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Preparation and spectroscopic studies on charge-transfer complexes of 2-hydroxypyridine with electron acceptors

Akmal S. Gaballa *

Faculty of Specific Education, Zagazig University, Zagazig, Egypt

HIGHLIGHTS

- Spectroscopic investigations on the interaction of 2-hydroxypyridine as an electron donor with σ- and π-acceptors.
- σ- and π-acceptors used in this study are iodine, chloranilic acid and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone.
- The prepared CT-complexes have the general formula [(HPyO)(acceptor)].
- Formation constant, charge transfer energy and thermal analyses data of CT-complexes are presented.

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ABSTRACT

The CT-interactions of electron acceptors such as iodine (I_2), chloranilic acid (H_2CA) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) with 2-hydroxypyridine (HPyO) have been investigated in the defined solvent. The data indicate the formation of CT-complexes with the general formula [(HPyO)(acceptor)]. The 1:1 stoichiometry of the (HPyO)–acceptors were based on elemental analysis, IR spectra and thermogravimetric analysis of the solid CT-complexes along with the photometric titration measurements for the reactions. The formation constants (K_{CT}) for the CT-complexes are shown to be strongly dependent on the type and structure of the electron acceptors. Factors affecting the CT-processes are discussed.

1. Introduction

Many charge-transfer complexes were formed between π- and *n*-donor [1–10]. Charge-transfer complexes exhibit certain properties, which could be important in biological systems and other various applications in electronics, solar cells, optical devices and others [11–13]. The mechanism of photosynthesis and oxidative phosphorylation are the object of much intense study [1–7]. CT-reaction is utilized for the assay of different pharmaceuticals [14,15].

2-Hydroxypyridine is an aromatic heterocyclic compound representing a very important class of compounds which possess a system of π- and *n*-electrons. This system in principle is able to form two types of charge-transfer complexes. Furthermore, CT complexes of 2-hydroxypyridine are particularly interesting because they provide an opportunity to examine the degree of interaction between π- and *n*-donor sites with different acceptors and the study of its CT interactions can help elucidate many chemical and biological phenomena they take part in. It is well known to form hydrogen bonded structures somewhat related to the base-pairing mechanism found in RNA and DNA. It is also a classic case of a molecule that exists as tautomers. The determination of which of the two tautomeric forms is present in solution has been the subject of many publications. The energy difference appears to be very small and is dependent on the polarity of the solvent. Non-polar solvents favor the formation of 2-hydroxypyridine whereas polar solvents such as alcohols and water favor the formation of 2-pyridone [16–19]. By considering the equilibrium between 2-pyridone and 2-hydroxypyridine, it is clear that this tautomerism is ruled by a proton transfer between nitrogen and oxygen, Fig. 1 [20–24].

We have been studying the synthesis and spectroscopic characterization of a variety of molecular donors and acceptors in order to fully understand the nature of their CT interactions [8,9,25–28]. In connection with such studies herein, we have prepared and spectroscopically investigated the interaction of 2-hydroxypyridine (HPyO) as an electron donor with iodine (I_2), chloranilic

* Tel.: +20 100 3627093.
E-mail addresses: akmalsg@yahoo.com, akmalsg@zu.edu.eg

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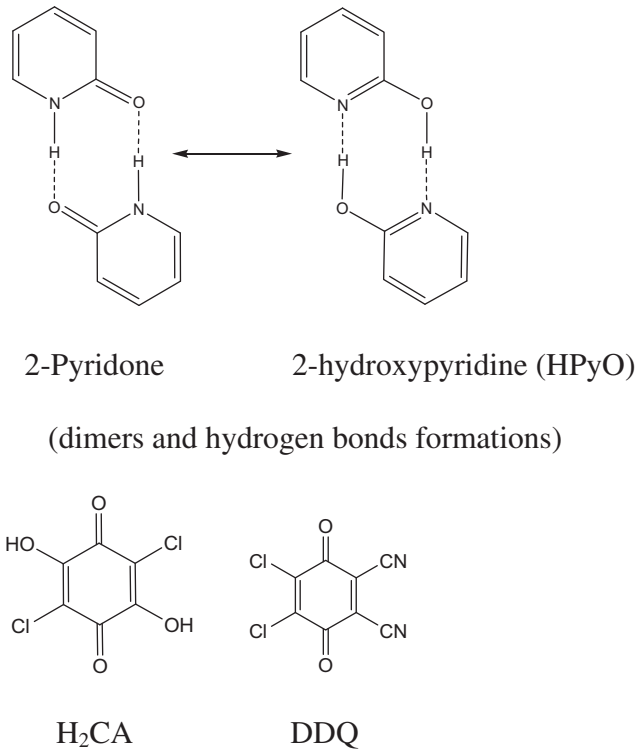

Fig. 1. Structure of the studied donor and acceptors.

acid (H_2CA) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) as electron acceptors to characterize the reaction products.

2. Experimental

2.1. Materials and spectral measurements

All chemicals used were of high grade. 2-Hydroxypyridine (HPyO) was obtained from Aldrich, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) was obtained from BDH while chloranilic acid (H_2CA) and Iodine were purchased from Merck Chemical Co. and were used as received.

The electronic absorption spectra were recorded in the region of 250–900 nm using UV–Vis. spectrophotometer model JASCO V-530 with quartz cell of 1.0 cm path length. The infrared spectra of the reactants and the obtained complexes were recorded using KBr disks on Perkin–Elmer 1430 ratio recording infrared spectrometer.

Photometric titrations at (294, 360), 520 and 396 nm were performed for the reactions of I_2, H_2CA and DDQ, respectively, with the donor (HPyO) in the defined solvent at 25 °C using a Helios Gamma Unicam UV–Vis. Spectrophotometer and Jenway Visible range spectrophotometer model 6300 as follows. The concentrations of HPyO (C_d) were kept fixed at 1.00×10^{-4} mol/L in the reaction with the acceptors I_2, H_2CA and DDQ, respectively, whereas the concentrations of the acceptors C_a were changed over a wide range of: 0.25×10^{-4}–3.00×10^{-4} mol/L for all acceptors. The acceptor–donor molar ratio (C_a:C_d) obtained in this case varies over the range 0.25:1.00–3.00:1.00. The peak absorbances appeared in the spectra that assigned to the formed CT-complexes were measured and plotted as a function of the ratio C_a:C_d according to the known method [29].

Elemental analyses were carried out in microanalysis unit of Cairo University, Egypt using CHNS-932 (LECO) and Vario EL elemental analyzers. Chlorine was determined by burning the substance in oxygen with platinum contact and following titration with mercuric nitrate towards diphenylcarbazide. The results of elemental analyses of the solid complexes were in accordance with the stoichiometric ratios obtained from photometric titrations.

Thermal analyses (TG, DTG) were carried out using a Shimadzu TGA-50 H computerized thermal analysis system. The system includes program which process data from the thermal analyzer with the ChromotPac C-R3A. The rate of heating of the samples was kept at 10 °C/min. Sample masses 2.066, 2.811 and 1.456 mg for HPyO and complexes **2** and **3**, respectively were analyzed under N_2 flow at 20 ml/min.

2.2. Preparation of the solid complexes

2.2.1. [(HPyO)I]·I (**1**),

To a solution of HPyO (47.6 mg, 0.50 mmol) in EtOH (10 mL), a solution of the acceptor (280.0 mg, 1.10 mmol I_2) in EtOH (50 mL) was added and stirred for 3 *h* then left overnight. The dark brown precipitate formed was filtered off, washed with the least amount of EtOH ($2 \times 1/2$ mL). The precipitate was also washed with Et_2O (3×1 mL) and dried in vacuo overnight over $CaCl_2$. Yield: 140.0 mg (80.16%).

Anal. found (Calcd. for $C_5H_5I_2NO$, 348.91): C, 16.98 (17.21); H, 1.51 (1.44); N, 4.11 (4.01).

2.2.2. [(H_2PyO)(HCA)] (**2**)

To a solution of HPyO (95.2 mg 1.0 mmol) in EtOH (20 mL), a solution of H_2CA (211.0 mg, 1.01 mmol) in EtOH (30 mL) was added at room temperature. The formed violet precipitate was filtered off, washed with the same solvent ($3 \times 1/2$ mL) and dried in vacuo overnight over $CaCl_2$. Yield: 240.0 mg (78.84%).

Anal. found (Calcd. for $C_{11}H_7Cl_2NO_5$, 304.08): C, 43.67 (43.45); H, 2.44 (2.32); N, 4.69 (4.61); Cl, 22.99 (23.32).

2.2.3. [(HPyO)(DDQ)] (**3**)

To a solution of HPyO (95.1 mg, 1.0 mmol) in EtOH (10 mL), a solution of DDQ (228.0 mg, 1.0 mmol) in EtOH (40 mL) was added at room temperature. The formed dark reddish-brown precipitate was filtered off, washed with EtOH ($3 \times 1/2$ mL) and air dried. Yield: 230.0 mg (71.41%).

Anal. found (Calcd. for $C_{13}H_5Cl_2N_3O_3$, 322.10): C, 48.52 (48.47); H, 1.61 (1.56); N, 13.23 (13.05); Cl, 22.52 (22.01).

3. Results and discussion

Three stable charge-transfer complexes, [(HPyO)I]·I (**1**), [(H_2PyO)(HCA)] (**2**) and [(HPyO)(DDQ)] (**3**) with the molar ratio of 1:1 (donor–acceptor) are obtained in good yields during the reaction of HPyO in EtOH with I_2, H_2CA and DDQ, respectively.

3.1. Electronic spectra

Figs. 2A–2D show the electronic absorption spectra of the donor HPyO and of the corresponding formed CT-complexes. The spectra revealed new absorption bands attributed to the CT-interactions. These bands are not present in the spectra of the free reactants and are observed at (294, 360), 520 and 396 nm for the complexes [(HPyO)I]·I, [(H_2PyO)(HCA)] and [(HPyO)(DDQ)], respectively. These absorptions are associated with the strong change in color observed upon mixing of reactants and reflect the electronic transitions in the formed CT-complexes. Furthermore, photometric titration measurements based on these characteristic CT-absorption bands of the CT-complexes, Figs. 3A, 3B, 3C confirmed the complex formation in a ratio, HPyO: acceptor of 1:1 in all cases. This is in good agreement with the obtained elemental analysis of the solid CT-complexes. Examination and comparison of the

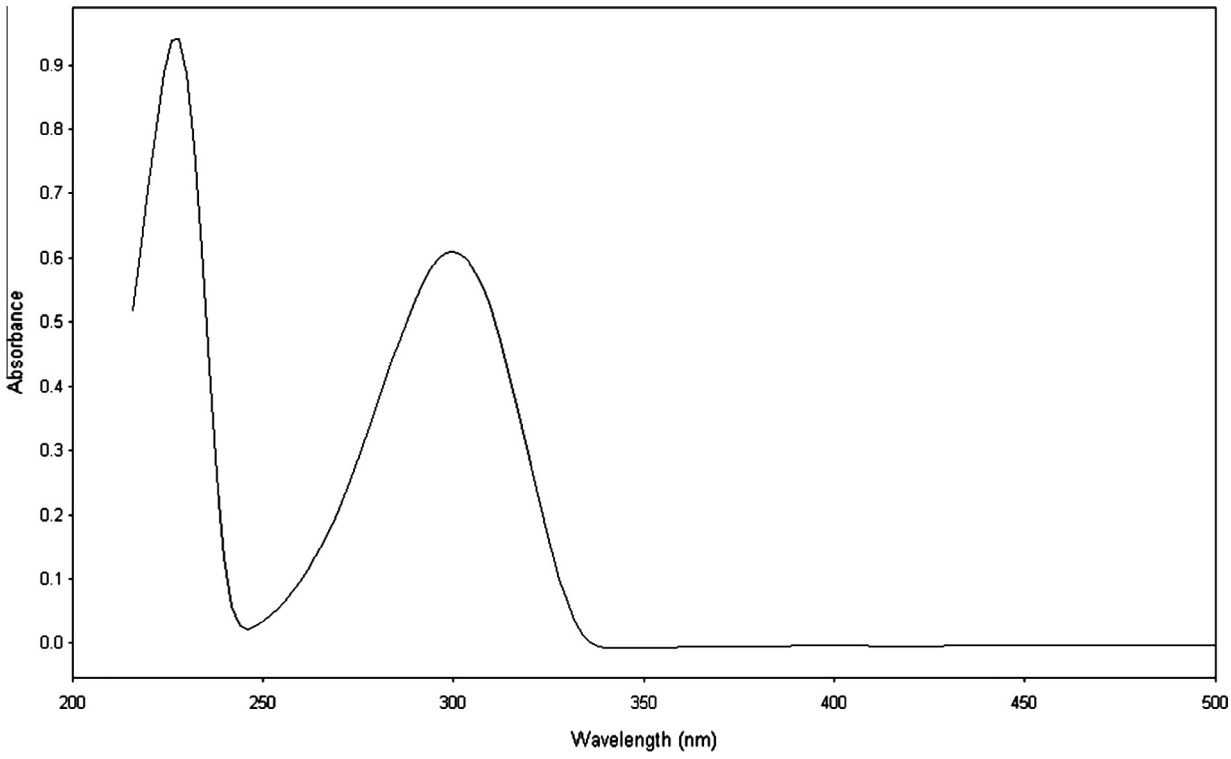

Fig. 2A. Electronic absorption spectrum of HPyO in EtOH, ([HPyO] = 1.0×10^{-4} M).

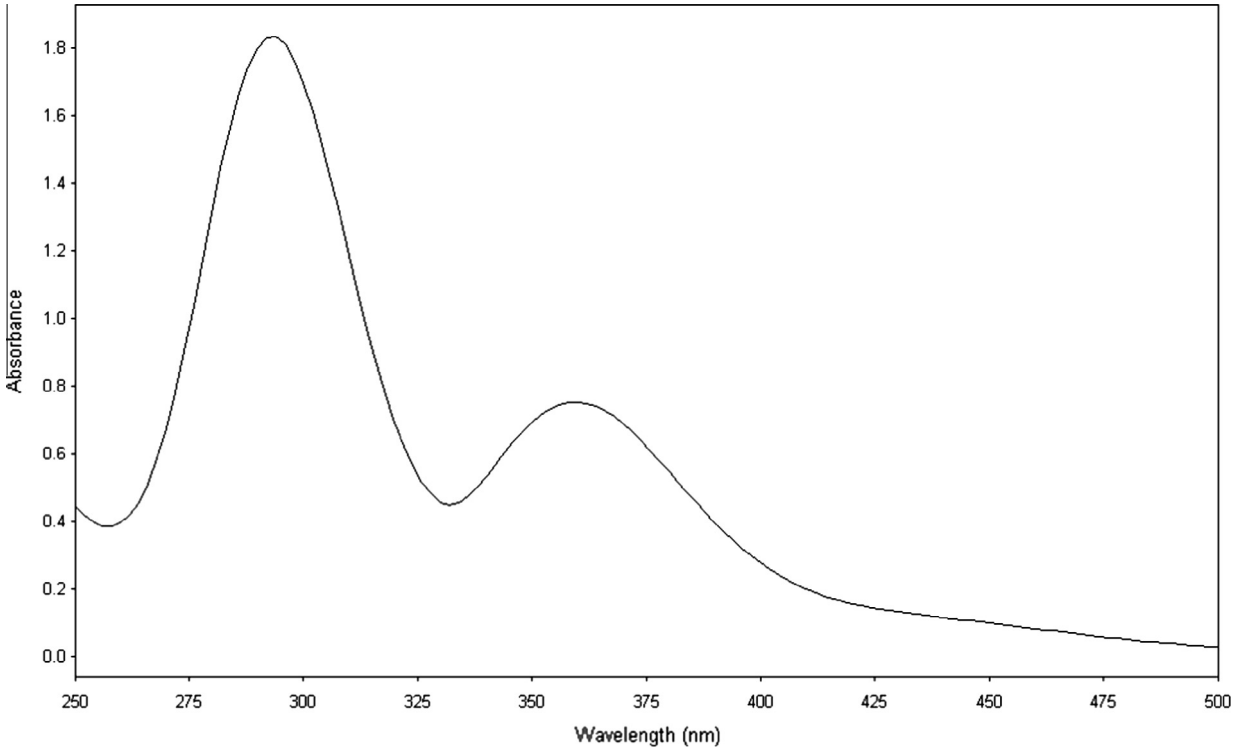

Fig. 2B. Electronic absorption spectrum of HPyO–I_2 reaction in EtOH ([HPyO] = 1.0×10^{-4} M and [I_2] = 1.0×10^{-4} M).

absorption spectra of the HPyO–acceptor systems reveal that the spectra are characterized by a maxima at the wavelengths (294, 360), 520 and 396 nm which are nearly similar to the same absorption bands of such acceptors with other donors [30–32].

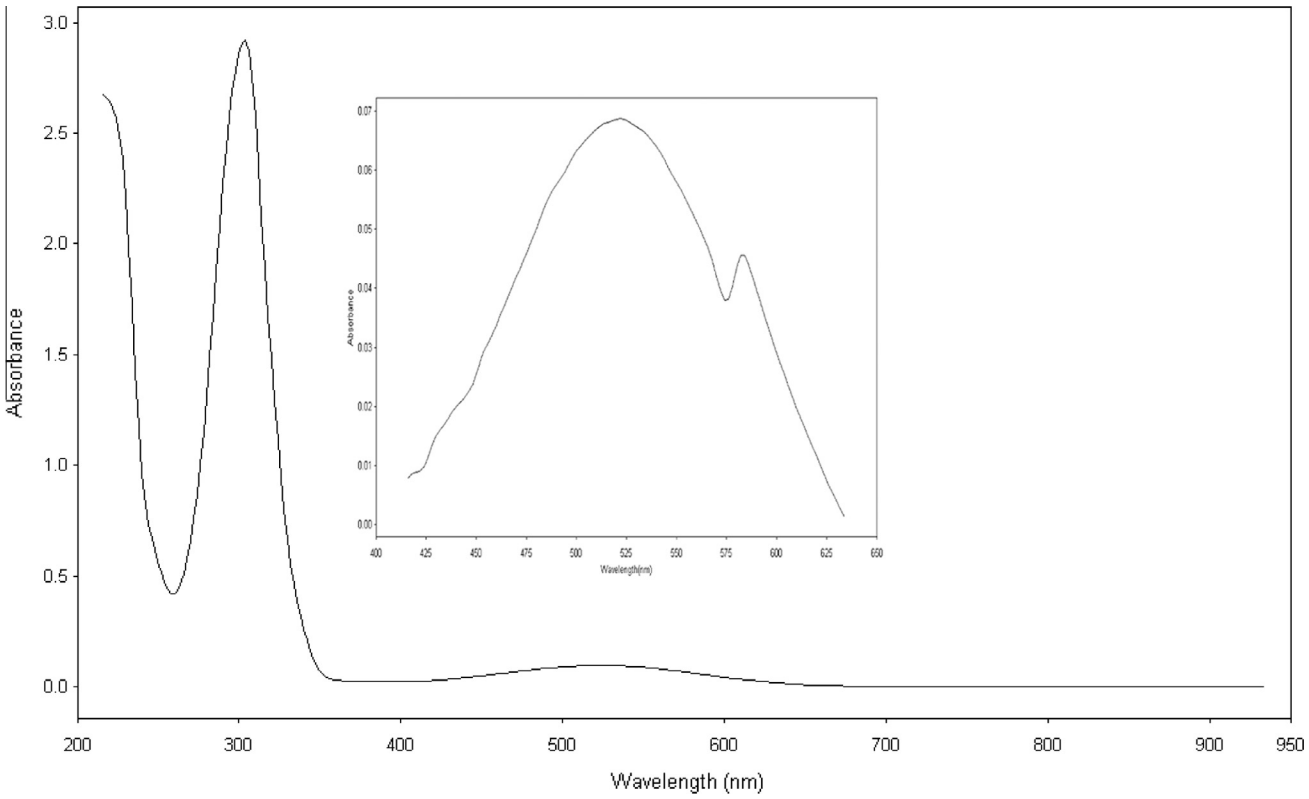

Fig. 2C. Electronic absorption spectrum of HPyO–H_2CA reaction in EtOH ([HPyO] = 1.0×10^{-4} M and [H_2CA] = 1.0×10^{-4} M).

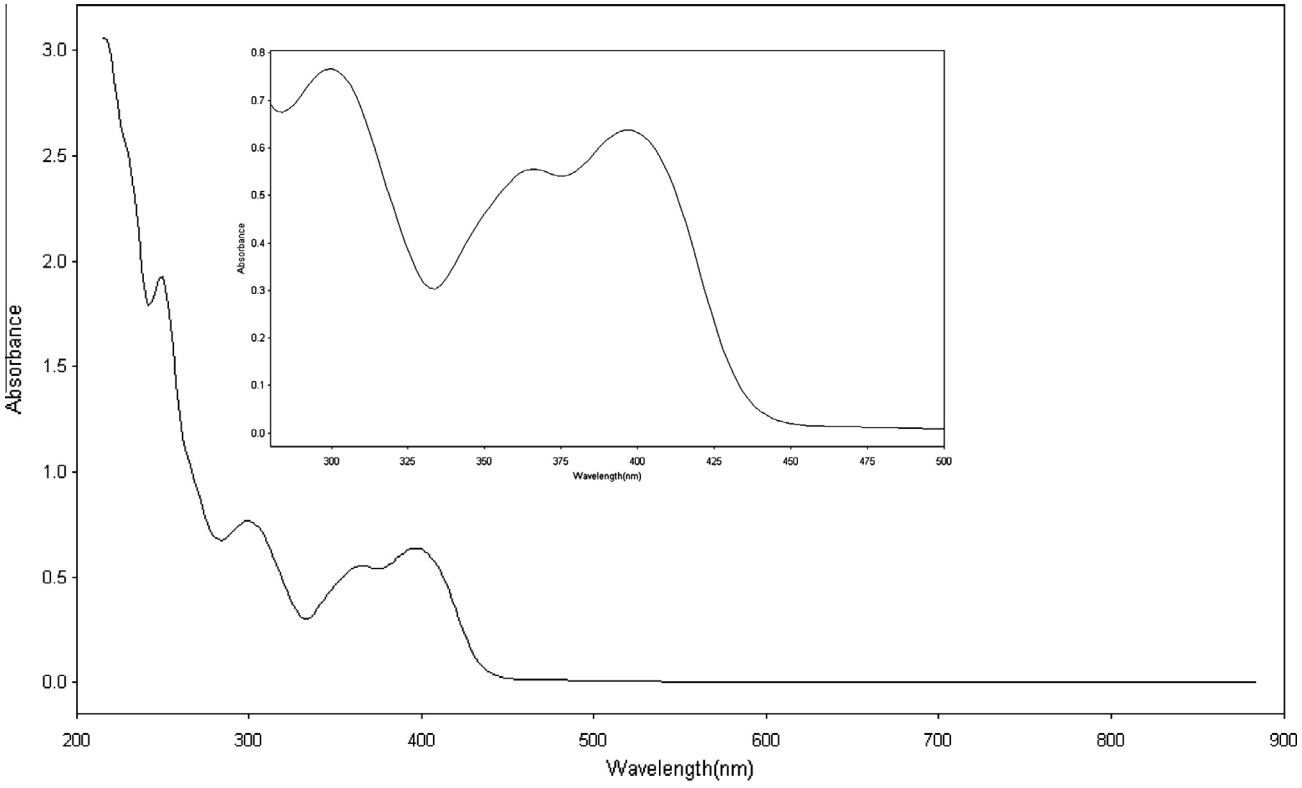

Fig. 2D. Electronic absorption spectrum of HPyO–DDQ reaction in EtOH ([HPyO] = 1.0×10^{-4} M and [DDQ] = 1.0×10^{-4} M).

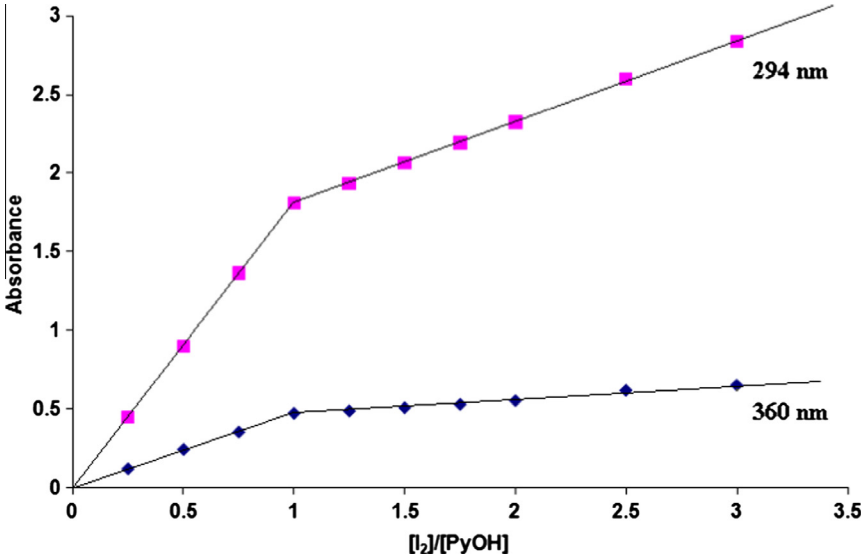

Fig. 3A. Photometric titration curves of HPyO–I_2 reaction in EtOH at 294 and 360 nm.

As previously indicated the absorption spectrum of the iodine complex, Fig. 2B, shows new strong absorption bands at 294 and 360 nm. Neither the free reactants HPyO nor iodine show these absorptions. These two absorptions of iodine complex are well known [4–7,28] to be characteristic of the iodide ion, I^-. Based on the reaction stoichiometry of 1:1 (HPyO:I_2) as well as on the elemental analysis data, the formed CT-complex of HPyO-iodide is identified as $[(HPyO)I]^+ \cdot I^-$. The formation of $[(HPyO)I]^+ \cdot I^-$ could be understood as follows:

(i) Formation of the outer complex, $(HPyO) + I_2 \rightarrow [(HPyO)]\ I_2$
(ii) This is followed by the formation of inner complex, $[(HPyO)]\ I_2 \rightarrow [(HPyO)I]^+\ I^-$.

Photometric titration for HPyO–DDQ system based on the absorption at 396 nm shows a reaction stoichiometry of 1:1 (HPyO:DDQ), indicate that this absorption belongs to the charge transfer and the complex could be formulated as [(HPyO)(DDQ)]. Similar complexes with 2-aminopridine and 3-aminopyridine were obtained with the same molar ratio [30b] which means that the donor has no effect on the reaction stoichiometries.

3.2. Formation constant and charge transfer energy of CT-complexes

The obtained spectrophotometric data, Table 1 were used to calculate the values of both equilibrium constants, K_C, and extinction coefficient, ε of the CT-complexes in EtOH for [(HPyO)I] I (**1**), [(H_2PyO)(HCA)] (**2**) and [(HPyO)(DDQ)] (**3**) for the 1:1 stoichiometry using following equation [33,34]:

$$\frac{C_d^\circ \cdot C_a^\circ}{A} = \frac{1}{\varepsilon K_c} + \frac{C_d^\circ + C_a^\circ}{\varepsilon} \quad (1)$$

where C_a° and C_d° are the initial concentration of the acceptor and the donor, respectively, and A is the absorbance of the CT band. Plotting $C_d^\circ \cdot C_a^\circ/A$ vs $(C_d^\circ + C_a^\circ)$ for the complexes **1**, **2** and **3**, straight lines were obtained supporting our conclusion of the formation of the 1:1 complexes, Figs. 4A–4C. In these plots, the slope and intercept for

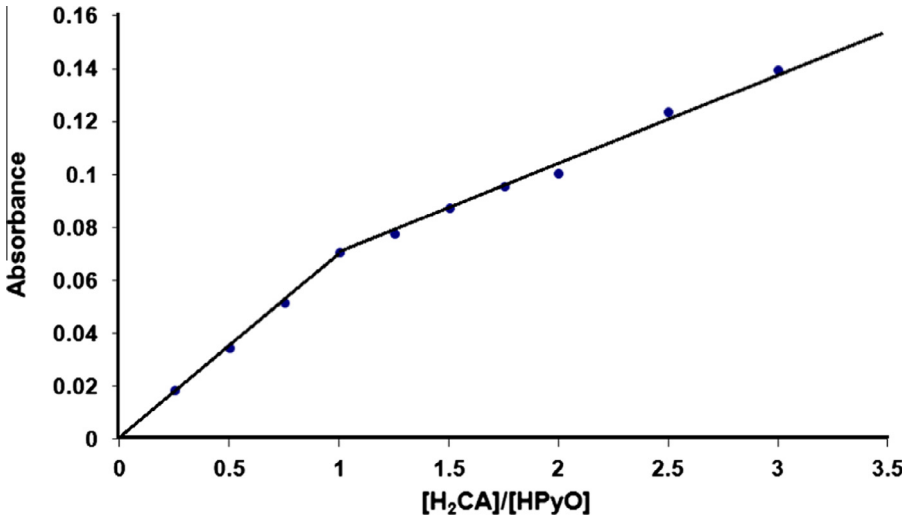

Fig. 3B. Photometric titration curves of HPyO–H_2CA reaction in EtOH at 520 nm.

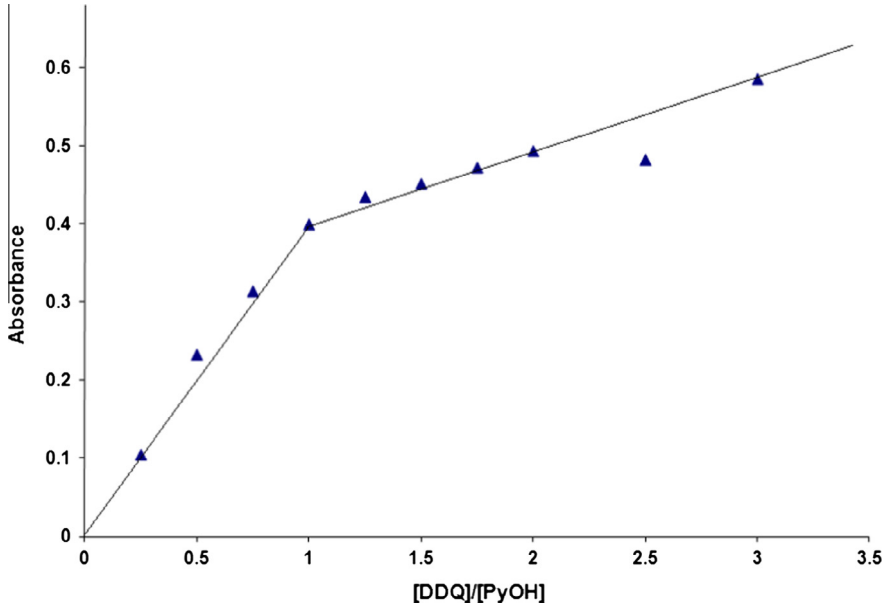

Fig. 3C. Photometric titration curves of HPyO–DDQ reaction in EtOH at 396 nm.

each case equal $1/\varepsilon$ and $1/\varepsilon K_C$, respectively. The values of both K_C and ε associated with the complexes are given in Table 2.

The high values of (K_C) reflects the high stability of the complexes as a result of the expected high donation of the HPyO which contains one hetero nitrogen atom and one hydroxyl group. The data also reveals that [(HPyO)(DDQ)] complex shows a higher value of the formation constant (K_C) in comparison with [(HPyO)I] I and [(H_2PyO)(HCA)] complexes. The values of the equilibrium constants are dependent on the nature of the acceptor including the type of electron withdrawing substituents such as cyano and halo groups.

The oscillator strength (f) was obtained from the following equation [35]:

$$f = 4.319 \times 10^{-9}(\varepsilon_{max} \cdot \Delta\upsilon_{1/2}) \quad (2)$$

where $\upsilon_{1/2}$ is the band-width for half-intensity in cm^{-1} and ε_{max} is the maximum extinction coefficient of the CT-band. The oscillator strength values are given in Table 2. The data resulted reveals several items: The HPyO–I_2, HPyO–H_2CA and HPyO–DDQ systems show different values of both formation constant (K_C) and molar absorptivity (ε). The different values of the oscillator strength, f, increases with increasing the accepting property of the acceptor. This result could also be explained on the basis of competitive solvent interactions with the acceptors [36].

The transition dipole moment (μ) which determines the transitions from a donor bonding orbital to an acceptor antibonding orbital is calculated using Eq. (3) [37–39]. A μ values were found in the following order for CT complexes, **1** > **3** > **2**.

$$\mu_{(Debye)} = 0.958\left(\frac{\varepsilon_{max} \cdot \Delta\upsilon_{1/2}}{\upsilon_{max}}\right)^{1/2} \quad (3)$$

The ionization potential (I_p) of the HPyO donor in the charge transfer complexes **1**, **2** and **3** are calculated using Eq. (4) derived by Aloisi and Pignataro [40–42];

$$I_{D(eV)} = 5.76 + 1.53 \times 10^{-4} \cdot \upsilon_{CT} \quad (4)$$

where υ_{CT} is the wavenumber in cm^{-1} corresponding to the CT band formed from the interaction between donor and acceptor. The electron donating power of a donor molecule is measured by its ionization potential which is the energy required to remove an electron from the highest occupied molecular orbital. I_p values were found in the following order for CT complexes, **1** > **3** > **2**.

Table 1
The values of $C_d^\circ \cdot C_a^\circ/A$ and $C_d^\circ + C_a^\circ$ for [(HPyO)(acceptors)] complexes.

V_a, ml (5.00×10^{-4} M)[a]	C_a° ($\times 10^{-4}$)	Ratio (a/d)	A				$C_d^\circ + C_a^\circ$ ($\times 10^{-4}$)	$C_d^\circ \cdot C_a^\circ$, ($\times 10^{-8}$)	$C_d^\circ \cdot C_a^\circ/A$ ($\times 10^{-8}$)			
			1, 294 nm	**1**, 360 nm	**2**, 520 nm	**3**, 390 nm			**1**, 294 nm	**1**, 360 nm	**2**, 529 nm	**3**, 390 nm
0.25	0.25	0.25	0.451	0.122	0.019	0.105	1.25	0.25	0.554	2.049	13.16	2.38
0.50	0.50	0.50	0.902	0.245	0.035	0.233	1.50	0.50	0.554	2.041	14.29	2.15
0.75	0.75	0.75	1.365	0.356	0.052	0.314	1.75	0.75	0.549	2.107	14.42	2.39
1.00	1.00	1.00	1.811	0.475	0.071	0.399	2.00	1.00	0.552	2.105	14.08	2.51
1.25	1.25	1.25	1.935	0.490	0.078	0.434	2.25	1.25	0.646	2.551	16.03	2.88
1.50	1.50	1.50	2.064	0.511	0.088	0.451	2.50	1.50	0.727	2.935	17.05	3.66
1.75	1.75	1.75	2.193	0.532	0.096	0.472	2.75	1.75	0.798	3.289	18.23	3.71
2.00	2.00	2.00	2.325	0.556	0.101	0.493	3.00	2.00	0.860	3.597	19.80	4.06
2.50	2.50	2.50	2.601	0.622	0.124	0.482	3.50	2.50	0.961	4.019	20.16	5.19
3.00	3.00	3.00	2.835	0.655	0.140	0.585	4.00	3.00	1.058	4.580	21.43	5.13

[a] V_d, is 1 ml (5.00×10^{-4} M); C_d° is 1.00×10^{-4} M in all systems.

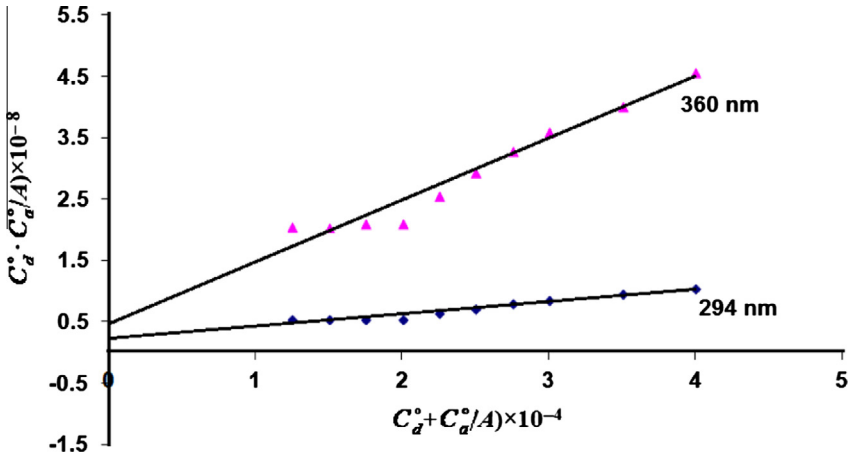

Fig. 4A. Relation between $C_d^\circ \cdot C_a^\circ/A$ and $C_d^\circ + C_a^\circ$ for HPyO–I_2 system in EtOH at 294 and 360 nm.

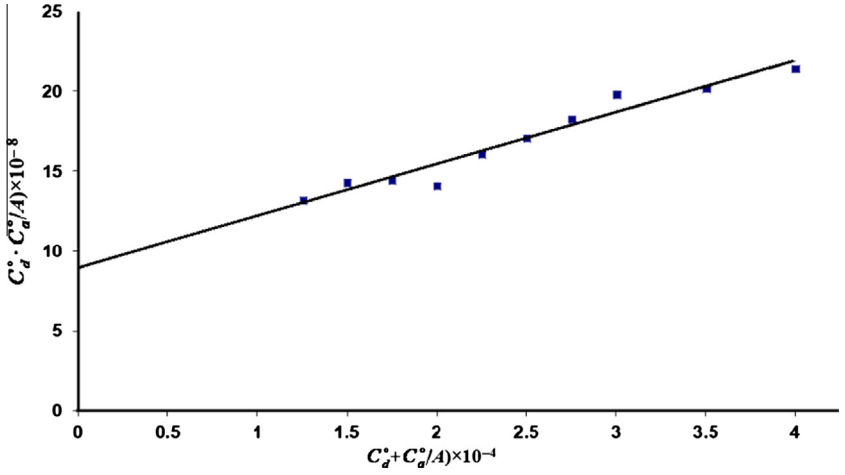

Fig. 4B. Relation between $C_d^\circ \cdot C_a^\circ/A$ and $C_d^\circ + C_a^\circ$ for HPyO–H_2CA system in EtOH at 520 nm.

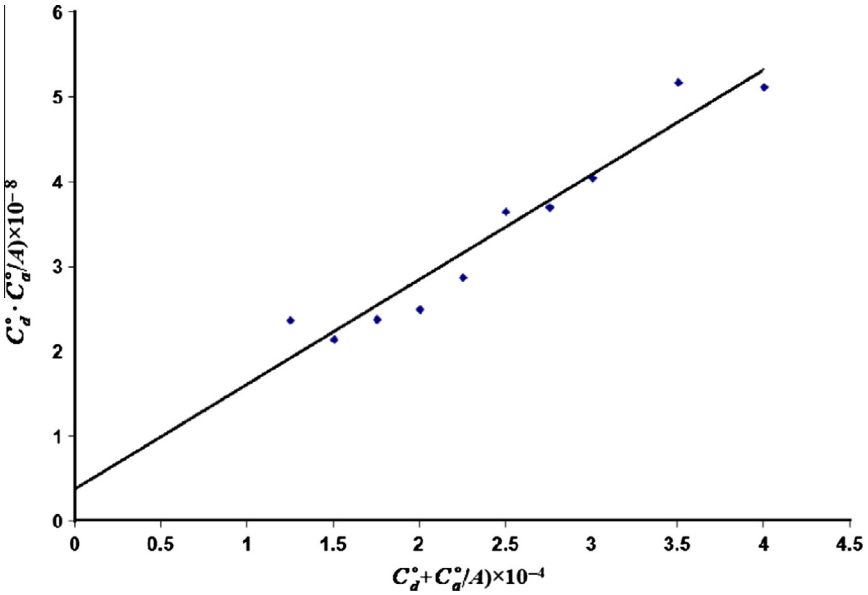

Fig. 4C. Relation between $C_d^\circ \cdot C_a^\circ/A$ and $(C_d^\circ + C_a^\circ)$ for HPyO–DDQ system in EtOH at 396 nm.

Table 2
Spectrophotometric results for HPyO CT-complexes in EtOH.

Complex	λ_{max} (nm)	K_C (l mol^{-1})	ε_{max} (l mol^{-1} cm^{-1})	E_{CT} (eV)	f	μ	I_p (eV)	ΔG° (25 °C) (k J mol^{-1})
[(HPyO)I]I	294	2.35×10^4	0.98×10^4	4.23	19.77	34.88	10.96	-2.49×10^4
	360	0.95×10^4	4.83×10^4	3.46	46.73	59.22	9.10	-2.27×10^4
[(H_2PyO)(HCA)]	520	0.36×10^4	0.31×10^4	2.39	1.08	11.01	8.67	-1.99×10^4
[(HPyO)(DDQ)]	396	3.83×10^4	0.81×10^4	3.14	5.04	19.63	9.89	-2.62×10^4

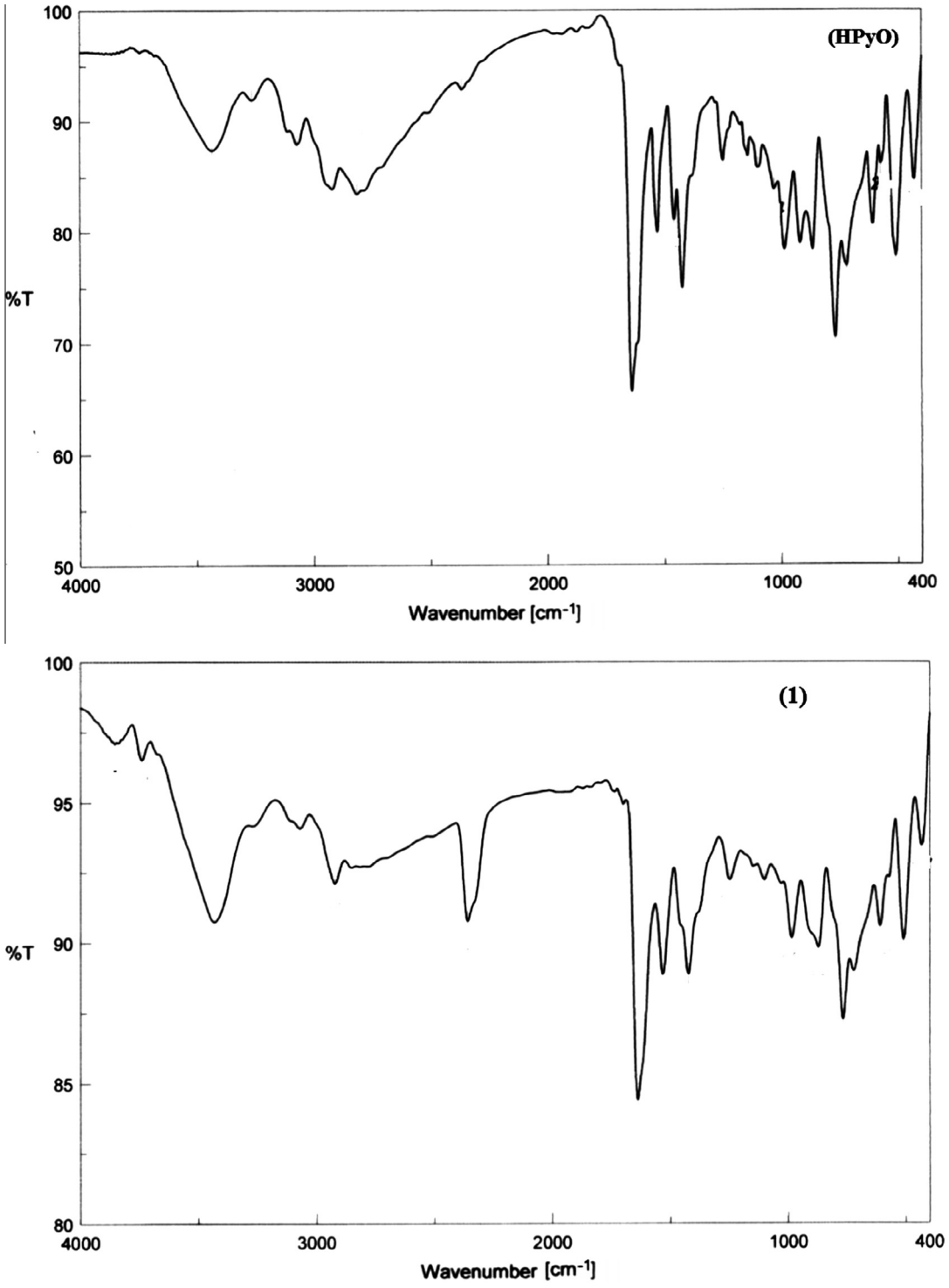

Fig. 5. Infrared spectra for HPyO and complexes (**1**, **2**, **3**).

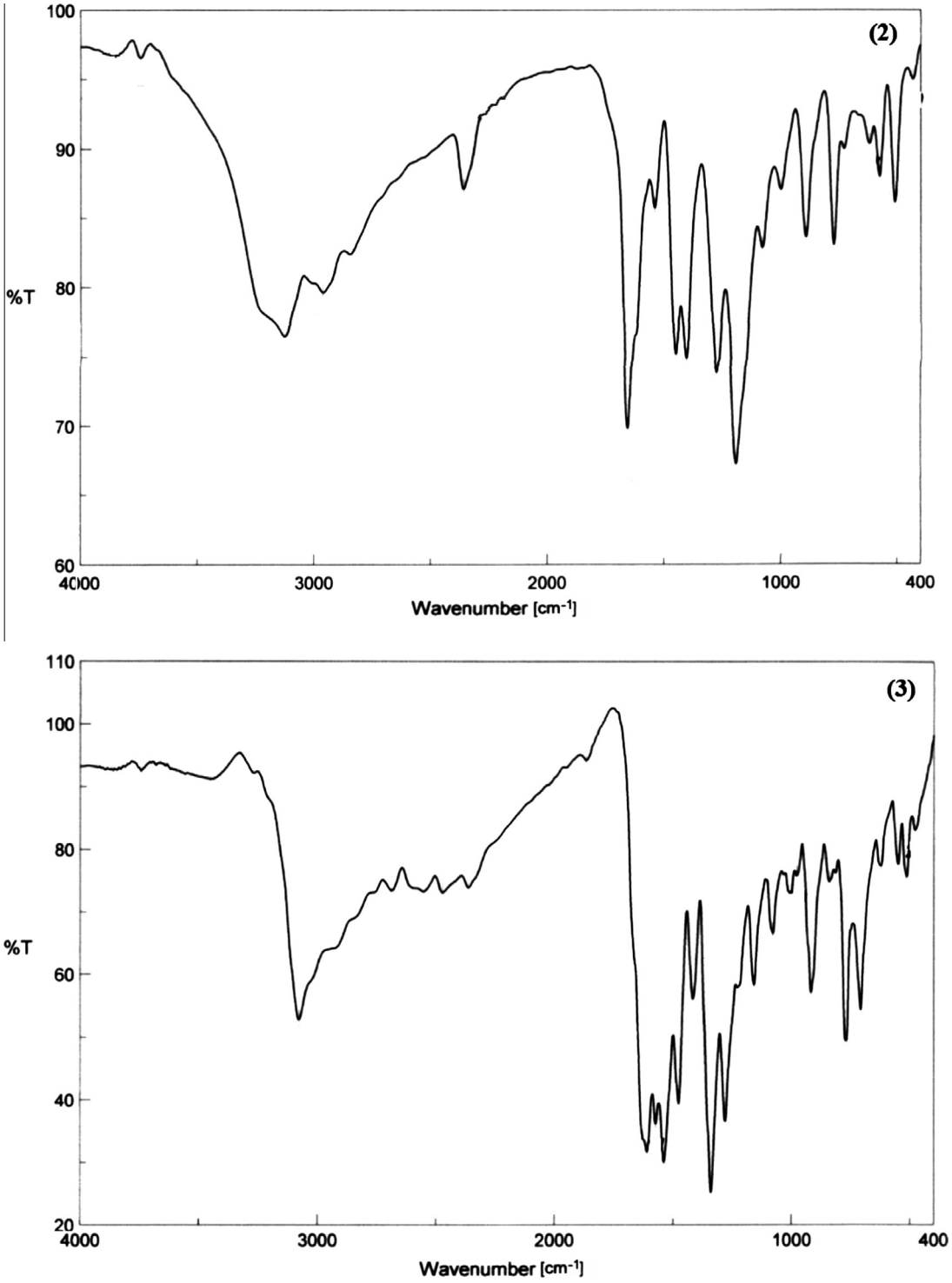

Fig. 5. (*continued*)

The energy of the charge-transfer complexes, E_{CT} of the HPyO complexes is calculated using following equation [37–39]:

$$E_{CT} = (h\upsilon_{CT}) = 1243.667/\lambda_{CT(nm)} \quad (5)$$

where λ_{CT} is the wavelength of the complexation band of the studied complexes.

The standard free energy changes of complexation (ΔG°) were calculated from the formation constants by following equation [43]:

$$\Delta G^{\circ} = -2.303RT \log K_{CT} \quad (6)$$

where R is the gas constant (8.314 J mol^{-1} K), T is the temperature in Kelvin degrees and K_C is the formation constant of the complexes at room temperature. ΔG° of interactions are negative in all CT complexes which indicate exothermic processes, Table 2.

Table 3
Characteristic infrared frequencies[a] (cm) and tentative assignments for complexes **1**, **2** and **3**.

H_2CA	DDQ	HPyO	**1**	**2**	**3**	Assignments
3235 mbr	3442 w	3436, br, m	3432, br		3430, br	ν(O—H); H bonded
	3339 w	3119, m	3243, m, br		3127, m	ν(N—H)
	3220 wbr	3072, m	3069, m	3077, vs, br		ν(C—H)
		2921, m	2926, w	2986, m	2961, br	ν_s(C—H)
		2815, m	2810, w			ν_{as}(C—H);
				2680, m		ν(N—H)
		2366, w	2363, w	2364, w	2360, m	Hydrogen bonding
	2234 w				2217, m	ν(C≡N)
		1682, s	1638, s	1866, vs	1715, sh	ν(C=O),
1665 m	1674 vs	1641, sh	1613, s	1610, s	1656, vs	ν(C=O), quinone
		1531, m				ν(C=N)
1632 s		1459, m		1572, vs	1540 w	ν(C=C)
	1554 s				1452 s	ring breathing bands
			1533, s			
			1463, w	1588, s	1406 s	C—H deformation
			1365, m	1476, m		
				1416, m		
1369 m		1425, m		1340, vs	1274, s	ν(C—C)
1290 vs	1268 ms	1364, sh	1249, m	1279, s		ν(C—N)
1225	1216 w	1250, w			1190 vs	ν(C—O)
1172 w	1174 vs	1144, w	1040, m	1159, w	1079 w	
	1073 vw	1101, w				
		1030, vw		1078, w		
982 vs		986, m	993, s	917, m	999 w	
	896 ms	919, m	883, w		891 m	C—H bend
			845, w			
853 m				840, m		ν(C—Cl)
	802 s		767, m	769 w	773 w	CH_2 Rock
752 m	722 ms	866, m	696, w	708 m		Skeletal vibration,
		769, s	560, w	622 m	620 w	ν(C—Cl)
690 m	623 vw	720, m	541, w	550 w	577 m	ν(C—O—C)
		609, m	511, w	513 w		
		575, vw				
		510, m				
571 ms					510 m	
		432, w	434w	479 w	433 w	CNC def.
	457 w					CH out of plan bend, skeletal vibration

[a] s, Strong; w, weak; m, medium; sh, shoulder; v, very; br, broad.

3.3. IR Analysis

The infrared absorption spectra of the donor and the formed complexes are shown in Fig. 5. Assignments of the well characterized bands in the infrared spectra of reactants and the obtained products are given in Table 3. The formation of CT-complexes during the reaction of HPyO with I_2, H_2CA and DDQ is strongly supported by observing of main infrared bands of the donor (HPyO) and acceptors (H_2CA, DDQ) in the product spectra. However, the bands of the donor and acceptors in the complexes spectra reveal small shifts in wavenumber values and intensities compared with those of the free donor and acceptors. This should be attributed to the expected symmetry and electronic structure changes upon the formation of CT-complexes.

Hydrogen bond formation in all CT complexes was confirmed with observation of medium to broad bands around 3430 cm^{-1} in the vibrational region of ν(O—H) and medium to week bands around 2360 cm^{-1} in the vibrational region of ν(N—H) [44].

In general for acid–base interaction, a proton transfer from the acceptor (acid) to the donor (base) is expected to occur in complex **2**. Such assumption is strongly supported by the appearance of a new band of medium intensity in the spectrum of complex **2**. This band is observed at 2680 cm^{-1} for HPyO–H_2CA CT-complex and may be due to the ν(N—H) stretching vibration of hydrogen against positively charged nitrogen [45]. We may suggest that, the acid–base interaction is associated with a proton migration followed by hydrogen bonding formation. The HPyO–H_2CA interaction involves a protonation for the basic nitrogen of the HPyO. Accordingly, we may formulate the complex as [(H_2PyO^+)(HCA^-)]. The increased electron density on the chloranilate unit as a result of charge transfer interaction and deprotonation of chloranilic acid, resulted in a pronounced shift to lower wavenumber in the ν(C—Cl) in [(H_2PyO)(HCA)] complex spectrum (840 cm^{-1}) compared with the free chloranilic acid (853 cm^{-1}) [46].

The significant shift of the CN stretching frequency from 2234 cm^{-1} towards lower frequency (2217 cm^{-1}) on complexation of DDQ with HPyO is indicative of charge transfer from HPyO to π^* of CN groups of DDQ which leads to a weakening of this bond. Similarly for DDQ, the CO stretching frequencies that appeared at 1674 cm^{-1} of the free acceptor was shifted to 1715 cm^{-1} and emerged with 1656 cm^{-1} upon complex formation.

3.4. Thermal analysis

The proposed structures for the complexes under investigation were confirmed by measuring TGA, and DTG thermograms (Fig. 6) under nitrogen flow. The thermal data obtained for complexes **2** and **3** together with the donor HPyO are summarized and given in Table 4.

The decomposition reactions of complex **2** occur in two expecting stages. The first stage of decomposition proceeds with a weight loss value of 29.50% at a lower temperature of approximately 150 °C in comparison with the thermogram of the free donor. This stage of decomposition might be associated with loss of the donor molecule in agreement with the calculated value of 31.27%. The second stage of decomposition proceeds at a maximum tempera-

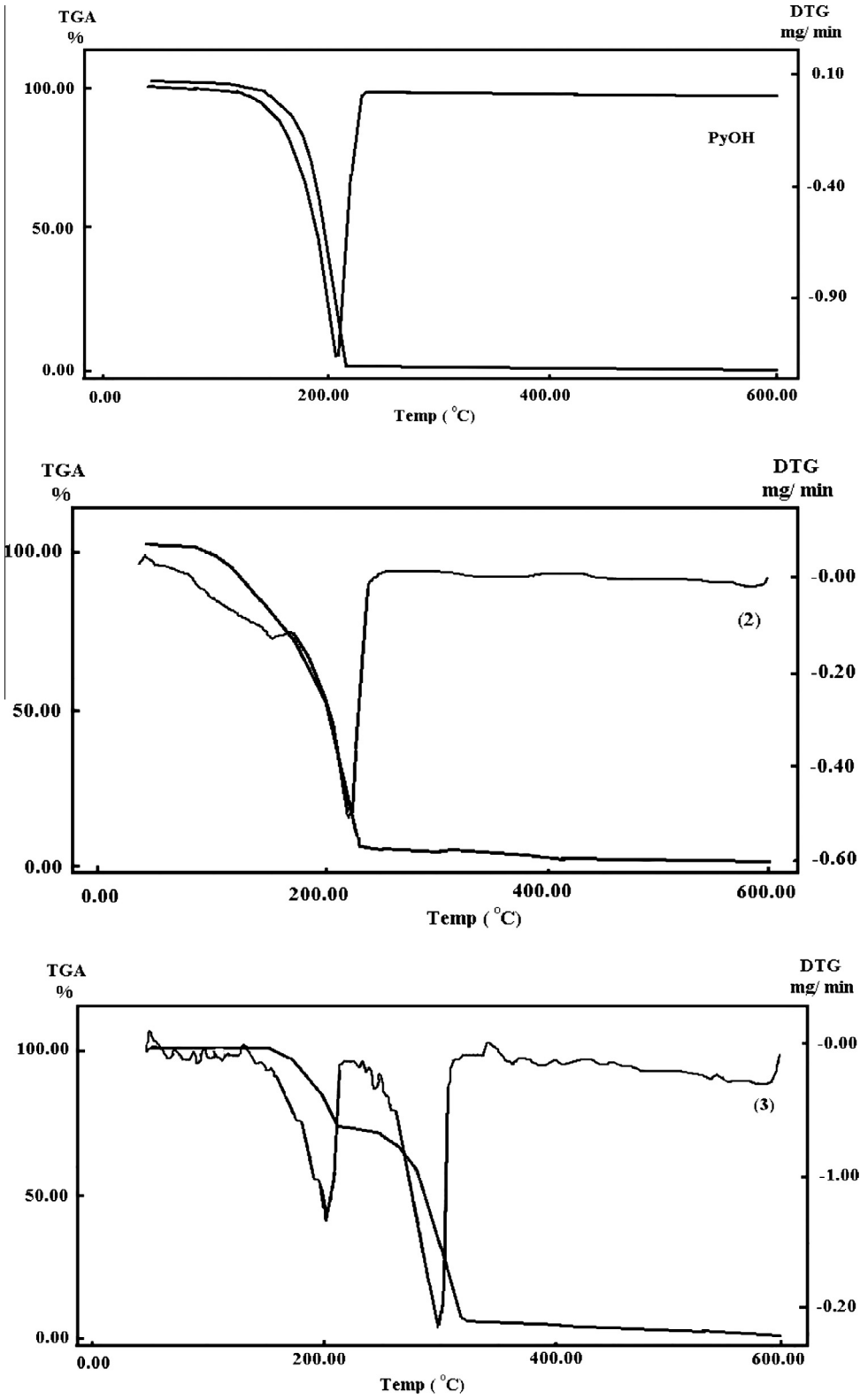

Fig. 6. Thermogravimeteric (TGA) and derivative (DTG) of HPyO and complexes **2** and **3**.

ture of 222 °C. This could be attributed to the loss of the acceptor, HCA. The weight loss associated with this stage of decomposition (70.50%) is in good agreement with the calculated value of 68.73%.

The obtained data for complex **3**, indicate that, the decomposition reactions occur in two stages. The donor molecule, HPyO is lost at a temperature maximum of 193.5 °C. The calculated weight loss of HPyO molecule in this complex corresponds to 29.52% in good agreement with the obtained value of 29.00%. The main second stage of decomposition proceeds at a maximum temperature of approximately 290 °C and associated with a weight loss value of 70.60%. This could be attributed to the loss of acceptor molecule, DDQ in agreement with the calculated values of 70.48%.

Table 4
The maximum temperature values for the decomposition along with the species lost in each step of the decomposition reactions of HPyO and complexes **2** and **3**.

Complex	Decomposition	T_{max}/°C	Lost species	% Weight loss	
				Found	Calc.
HPyO	First step (total loss) residue	207	C_5H_5NO	99.86 00.14	100.00 00.00
$[(H_2PyO)(HCA)]$ (**2**)	First step	150	C_5H_5NO	29.50	31.27
	Second step	222	$C_6H_2Cl_2O_4$	70.50	68.73
	Total loss		$C_{11}H_7Cl_2NO_5$	100.00	100.00
	Residue		–	00.00	00.00
[(HPyO)(DDQ)] **(3)**	First step	193.50	C_5H_5NO	29.00	29.52
	Second step	290.00	$C_8Cl_2N_2O_2$	70.60	70.48
	Total loss		$C_{13}H_5Cl_2N_3O_3$	99.60	100.00
	Residue		–	00.40	00.00

Comparing the weight loss (lost species) at each stage of decomposition (temperature maximum) of the free donor with that of the formed CT-complexes (**2**, **3**) confirmed the formation of 1:1 CT-complexes not new compounds or other adducts which agree quite well with the data obtained from microanalyses and photometric titration measurements.

4. Conclusion

A comprehensive study of the charge transfer interactions of the donor 2-hydroxypyridine (HPyO) with the σ-acceptor, Iodine and π-acceptors, H_2CA and DDQ, was conducted in Ethanol. We were able to show that the reaction stoichiometry donor:acceptor is the same for all acceptors, 1:1 and the resulting CT-complexes were shown to have the formulas: [(HPyO)(acceptor)]. Our obtained results indicate that the nitrogen atom and hydroxyl group in 2-hydroxypyridine are involved in the complexation with acceptors. In comparison with the previous studies of similar CT-complexes, changing of derivative on the ligand (—OH instead of —NH_2), has no effect on complexation with π-acceptors [30b]. The type of solvent (ethanol) played important role in complex formation with I_2 as σ-acceptor and resulted in formation of new type of CT-complex with iodine in comparison with using dichloromethane solution [47]. Spectrophotometric results (λ_{max}, K_C, ε_{max}, E_{CT}, f, μ, I_p, ΔG°) for the new prepared HPyO CT-complexes are dependant on the nature of acceptor used.

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