

# Reactor Design for the Synthesis of Cobalt(II/III) Carboxylate Redox Couple and its Optimization

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**Abstract.** In the present study the method for the preparation of redox couple of cobalt Co(II)/Co(III) has been developed at different reaction conditions (time, initial concentration of Co(II) and potassium chlorate), using glacial acetic acid as a solvent, redox couple was generated in different concentrations by varying the amount of potassium chlorate. An experimental setup was organized and jacketed glass reaction vessel was designed to carry out such reaction. Such redox couple has widespread application in the production of hydroperoxides which is subsequently used in catalytic oxidation of hydrocarbons. At the time of titration the pH of the reaction is essentially maintained by the addition of sodium acetate solution to avoid hindrance of chloride ions which are present in the system as a reaction product.

**Keywords:** oxidation, reduction, cobalt, transition metal, catalysis

## Introduction

The oxidation catalysis is one of the most important processes in industrial chemistry (Cornils *et al.*, 2018; Sies, 2017; Vasilios *et al.*, 2016; Jan and Stefano, 2015; Mario and Oxana, 2013; Howard, 2000) which have several research papers and patents give evidence to the fact that the role of catalysis in exploration of new industrial processes has been phenomenal. Redox reactions have extensively been employed in building of new catalytic processes. Simultaneously, these reactions have widely been studied and investigated in research laboratories. Catalytic processes usually require transition metal ions and their complexes as oxidation catalyst to produce desired product with high selectivity and yield (Gorlin *et al.*, 2017; Stanley, 2017; Zheng *et al.*, 2017; Punniyamurthy *et al.*, 2005).

Transition metals ions and their complexes have been established to use as an efficient oxidation catalyst when used in homogenous reaction system (Breuil *et al.*, 2015; Catherine and Kogularamanan, 2015; Janes, 2015; Slone *et al.*, 1999; Couty and Hall, 1996). Among hundreds of transition metal complexes, cobalt ions Co(II) and Co(III) and its complexes and redox couple Co(II)/Co(III) has widely been studied during last few years (Li and Ackermann, 2015; Zhang *et al.*, 2014; Westerhaus *et al.*, 2013) low valent Co(II) is used for C-H transformations and high valent Co(III) is employed as C-H functionalization. Their redox couple is efficiently

used in hydrosilylation of alkenes (Hui *et al.*, 2016; Hui *et al.*, 2016; Jie, 2016; Ruhuai *et al.*, 2016; Ruhuai *et al.*, 2016; Zell *et al.*, 2015; Li and Ackermann, 2015; Parthasarathy and Chien-Hong, 2015). This couple is also employed as oxidation catalyst in the production of hydroperoxides which is subsequently used in petroleum industry (Khan and Naqvi, 2021).

## Materials and Methods

**Glass ware.** All experiments were performed using standard laboratory class A Pyrex volumetric glassware.

**Chemicals.** Cobalt(II) acetate tetrahydrate pro-analysis grade, potassium iodide extra pure, sodium thiosulphate were supplied by Merck, potassium chlorate AnalaR Grade by BDH, potassium chloride by Baker, J.T., sodium carbonate extra pure by Scharlau, glacial acetic acid and propanol were supplied by Sigma Aldrich. All chemicals were prepared in triple distilled water except Cobalt(II) acetate which was prepared in glacial acetic acid.

**Experimental setup.** Experimental setup is schematically described in Fig. 1.

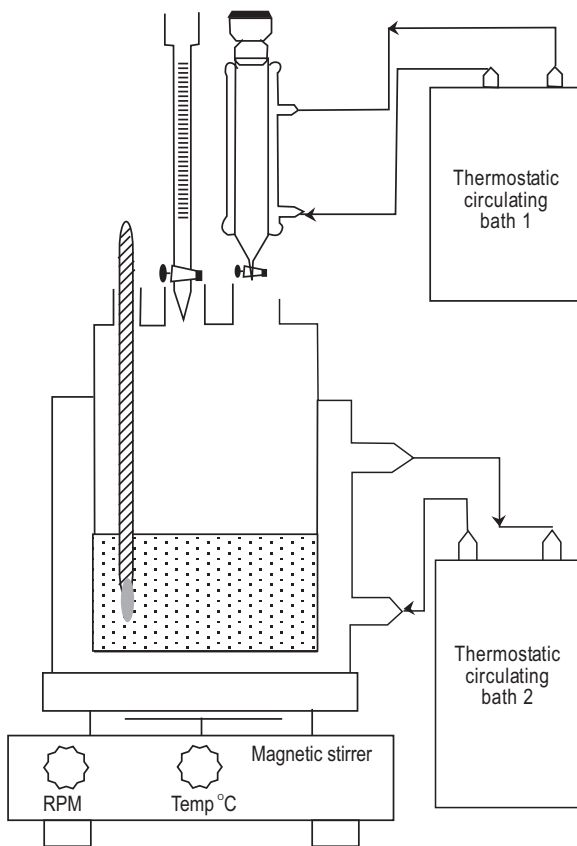
**Designing and fabrication of jacketed reaction vessel.** A 50 mL jacketed glass reaction vessel has indigenously been designed and fabricated to study the electron transfer reaction between Cobalt(II) and chlorate ions. Vessel is designed with the provision of three necks. Thermometer is placed with stopcock in first neck. Burette containing sodium thiosulfate for titration is

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allowed to enter from second neck and reaction quenching reagent is transferred from jacketed column, which is adjusted at the third neck of the reactor.

Jacketed reaction vessel is placed over magnetic stirrer for providing uniform stirring by means of magnetic follower which is rotating inside the reaction vessel. Automatic pipettes are employed for the transfer of reactants into the reactor. All the reactions are carried out at constant temperature, for this purpose the outer jacket is connected with thermostatic bath 1 to provide counter current flow of water at required temperature. The reaction quenching jacketed column is also connected with another thermostatic bath 2.

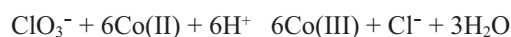
**Preparation of reaction quenching reagent.** At specified time, reaction between cobalt(II) and potassium chlorate is quenched with specially prepared reagent. This reaction is highly pH dependent favoured by low pH. This adjustment of pH is going to be achieved by dissolving sodium carbonate in aqueous acetic acid



**Fig. 1.** Schematic diagram of jacketed glass reaction vessel.

solution heating is provided to expel carbon dioxide, resulting solution contains sodium acetate buffer. Calculated amount of potassium iodide is also introduced into the reagent. Reaction is instantaneously quenched by transferring the quenching reagent directly into the reactor from jacketed column at specified time. The pH of reagent is going to facilitate iodine liberation which is then titrated against standardized sodium thiosulphate and turns greenish colour of cobalt(III) to vibrant purple.

**Production of redox couple.** Kinetic analysis of the reaction between potassium chlorate (used as an oxidizing agent) and cobalt(II) acetate tetra hydrate follows a simple and single phase ionic reaction:



This reaction generates a redox couple of Co(II) / Co(III) usually named as partially oxidized catalyst (POC), provides a method for the preparation and purification of Co(III) ions.

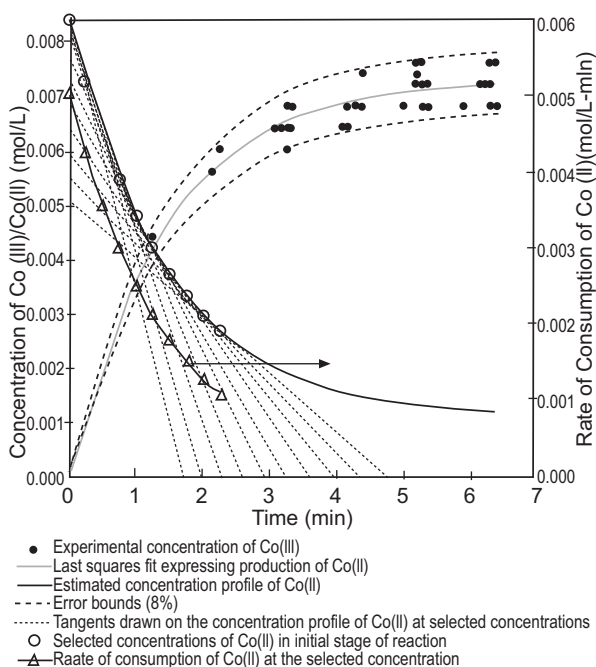
**Design of experiment (DOE).** A central composite design (CCD) of experiment (DOE) has been constructed to vary the concentrations of Co(II) and chlorate in a systematic way during kinetic experiments. It was necessary to carefully study the effects of the concentration of reactants upon the concentration of Co(III) and the rate of production in time domain during reaction system design of experiment (DOE) was introduced at the early stage of experimental work for the exact determination of redox couple of Co(II)/Co(III). This DOE gives simple and easy understanding of the reaction pattern. All the experiments are designed on the basis of central composite design which incorporates partial factorial design, star design and replication.

This DOE not only used for the development of analytical technique for the estimation of redox couple but also provide reduced number of experiments with the possibilities to evaluate interactions among variables. These techniques also enable the selection of optimal experimental conditions, helping to avoid trivial mistakes during optimization.

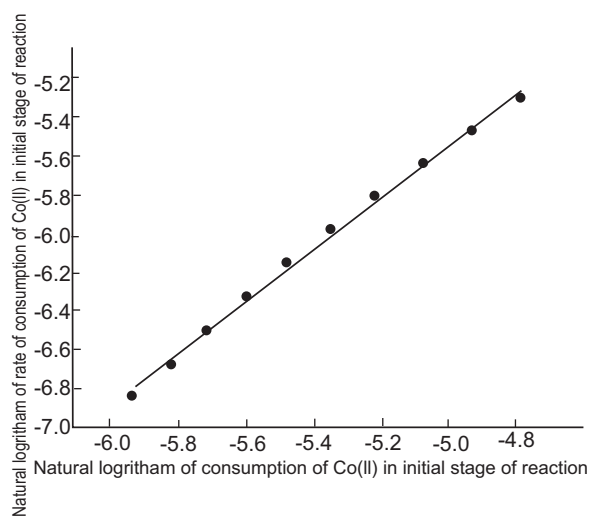
## Results and Discussion

A significant part of this academic research has been dealt with the collection of experimental kinetic data during the oxidative conversion of Co(II) to Co(III) using chlorate as an oxidizing agent in acetic acid solution. Such kinetic data consist of the concentrations of Co(III) in the time domain and the corresponding

rates of production there of as function of temperature and initial concentrations of the reactants.

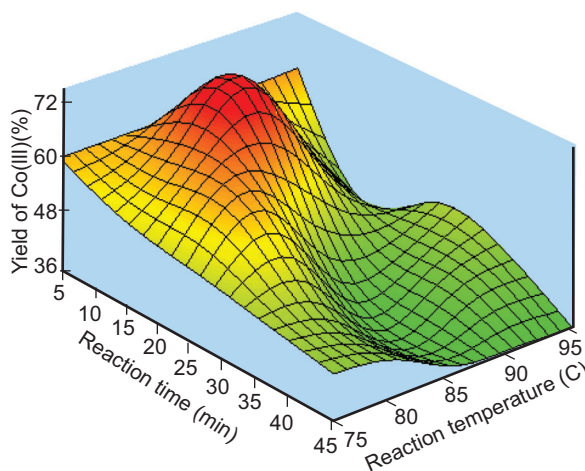


**Fig. 2.** Kinetic analyses of the experimental kinetic data, reaction conditions:  $T = 85\text{ }^{\circ}\text{C}$ ,  $C_{\text{Co(II)}} = 8.3979 \times 10^{-3}\text{ mol/L}$ ,  $C_{\text{H}_2\text{O}} = 0.5\text{ mol/L}$ ,  $V_R = 30\text{ mL}$ .



**Fig. 3.** Linear relation ( $R^2 = 0.9971$ ) between initial rate and concentration of Co(II), reaction conditions:  $T = 85\text{ }^{\circ}\text{C}$ ,  $C_{\text{Co(II)}} = 8.3979 \times 10^{-3}\text{ mol/L}$ ,  $C_{\text{H}_2\text{O}} = 0.5\text{ mol/L}$ ,  $V_R = 30\text{ mL}$ .

The reaction was studied under time domain for 45 min. The data was collected at 75, 80, 85, 90 and 95  $^{\circ}\text{C}$ . 3-D surface plot (Fig. 4) shows the response of Co(III) yield against time and temperature. The red peak shows the maximum conversion of Co(II) into Co(III). This peak is observed at 85  $^{\circ}\text{C}$  maximum yield is obtained during first 10 min. This method gives the flexibility of generating of redox couple Co(II)/Co(III) of different compositions. In (Fig. 2) differential kinetic analyses is used for fitting the kinetic data. Concentration of redox couple and rate of consumption of Co(II) is then plotted against time. Rate of conversion of Co(II) to Co(III) is calculated by drawing tangents at selected concentrations. In (Fig. 3) plot between natural logarithm of rates against natural logarithm of concentrations of Co(II) follows the equation of straight line, slope gives the order of reaction and rate constant is obtained from y-intercept.



**Fig. 4.** Response surface shows the yield of Co(III) with respect to time and temperature.

Based on the present research work it is concluded that a straight forward and ample technique has been established for the production of redox couple which is used as a potent catalyst in the formation of hydro peroxides which is a well known intermediate in homogenous catalytic oxidation of hydrocarbons. This technique also provides a sophisticated and reliable method for the determination of Co(III) ions.

**Conclusion**

It is also concluded that the kinetics of above reaction has been keenly observed and studied and a compre-

hensive method is developed to get the overall order of the reaction with respect to time. Present research has pointed out the necessary requirement for a good reaction medium and recommended the use of glacial acetic acid.

**Conflict of Interest.** The authors declare they have no conflict of interest.

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