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A Structural Study of the Intermolecular Interactions of Tyramine with Some π-Acceptors: Quantification of Biogenic Amines Based on Charge-Transfer Complexation[1]

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Abstract—In this paper, we report the synthesis and characterization of four CT complexes of Ty with picric acid (PA), chloranilic acid (CLA), quinol (QL), and 1,3-dinitrobenzene (DNB), and present their thermal decomposition behavior. These complexes were structurally characterized to interpret the behavior of interactions using elemental analysis; IR and ^{1}H NMR spectroscopy. Finally, the thermal behavior of the obtained complexes and the kinetic thermodynamic parameters (E^*, A, ΔS^*, ΔH^*, and ΔG^*) were also investigated using Coats–Redfern and Horowitz–Metzger equations.

Keywords: biogenic amines, tyramine, charge-transfer complex, thermal decomposition

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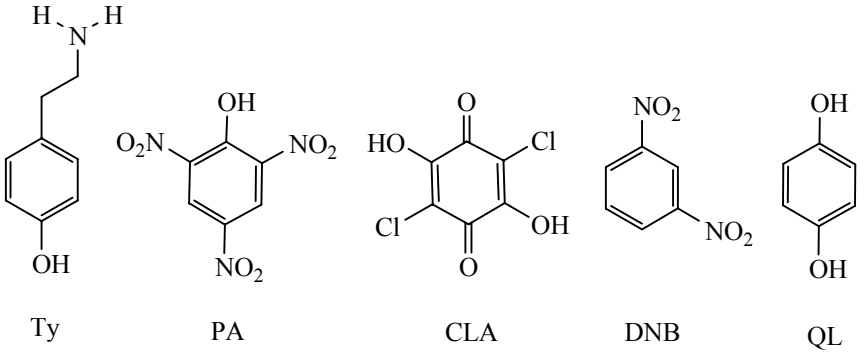
INTRODUCTION

Tyramine (Ty, Scheme 1), is the most important biogenic amine in fermented dairy products, in which it produced through the microbial enzymatic decarboxylation of tyrosine [1]. In addition, it is also one of the most biologically active of all biogenic amines [2]. It is found commonly in fermented foods, beverages, meat, fish, seafood and dairy products [3]. Ty is an indirectly acting sympathomimetic amine which releases norepinephrine from a sympathetic nerve ending. It is widely used as pharmacological tool to understand and evaluate the role of the sympathetic nervous system on human physiology and pathology and its influence on the cardiovascular system [4]. The ingestion of foods containing large amounts of Ty has toxicological effects, causing symptoms such as migraine, hypertension, brain haemorrhage, heart failure and diarrhea [5, 6]. For this reason, the development of a new method to measure Ty concentrations in foods would be important. Many techniques have been developed and improved for detection and quantification of Ty in different food products, including fluorometry, thin layer chromatography, capillary electrophoresis, high-performance liquid chromatography (HPLC) and electrochemical methods [7–10].

Charge-transfer (CT) complexation is of great importance in chemical reactions, including addition, substitution, condensation [11], biochemical and bioelectrochemical energy-transfer processes [12], biological systems [13], and drug–receptor binding mechanisms. For example, drug action, enzyme catalysis, ion transfers through lipophilic membranes [14], and certain π-acceptors have been successfully utilized in the pharmaceutical analysis of some drugs in pure form or in pharmaceutical preparations [15–17]. Furthermore, CT complexation is also of great importance in many applications and fields, such as non-linear optical materials, electrically conductive materials,

[1] The text was submitted by the authors in English.

Scheme 1. Tyramine and acceptors



second-order non-linear optical activity, micro-emulsions, surface chemistry, photocatalysts, dendri-mers, solar energy storage, organic semiconductors, and the investigation of redox processes [18–23].

The aim of this work was to provide basic data that can be used for the detection and quantification of Ty based on charge-transfer (CT) complexation.

EXPERIMENTAL

Materials and methods. All of the chemicals used throughout this study were of high reagent grade. Tyramine (Ty), picric acid (PA), chloranilic acid (CLA), quinol (QL), and 1,3-dinitrobenzene (DNB) acceptors (Scheme 1) were purchased from Sigma-Aldrich and were used without further purification. The elemental analyses for carbon, hydrogen and nitrogen contents were performed with the Micro analyzer Perkin-Elmer CHN 2400 (USA) at Cairo University, Egypt. Infrared spectra were measured in KBr discs within the range of 4000–400 cm^{-1} on a Shimadzu FT-IR spectrophotometer with 30 scans at 2 cm^{-1} resolution at Taif University, Saudi Arabia. ^1H NMR spectra were collected by the Analytical Center at King Abdul Aziz University, Saudi Arabia, on a Bruker DRX-250 spectrometer operating at 250.13 MHz with a dual 5 mm probe head. The measurements were performed at ambient temperature using DMSO-d_6 as a solvent and TMS as an internal reference. The thermogravimetric analysis (TG) was carried under a static air atmosphere to a temperature of 800°C at a heating rate of 10°C/min using a Shimadzu TGA–50H thermal analyzer in the Central Lab at the Ain Shams University, Egypt.

Synthesis. The solid Ty complexes with PA, CLA, QL or DNB acceptors were prepared by mixing equimolar amounts of the Ty donor with each acceptor in pure–grade methanol. The resulting solutions were stirred for approximately 30 min and allowed to evaporate slowly at room temperature. The separated solid complexes were filtered, washed well with methanol and dried over anhydrous calcium chloride for 24 h in desiccator. All the complexes are insoluble in cold and hot water, but easily soluble in DMF and DMSO.

RESULTS AND DISCUSSION

Elemental analyses (C, H, and N) of the Ty CT complexes were performed, and the obtained analytical data are as follows: **[(Ty)(PA)].** Calculated, %: C 45.91, H 3.85, N 15.30. $C_{14}H_{14}N_4O_8$. Found, %: C 45.95; H 3.81; N 15.27. M_w 366.28. **[(Ty)(CLA)].** Calculated, %: C 48.58; H 3.79; N 4.05. $C_{14}H_{13}Cl_2NO_5$. Found, %: C 48.55; H 3.82; N 4.00. M_w 346.16. **[(Ty)(QL)].** Calculated, %: C 68.00; H 6.93; N 5.66. $C_{14}H_{17}NO_3$. Found, %: C 68.05; H 7.00; N 5.63. M_w 247.29. **[(Ty)(DNB)].** Calculated, %: C 55.08; H 4.95; N 13.76. $C_{14}H_{15}N_3O_5$. Found, %: C 55.12; H 4.90; N 13.79. M_w 305.29.

The elemental analyses data for the prepared CT complexes are in agreement with the molar ratio obtained from the spectrophotometric titrations. The stoichiometry of all the Ty CT complexes was found to have a 1 : 1 ratio. Based on the obtained data, the prepared Ty CT complexes were formulated as [(Ty)(PA)], [(Ty)(CLA)], [(Ty)(QL)], and [(Ty)(DNB)]. The formation of 1 : 1 complexes was strongly supported by IR, ^1H NMR, and thermal analyses data.

Interpretation of the IR spectra. The IR absorption spectra of the Ty solid CT complexes which registered in the frequency range 4000–400 cm^{-1} using KBr disc are are provided in Table 1. The spectrum of free Ty donor displays a series of significan bands as:

Table 1. IR spectral data (ν, cm^{-1}) and tentative assignments for Ty donor, acceptors, and their complexes

Ty donor	Acceptor				Complexes				Assignments[a]
	PA	CLA	QL	DNB	PA	CLA	QL	DNB	
3339	3374	3235	3262	–	3424	3282	3192	3632	ν(O–H)
3283				–	3272	3236	–	–	ν(N–H)
3056			3031	3110	3076	3018	–	3105	ν(C–H), arom.
2998	2928	–	2857	–	2908	2987	2944	2874	ν_s(C–H) + ν_{as}(C–H)
2916	2861		2836			2933			
–	–	–	–	–	2723	2669	2733	2740	Hydrogen bond
					2628	2601	2626	2490	
					2524	2492	2436	2437	
					2460				
–	–	1663	–	–	–	1665	–	–	ν(C=O), CLA, complex
		1629				1633			
–	1616	–	–	1608	1612	–	1612	1608	$\nu_{as}(NO_2)$; PA, DNB, complex
1596	-	–	–	–			1595		δ(N–H)
1518	1567	–	–	–	1569	1541	1515	1536	Ring breathing bands
					1544				
1484	1541	–	1518	1538	1490	1498	1468	1350	ν(C=C)
	1492		1477		1432	1370			δ(C–H) deformation
	1442								
	1416								
1267	1357	1368	1244	1364	1364	1274	1355	1273	ν(C–C) + ν(C–O) + ν_{as}(C–N)
1174	1303	1263	1222	1150	1336	1226	1220	1222	
1114	1276	1207	1210	1069	1268		1089	1068	
1071	1226	1168	1164		1197		1041		
	1180		1097		1161				
	1108				1083				
	1078								
	1021								
968	888	981	827	914	909	982	945	909	δ(C–H) in-plane bending
944	832	838	759	837	824	834	831	836	ν(C–Cl); CLA, complex
823	805	751		727	711	754	762	714	
755	699								
550	626	–	–	–	592	693	614	653	δ(C–N) out-of-plane bending
528	–	690		–		575	553	–	skeletal vibration
	543	569		663	554	–	–	508	δ(ONO); PA, DNB, complex
						505	520		CNC deformation

[a] (ν) stretching; (ν_s) symmetrical stretching; (ν_{as}) asymmetrical stretching; (δ) bending.

3339, 3283, and 1596 cm^{-1}, which may assign to ν(OH), ν(NH), and δ(NH). In the IR spectra of the CT complexes, these significant bands are shifted and decreased in intensity. This result could be attributed to the expected changes in symmetry and electronic structure changes upon the formation of the CT complexes. The outlined changes in (N–H) in the Ty donor upon complexation clearly confirm the involvement of the NH_2 group in hydrogen bonding with acceptors. This bonding is confirmed by the appearance of a weak absorption bands that appears between 2400 and 2800 cm^{-1}, representing the H-

bonded NH_2 group. These group of bands were observed at 2723, 2628, 2524, and 2460 cm^{-1} for PA complex (Scheme 1), at 2669, 2601, and 2492 cm^{-1} for CLA complex (Scheme 2), at 2733, 2626, and 2436 cm^{-1} for QL complex and 2740, 2490, and 2437 cm^{-1} for DNB complex. These bands are due to hydrogen bonding in the complex which clearly indicates that the complexation occurs through the formation of intermolecular H-bond between the NH_2 group in the Ty donor and acceptors [24–32]. Furthermore, in CLA complex, the carbonyl stretching vibration bands; ν(C=O) appeared at 1665 and 1633 cm^{-1}, slightly shifted with respect to those of CLA (1663 and 1629 cm^{-1}); this is probably due to intermolecular H-bond with Ty. The electron density around protons depends on the degree of electro negativity for atoms attached with protons; therefore, the two withdrawing nitro groups attached to DNB acceptor decrease the electron density around the proton flanked between the nitro groups, and increase the acidic character of this proton which facilitates to make intermolecular hydrogen bond with the lone pair of electron on the nitrogen atom of the Ty donor [33, 34].

Interpretation of the ^{1}H NMR spectra. The nuclear magnetic resonance spectra present the persuasive confirmation of the complexation pathway. The chemical shifts (δ) of the different types of protons of the CT complexes are given below. The free Ty donor produced signals: 2.53 t (2H, $NH_2C\underline{H}_2$), 2.70 t (2H, $C\underline{H}_2$–Ph), 4.14 b (3H, NH_2 and OH), 6.68 t (2H, phenol $C^{3,5}H$), 6.9 t (2H, phenol $C^{2,6}H$). The ^{1}H NMR spectrum of free Ty donor displays a characteristic broad signal at 4.14 ppm, corresponding to the protons of NH_2 and OH groups. On complexation with PA and CLA acceptors, these two signals appeared at new δ values. The reaction of Ty donor with PA acceptor yielded a new CT complex, which produced signals: 2.45 s (3H, tyramine NH_2 and OH), 2.69 t (2H, $C\underline{H}_2$–Ph), 2.94 t (2H, $NH_2C\underline{H}_2$), 6.68 t (2H, phenol $C^{3,5}H$), 6.92 t (2H, phenol $C^{2,6}H$), 7.70 s (1H, hydrogen bonded OH of picric acid), 8.59 s (2H, picric acid protons). The signals attributed to NH_2 and OH protons in this complex appeared at 2.45 ppm. The peak at 11.94 ppm, which is assigned to the OH proton of free picric acid [35], was upfield shifted to 7.70 ppm in the spectrum of this complex. Together, these data indicate that NH_2 group in Ty and OH group in PA are involved in the formation of the CT complex between Ty donor and PA acceptor. The reaction of Ty donor with CLA acceptor formed a new CT complex. This compound produced signals: 2.45 s (3H, tyramine NH_2 and OH), 2.69 t (2H, $C\underline{H}_2$–Ph), 2.94 t (2H, $NH_2C\underline{H}_2$), 5.04 s (1H, chloranilic acid OH), 6.69 t (2H, phenol $C^{3,5}H$), 7.01 t (2H, phenol $C^{2,6}H$), 7.96 s (1H, hydrogen bonded OH of chloranilic acid). When Ty donor complexed with CLA acceptor, the signals of OH and NH_2 protons appeared at δ = 2.45. The high upfield shift of this characteristic signal confirms the formation of CT complex between Ty and CLA. It has been found that, the phenolic proton signal, which is observed at approximately ~9.15 ppm in the spectrum of the free CLA acceptor [36] , decreased in intensity with a high up-field shift for the nonhydrogen-bonded one (δ ~5.04) in the spectrum of this complex. Instead, the peak appeared at 7.96 ppm, is attributed to the hydrogen bonded OH of CLA. This situation confirmed the formation of the CT complex between one of the phenolic protons of CLA to the –NH_2 group of Ty.

Thermal analyses results. Thermal analysis (TG) was carried out in order to confirm the composition and structures of the formed CT complexes. The possible thermal degradation data for these complexes are provided in Table 2. Fairly close values of the calculated and experimental percentage of the moieties expelled from these complexes strongly support the stoichiometry and the structures proposed for the complexes. The TG thermogram of the PA complex indicated that it was thermally decomposes in two degradation steps. The first decomposition step in the temperature range of 200–350°C has a weight loss of approximately 62.52% and is attributed to the loss of the acceptor moiety (PA). The second decomposition step occurred within the 350–690°C temperature range and was assigned to the removal of the donor moiety (Ty). The thermal degradation of the CLA complex occurs in two degradation stages within the 210–700°C temperature range. The first stage of decomposition corresponds to the loss of the acceptor moiety with a weight loss of 60.25%. The second stage of decomposition corresponds to the loss of the donor moiety with a weight loss of 39.66%, which is very close to the calculated value (39.63%). The thermal degradation of the QL complex occurs in two degradation stages within the 50–800°C temperature range. The first stage of decomposition corresponds to the loss of the donor moiety with a weight loss of 55.50% very close to the expected theoretical value of 55.47%. The second stage of decomposition corresponds to the loss of the acceptor moiety with a weight loss of 44.00%,

Table 2. Thermal decomposition data for the Ty–CT complexes

Complex	Stage	TG range, °C	TG, weight loss, %		Lost fragments
			found	calculated	
[(Ty)(PA)]	I	200–350	62.52	62.55	PA acceptor
	II	350–690	37.41	37.45	Ty donor
[(Ty)(CLA)]	I	210–400	60.25	60.37	CLA acceptor
	II	400–700	39.66	39.63	Ty donor
[(Ty)(QL)]	I	50–305	55.50	55.47	Ty donor
	II	305–800	44.00	44.53	QL acceptor
[(Ty)(DNB)]	I	120–345	99.96	100.0	Ty + DNB

which is in good agreement with the calculated value (44.53%). The TG thermogram of the DNB complex indicated that it is thermally stable in the 25–120°C temperature range. The thermal decomposition of this complex proceeds via one degradation step. The decomposition begins at ~120°C and completes at ~345°C, and the observed weight loss associated with this step is (found 99.94, calculared 100.0%), which can be attributed to the loss of the $C_{14}H_{15}N_3O_5$ moiety (Ty + DNB).

Thermodynamic results. Nowadays, there has been increasing interest in determining the rate-dependent parameters of solid-state non-isothermal decomposition reactions by analysis of the TG curves. Several equations have been proposed to analyze a TG curve and to obtain the kinetic thermodynamic parameters. Two different methods were employed to evaluate the kinetic thermodynamic parameters: the Coats–Redfern method [37] and the Horowitz–Metzger method [38]. The thermodynamic parameters

Scheme 2.

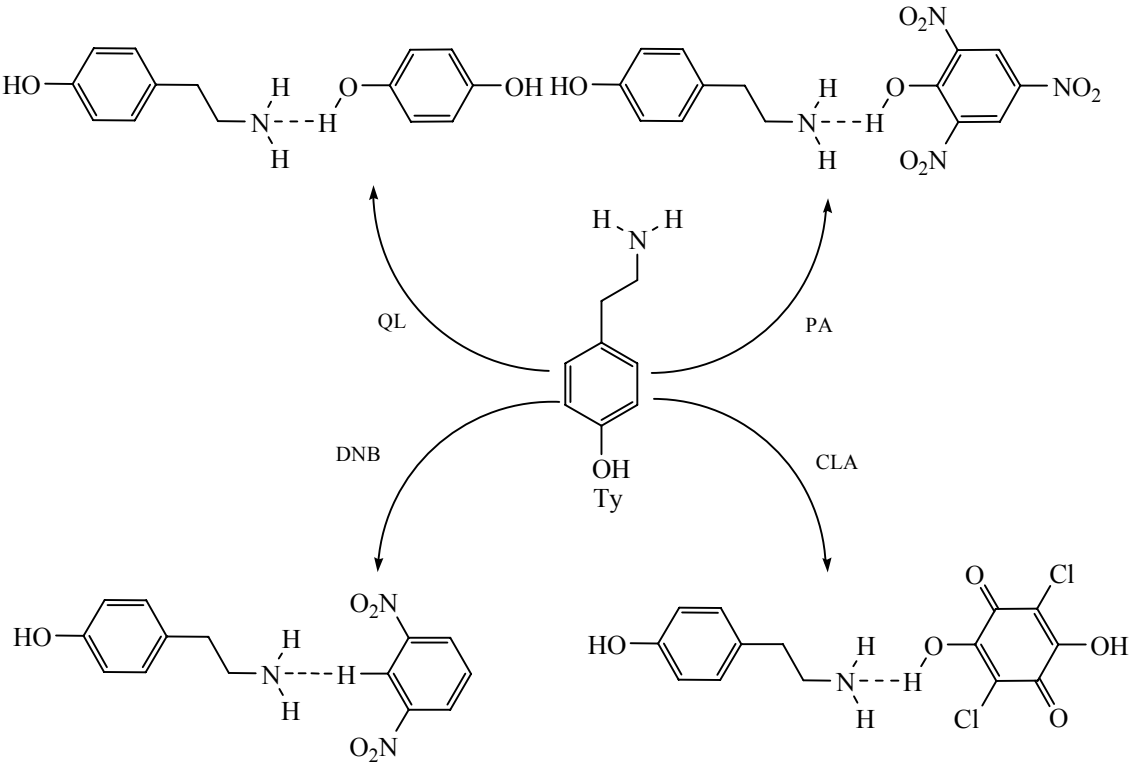


Table 3. Kinetic parameters determined using the Coats–Redfern (CR) and Horowitz–Metzger (HM) methods

Complex	Parameter[a]	Methods	
		CR	HM
QL complex	r	0.9954	0.9922
	E, kJ/mol	2.55E+05	2.65E+05
	A, s^{-1}	6.04E+14	5.01E+15
	ΔS, J mol^{-1} K^{-1}	–3.04E+01	–4.98E+01
	ΔH, kJ/mol	2.41E+05	2.62E+05
	ΔG, J/mol	2.23E+05	2.20E+05
DNB complex	r	0.9940	0.9932
	E, kJ/mol	2.75E+05	2.82E+05
	A, s^{-1}	4.90E+15	3.85E+16
	ΔS, J mol^{-1} K^{-1}	–4.70E+01	–6.11E+01
	ΔH, kJ/mol	2.64E+05	2.70E+05
	ΔG, J/mol	2.30E+05	2.22E+05
PA complex	r	0.9990	0.9981
	E, kJ/mol	1.62E+05	1.80E+05
	A, s^{-1}	2.64E+08	8.92E+09
	ΔS, J mol^{-1} K^{-1}	–9.32E+01	–6.33E+01
	ΔH, kJ/mol	1.62E+05	1.82E+05
	ΔG, J/mol	2.30E+05	2.42E+05
CLA complex	r	0.9932	0.9941
	E, kJ/mol	3.20E+05	3.38E+05
	A, s^{-1}	3.21E+18	8.30E+19
	ΔS, J mol^{-1} K^{-1}	–1.11E+02	–1.22E+02
	ΔH, kJ/mol	3.15E+05	3.42E+05
	ΔG, J/mol	2.22E+05	2.41E+05

[a] (r) correlation coefficient of the linear plot.

[i.e., the activation energy (E^*), the frequency factor (A), the enthalpy of activation (H^*), the entropy of activation (S^*), and the Gibbs free energy of activation (G^*)] associated with the complexes were evaluated graphically by employing the Coats–Redfern and Horowitz–Metzger methods, and the evaluated data are listed in Table 3. The kinetic data obtained from the two methods are comparable and can be considered in good agreement with each other. The activation energy (E^*) of the complexes is expected to increase with the increasing thermal stability of complexes. Therefore, the E^* value for the CLA complex is higher compared to the other complexes, which indicates the higher thermal stability of the CLA complex. By comparing the E^* values for the main decomposition stage of the Ty complexes, we observed the following trend for the different acceptors: CLA > DNB > QL > PA. These differences may be due to the reactivity of the complexes and the electronic configuration of the acceptor when complexed with the Ty donor. The entropy of activation (ΔS^*) is found to be negative in all cases, which indicates that the decomposition reactions proceed spontaneously and the activation complexes have more ordered structure than the reactants. The ΔS* values of the Ty CT complexes occur in a decreasing order as follows: QL complex > DNB complex > PA complex > CLA complex. The satisfactory values for the correlation coefficients from the Arrhenius plots of the thermal decomposition steps were observed to be $r \sim 1$ for all cases, which indicates a good fit with the linear function and reasonable agreement between the experimental data and the kinetic parameters.

Complexation pathway. Based on the above data the proposed complexation mechanism of these CT complexes between Ty donor with acceptors can be illustrated by the Scheme 2.

CONCLUSIONS

This study has demonstrated the complexation behavior of this bioactive amine with PA, CLA, QL and DNB π-acceptors. The solid CT complexes were isolated and structurally characterized using elemental analysis, IR, ^{1}H NMR, and thermogravimetric (TG) analysis. The kinetic parameters (E^*, A, ΔS^*, ΔH^*, and ΔG^*) have been estimated. It was observed that the reaction stoichiometry is 1 : 1, and the resulting CT complexes were shown to have the general formula: [(Ty)(acceptor)]. The interaction between the Ty and the acceptors was taking place by the formation of intermolecular hydrogen bond. The TG analysis indicates that the formation of complexes was thermally stable, exothermic, spontaneous. The data obtained herein, can be used in further studies to assessment of Ty quantitatively in food products.

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