acid and diluting it to 100 ml. by distilled water and standardised by established methods."
- (8) PALLADIUM CHLORIDE SOLUTION: The solution was prepared by dissolving 1 gm. palladium chloride (J.M.) in 100 ml. distilled water in presence of hydrochloric acid (2ml) and standardised. 2
- (9) IRIIDIUM TRICHLORIDE SOLUTION: Iridium trichloride (hydrated) (J.M.) solution was prepared by the standard method.
- (10) PLATINUM (IV) CHLORIDE SOLUTION: 1 gm. chloroplatinic acid (J.M.) was dissolved in 100 ml. distilled water containing 2 ml. dilute hydrochloric acid and standardised."

BUFFER SOLUTIONS:

The buffer solution solutions of different pH (2-6) were prepared by mixing, the appropriate vol of 0.5 M sodium acetate and 0.5 M acetic acid solution. The buffer solutions of higher pH were prepared by mixing 0.1 M acetic acid and .01 M NaOH solution's Buffer solution of (pH 9,10). were prepared by mixing appropriate amount of borax and hydrochloric acid.

ISOLATION OF CHELATES:

Metal Chelates of pot propyl xanthate pot isopropyl xanthate, pot butyl xanthate and pot butyl xanthate were isolated by mixing the aqueous solution of the metal ion with respective xanthate solution. The details of the isolation of complexes are as follows:

Fe (III) Complexes:

The equimolar solutions of Fe(III) and respective xanthate were mixed together in 1:4 ratio at pH 3-6. The brown complex so formed was filtered, washed with distilled water. The complex was then shaken with nbutanol and crystallised out by eveporating solvent in vaccum.

Co (III) Complex:

The green complex of cobalt (III) was isolated by mixing metal solution with respective xanthate solution in a stoichiometric ratio 1:4 at pH 4.0. The complex so formed was shaken with n-butanol and alcoholic layer removed. It was washed repeatedly with water and obtained by evaporation in vaccum.

Ni (II) Complexes:

The yellow complex was isolated by mixing nickel sulphate solution with xanthate solution in a stoichiometric ration 1:3 (ligand was in slight excess) at pH 5. The complex so formed was extracted with n-butanol and the alcoholic layer removed. It was washed with distilled water and obtained by evaporation in vaccum.

Cu (II) Complexes:

The yellow complex was isolated by mixing the aqueous solution of copper sulphate and respective xanthate solution in a stoichiometric ratio 1:4 at pH 5. The precipitate was filtered, washed with distilled water and then shaken with n-butanol. The complexes obtained by evaporation under vaccum.

Ru (III) Complexes:

The brown complex was isolated by mixing aqueous solution of ruthenium trichloride solution and respective xanthate solution in a stoichiometric ratio 1:4 at pH 4. The complex so formed was shaken with n-butanol and alcoholic layer removed. The organic layer was washed repeatedly with distilled water and obtained by evaporation in vaccum.

Rh(III) Complexes:

The pink complexes was isolated by mixing rhodium trichloride solution and respective xanthate solution in stoichiometric ratio 1:4 (reagent in slight excess) at the pH 4.5. The complexes was shaken with n-butanol and alcoholic layer removed and washed with distilled water. The metal xanthate was obtained by evaporation in vaccum.

Pd (II) Complexes:

The yellow coloured complexes was isolated by the interaction of palladium chloride solution and respective xanthate solution in a the stoichiometric ratio 1:3 at the pH 3.5. The complex was shaken with n-butanol, washed with distilled water repeatedly. The metal xanthate was isolated by evaporating the solvent in vaccum.

Ir(III) Complexes:

The yellow complexes was formed by mixing the iridium trichloride solution with respective reagent solution in a stoichiometric ratio 1:3 in aqueous medium at pH=7.5. The complex so formed was shaken with n-butanol. After separating the organic layer it was washed with distilled water. The complex was isolated by evaporation in vaccum.

Pt (IV) Complexes:

It was isolated by mixing the chloroplatinic acid solution with respective xanthate in aqueous medium at pH 4.5. The precipitate was filtered, washed repeatedly with distilled water and dried under vaccum at 80°C.

Metal Xanthates of Propyl and Iso-propyl Alcohol

S.No.	Metal ion	Formula of complex	Abriviation	Colour	pH	Stability
1.	Fe (III)	$\text{Fe}(\text{C}_4\text{H}_7\text{OS}_2)_3$	$\text{Fe}(\text{PX})_3$	Brown	3-5	Unstable
	"	$\text{Fe}(\text{C}_4\text{H}_7\text{OS}_2)_3$	$\overset{ }{\text{Fe}}(\text{PX})_3$	Brown	3-5	Unstable
2.	Co (II)	$\text{Co}(\text{C}_4\text{H}_7\text{OS}_2)_3$	$\text{Co}(\text{PX})_3$	Dar Green	3.5-6.5	Unstable
	"	$\text{Co}(\text{C}_4\text{H}_7\text{OS}_2)_2$	$\overset{ }{\text{Co}}(\text{PX})_3$	Green	3.5-6.5	Unstable
3.	Ni (II)	$\text{Ni}(\text{C}_4\text{H}_7\text{OS}_2)_3$	$\text{Ni}(\text{PX})_2$	Yellow	4.5-6.5	Stable
	"	$\text{Ni}(\text{C}_4\text{H}_7\text{OS}_2)_3$	$\overset{ }{\text{Ni}}(\text{PX})_2$	Yellow	4.5-6.5	Stable
4.	Cu (II)	$\text{Cu}(\text{C}_4\text{H}_7\text{OS}_2)_2$	$\text{Cu}(\text{PX})_2$	Light	4-6	Stable
	"	$\text{Cu}(\text{C}_4\text{H}_7\text{OS}_2)_2$	$\overset{ }{\text{Cu}}(\text{PX})_2$	Yellow	4-6	Stable
				Light Yellow		
5.	Ru (III)	$\text{Ru}(\text{C}_4\text{H}_7\text{OS}_2)_3$	$\text{Ru}(\text{PX})_3$	Brown	4-6	Unstable
	"	$\text{Ru}(\text{C}_4\text{H}_7\text{OS}_2)_3$	$\overset{ }{\text{Ru}}(\text{PX})_3$	Brown	4-6	Unstable
6.	Rh (III)	$\text{Rh}(\text{C}_4\text{H}_7\text{OS}_2)_3$	$\text{Rh}(\text{PX})_3$	Light	4.5-7	Unstable
	"	$\text{Rh}(\text{C}_4\text{H}_7\text{OS}_2)_3$	$\text{Rh}(\text{IPX})_3$	Orange	4.5-7	Unstable
				Light Orange		
7.	Pd (II)	$\text{Pd}(\text{C}_4\text{H}_7\text{OS}_2)_2$	$\text{Pd}(\text{PX})_2$	Yellow	3-7	Unstable
	"	$\text{Pd}(\text{C}_4\text{H}_7\text{OS}_2)_2$	$\overset{ }{\text{Pd}}(\text{PX})_2$	Yellow	3-7	Unstable
8.	Ir (III)	$\text{Ir}(\text{C}_4\text{H}_7\text{OS}_2)_3$	$\text{Ir}(\text{PX})_3$	Light	5-8	Unstable
	"	$\text{Ir}(\text{C}_4\text{H}_7\text{OS}_2)_3$	$\text{Ir}(\text{IPX})_3$	Brown	5-8	Unstable
				Light Brown		
9.	Pt (IV)	$\text{PtCl}(\text{C}_4\text{H}_7\text{OS}_2)_3$	$\text{PtCl}(\text{PX})_3$	Brown	4-5.5	Unstable
	"	$\text{PtCl}(\text{C}_4\text{H}_7\text{OS}_2)_3$	$\text{PtCl}(\text{IPX})_3$	Brown	4-5.5	Unstable

Metal Xanthates of Butyl and Iso-butyl Alcohol

S.No.	Metal ion	Formula of complex	Abriviation	Colour	pH	Stability
1.	Fe (III)	Fe(C ₅ H ₉ OS ₂) ₃	Fe(BX) ₃	Brown	3-5	Unstable
	"	Fe(C ₅ H ₉ OS ₂) ₃	Fe(IBX) ₃	Brown	3-5	Unstable
2.	Co (III)	Co(C ₅ H ₉ OS ₂) ₃	Co(BX) ₃	Dark Green	3.5-6.5	Unstable
	"	Co(C ₅ H ₉ OS ₂) ₃	Co(IBX) ₃	Green	3.5-6.5	Unstable
3.	Ni (III)	Ni(C ₅ H ₉ OS ₂) ₃	Ni(BX) ₃	Yellow	4-6	Stable
	"	Ni(C ₅ H ₉ OS ₂) ₃	Ni(IBX) ₃	Yellow	4-6	Stable ✓
4.	Cu (II)	Cu(C ₅ H ₉ OS ₂) ₂	Cu(BX) ₂	Light	4-6	Stable
				Yellow	4-6	Stable ✓
		Cu(C ₅ H ₉ OS ₂) ₂	Cu(IPX) ₂	Light		
				Yellow		
5.	Ru (III)	Ru(C ₅ H ₉ OS ₂) ₃	Ru(PX) ₃	Brown	4.5-7	Stable
	"	Ru(C ₅ H ₉ OS ₂) ₃	Ru(IBX) ₃	Brown	4.5-7	Stable
6.	Rh (III)	Rh(C ₅ H ₉ OS ₂) ₃	Rh(BX) ₃	Light Orange	4.5-7	Stable
	"	Rh(C ₅ H ₉ OS ₂) ₃	Rh(IPX) ₃	Light Orange	4.5-7	Stable
7.	Pd (II)	Pd(C ₅ H ₉ OS ₂) ₂	Pd(BX) ₃	Yellow	3-7	Stable
	"	Pd(C ₅ H ₉ OS ₂) ₂	Pd(IBX) ₃	Yellow	3-7	Stable
8.	Ir (IV)	Ir(C ₅ H ₇ OS ₂) ₃	Ir(BX) ₃	Yellowish	5-8	Stable
				Brown	5-8	Stable
		Ir(C ₅ H ₇ OS ₂) ₃	Ir(IBX) ₃	Yellowish		
9.	Pt (IV)	PtCl(C ₅ H ₉ OS ₂) ₃	PtCl(BX) ₃	Brown	4-5.5	Stable
	"	PtCl(C ₅ H ₉ OS ₂) ₃	PtCl(IBX) ₃	Brown	4-5.5	Stable

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