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Studies of Physical and Chemical Compounds Charge Transfer Between Amino Acids and Iodine and its Applications in the Industry of Unconventional Organic Connectors

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Abstract: ***Tri-iodide charge-transfer complexes synthesized upon the chemical interaction between iodine and tryptophan or tyrosine were characterized using different spectroscopic techniques (e.g., infrared, Raman, electronic, X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The triiodide charge-transfer complexes were prepared by dry grinding of potassium iodide, iodine and amino acid with 1:1:1 molar ratio in presence of few drops of methylene chloride solvent. The electronic spectra exhibit two absorption bands around 360 and 280 nm due to the formation of the triiodide ion (I_3^-). The Raman spectra show the characteristic bands for the triiodide ion at 160, 126 and 100 cm^{-1}, which are assigned to ν_{as} (I-I), ν_s (I-I) and δ (I_3^-), respectively. The iodine complexes were shown to contain the triiodide species based on the electronic absorptions as well as on the Raman absorption bands characteristic for the non-linear triiodide species, I_3^-, with C_{2v} symmetry. The proposed structures of these complexes are further supported by thermal analyses measurements. The DC electrical properties as a function of temperature of these charge transfer complexes have been studied.***

Keywords: Tryptophan; tyrosine; iodine; charge-transfer complexes; DC electrical; Raman spectroscopy

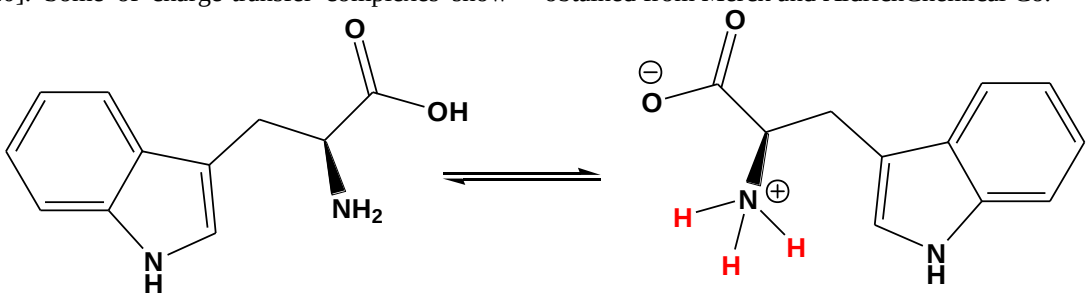
1. Introduction

Charge-transfer complexes may be performed between electron donor molecule and an electron acceptor molecule in their ground states and almost charge transfer complexes have unique absorption bands in the ultraviolet-visible region of spectra [1-4]. The interaction between donor and acceptor is not only a charge-transfer interaction but also an expression of electrostatic force action [5-7]. The interaction between donor and acceptor is usually much weaker than interactions responsible for formation of the hydrogen bond and the covalent bond, but nevertheless it is useful for constructing crystal structure [6-10]. The solid charge-transfer complexes formed between iodine and several types of electron donors such as aromatic hydrocarbons, polycyclic amines, mixed oxygen/nitrogen-containing cyclic bases, aromatic/aliphatic amines have been studied and classified [1-10]. The triiodide ion I_3^-, pentaiodide ion I_5^-, and nonaiodide ion I_9^- were formed in the reaction of iodine with various donors, such as metal acetylacetonates [11-13], polyazacyclic [14-16], and crown ethers [17-20]. Some of charge-transfer complexes show very interesting applications in the analysis of some drugs in pure form or in pharmaceutical preparations [21, 22]. The charge-transfer in fullerene-based [23, 24] compounds is currently of great interest since these materials can be utilized as superconductors [25] and produce non-linear optical activity [26]. In continuation of our studies on the intermolecular charge-transfer complexes [27-34], we report herein the results obtained from the electronic, infrared, and Raman spectra of the two charge transfer complexes formed from the reaction of iodine with the donors like tryptophan or tyrosine. The aim of the work is to study the supposed structures and bonding of the resulting two iodine-amino acid complexes and also to study the electrical conductivity behavior.

2. Experimental

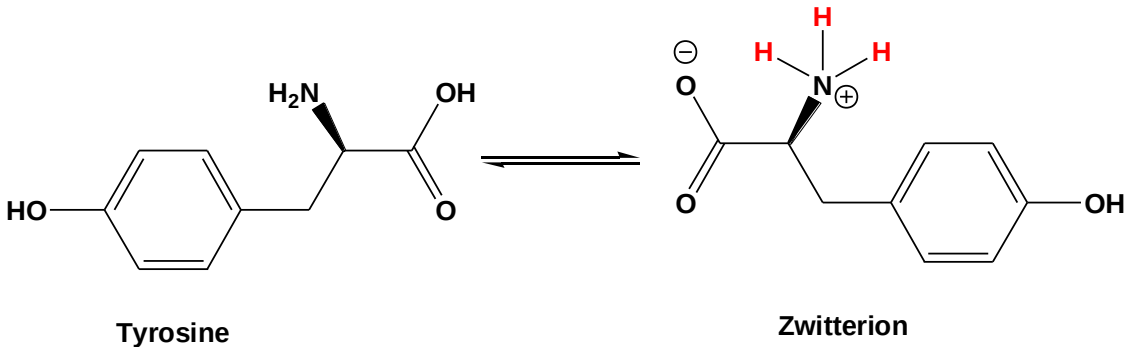
2.1 Chemicals

All chemicals used in this study were of high purity grade. Iodine and potassium iodides were obtained from BDH, tryptophan (Formula I) and tyrosine (Formula II) were obtained from Merck and AldrichChemical Co.



Tryptophan Zwitterion

Formula I: Tryptophan and its zwitterion structure



Formula II: Tyrosine and its zwitterion structure

2.2 Synthesis

The solid brown tryptophan and tyrosine triiodide charge-transfer complexes were synthesized by mixing 1 mmol of iodine, 1 mmol of KI and 1 mol of amino acids (tryptophan and tyrosine). Add tryptophan or tyrosine to the definite weight of both iodine and KI in porcelain mortar with continuous grinding in presence of few drops of methylene chloride solvent. Dry the reactions of amino acids with KI/I_2 systems by continuous suction and transfer them to a dry beaker. Store the beaker overnight in a desiccators filled with activated anhydrous calcium chloride, then transfer solid powders of iodine complexes to clean vial. The vial was capped well to exclude moist air. The contents of carbon, hydrogen, nitrogen, and I of the solid reaction products are a good agreement with the mixing molar ratios.

2.3 Instrumentals

The elemental analyses of the carbon, hydrogen and nitrogen contents were performed using a Perkin-Elmer CHN 2400 (USA). The electronic absorption spectra of methylene chloride solvent of the amino acids, iodine and resulting charge transfer complexes were recorded over a wavelength range of 200-800 nm using a UV/Vis double-beam JASCO-V-670 spectrophotometer. The instrument was equipped with a quartz cell with a 1.0 cm path length. The molar conductivities of freshly prepared 1.0 $\times 10^{-3}$ mol/cm^{3}dimethylsulfoxide (DMSO) solutions were measured for the dissolved free amino acids and its iodine charge-transfer complexes using Jenway 4010 conductivity meter. The mid-infrared (IR) spectra within the range of 4000-400 cm^{-1} for the solid powder of free amino acids and its iodine charge-transfer complexes were recorded on a Bruker FT-IR spectrophotometer with 30 scans at 2 cm^{-1} resolution, while, Raman laser spectra of samples were measured on the Bruker FT-Raman with laser 50 mW. Thermogravimetric analysis (TG/DTG) was performed under static nitrogen atmosphere between room temperature and 800 °C at a heating rate of 10 °C/min using a Shimadzu TGA–50H thermal analyzer. Scanning electron microscopy (SEM) images were taken in Quanta FEG 250 equipment. The X-ray diffraction patterns for the complexes were recorded on X 'Pert PRO PAN analytical X-ray powder diffraction, target copper with secondary monochromate. The d.c. measurements were done with the help of a Source-Measure Unit (Keithley model-236). The a.c. measurements were done on LCZ meter (Keithley model-3330). Platinum was used as contact for all the measurements.

3. Results and Discussion

3.1Molar conductance

The solid mixing process between amino acids (tryptophan and tyrosine) as a donation source, potassium iodide and iodine give a stable triiodide charge transfer complexes with general formula $[(\text{amino acid-K})]^+\cdot I_3^-$. The molar conductance values of both tryptophan and tyrosine triiodide charge–transfer complexes dissolved in DMSO solvent at 10^{-3} molar concentrations were obtained within the range 80 $\Omega^{-1}cm^2mol^{-1}$, this result discussed that the resulted complexes is electrolytic behaviour. These data was assigned to the formation of dative $D^+—A^-$ complex between amino acid donor and triiodide (I_3^-) molecule, which is matched with the general structures were suggested.

3.2 Electronic Spectra

The electronic spectra of $[(\text{tryptophan-K})]^+\cdot I_3^-$ and $[(\text{tyrosine-K})]^+\cdot I_3^-$ charge transfer complexes in methylene chloride solvent with 1×10^{-4} M concentration were scanned as presented in Fig. 1. The spectra of both charge transfer complexes were collected a real absorption bands that do not exist in the spectra of the free reactants. The tryptophan and tyrosine triiodide charge transfer complexes have new bands at (280 and 354) nm and (276 and 378) nm, respectively. These bands were formed upon the reaction of tryptophan and tyrosine with KI/I_2 in methylene chloride solvent. The band gap value for $[(\text{tryptophan-K})]^+\cdot I_3^-$ and $[(\text{tyrosine-K})]^+\cdot I_3^-$ complexes are 2.07 and 2.76 eV, respectively. The values of band gap can vary depending on particle size of the composite, with smaller band gap values indicative of relatively densely packed crystalline structures [35].

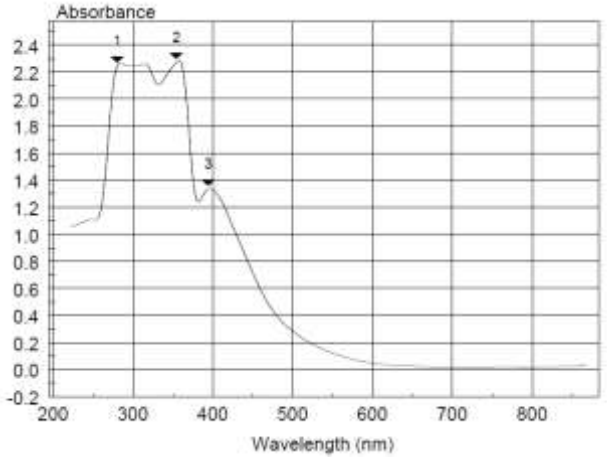


Figure 1A

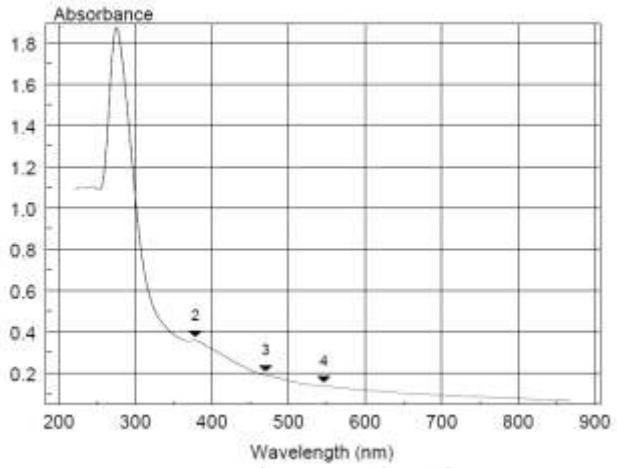


Figure 1B

Figure 1: Electronic spectra of A: $[(\text{tryptophan-K})]^{+}\cdot I_3^{-}$ and B: $[(\text{tyrosine-K})]^{+}\cdot I_3^{-}$ complexes in methylene chloride solvent.

3.3 Infrared and Raman Spectra

The infrared spectra (4000-400 cm^{-1}) of the $[(\text{tryptophan-K})]^{+}\cdot I_3^{-}$ and $[(\text{tyrosine-K})]^{+}\cdot I_3^{-}$ charge transfer complexes were performed. The spectra are shown in Fig. 2A-B. The spectral bands are discussed and assigned to their vibrational modes and listed in Table 1. The absorption bands characteristic of tryptophan and tyrosine acting as donor moieties in the mentioned triiodide complexes are detected with small changes in band intensities and wavenumber values. The sharp singlet peak at 3403 and 3207 cm^{-1} are assigned to the –NH of indol ring of tryptophan and –OH of tyrosine moiety, respectively. The strong-medium-weak bands existed within the range of 3000-2800 cm^{-1} was due to C–H stretching vibration motions of aliphatic and aromatic moieties. The infrared absorption bands due to different kind of deformation motions were observed at 1300-400 cm^{-1} [36-38]. The important absorption bands assigned to the asymmetric and symmetric stretching of NH_3^{+} as zwitterionic form of amino acid occurred at 1590-1570 cm^{-1} and (2680-2790 cm^{-1} and 2100-2150 cm^{-1}) [38], respectively. The asymmetric and symmetric stretching vibration motions of NH_3^{+} are decreasing in their intensities and also shifted to lower wavenumbers. These are assigned to the formation of intermolecular charge-transfer electrostatic binding between triiodide ions (I_3^{-}) and NH_3^{+} zwitterion (Fig. 3). The asymmetric stretching at (1500-1400 cm^{-1}) and also symmetric stretching at (1410-1310 cm^{-1}) of COO^{-} were also observed showing the zwitterionic nature of tryptophan and tyrosine. The stretching vibration motions of C–C were assigned at (1130-1150 and 920-890 cm^{-1}), deformation vibrations at (420-540 cm^{-1}) and CH_2 twisting vibrations at (1220-1270 cm^{-1}) [38] were also assigned.

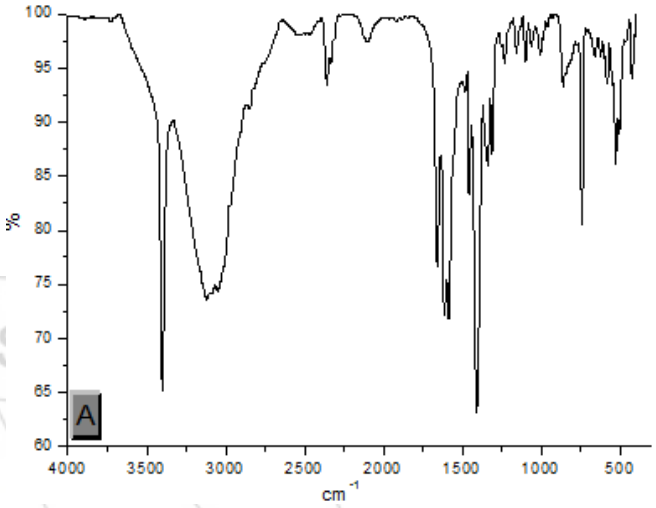


Figure 2A

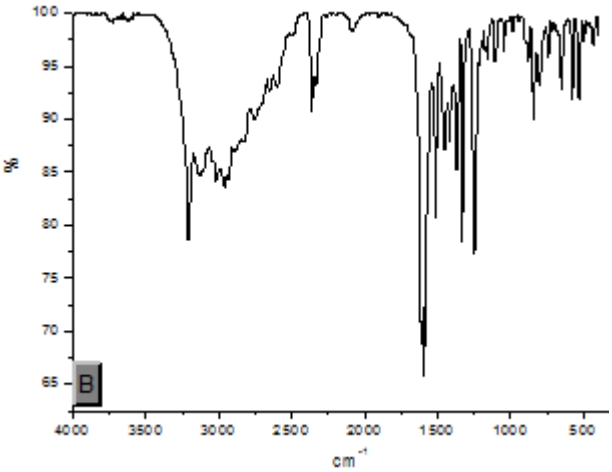


Figure 2B

Figure 2: Infrared spectra of A: $[(\text{tryptophan-K})]^{+}\cdot I_3^{-}$ and B: $[(\text{tyrosine-K})]^{+}\cdot I_3^{-}$ complexes.

Table 1: Infrared absorption frequencies (cm^{-1}) and tentative assignments of the free amino acid reactants and their charge transfer complexes.

Tryptophan	Tyrosine	$[(\text{tryptophan-K})]^{+}\cdot I_3^{-}$	$[(\text{tyrosine-K})]^{+}\cdot I_3^{-}$	Assignment
3403	3207	3400	3211	-NH indol; tryptophan -OH; tyrosine
3053 2965 2907 2849	3041 3025 2963 2834	3104 3054 2848	3129 2960 2892 2829	CH_2 asymmetric stretching
2736	2651	2770	2753 2717	NH_3^{+} symmetric stretching
2643	2603	2522 2472	2647 2597	NH stretching

2103	2100	2102	2077	NH_3^+ symmetric stretching
1612	1607	1601	1595	NH_3^+ asymmetric stretching
1555	1533	1576	1519	COO^- asymmetric stretching
1416	1416	1407	1413	COO^- symmetric stretching

1316 1232 1167	1328 1267 1246	1345 1306 1225	1369 1332 1250	CH_2 deformation
1097	1111	1100	1100	C-C stretching
547 505	575 536	524 424	524 430	C-C deformation

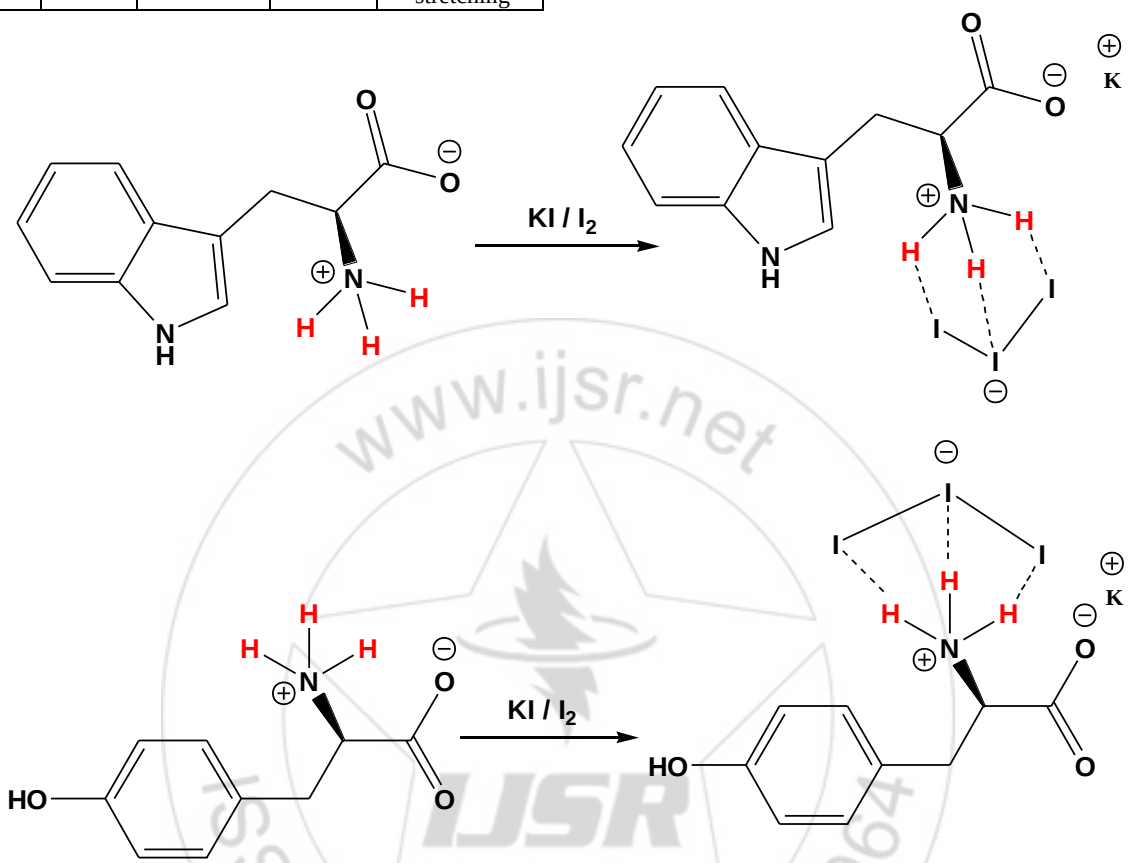
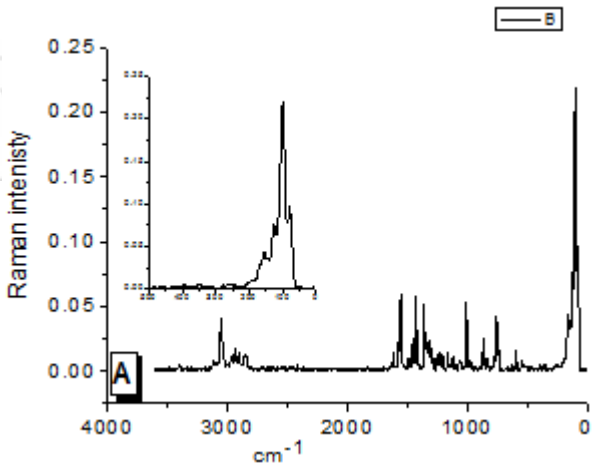


Figure 3: Suggested structures of $[(tryptophan\text{-}K)]^+ \cdot I_3^-$ and $[(tyrosine\text{-}K)]^+ \cdot I_3^-$ charge transfer complexes.

The Raman spectra of $[(tryptophan\text{-}K)]^+ \cdot I_3^-$ and $[(tyrosine\text{-}K)]^+ \cdot I_3^-$ are exhabited in Fig. 4 and the recorded absorption frequencies refer to the presence of triiodide ion, I_3^- [39-43]. The medium-to-strong peaks at 160 cm^{-1} is assigned to the asymmetric stretching vibrations $\nu_{as}(I–I)$; I_3^-. Observed very intence band assigned to the symmetrical stretching vibrations $\nu_s(I–I)$; I_3^- is located at 126 cm^{-1}. The third shoulder band existed at 100 cm^{-1} is due to $\delta(I_3^-)$. Since both the ν_s and ν_{as} of the triiodide ion are found in the Raman spectra, the I_3^-unit appears to be non-linear with C_{2v} symmetry. General mechanism for the formation of both $[(tryptophan\text{-}K)]^+ \cdot I_3^-$ and $[(tyrosine\text{-}K)]^+ \cdot I_3^-$ complexes are proposed as follows:

$[(tryptophan)] + I_2 + KI \rightarrow [(tryptophan\text{-}K)]^+ \cdot I_3^-$

$[(tyrosine)] + I_2 + KI \rightarrow [(tyrosine\text{-}K)]^+ \cdot I_3^-$



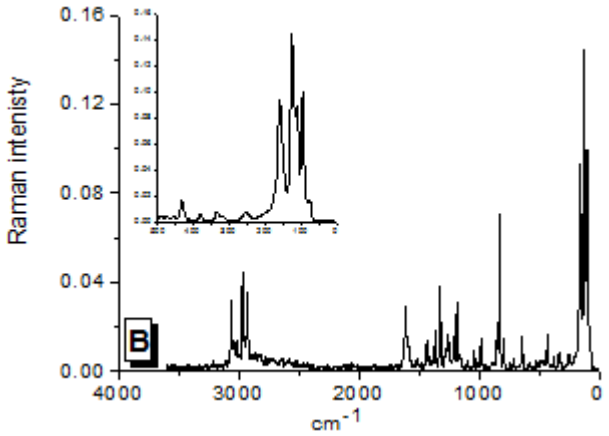


Figure 4: Raman spectra of A: $[(\text{tryptophan-K})]^{+}\cdot I_3^{-}$ and B: $[(\text{tyrosine-K})]^{+}\cdot I_3^{-}$ complexes

3.4 XRD and SEM studies

X-ray powder diffraction patterns can be used to identify about the crystallinity. Fig. 5 shows amorphous shape of the synthesized $[(\text{tryptophan-K})]^{+}\cdot I_3^{-}$ and their aggregates.It is clear from the SEM image that the synthesized tryptophan triiodide complex is almost irregular shape as presented in Fig. 6.

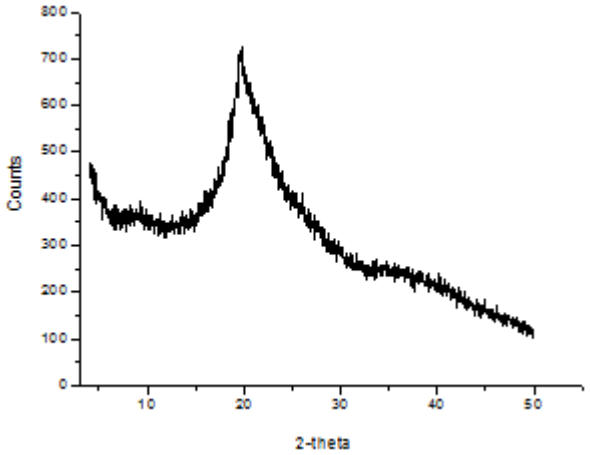


Figure 5: XRD patterns of $[(\text{tryptophan-K})]^{+}\cdot I_3^{-}$ complex.

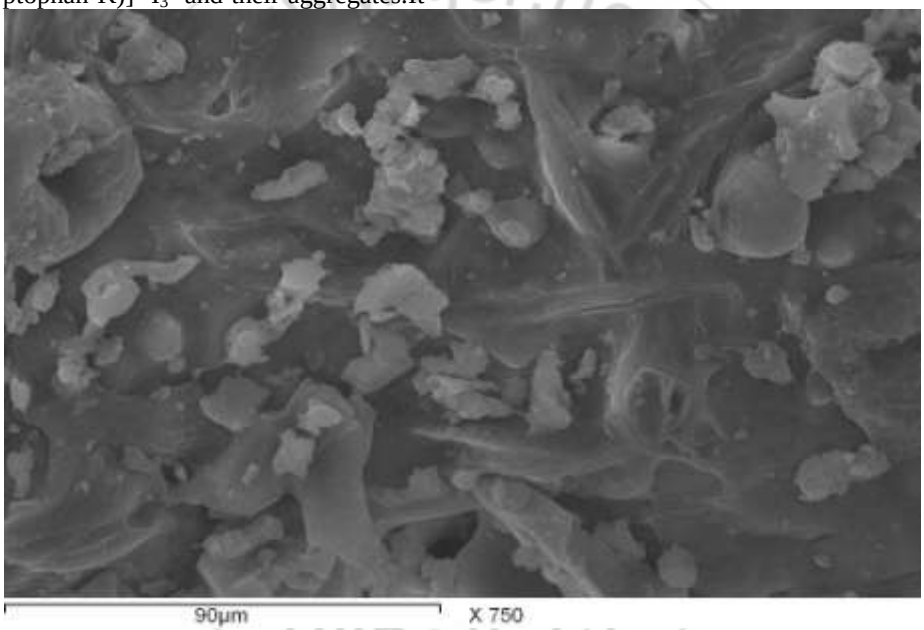


Figure 6: SEM image of $[(\text{tryptophan-K})]^{+}\cdot I_3^{-}$ complex.

3.5 Thermal analysis

The thermal behaviors of $[(\text{tryptophan-K})]^{+}\cdot I_3^{-}$ and $[(\text{tyrosine-K})]^{+}\cdot I_3^{-}$ charge transfer complexes have been studied as a function of temperature. The decomposition nature of suggested structures with temperature and the residual products are discussed. Thermal steps of both complexes were discussed upon TG diagrams corresponding to these complexes are shown in Fig. 7. The differential thermogravimetry (DTG) data of the iodide complexes have three exothermic decomposition steps in the range of 100-300 ^{o}C, 300-500^{o}C, and 500-800 ^{o}C with DTG_{max}= (110 ^{o}C, 315^{o}C and 600^{o}C) with total weight loss equal 89.97 % and (310 ^{o}C, 400^{o}C and 550^{o}C) with total weight loss equal 89.27%, for $[(\text{tryptophan-K})]^{+}\cdot I_3^{-}$ and $[(\text{tyrosine-K})]^{+}\cdot I_3^{-}$ charge-transfer complexes, respectively, attributed to loss of one amino acid moiety and iodide molecule, further leaving potassium oxide residual contaminated with polluted carbons.

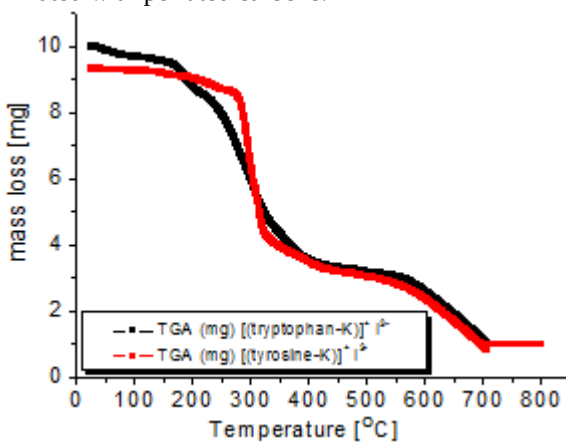


Figure 7: TGA curves of A: $[(\text{tryptophan-K})]^{+}\cdot I_3^{-}$ and B: $[(\text{tyrosine-K})]^{+}\cdot I_3^{-}$ complexes.

3.6 Kinetic Studies

The kinetic thermodynamic parameters (Table 2) of the resulted charge–transfer triiodide complexes can be calculated using the Coats-Redfern method [44] as follows:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left(\frac{ZR}{\varphi E}\right) - \frac{E}{RT}$$

Where α, and φ are the fraction of the sample decomposed at time t and the linear heating rate, respectively. R is the gas constant and E is the activation energy in kJ mol^{-1}. A plot of $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$ against $1/T$ (Fig. 8) was found to be linear from the slope of which E and Z (Arrhenius constant) can be deduced from the slope and intercept, respectively. The enthalpy of activation, ΔH, and the free enthalpy of activation, ΔG, can be calculated via the following equation:

$$\Delta H = E - RT_m \; ; \Delta G = \Delta H - T_m \Delta S$$

Accordingly, the kinetic data in Table 2, the [(tryptophan-K)]$^+\cdot I_3^-$ and [(tyrosine-K)]$^+\cdot I_3^-$ charge-transfer complexes has −ve entropy, which indicates that activated triiodide complexes have more ordered system than reactants. Also, it was found that the [(tryptophan-K)]$^+\cdot I_3^-$ complex has a higher thermal stability, because of the tryptophan donor has a high molecular weight and high melting point rather than tyrosine donor.

Table 2: Kinetic and thermodynamic parameters of the [(tryptophan-K)]$^+\cdot I_3^-$ and [(tyrosine-K)]$^+\cdot I_3^-$ complexes.

Complex	Parameter					r
	E (kJol^{-1})	A (s^{-1})	ΔS (J mol^{-1}K^{-1})	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	
[(tryptophan-K)]$^+\cdot I_3^-$	1.42×10^5	4.70×10^{12}	-67.5	1.40×10^5	1.45×10^5	0.9990
[(tyrosine-K)]$^+\cdot I_3^-$	1.12×10^5	7.55×10^7	-99.2	1.10×10^5	1.70×10^5	0.9992

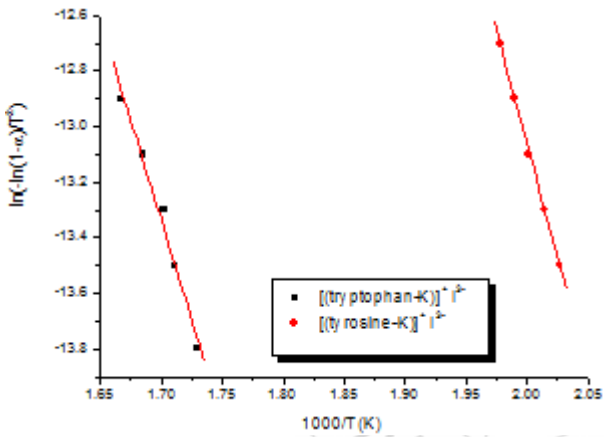


Figure 8: Coats-Redfern (CR) plots of the A: [(tryptophan-K)]$^+\cdot I_3^-$ and B: [(tyrosine-K)]$^+\cdot I_3^-$ complexes.

3.7 Solid electrical conductivity studies

The [(tryptophan-K)]$^+\cdot I_3^-$ and [(tyrosine-K)]$^+\cdot I_3^-$ charge transfer complexes were compressed in pellet form to measure the DC electrical conductivity. The temperature dependence of the DC electrical conductivity (σ) of the complexes was carried out in the temperature range 300-373 K. It was found that the values of σ increase with increasing the temperature according to the Arrhenius relation.

$$\sigma = \sigma_o \exp(-E_a/KT)$$

Where E_a is the activation energy of the conduction process and σ_o is constant, K Boltzmann constant and T is the absolute temperature. Fig. 9 shows the plot of log σ vs (1000/T)which are found to be linear in the used temperature range. This indicates that the two triiodide charge transfer complexes have a semiconducting nature [45]. The activation energy of these complexes was calculated from the slope of the lines in Fig. 9. The E_a of [(tryptophan-K)]$^+\cdot I_3^-$ complex was found to be 0.65 eV. The value of E_a of [(tyrosine-K)]$^+\cdot I_3^-$ is 2.41eV which is relatively large compared with that of the other [(tryptophan-K)]$^+\cdot I_3^-$ complex.

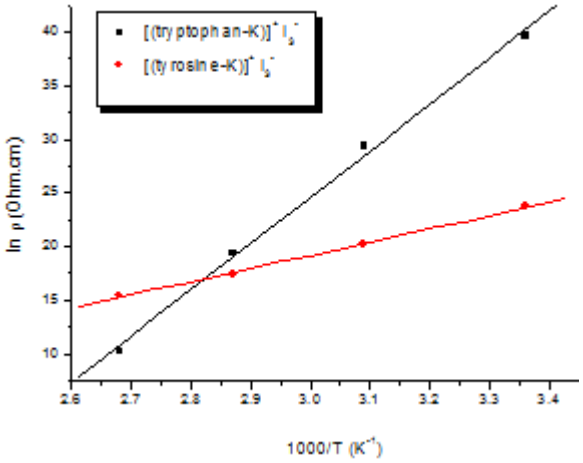


Figure 9: Curves of temperature dependence (25, 50, 75 and 100°C) of the electrical conductivity of the CT complexes.

4. Acknowledgement

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