# Electrochemical Behaviour of 4-Tertbutylcyclohexanone Semicarbazone and its Co(II) Complex

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**Abstract**

The electrochemical behaviour of 4-tertbutylcyclohexanone semicarbazone (TBCHSC) and its Co(II) complex was investigated by a glassy carbon electrode, cyclic voltammetry technique. Semicarbazone synthesized from the condensation of 4-tertbutylcyclohexanone and semicarbazide hydrochloride (1:1 molar ratio) was further treated with cobalt(II) acetate (2:1 molar ratio), to form the Co(II)-semicarbazone complex. The semicarbazone was studied in buffer solutions (Britton-Robinson universal buffer and phosphate buffer), with a pH in the range of 3 to 11. The reduction process was found to be irreversible and diffusion controlled, for both semicarbazone and its Co(II) complex. The effects of change on the sweep rate, concentration, pH and solvent were evaluated. The semicarbazone reduction mechanism was suggested on the basis of the obtained results. Kinetic parameters, such as charge transfer coefficient ($\alpha_n$), diffusion coefficient ($D_0^{1/2}$), and rate constant ($k^\circ_{f,h}$), were calculated from cyclic voltammetric measurements. Semicarbazone and its Co(II) complex were tested against bacterial and fungal species. The metal complex had higher activity than the free ligand.

*Keywords:* 4-tertbutylcyclohexanone semicarbazone, Co(II) complex, cyclic voltammetry, kinetic parameters, antimicrobial activities.

**Introduction**

The electrochemical technique is one of the greener, more economic, specific and selective approaches [1-2]. Electrochemical reactions are most often studied with standard three electrode techniques, such as cyclic voltammetry, polarography, etc. Cyclic voltammetry has gained extensive use in providing information about the reduction, oxidation and formation of intermediates, and also on the reversible nature of the electrode transfer processes. Cyclic voltammograms provide valuable information regarding electrode processes [3-4]. Semicarbazones are amongst the most widely studied nitrogen and oxygen/sulphur donor ligands. They have been a subject of interest in recent decades, due to their biological activity, good complexing properties and analytical applications [5-9]. Systematic perusal of earlier literature reveals that,

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in spite of the variegated importance associated to semicarbazones compounds, relatively few reports exist on their electrochemical behaviour [10-16]. Hence, efforts have been made to undertake cyclic voltammetric studies on 4-tertbutylcyclohexanone semicarbazone (TBCHSC). In this process, TBCHSC's imine group (-C=N-) has been reduced into the amine group (-CH-NH$_2$), in a protic solvent such as CH$_3$OH, by the transfer of 4e$^-$ [17-18]. In this paper synthesis, spectral analysis, cyclic voltammetric and antimicrobial activity studies of TBCHSC and its Co(II) complex have been carried out.

**Experimental**
All employed chemicals were of analytical grade. Methanol was freshly distilled prior to use. IR spectra were acquired using an A-8400 S, Shimadzu Spectrophotometer model, and KBr optics.

*Ligand synthesis*
Semicarbazone was synthesized mixing 4-tertbutylcyclohexanone, semicarbazide hydrochloride and sodium acetate trihydrated (equimolar ratio) in methanol (Scheme I). TBCHSC was synthesized by the standard procedure, as available in the literature [19-20].
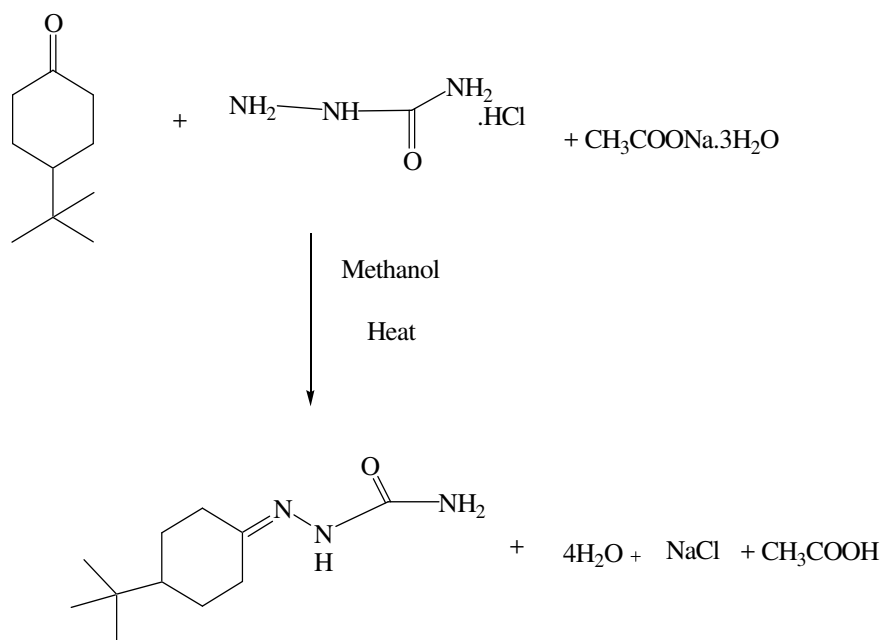


**Scheme I.** Synthesis of 4-tertbutylcyclohexanone semicarbazone.

*Synthesis of the complex*
The TBCHSC cobalt complex was synthesized in a methanolic solution of TBCHSC, by mixing it with a methanolic solution of Co(II) acetate (2:1 molar ratio), refluxing the mixture for 5 hours, and drying it in vacuum over fused CaCl2 (Scheme II).
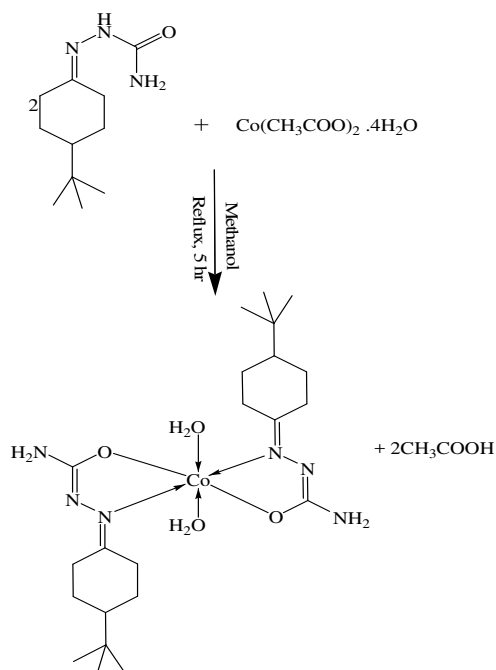
**Scheme II.** Synthesis of the TBCHSC Co(II) complex.

### Cyclic voltammetric study of TBCHSC and its Co(II) complex

Semicarbazone's stock solutions ($1 \times 10^{-2}$ M) in dimethylformamide (AR) and methanol were prepared. Britton-Robinson and phosphate buffers were prepared in double distilled water. In the typical cyclic voltammetric experiment, a reaction mixture consists of a compound solution, solvent (the minimum volume necessary to keep the compound in the solution) and a buffer solution (keeping the overall volume constant at 10 mL).

The stock solution of the complex was prepared in alcohol and DMF. 1 M NaClO₄ was prepared in double distilled water, and used as supporting electrolyte. The working solution was prepared by taking 1 mL of the stock solution (0.01 M) of the complex and 1 mL of the supporting electrolyte solution (1 M NaClO₄ ). The final solution was made up to 10.0 mL, by adding alcohol or DMF to get 1 mM concentration of the experimental solution.

A stream of nitrogen gas was passed over the reaction mixture. The three electrodes (glassy carbon electrode-working electrode, Ag/AgCl-reference electrode and a Pt wire-auxiliary electrode) were connected to the electrochemical cell. Required scan rates, current sensitivity, initial potential and final potential were applied, and the resulting current was measured as a function of the applied potential.

The electrochemical reduction behaviour of the synthesized TBCHSC was studied on a glassy carbon electrode in DMF and $CH_3OH$ media, using phosphate and B-R buffers, at various sweep rates, pH values and electroactive species concentrations. The compound exhibited one irreversible reduction peak in the cathodic direction. Thus, kinetic parameters, such as charge-transfer coefficient ($\alpha_n$), diffusion coefficient ($D_0^{1/2}$) and rate constant ($K^0_{f,h}$) were calculated for an irreversible and diffusion controlled reduction, by using the following equations [21-24]:

$$\left| E_p - E_{p/2} \right| = \frac{1.857RT}{\alpha_n F} = \left( \frac{47.7}{\alpha_n} \right) mV \qquad (1)$$

$$I_P = 3.01 \times 10^5 \, n \, (\alpha_n)^{1/2} \, A \, C \, D_0^{1/2} \, v^{1/2} \qquad (2)$$

$$E_P = -\frac{RT}{\alpha_n F} \left[ 0.78 + \ln\left( \frac{D_0^{1/2}}{k^{\circ}_{f,h}} \right) + \ln\left( \frac{\alpha_n F v}{RT} \right)^{1/2} \right] \qquad (3)$$

Most of the cyclic voltammograms were recorded with an initial potential (Ei) value of +500 and a switching potential value (Es) of -1100 mV for semicarbazone. For the complex, the Ei value was + 500 and the Es value was -1000 mV, at the scan rates of 50-250 mV/sec. The various parameters employed to evaluate the electrochemical reversibility are listed in Tables 1 to 6.

### Antimicrobial studies
*In vitro* antibacterial activity of the compounds was studied against gram positive and gram negative bacterial strains, by the agar well diffusion method. Mueller Hinton agar no. 2 was used as bacteriological medium. The antifungal activity of the experimental compounds was investigated by the agar well diffusion method. The yeasts and saprophytic fungi were sub cultured onto Sabouraud's dextrose agar (SDA) (Merck, Germany). The activity index was calculated by the standard zone of inhibition [25-28].

## Results and discussion
### Cyclic voltammetry studies
The cyclic voltammetric results for semicarbazone are given in Tables 1 to 4, and its voltammograms are depicted in Figs. 1 to 4.

**Table 1.** Effect of the sweep rate on the voltammetric parameters of 1 mM 4-tertbutylcyclohexanone semicarbazone in a $CH_3OH^-$ phosphate buffer, at different pHs (5.8, 7 and 8).

| pH | $v$ (mVs$^{-1}$) | $E_{pc}$ (mV) | $I_{pc}$ ($\mu$A) | $E_{p/2}$ (mV) | $I_{pc}/v^{1/2}$ | $\alpha_n$ | $D_0^{1/2}$x10$^3$ (cm$^2$s$^{-1}$) | $k^{\circ}_{f,h}$ (cm.s$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| | 50 | -475.81 | 09.10 | -149.28 | 1.30 | 0.1460 | 10.59762 | $8.22684 \times 10^{-4}$ |
| | 100 | -510.93 | 17.18 | -173.42 | 1.84 | 0.1413 | 14.39066 | $1.39865 \times 10^{-3}$ |
| **5.8** | 150 | -518.79 | 22.50 | -188.78 | 1.89 | 0.1445 | 15.20863 | $1.64316 \times 10^{-3}$ |
| | 200 | -544.83 | 26.15 | -265.04 | 1.85 | 0.1704 | 14.09507 | $9.51096 \times 10^{-4}$ |
| | 250 | -572.17 | 29.60 | -300.03 | 1.87 | 0.1752 | 14.07352 | $8.06756 \times 10^{-4}$ |
| | 50 | -540.76 | 14.32 | -230.72 | 2.03 | 0.1538 | 16.25011 | $7.59562 \times 10^{-4}$ |
| | 100 | -590.32 | 21.47 | -270.27 | 2.14 | 0.1490 | 17.50362 | $9.45156 \times 10^{-4}$ |
| **7.0** | 150 | -606.08 | 27.92 | -294.62 | 2.28 | 0.1531 | 18.33405 | $1.01787 \times 10^{-3}$ |
| | 200 | -617.67 | 29.89 | -321.50 | 2.11 | 0.1610 | 16.57592 | $8.40880 \times 10^{-4}$ |
| | 250 | -621.05 | 34.19 | -350.16 | 2.16 | 0.1760 | 16.21889 | $6.54659 \times 10^{-4}$ |
| | 50 | -706.22 | 13.79 | -369.99 | 1.95 | 0.1418 | 16.29719 | $3.77331 \times 10^{-4}$ |
| | 100 | -718.35 | 20.60 | -372.10 | 2.00 | 0.1377 | 17.46839 | $5.91325 \times 10^{-4}$ |
| **8.0** | 150 | -747.26 | 26.72 | -405.96 | 2.18 | 0.1397 | 18.36735 | $6.19647 \times 10^{-4}$ |
| | 200 | -758.08 | 27.95 | -422.24 | 1.98 | 0.1420 | 16.50532 | $5.71478 \times 10^{-4}$ |
| | 250 | -799.14 | 39.20 | -426.46 | 2.48 | 0.1279 | 21.81098 | $9.88632 \times 10^{-4}$ |

**Table 2.** Effect of the sweep rate on the voltammetric parameters of 4-tertbutylcyclohexanone semicarbazone in a $CH_3OH$-BR buffer at different pH (3, 5 and 9).

| pH | $Nm$ $Vs^{-1}$ | $E_{pc}$ (mV) | $I_{pc}$ (µA) | $E_{p/2}$ (mV) | $I_{pc}/v^{1/2}$ | $\alpha_n$ | $D_0^{1/2}$x$10^3$ (cm²s⁻¹) | $k°_{f,h}$ (cm.s⁻¹) |
|---|---|---|---|---|---|---|---|---|
| **3.0** | 50 | -371.53 | 08.127 | -133.70 | 1.1490 | 0.20056 | 8.077375 | 6.04479×10⁻⁴ |
| | 100 | -408.79 | 14.72 | -168.70 | 1.4720 | 0.19867 | 10.39415 | 8.43410×10⁻⁴ |
| | 150 | -414.83 | 16.53 | -190.20 | 1.3500 | 0.21234 | 9.218462 | 7.24723×10⁻⁴ |
| | 200 | -445.85 | 23.13 | -223.42 | 1.6357 | 0.21444 | 11.11616 | 7.56498×10⁻⁴ |
| | 250 | -464.88 | 26.42 | -237.43 | 1.6736 | 0.20971 | 11.48419 | 8.03030×10⁻⁴ |
| **5.0** | 50 | -664.84 | 19.77 | -322.14 | 2.7970 | 0.13919 | 23.59254 | 7.28920×10⁻⁴ |
| | 100 | -713.15 | 24.84 | -435.05 | 2.4844 | 0.17152 | 18.88041 | 2.87094×10⁻⁴ |
| | 150 | -765.63 | 33.30 | -443.20 | 2.7210 | 0.14794 | 22.25396 | 5.47605×10⁻⁴ |
| | 200 | -782.34 | 39.62 | -463.81 | 2.8019 | 0.14975 | 22.78574 | 5.59838×10⁻⁴ |
| | 250 | -788.49 | 46.30 | -444.24 | 2.9289 | 0.13856 | 24.76309 | 8.90162×10⁻⁴ |
| **9.0** | 50 | -859.26 | 12.78 | -515.48 | 1.8079 | 0.13875 | 15.27371 | 1.66648×10⁻⁴ |
| | 100 | -974.09 | 18.44 | -600.11 | 1.8440 | 0.12754 | 16.25118 | 1.97765×10⁻⁴ |
| | 150 | -995.80 | 24.84 | -564.61 | 2.0290 | 0.11062 | 19.19271 | 4.61022×10⁻⁴ |
| | 200 | -1030.6 | 31.54 | -550.54 | 2.2300 | 0.09936 | 22.26835 | 7.91779×10⁻⁴ |
| | 250 | -1082.4 | 35.44 | -553.51 | 2.2400 | 0.09018 | 23.49177 | 1.07196×10⁻³ |

**Table 3.** Effect of the sweep rate on the voltammetric parameters of 1 mM 4-tertbutylcyclohexanone semicarbazone in a DMF-phosphate buffer at different pHs (5.8, 7 and 8).

| pH | $v$ (mVs⁻¹) | $E_{pc}$ (mV) | $I_{pc}$ (µA) | $E_{p/2}$ (mV) | $I_{pc}/v^{1/2}$ | $\alpha_n$ | $D_0^{1/2}$x$10^3$ (cm²s⁻¹) | $k°_{f,h}$ (cm.s⁻¹) |
|---|---|---|---|---|---|---|---|---|
| **5.8** | 50 | -772.87 | 06.10 | -447.81 | 0.86 | 0.14674 | 7.087903 | 9.97320×10⁻⁵ |
| | 100 | -784.32 | 09.81 | -450.50 | 0.98 | 0.14289 | 8.167991 | 1.68979×10⁻⁴ |
| | 150 | -798.88 | 13.09 | -459.12 | 1.06 | 0.14039 | 8.977866 | 2.24739×10⁻⁴ |
| | 200 | -828.11 | 20.27 | -483.26 | 1.43 | 0.13832 | 12.12951 | 3.17084×10⁻⁴ |
| | 250 | -844.57 | 24.20 | -504.62 | 1.53 | 0.14031 | 12.86021 | 3.24495×10⁻⁴ |
| **7.0** | 50 | -742.01 | 07.26 | -511.07 | 1.03 | 0.20654 | 7.110444 | 2.51440×10⁻⁵ |
| | 100 | -818.78 | 18.68 | -510.42 | 1.80 | 0.15469 | 14.95154 | 1.82343×10⁻⁴ |
| | 150 | -834.24 | 22.13 | -539.55 | 1.81 | 0.16187 | 14.13513 | 1.55824×10⁻⁴ |
| | 200 | -844.10 | 25.44 | -556.45 | 1.80 | 0.16582 | 13.90371 | 1.47827×10⁻⁴ |
| | 250 | -868.79 | 31.90 | -588.10 | 2.02 | 0.16993 | 15.40398 | 1.37520×10⁻⁴ |
| **8.0** | 50 | -789.39 | 07.12 | -558.03 | 1.00 | 0.20617 | 6.988405 | 1.70580×10⁻⁵ |
| | 100 | -827.50 | 10.28 | -604.03 | 1.02 | 0.21345 | 7.007899 | 1.43350×10⁻⁵ |
| | 150 | -843.98 | 13.44 | -639.74 | 1.18 | 0.23355 | 7.147319 | 8.43400×10⁻⁶ |
| | 200 | -854.64 | 17.13 | -655.26 | 1.21 | 0.23924 | 7.79786 | 8.07600×10⁻⁶ |
| | 250 | -881.24 | 18.08 | -685.22 | 1.11 | 0.24334 | 7.296539 | 5.77700×10⁻⁶ |

**Table 4.** Effect of the concentration on the cathodic peak potential and peak current for 4-tertbutylcyclohexanone semicarbazone (mM) in an alcohol phosphate buffer at pH 5.8.

| $v$ mV/s | Concentration of 4-tertbutylcyclohexanone semicarbazone (mM) in an alcohol phosphate buffer at pH 5.8 | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 mM | | 2 mM | | 3 mM | | 4 mM | |
| | $E_{p,c}$ (mV) | $I_{p,c}$ (µA) | $E_{p,c}$ (mV) | $I_{p,c}$ (µA) | $E_{p,c}$ (mV) | $I_{p,c}$ (µA) | $E_{p,c}$ (mV) | $I_{p,c}$ (µA) |
| 50 | -475.810 | 09.19 | -535.50 | 14.211 | -630.78 | 09.61 | -680.87 | 11.18 |
| 100 | -510.92 | 17.18 | -590.32 | 21.47 | -668.45 | 23.43 | -688.88 | 18.79 |
| 150 | -518.94 | 22.50 | -634.18 | 27.55 | -710.00 | 26.00 | -729.46 | 26.50 |
| 200 | -544.833 | 26.15 | -658.58 | 39.26 | -739.83 | 37.86 | -797.71 | 33.58 |
| 250 | -572.173 | 29.61 | -676.56 | 45.08 | -744.05 | 46.11 | -903.633 | 38.14 |
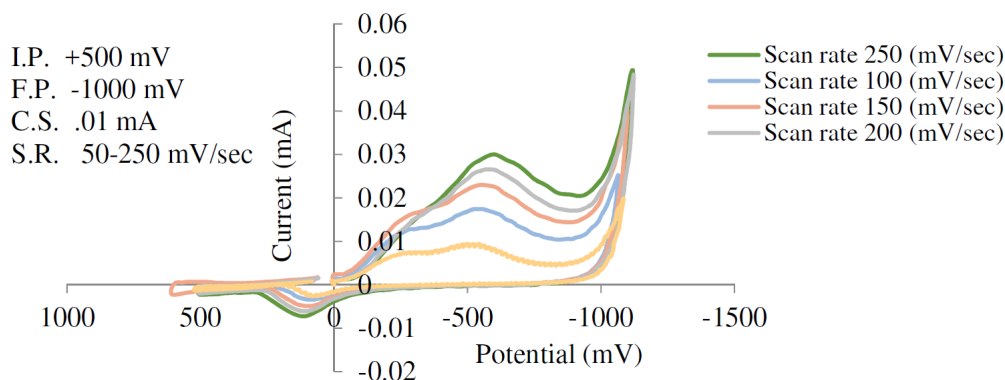
**Figure 1.** TBCHSC cyclic voltammograms in a methanolic medium containing a phosphate buffer (pH 5.8).
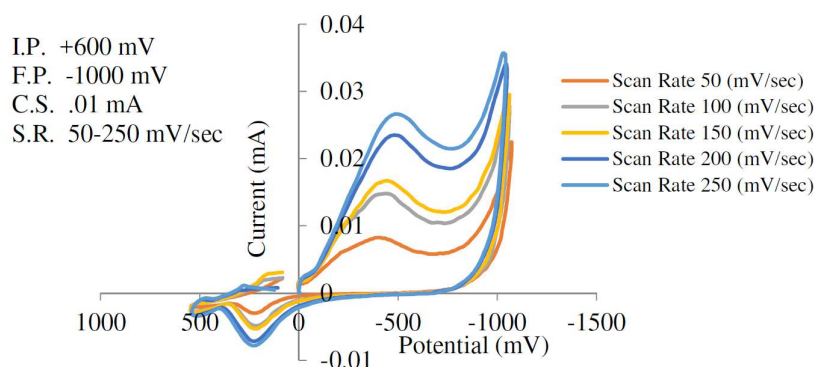


**Figure 2.** TBCHSC cyclic voltammograms in a methanolic medium containing a BR buffer (pH 3).
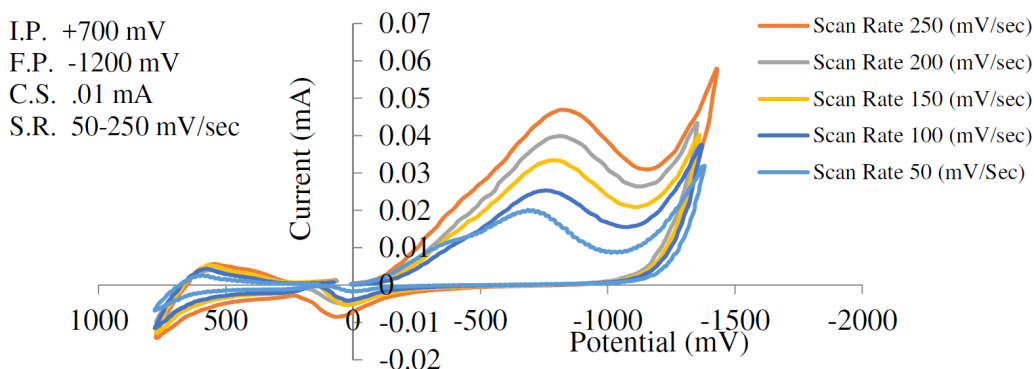


**Figure 3.** TBCHSC cyclic voltammograms in a methanolic medium containing a BR buffer (pH 5).

The cyclic voltammetric results for the complex are presented in Tables 5 to 6, and its voltammograms are displayed in Figs. 5 to 6.
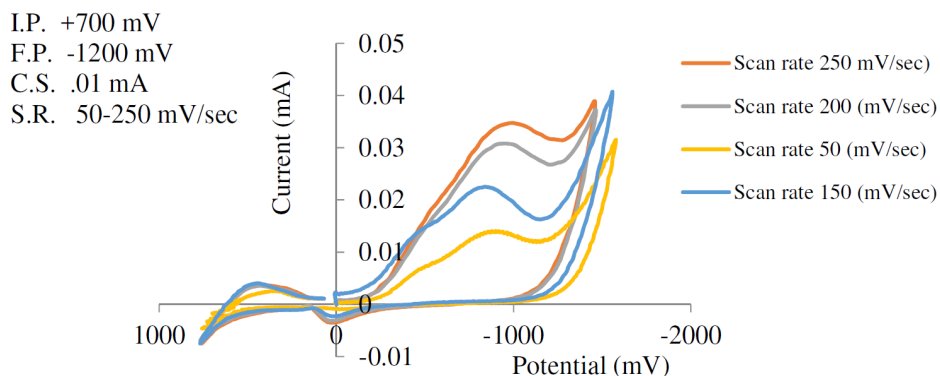
**Figure 4.** TBCHSC cyclic voltammograms in a DMF medium containing a phosphate buffer (pH 7).

**Table 5.** Effect of the sweep rate on the voltammetric parameters of the Co(II) complex of 4-tertbutylcyclohexanone semicarbazone in methanol-NaClO$_4$, at different concentrations.

| Complex conc. | $v$ (mVs$^{-1}$) | $E_{pc}$ (mV) | $E_{p1/2}$ (mV) | $I_{p,c}$ (µA) | $I_{p,c}/v^{1/2}$ |
|---|---|---|---|---|---|
| 1 mM | 50 | -688.29 | -592.46 | 09.18 | 1.298 |
| | 100 | -745.50 | -624.68 | 11.75 | 1.175 |
| | 150 | -747.50 | -621.84 | 15.70 | 1.282 |
| | 200 | -751.71 | -584.20 | 18.26 | 1.291 |
| | 250 | -781.70 | -642.72 | 22.20 | 1.400 |
| 2 mM | 50 | -704.03 | -617.43 | 12.58 | 1.779 |
| | 100 | -741.89 | -641.89 | 15.39 | 1.539 |
| | 150 | -748.12 | -635.61 | 20.21 | 1.650 |
| | 200 | -765.01 | -647.71 | 26.51 | 1.874 |
| | 250 | -793.40 | -652.67 | 30.60 | 1.935 |
| 3 mM | 50 | -711.57 | -638.57 | 16.84 | 2.381 |
| | 100 | -732.58 | -646.73 | 20.10 | 2.010 |
| | 150 | -756.67 | -653.72 | 26.14 | 2.135 |
| | 200 | -777.15 | -660.05 | 32.86 | 2.323 |
| | 250 | -797.55 | -685.22 | 37.37 | 2.363 |
| 4 mM | 50 | -725.58 | -642.37 | 21.35 | 3.019 |
| | 100 | -736.89 | -642.26 | 24.65 | 2.465 |
| | 150 | -757.64 | -650.38 | 31.86 | 2.602 |
| | 200 | -785.86 | -667.38 | 40.80 | 2.885 |
| | 250 | -806.41 | -676.50 | 47.60 | 3.010 |

**Table 6.** Effect of the sweep rate on the voltammetric parameters of the Co(II) complex of 4-tertbutylcyclohexanone semicarbazone in DMF-NaClO$_4$.

| Complex conc. | $v$ (mVs$^{-1}$) | $E_{pc}$ (mV) | $E_{p1/2}$ (mV) | $I_{p,c}$ (µA) | $I_{p,c}/v^{1/2}$ |
|---|---|---|---|---|---|
| 1 mM | 50 | -697.82 | -580.39 | 15.63 | 2.210 |
| | 100 | -746.23 | -603.45 | 20.27 | 2.027 |
| | 150 | -749.80 | -607.20 | 28.27 | 2.300 |
| | 200 | -765.19 | -620.63 | 33.00 | 2.330 |
| | 250 | -812.82 | -612.78 | 45.17 | 2.857 |

I.P.  +500 mV
F.P.  -1000 mV
C.S.  .01 mA
S.R.   250 mV/sec
Conc. 1 mM- 4 mM

— for 1 mM conc. at scan rate 250  (mV/sec)
— for 4 mM conc. at scan rate 250  (mV/sec)
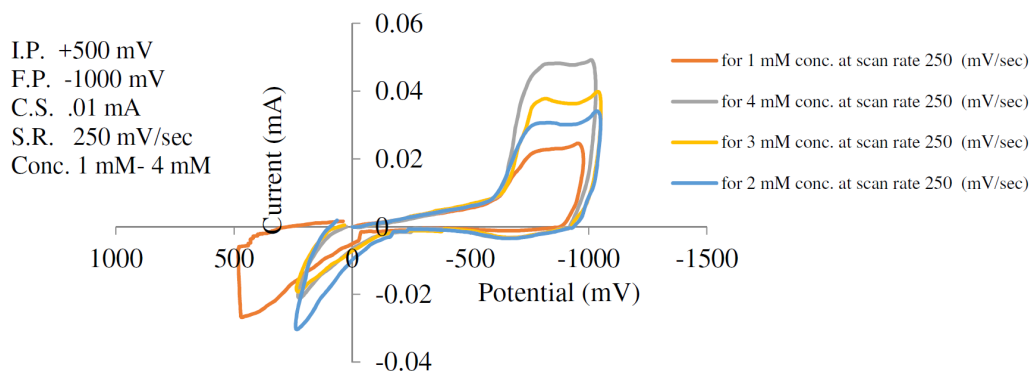— for 3 mM conc. at scan rate 250  (mV/sec)
— for 2 mM conc. at scan rate 250  (mV/sec)

**Figure 5.** Cyclic voltammograms of the TBCHSC Co(II) complex in a methanolic medium with 1 mM-4 mM conc., at the scan rate of 250.
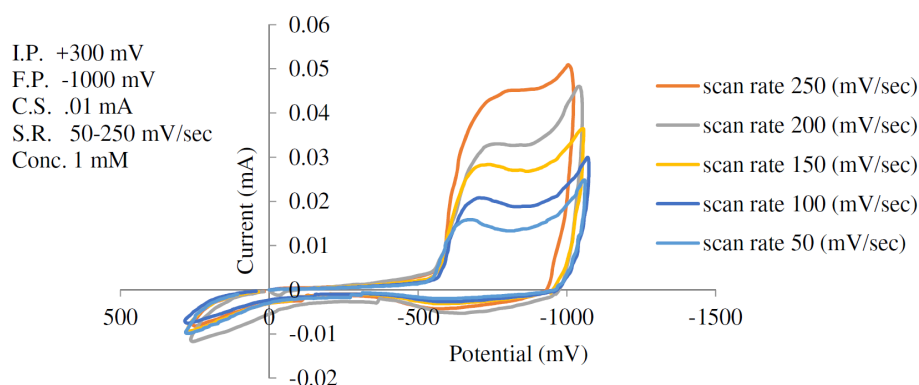
I.P.  +300 mV
F.P.  -1000 mV
C.S.  .01 mA
S.R.   50-250 mV/sec
Conc. 1 mM

— scan rate 250 (mV/sec)
— scan rate 200 (mV/sec)
— scan rate 150 (mV/sec)
— scan rate 100 (mV/sec)
— scan rate 50 (mV/sec)

**Figure 6.** Cyclic voltammograms of the Co(II) complex of TBCHSC in a DMF medium with 1 mM conc.

The cyclic voltammograms were recorded by varying the scan rate, keeping the pH and the solution concentration constant; the data exhibited one irreversible reduction peak at all scan rates. The peak potential value shifted towards the more negative direction, with an increase in the scan rate, indicating that the electrochemical process was irreversible (Fig. 8). The peak current was also increased as the scan rate increased for the compounds. The linear nature of the $I_{pc}$ v/s $\nu^{1/2}$ plot, with an intercept different of zero, showed that TBCHSC reduction was diffusion controlled (Fig. 7).

The concentration effect on the reduction potential was studied by varying the compound concentration from 1 mM to 4 mM, keeping the scan rate constant. The cathodic peak current was found to linearly increase with an increase in the compound concentration. The plot of $I_{pc}$ vs. concentration showed linearity, further indicating that the electrode process was diffusion controlled. It was also observed that the peak potential ($E_{pc}$) shifted towards more negative values, as the compound concentration increased (Table 4). This $E_{pc}$ shifts in the cathodic direction, with an increasing concentration, indicated that the reduction products were adsorbed onto the electrode surface; this kind of shift has been theoretically predicted and experimentally observed [29-30].
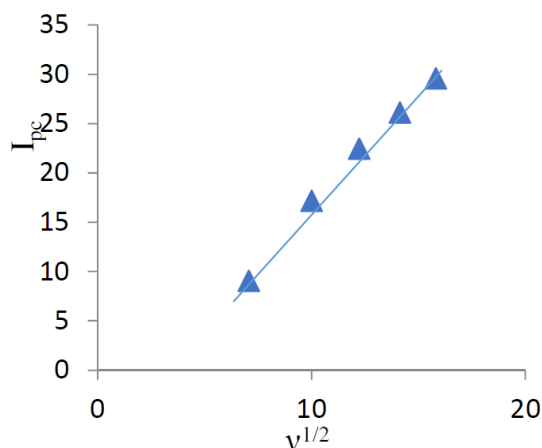
**Figure 7.** TBCHSC current ($I_{pc}$) vs. $v^{1/2}$ in a methanolic medium containing phosphate buffer (pH 8).

The pH effect upon TBCHSC reduction was investigated (Tables 1 to 3, and Fig. 8). The peak potential values of the compounds were found to change with the solution's pH value. This dependence of the peak potential on the pH indicates that the proton transfer took place during the electrode reaction. The peak potential shifts towards more negative values depended upon the solution's pH. This meant that the reduction was easier in acidic media, and difficult in media where the proton concentration was low. The ease of reduction was found to be greater in an acidic pH than in an alkaline pH, which might be because of the formation of an easily reducible protonated intermediate.
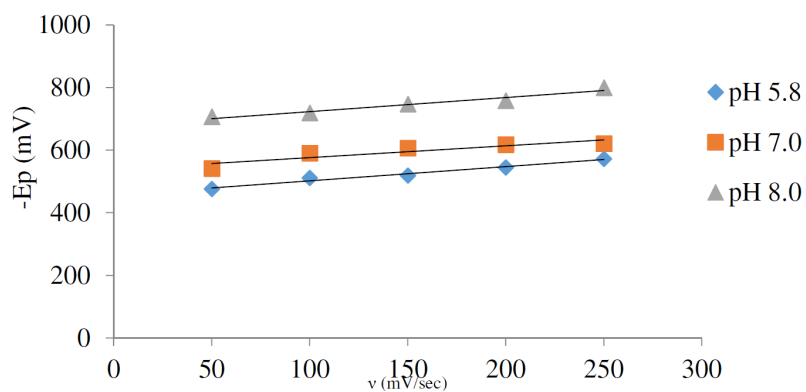


**Figure 8.** Potential vs. scan rate in a methanolic medium with a phosphate buffer (pH 5.8, 7 and 8).

Cyclic voltammograms were recorded in two different media: a DMF-phosphate buffer and a $CH_3OH$-phosphate buffer. It was observed that the peak potential shifted towards more negative values in the presence of an aprotic solvent (DMF), and the shift magnitude depended on the solvent nature. The shift order observed in the present study was DMF-phosphate > $CH_3OH$-phosphate buffer. This trend paralleled the trend observed in the solvent viscosity (DMF 0.796 > methanol 0.544).

In this process, the imine group (-C=N-) 4-tertbutylcyclohexanone semicarbazone was reduced into the amine group (-CH-NH$_2$), in a protic solvent

such as $CH_3OH$. Since all steps involved in the reaction mechanism took place at the same potential, it occurred a single reduction peak corresponding to the transfer of four electrons (Scheme III).
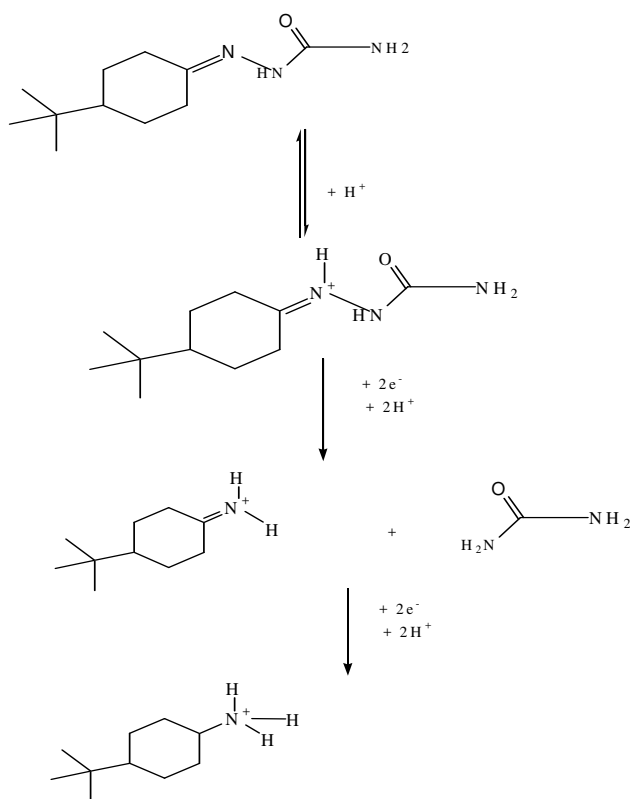


**Scheme III.** Proposed reduction mechanism for 4-tertbutylcyclohexanone semicarbazone.

In the case of the complex, no anodic peak appeared, indicating the irreversible nature of the electrode process [31]. The electrode nature was also confirmed from the peak potential value that shifted towards the more negative direction, with an increase in the scan rate. The peak current also increased as the scan rate increased for the compounds. The effect of the concentration on the reduction potential was studied by varying the compound concentration from 1 mM to 4 mM, keeping the scan rate constant. It was observed that the peak potential ($E_{pc}$) shifted towards more negative values, and the cathodic peak current was found to linearly increase as the compound concentration increased. It was also observed that the peak potential shifted to more negative values in the presence of an aprotic solvent, and the shift magnitude depended on the solvent nature (Tables 5 to 6). If the reduction of the Co(II) complex and that of the ligand in alcoholic acidic pH were to be compared, it would be observed that the former would be more difficult than the latter, suggesting that the ligand reduction was proton dependant.

### *Infrared study*
The absence of a $\upsilon$(C=O) band (1745 cm$^{-1}$) of ketone, and the presence of a $\upsilon$(C=N) band occurred [32] at 1622-1632 cm$^{-1}$ in the ligand spectra, indicated

condensation between the ketonic group and the amino group of semicarbazide. In comparison with the semicarbazone spectra, the Co(II) complex exhibited the $\nu$(C=N) band in the 1590–1603 cm$^{-1}$ region, showing the band shift to lower wave numbers, and indicating that the nitrogen was coordinated to the metal ion. The $\upsilon$(C=O) band disappearance at 1700 ± 100 cm$^{-1}$ (initially present in the semicarbazone spectra), in the Co(II) complex spectra, indicated that the participation of ketonic oxygen resulted in a bond formation. The appearance of new bands in the 579–560 and 386-322 cm$^{-1}$ regions assignable to $\upsilon_{M-O}$ and $\upsilon_{M-N}$, respectively, reflected the bonding of the metal ions to oxygen and nitrogen atoms [33-36].

*Elemental analysis*
This section deals with the elemental (CHNO) analysis of the ligand and its complex (Table 7).

**Table 7.** Elemental analysis.

| Sr. No | Specification | Colour and state | Elemental analysis ( %) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | C found (calcd.) | H found (calcd.) | N found (calcd.) | O found (calcd.) | Co found (calcd.) | M. Wt found (calcd.) |
| 1 | 4-terbutylcyclohexanone semicarbazone ($C_{11}H_{21}N_3O$) | Creamish solid | 62.52 (62.87) | 10.02 (10.51) | 19.89 (20.05) | 7.57 (7.89) | 0 | 211.30 (212.46) |
| 2. | 4-terbutylcyclohexanone semicarbazone) Co(II) complex ($C_{22}H_{44}Co\ N_6O_4$) | Light purple solid | 51.25 (51.99) | 8.60 (8.98) | 16.30 (16.47) | 12.41 (12.93) | 11.43 (12.02) | 515.56 (516.17) |

*Antimicrobial studies*
This section deals with the recent biological studies of semicarbazone and its cobalt(II) metal complex. The results of the antifungal study of TBCHSC and its Co(II) complex on *Fusarium oxysporium, Trichoderma reesei* (Table 8) and on Gram positive bacteria (*Bacillus subtilis)* and Gram negative bacteria (*Escherichia coli*) are recorded in Table 9. From Tables 8 to 9, it is clear that the inhibition was much larger for the metal complex than for semicarbazone.

**Table 8.** Antifungal studies of semicarbazone and its Co(II) complex.

| | *Fusarium oxysporium* | | | | *Trichoderma reesei* | | | |
|---|---|---|---|---|---|---|---|---|
| Anti-fungal | TBCHSC | | Co(II) complex | | TBCHSC | | Co(II) complex | |
| Stock conc. µg/mL | Zone of inhibition (mm) | Activity index | Zone of inhibition (mm) | Activity index | Zone of inhibition (mm) | Activity index | Zone of inhibition (mm) | Activity index |
| 20 | 07 | 0.31 | 14 | 0.636 | 15 | 0.68 | 19 | 0.86 |
| 40 | 20 | 0.90 | 19 | 0.863 | 15 | 0.68 | 18 | 0.81 |
| 60 | 20 | 0.90 | 30 | 1.360 | 16 | 0.72 | 22 | 1.00 |
| 80 | 24 | 1.09 | 20 | 0.900 | 35 | 1.59 | 22 | 1.00 |

**Table 9.** Antibacterial studies of semicarbazone and its Co(II) complex.

| | *Bacillus subtilis* | | | | *Escherichia coli* | | | |
|---|---|---|---|---|---|---|---|---|
| Anti-bacterial | TBCHSC | | Co(II) complex | | TBCHSC | | Co(II) complex | |
| Stock conc. µg/mL | Zone of inhibition (mm) | Activity index | Zone of inhibition (mm) | Activity index | Zone of inhibition (mm) | Activity index | Zone of inhibition (mm) | Activity index |
| 20 | 05 | 0.25 | 16 | 0.8 | 04 | 0.20 | 08 | 0.40 |
| 40 | 09 | 0.45 | 12 | 0.6 | 03 | 0.15 | 04 | 0.20 |
| 60 | 12 | 0.60 | 14 | 0.7 | 03 | 0.15 | 04 | 0.20 |
| 80 | 15 | 0.75 | 16 | 0.8 | 09 | 0.45 | 10 | 0.50 |

## Conclusion

From the electrochemical studies, it was concluded that the semicarbazone reduction and its Co(II) complex is irreversible. Keeping in view the feasibility of the reduction site, and on the basis of cyclic voltammetric results, the reduction mechanism shown in the Scheme III may be suggested for the electro reduction of 4-tertbutylcyclohexanone semicarbazones, similar to that reported in the literature [21-24]. The mechanism finds support from the $E_{pc}$ and $E_{p1/2}$ shifts towards the negative potential, with pH, as protons are consumed in the reduction. The antimicrobial activity of the complex is higher in comparison to semicarbazone, which indicates that metallation increases biological activity.

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