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KINETICS AND MECHANISM OF OXIDATION OF (E)-1,5-DIPHENYLCARBAZONE COBALT(II) [Co^{II}ArNNCONNAr] BY N-CHLORO-p-TOLUENESULPHONAMIDE

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ABSTRACT

The (E)-1,5-diphenylcarbazone cobalt(II) [CoIIArNNCONNAr] was synthesized by addition of (E)-1,5-diphenylcarbazone 2[ArNHNHCO=NAr] to cobalt diacetate with reflex to 24 hrs. The kinetics of oxidation of Cobalt(II) of [Co^{II}ArNNCONNAr] by N-chloro-p-toluenesulphonamide Chloramine-T to Cobalt(III) have been investigated at 25 °C. The reaction is consecutive first order with respect to both [Cobalt(II)Complex] and Chloramine-T. The order of the reaction in [H^+] was fractional and the rate constant was unaffected by the ionic strength. Rate law of the suggested mechanism including all factors affecting the rate of reaction was derived.

Keywords: (E)-1,5-diphenylcarbazone, Cobalt diacetate, N-chloro-p-toluenesulphonamide Chloramine-T, kinetics of oxidation.

INTRODUCTION

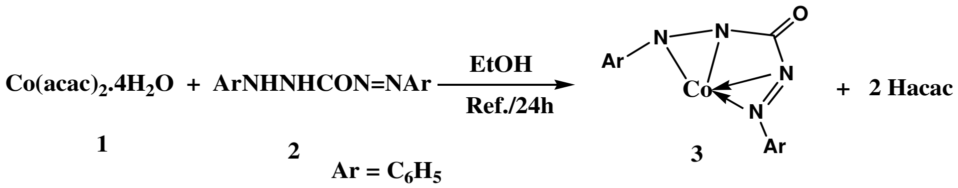
The diverse nature of the chemistry of organic-N-halogen reagents[1] is due to their ability to act a sours of halogenium cations , hypohalite species and nitrogen anions which act both as bases and nucleophiles under different condition, these N-halo-compounds also reacted with olefins to add halide to the double bond or act are a source of hypohalous acids in aqueous solution.[2] The N-halo compounds have been used successfully not only as halogenating agents, but several of them have been found to be effective agents for oxidations and dehydrogenation[3-4] but its use for oxidizing inorganic compounds has received very little attention.[5-12] N-bromosuccinmide (NBrS) has been used to oxidize chromium (III) complexes [Cr^{III}(HEDTA)].[11-13] It was assumed that electron transfer takes place through an inner-sphere mechanism with the hydroxyl ligand of chromium(III) complex bridging the two reactants. Recently the oxidation of [Co^{III} (EDTA)]$^{-2}$,[9] and [Co^{II} (HEDTA)]$^{-}$,[10] by N-halosuccinimide in aqueous solution were studied, and these reaction were found to proceed via an inner-sphere mechanism. The kinetics and mechanism of oxidation of Cr^{III} dipicolinic acid complex by N-halo succinimide were investigated. [15-16] Chloramine-T is the sodium salt of the acid N-chloro-p-toluene sulphonimide was used successfully as an oxidimetric titrant in aqueous solution.[15-21]

In this paper the kinetics of oxidation of [Co^{II}ArNNCONNAr] by Chloramine-T studied in order to assume the effect of complex formation on the resistance of cobalt(II) towards oxidation.

EXPERIMENTAL

The synthesis of **(3)** was achieved by slow addition of a solution of the (E)-1,5-diphenylcarbazone(2) in 150 ml of EtOH to a stoichiometric amount of [$Co(acac)_2.4H_2O$] in 150 ml of EtOH at room temperature, then was heated up to reflex for 24 hours resulted of [Co^{II}ArNNCONNAr](3) as pink color (Scheme-1).

The UV-visible absorption spectra of oxidation of [Co^{II}ArNNCONNAr] by Choramine-T wear recorded on shimadzu UV-spectrophotometer, UV-spectra for the reaction between cobalt(II) diacetate and [ArNNCONNAr] are shown in the following Scheme-1.



Scheme-1

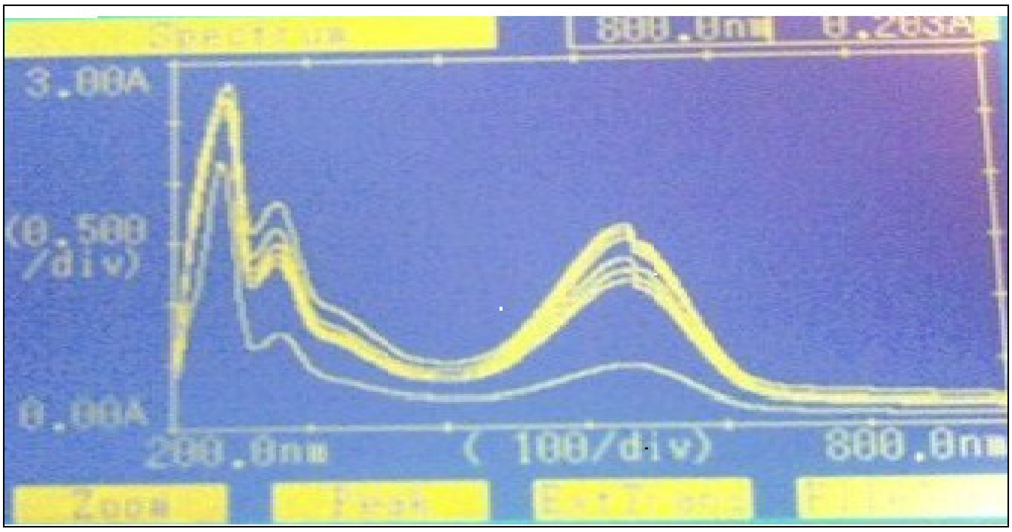


Fig.-1: UV. Spectra for the reaction between [Co(acac)$_2$] and [ArNNCONNAr]

Organic test for presence of the acetate in [Co^{II}ArNNCONNAr] have been investigation in both the formed precipitation and the filtered solvent. The test showed that, acetate is available in solvent by adding $AgNO_3$ and also by adding dilute sulphuric acid which they gave precipitation with the solvent.

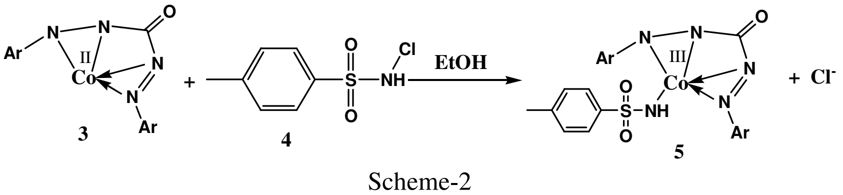
Consecutive first order reaction was maintained in all runs by the presence of a large excess of chloramine-T. The ionic strength was kept constant by addition of NaCl. The pH profile of reaction mixture was found to be constant during the reaction run.

The dark pink color of [Co^{II}ArNNCONNAr] in ethanol during oxidation turned gradually open green to colorless at 533nm and the wave length at 280nm shift little to 284nm. The presence of isosbestic point at 300nm in the adsorption spectra indicated the existence of two species at equilibrium.

Known excess of ([Choramine-T] 10 fold>) was added to [Co^{II}complex] 24hr after the onset of the reaction, the number of moles of cobalt(II)complex was calculated using iodometric titration method .

RESULTS AND DISCUSSION

The overall stoichiometry of reaction was characterized as one mole of chloroamine-T (4) per mole of cobalt (II) complex (3) as followed Scheme-2:



Scheme-2

Oxidation of cobalt(II) complex (3) over pH range (5.5- 6.6) was studied at ionic strength (0.1- 0.5 M) using different concentrations of chloramines-T (4) and cobalt(II) complex . (Figure 2) shows the oxidation process of Co^{II} complex by chloramine-T at interval time. The graph shows the normal curve of decreasing the concentration of Co^{II} Complex.

Plots of [ln (A∞-At)] versus time , where A∞ and At are absorbance at infinity and t time, respectively showed marked deviation from linearity and give good guide that it's the reaction is complex and the rate law of simple first order dose not obey this application others applications of zero and second and third order were tested and showed deviation again .The results were obey consecutive first order reaction , two steps of reaction were noticed . The first step was fast followed by slow second step Fig.- 3 and 4.

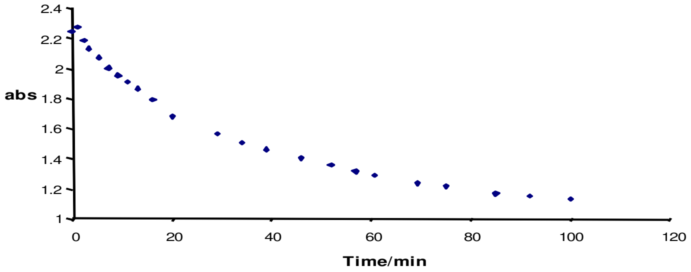


Fig.-2: Shows the decrease in concentration of [Co^{II}ArNNCONNAr] oxidized by Chloroamine-T with time

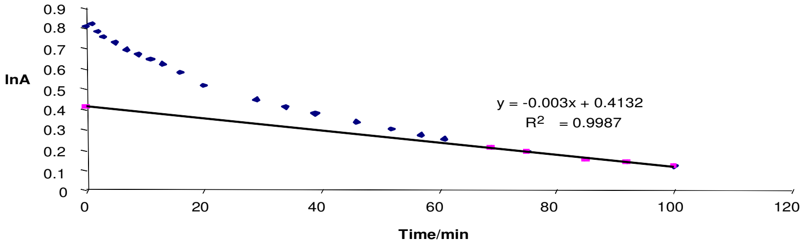


Fig.-3: Shows the second step of the consecutive first order reaction of [Co^{II}ArNNCONNAr] with chloroamine-T

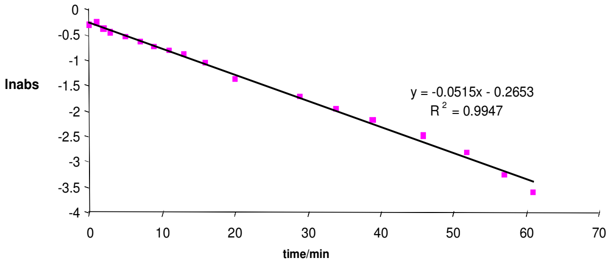


Fig.-4: Shows the first step of the consecutive first order reaction of [Co^{II}ArNNCONNAr] with Chloromine-T

The rate constants of first and second steps are shown in table (1), The results (table 1) show that k (rate constants) were unaffected when concentration of cobalt(II)complex was varied at constant chloroamine-T concentration indicating, First order dependence on the complex concentration .

Table-1: Kinetics data for the oxidation of Co(II)Complex by Chloroamine-T at 25°C, [Chloroamine-T]= 0.06M

Conc.Of [Co^{II}ArNNCONNAr] Complex	k_1/ min^{-1}	k_2/min^{-1}
0.004	0.0899	0.00366
0.006	0.0902	0.00370
0.008	0.0945	0.00405
0.010	0.0900	0.00330

Table-2 shows that the rate of reaction increases with increasing concentration of Chloroamine-T at constant [H^+] and ionic strength , plotting these results by using differential methods the order was found to be the first (Fig 5) and the overall the reaction will be second order.

Table-2: Kinetics data for the oxidation of Co(II)Complex by chloroamine-T at 25°C, of [Co^{II}ArNNCONNAr]= 0.06M

Conc. Of Chloroamine-T	k_1/ min^{-1}	k_2/min^{-1}
0.01	0.0082	0.00094
0.02	0.0132	0.00188
0.04	0.0515	0.00300
0.06	0.0902	0.00405

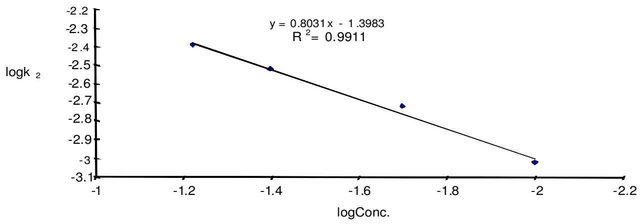


Fig.-5: Plot of $\log k_2$ against log(conc.) of Chloroamine-T for the oxidation reaction of [Co^{II}ArNNCONNAr]

Plots of log k_2 versus pH's, Fig.-6 shows that the rate of reaction increases with increasing pH (Table- 3). The order of reaction in [H^+] was fractional, However (k) was unaffected by ionic strength since the reaction is taking place between charged and uncharged species .

Table-3: Kinetics data for the oxidation of Co(II)Complex by Chloroamine-T at 25°C and at different pH,s [Chloroamine-T] = 0.06M , [Co^{II}ArNNCONNAr]= 0.08M

pH	k_1/ min^{-1}	k_2/min^{-1}
5.5	0.0945	0.00405
5.8	0.1101	0.00570
6.2	0.1283	0.00830
6.6	0.1354	0.0108

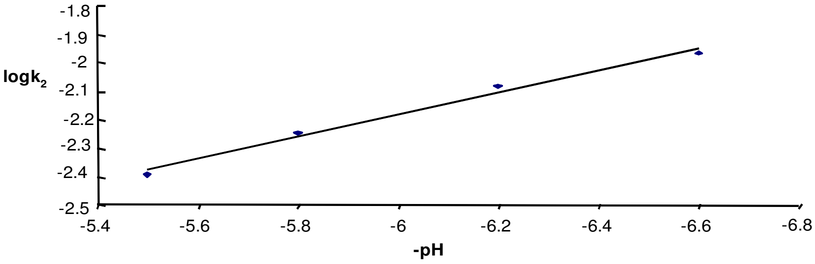


Fig.-6: Plot of ($\log k_2$) against (-pH) for the oxidation of [Co^{II}ArNNCONNAr] by Chloroamine-T

The following scheme can be proposed for the oxidation of [Co^{II}ArNNCONNAr] by Chloroamine-T

$$RNCl^- (4) + H^+ \leftrightarrow RNHCl$$
$$RNHCl + \text{cobalt(II)complex } (3) \leftrightarrow X$$
$$X \rightarrow \text{Product } (5) \quad \text{(slow and rate determing step)}$$

Scheme-3

According to the above (Scheme-3) the total concentration of Chloroamine-T equal to [$RNCl^-$][$RNHCl^-$] and X , the rate law can be derived -

$$-d[\text{Chloroamine-T}] / dt =$$
$$\{ K_3 K_1K_2[\text{chloroamine-T}][\text{Cobalt Complex}][H^+]\} / \{1+K_1 [H^+]+K_1K_2[\text{Chloroamine-T}][H^+]\}$$

CONCLUSION

The reaction is a complex and the results were obtained follows consecutive first order with two steps of reaction, fast step reaction followed by slow step reaction, (rate determining step).

The rates constants were unaffected by the increase of ionic strength , this mean the formed complex is neutral, and no effect of the charged on the reaction. The complex formation depends on the concentration of chloramine-T.

Increasing concentration of chloramines-T leads to increase the rate of complex formation and the equivalent state of CoII will be changed to the CoIII, also the new complex formation CoIII complex is depending on the concentration of the CoII complex it self. The effect of pH was clear even within small change of pH, since, the availability of proton give us the free acid of chloramines-T which is more active toward oxidation of Co(II)complex and taking electron from cobalt.

The oxidized cobalt(II)complex by choramine-T to cobalt(III)complex has the over all stoichiometry of reaction as one mole of chloramineT to one mole of cobalt(II)complex. In general the rate law deduced shows that the reaction depends on the concentration of chloramine-T and complex and hydrogen ions.

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