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# Study of Electrical and Thermal Properties of Triazine Schiff's Base Complexes with Transition Metal(II) Ions

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## ABSTRACT

In this investigation, the electrical and thermal properties of newly synthesized Schiff bases from TRIPOD with different substituted aniline and complexes of TRIPOD-SBNA with transition metal(II)ions were studied. An examination of the thermograms of Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD-SBNA with transition metal(II)complexes indicates that they are with varying thermal stability undergoing decomposition at different temperatures. Their percent weight loss as computed from the thermograms suggests that the final product of decomposition in them corresponds to respective metal oxide. Further, the thermogravimetric results offer supports to the composition of the complex polymer conjugates. The electrical conductivity of Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD-SBNA with transition metal (II) complexes showed a tendency to increase by increasing the temperature upto 407 K and indicates their semiconducting behavior.

Key words: Complexes, TRIPOD, Tripodal Schiff's Bases, TRIPOD-SBNA.

#### **1. INTRODUCTION**

1,3,5-triazine is a very important class of six-membered aromatic heterocyclic compounds receiving much attention in scientific research [1]. There has been a growing interest on synthesis, structural studies, and applications of transition metal complexes of substituted Triazines due to their interesting electronic and optical features with excellent pharmacological properties [2-6]. A further interesting aspect of S-Triazine is the redox properties, which makes 2,4,6-trisubstitutedtriazines as important building blocks in electronic and polymeric materials. With a delocalized electron system Triazine based ligands have been studied as materials for non-linear optical applications. On the basis of the above-mentioned background in this investigation, the electrical and thermal and properties of Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD-SBNA with transition metal(II)complexes were studied [2,6-11].

#### 2. MATERIALS AND METHODS

In this work, the electrical thermal and properties of Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD-SBNA with transition metal(II)complexes were studied. It is discussed one by one in detail.

#### 2.1. Electrical Properties of Tripod Schiff's Bases

The possibility of improving the conductivity of heterocyclic compounds, which are conventionally insulators, to metallic levels has attracted not only chemists but also physicists and even material scientists. Many researchers have tried to combine the process ability and other attractive properties of heterocyclic compounds with the electronic properties of metals or semiconductors. Conducting polymers are different from electrically conductive polymers as they are conductive only if the individual conductive particles are in contact and form a coherent phase [12]. For significant electrical conductivity

in heterocyclic compounds, there has to be the correct combination of both structural and electrical features.

The shape of the heterocyclic compounds must be such that extensive inter-complex interaction can occur in solid state. Electron transport will be facilitated by the close approach of the matrix and therefore the absence of bulky non-electrolytic polymer is an advantage. Detailed structural studies have shown the importance of inters tack interaction (e.g. H-bonded, polymer-polymer bonding) in stabilizing these structures and these interactions can also have an important role on the electrical conduction properties. Heterocyclic compounds can conveniently be divided into two categories: semiconductor and metallic behavior.

Semiconductor type behavior: Semiconductors are characterized by relative low conductivity and a positive temperature-dependent conductivity. The most heterocyclic compounds exhibit detectable electrical conductivity belonging to this class. The temperature dependence of the conductivity is given by:

$$\sigma = \sigma_0 \exp\left[-\text{Ea/kT}\right]$$

Where  $\sigma$  is the conductivity Ea is the thermal activation energy for the electrical conduction,  $\sigma_0$  is the parameter depending on the semiconductor nature and k is the Boltzmann constant.

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**Received**: 20<sup>th</sup> September 2021; **Revised**: 20<sup>th</sup> December 2021; **Accepted**: 02<sup>nd</sup> January 2022 The electrical conductivity of the heterocyclic compounds has a positive temperature coefficient. That is, with the increase in temperature, conductivity increases exponentially. The increase starts when charge carriers have enough activation energy. Also, during the increase of temperature, the mobility of these carriers increases. This is a property of typical semiconductivity. The temperature dependence of semiconductors has the general form

$$\sigma = \sigma_0 \exp\left[-Ea/kT\right]$$

Where Ea is the thermal activation energy for the electrical conduction,  $\sigma_0$  is the parameter depending on the semiconductor nature and k is the Boltzmann constant.

A versus 1000/T yields a straight line whose slope can be used to determine the  $\sigma$  A plot of ln thermal activation energy of the heterocyclic compounds (Triazines).

#### **3. EXPERIMENTAL PROCEDURE**

Voltage drop method was used for the measurement of the resistance of pellet using a Systronic microvoltmeter as a function of temperature in the range 1V to 100 V. The connecting wires of the sample holders from the furnace were connected to the two terminals of the instrument. In this way, the corresponding resistance (R) of the pellet was measured directly by keeping the pellet in the sample holder.

$$\mathbf{R} = \left(\frac{\mathbf{V}_{\mathrm{T}} - \mathbf{V}_{\mathrm{R}}}{\mathbf{V}_{\mathrm{R}}}\right) \times 10^{-5} \,\Omega$$

Where,  $V_T$  = total voltage range applied  $V_R$  = actual voltage across resistance R = resistance of the pellet. Resistivity ( $\rho$ ) was then calculated using the relation

 $\rho = (\mathbf{R} \times \mathbf{A})/t$ 

Where, A = surface area of pellet t = thickness of pellet

The electrical conductivity ( $\sigma$ ) varies exponentially with the absolute temperature according to well-known relation

$$\sigma = \sigma_0 \exp\left(-Ea/kT\right)$$

Where,  $\sigma$  = electrical conductivity at temperature T  $\sigma_0$  = electrical conductivity at temperature T =  $\infty$ Ea = activation energy of electrical conduction k = Boltzmann constant of electrical conduction T = absolute temperature

This relationship has been modified as -

$$\log \sigma = \log \sigma_0 + [-Ea/2.303 \text{ kT}]$$

According to this relation, a plot of a log  $\sigma$  versus 1/T would be linear with a negative slope. The slope of the straight-line part of the plot ln  $\sigma$  versus 1000/T has been used in determining the thermal activation energies of the polymer conjugates. Such plots were made on the basis of each set of data. The plots of temperature dependence of electrical conductivity of the Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD- SBNA with transition metal (II) complexes have been drawn.

The d. c. electrical resistivity was determined as a function of temperature in the range 305 K  $\leq$  T  $\leq$ 407 K. The results of electrical conductivity and activation energy are incorporated in Table 1. The temperature dependence of the electrical conductivity of Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD-SBNA with transition metal (II) complexes are shown in Figure 1.

**Table 1:** Electrical conductivity and activation energy

 TRIPOD compounds.

S. No.	Samples	$\sigma \left( \Omega^{-1} cm^{-1} \right)$	Ea (eV)
1.	TRIPOD	$1.17 \times 10^{-7}$	0.579
2.	TRIPOD-SBNA	$5.42 \times 10^{-7}$	0.878
3.	TRIPOD-SBCA	$3.19 \times 10^{-7}$	0.873
4.	TRIPOD SBNA-Co (II)	$4.88 \times 10^{-7}$	0.897
5.	TRIPOD SBNA-Ni (II)	$5.57 \times 10^{-7}$	0.711
6.	TRIPOD SBNA-Cu (II)	$6.53 \times 10^{-7}$	0.879





#### 4. RESULTS AND DISCUSSION

## 4.1. Electrical Conductivity of Schiff Bases and Complexes Synthesized from TRIPOD

The electrical conductivity and activation energy of Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD-SBNA with transition metal (II) complexes are cited in Table 1 and the temperature dependence of log  $\sigma$  of these compounds is shown in Figure 1.

It is observed that,

- 1. The plots of log  $\sigma$  versus  $10^3/T$  are found to be linear in the studied temperature range 305-407 K [13,14]
- 2. Electrical conductivity of the Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD- SBNA with transition metal (II) complexes lies in the range of  $1.17 \times 10^{-7}$ – $6.53 \times 10^{-7} \Omega^{-1} cm^{-1}$
- The electrical conductivity of these Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD-SBNAwithtransitionmetal(II)complexes follows the order, TRIPOD
   TRIPOD-SBCA<TRIPODSBNA-Co(II)</p>
   TRIPOD SBNA-Ni(II)
   TRIPODSBNA-Cu(II)
- 4. The activation energy of electrical conduction of the Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD- SBNA with transition metal (II) complexes has been found to increase in the order, TRIPOD <TRIPODSBNA-Ni(II) < TRIPOD-SBCA < TRIPOD-SBNA< TRIPODSBNA-Cu(II) <TRIPODSBNA-Co(II).</p>

#### 4.2. Thermal Properties of Tripod Schiff 'S Bases

This part of chapter deals with the thermal properties of Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD- SBNA with transition metal (II) complexes. Thermal

Table 2:	Thermal	data of	TRIPOL	J-Schiff s	bases.	

Samples	Half decomposition temperature (°C)	Activation energy (KJ/mole)	Frequency factor Z (s <sup>-1</sup> )	Entropy change – ΔS (J/mol/K)	Free energy change ∆G (k J/mol)
TRIPOD	275	73.00	16.17	951	545.43
TRIPOD- SBNA	532	27.11	27.41	236.27	145.47
TRIPOD- SBCA	396	35.98	80.31	295.35	127.98
TRIPOD SBNA-Co (II)	616	23.42	155.70	211.85	159.27
TRIPOD SBNA-Ni (II)	337	19.15	147.39	208.27	80.97
TRIPOD SBNA-Cu (II)	614	23.23	156.09	210.73	158.97

analysis is a branch of material science where the properties of material are studied as they change with temperature.

The TGA technique finds wide applications, especially in analytical chemistry. Qualitative and quantitative analysis for wide range of sample types, especially for inorganic materials. Kinetic studies where weight changes can be clearly attributed reactions, volatilizations, and adsorption and desorption may be studied. There are three types of thermogravimetry.

In the present investigation, non-isothermal or dynamic thermogravimetric analysis is carried out for thermal analysis of Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD- SBNA with transition metal (II) complexes. During the thermal analysis of the compounds. The following types of reaction may generally occur.

## 4.3. Determination of Water Molecules from Thermal Decomposition

The TG data gives important information about stoichiometry, thermal stability, and nature of water molecules. According to Nikolaev [17], water eliminated below 140°C can be considered as lattice (crystal) water and water eliminated above 150°C may be due to the coordinated to the metal ion.

#### 4.4. Determination of Kinetic Parameters

In the present investigation, the Horowitz-Metzger method has been used for the evaluation of kinetic parameters of newly synthesized Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD- SBNA with transition metal (II) complexes.

## 4.5. Horowitz-Metzger Method

In the present investigation, the newly synthesized Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD- SBNA with transition metal (II) complexes were studied by thermogravimetric analysis to suggest the presence of water molecule (lattice/coordinated) and to compare the thermal stability of the compounds. The thermograms, gave information about its nature and percent weight losses at various temperatures. The kinetics of thermal decomposition steps were investigated by the non-isothermal method. Table 2 gives the results of the thermogravimetric analysis are discussed for each newly synthesized Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD-SBNA with transition metal (II) complexes [15,16].

#### 4.6. Thermal Study of Tripod-Schiff's Bases

An analysis of the thermograms of all Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD-SBNA with transition metal (II) complexes as shown in Figure 2 and indicate that these Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD-SBNA with transition metal



Figure 2: Thermograms of TRIPOD -Schiff's bases.

(II) complexes undergo single step decomposition after dehydration, while TRIPOD undergo two steps decomposition. In all the Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD- SBNA with transition metal (II) complexes rapid weight loss has been observed.

On the basis of half decomposition temperature, the thermal stability order of compounds was found to be, TRIPOD <TRIPODSBNA-Ni(II) < TRIPOD-SBCA< TRIPOD-SBNA< TRIPODSBNA-Cu(II) <TRIPODSBNA-Co(II)

An examination of the thermogram of the Schiff's bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD-SBNA with transition metal(II)complexes indicates that they are with varying thermal stability undergoing decomposition at different temperatures. The percent weight loss as computed from the thermograms of the Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD-SBNA with transition metal(II) complexes suggests that the final product of decomposition in them corresponds to respective metal oxide. Further, the thermogravimetric results offer supports to the composition of the complex polymer conjugates. The value of thermodynamic parameters is nearly the same for each Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD-SBNA with transition metal(II) complexes. This similarity indicates that the basic steps involved in the thermal degradation of Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD-SBNA with transition metal(II) complexes are the same. The negative values of apparent energy of activation indicate that the activated Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD-SBNA with transition metal(II) complexes have a more ordered or more rigid structure than the reactants or intermediates and the reactions are slower than normal [18,19].

### 5. CONCLUSION

From the results of electrical conductivity of all the polymer matrixes under investigation, the following conclusions can be drawn,

- 1. The electrical conductivity of Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD-SBNA with transition metal (II) complexes showed a tendency to increase by increasing the temperature upto 407 K and obeyed log  $\sigma$  versus 1/T relation indicates their semiconducting behavior [20-23]
- 2. The variation in the electrical conductivity and activation energy of electrical conduction with the metal ions in TRIOPDSBNA complexes may be explained on the basis of influence of the incorporation of different metal ions in the Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD-SBNA with transition metal (II) complexes which increases the ionization tendency [24]
- 3. Activation energy is a direct measure of the band gap of semiconductors, lower the activation energy, lower will be the band gap [25-28].

An examination of the thermogram of the TRIPOD compounds indicates that they are with varying thermal stability undergoing decomposition at different temperatures. The percent weight loss as computed from the thermograms of the complex TRIPOD compounds suggests that the final product of decomposition in them corresponds to respective metal oxide. Further, the thermogravimetric results offer supports to the composition of the complex TRIPOD compounds. The value of thermodynamic parameters is nearly the same for each TRIPOD compounds. This similarity indicates that the basic steps involved in the thermal degradation of TRIPOD compounds are the same. The negative values of apparent energy of activation indicate that the activated TRIPOD compounds have a more ordered or more rigid structure than the reactants or intermediates and the reactions are slower than normal [29-33]. In the present investigation, synthesis and characterization of Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD- SBNA with transition metal (II) complexes have been attempted due to their wide range of applications in various fields science. The present investigation is summarized in the form of the following conclusions, Electrical properties show that the Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD- SBNA with transition metal (II) complexes is semiconductor nature. The thermogram of the Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD- SBNA with transition metal (II) complexes indicate that they have varying degree of thermal stability and undergo decomposition at different temperatures. The percent weight loss as computed from the thermograms of the Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD-SBNA with transition metal (II) complexes suggest that the final product of decomposition in them corresponds to respective metal oxide. Further, the thermogravimetric results offer supports to the composition of Schiff bases synthesized from TRIPOD with different substituted aniline and ligand TRIPOD- SBNA with transition metal (II) complexes. The experimental studies in the present investigation show that the use of TRIPOD-SBNA and TRIPOD-SBCA brings some changes in structure and enhance electrical properties, thermal stability, properties of the TRIPOD compounds [34-38].

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