CHARGE-TRANSFER COMPLEXES OF SOME HETEROARYLTHIOUREA DERIVATIVES WITH π-ACCEPTORS

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Received October 15, 1992
Accepted May 12, 1993

Charge-transfer complexes of some heteroarylthiourea derivatives with π-acceptors have been studied spectrophotometrically in CH_2Cl_2. Spectral data, stability constants and enthalpies of complexation are reported. From the energies of the CT transition, ionization potentials of the donors have been obtained. Effects of donor molecular structure, π-acceptor electron affinity and nature of solvent on K_{CT} of complexes are investigated and discussed. It is deduced that the formed CT complexes are of *n*–π kind and of 1 : 1 stoichiometry.

Due to the wide use of thiourea derivatives in many biological, pharmaceutical and industrial applications[1], a lot of work has been carried out on CT complexes of thiourea derivatives as well as of some related sulfur compounds with iodine as σ-acceptor[2 – 9]. It was concluded that the complexes formed are of *n*–σ type with the site of *n*-donor action at the sulfur atom. On the other hand, little attention has been focused on the interaction of π-acceptors with thiourea derivatives. Misra et al.[10] has studied the CT complexes of thiourea with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) by conductometric measurements in methanol. It was deduced that the stoichiometry of thiourea–DDQ complex is 2 : 3. Recently, we have investigated the CT complexes of some thiocarbanilides and alkylthioureas with some π-acceptors as DDQ, tetracyanoethylene (TCNE) and 2,3,5,6-tetrachloro-1,4-benzoquinone (CHL) in dichloromethane[11,12]. It is deduced that these CT complexes are of *n*–π type. In order to elucidate the role of heterocyclic moiety in these donor molecules on their magnitude of donor–acceptor interaction, it would be of interest to study the CT complexes of some heteroarylthiourea derivatives with π-acceptors. In view of the limited information on such systems in the literature the present article is devoted to the study of CT complexes of some heteroarylthiourea derivatives with some π-acceptors. These donors have the following formula: R^1–NH–CS–NHR^2, where R^1 = 2-pyridyl, R^2 = CH_3 (*I*); R^1 = 2-pyridyl, R^2 = Ph (*II*); R^1 = 2-pyrimidyl, R^2 = Ph (*III*).

EXPERIMENTAL

Materials and Solutions

The electron donors *I* – *III* were prepared by the reaction of methylisothiocyanate and phenylisothiocyanate with 2-aminopyridine and 2-aminopyrimidine in pyridine. The reaction mixture was refluxed for 30 min and cooled, the precipitate was recrystallized from ethanol. The purity of the compounds was checked by elemental analysis and thin layer chromatography.

Compound I: For $C_7H_9N_3S$ (167.1) calculated: 50.26% C, 5.43% H, 25.14% N, 19.18% S; found: 50.20% C, 5.40% H, 25.20% N, 19.20% S; m.p. 145 °C.

Compound II: For $C_{12}H_{11}N_3S$ (229.3) calculated: 62.84% C, 4.84% H, 18.34% N, 13.99% S; found: 62.70% C, 4.80% H, 18.40% N, 13.90% S; m.p. 171 °C.

Compound III: For $C_{11}H_{10}N_4S$ (230.2) calculated: 57.35% C, 4.38% H, 24.34% N, 13.93% S; found: 57.30% C, 4.40% H, 24.40% N, 13.80% S; m.p. 198 – 200 °C.

The electron acceptors, tetracyanoethylene (TCNE), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and 2,3,5,6-tetrachloro-1,4-benzoquinone (CHL) were Aldrich products and were recrystallized from chlorobenzene, dry methylene chloride and dry benzene, respectively.

The solvents methylene chloride, ethylene chloride, and chloroform were of spectral grade. Stock solutions of donor or acceptor were freshly prepared in the proper deoxygenated solvent prior to use in order to avoid any contamination.

Synthesis of the Solid CT Complexes (1 : 1)

Equimolar ammounts of donor (*I*, *II* and *III*) and acceptor (DDQ and TCNE) were dissolved separately at room temperature in a minimum volume of dry methylene chloride. The two solutions were mixed and the resulting mixture was left at room temperature for 4 h. The solid CT complexes which separated out were recrystallized from absolute ethanol. The analytical data of the prepared complexes and some of their physical properties are listed in Table I.

Several attempts were made to preapre the CT complexes of donors *I* – *III* with CHL but all failed.

RESULTS AND DISCUSSION

Chemical Analysis and Infrared Spectra

The chemical analysis of the isolated solid CT complexes (Table I) clearly indicates the formation of 1 : 1 type of such CT complexes. Selected IR spectral bands of both donors (*I*, *II* and *III*) and acceptors (DDQ and TCNE) with the corresponding ones that appear in the IR spectra of the isolated complexes clearly were compared. The IR bands of the donors *I* – *III* which appeared at 3 150 – 3 300 ν(NH), 1 345 – 1 350 ν(NCSN) and 1 005 – 1 090 ν(CS) cm^{-1}, respectively, are shifted to lower frequencies on complexes formation. The observed large shift of ν(C=S) to lower frequencies on complexation suggests that the *n*-electrons involved in the CT transition belong to the sulfur thiocarbonyl group. Moreover, the $\nu(C\equiv N)$ of the acceptors DDQ and TCNE (at 2 237 and 2 225, 2 260 cm^{-1}, respectively), $\nu(C=O)$ and $\nu(C-Cl)$ of DDQ which appeared at 1 678 and 802 cm^{-1}, respectively, are shifted also to lower frequencies. This behavior is in accordance with charge migration from donor to acceptor.

Electronic Spectra

The absorption spectra of the studied heteroarylthioureas–TCNE complexes in CH_2Cl_2 display one broad absorption band that absorbed in the visible region (400 – 700 nm), in which neither the donor nor the acceptor separately absorbed (Fig. 1, Table II). In addition the CHL–*II* CT complex solution displays one broad CT band at 510 nm. On the other hand, the CT complex solution of donor *II* with DDQ shows a group of absorption bands at 448 sh, 472, 516, and 587 (Fig. 2). Such absorption bands can be ascribed to the absorption of the radical anion DDQ^- (refs[13 – 16]). Thus one can deduce that the DDQ–*II* CT complex exists predominantly in an ionic structure (D^+, A^-).

TABLE I
Microanalysis data, colour and melting points for the solid CT complexes of donor *I* – *III* with π-acceptors TCNE and DDQ

Complex	Colour M. p., °C	Calculated/Found				
		% C	% H	% N	% S	% Cl
I–TCNE	brown 180^a	52.84 52.90	3.07 3.09	33.21 33.35	10.86 10.70	–
II–TCNE	reddish brown 140^a	60.46 60.53	3.10 3.12	27.44 27.50	8.97 8.85	–
III–TCNE	brown 150	56.94 56.98	2.81 2.88	31.27 31.35	8.94 8.81	–
I–DDQ	yellow 155^a	45.66 45.70	2.30 2.33	17.76 17.80	8.13 8.20	17.98 17.87
II–DDQ	yellow 210^a	52.61 52.71	2.43 2.47	15.35 15.40	7.03 7.10	15.54 15.60
III–DDQ	yellow 230^a	49.87 49.83	2.20 2.25	18.38 18.43	7.01 7.08	15.51 15.58

[a] Decomposed.

TABLE II

Spectral characteristics, formation constants (K_{CT}) and thermodynamic parameter (ΔH) values for the CT complexes of heteroarylthioureas with π-acceptors at different temperatures in CH_2Cl_2 as well as the ionization potentials of the donors

Complex	λ_{max} nm	E_{CT} eV	IP eV	K_{CT}, dm^3 mol^{-1}				ε_{CT}, dm^3 mol^{-1} cm^{-1} 10 °C	$-\Delta H$ kcal mol^{-1}	$(b/a)^2$
				10 °C	15 °C	20 °C	25 °C			
I–TCNE	540	2.286	8.27	18.9 ± 3.5	14.55 ± 2.15	12.83 ± 1.35	8.28 ± 2.59	492.00 ±87.00	8.70 ± 1.47	0.165
II–TCNE	540	2.286	8.27	12.45 ± 1.44	10.69 ± 1.07	9.32 ± 0.90	7.63 ± 1.65	443.00 ± 55.00	5.38 ± 0.36	0.102
III–TCNE	525	3.352	8.35	10.71 ± 2.14	7.14 ± 1.95	5.10 ± 0.94	3.31 ± 0.74	329.00 ± 37.00	12.93 ± 0.48	0.239
II–CHL	510	2.421	8.00	–	–	–	–	–	–	–

Ionization Potentials of the Donors

The ionization potentials of HOMO(n) of the donors *I* – *III* were estimated from CT energies of their complexes with TCNE or CHL by adopting the empirical equations as reported by Aloisi and Pignataro[17] and the values are listed in Table II. Comparison of the ionization potential values calculated from the CT energies (8.27 – 8.35 eV in case of TCNE) with those of the corresponding ones on tetramethylthiourea and thiourea (8.12 and 8.5 eV, respectively, by electron impact mass spectrometric technique[5,18], reveals that the HOMO of the donors *I* – *III* that is involved in the CT interaction have the same nature as tetramethylthiourea and thiourea (*n*-type).

Formation Constants (K_{CT}) of CT Complexes

The formation constant values (K_{CT}) of the CT complexes of donors *I* – *III* with TCNE as π-acceptor in temperature range 10 – 25 °C were determined spectrophotometrically[19] in CH_2Cl_2 and calculated by linear least squares method. The K_{CT} and ε_{CT} values obtained are given in Table II. It is evident that the stability of the formed CT complexes of three donors with TCNE are *I* > *II* > *III*. This behavior can be attributed to the expected low donor ability of sulfur thiocarbonyl group. The high donor ability of

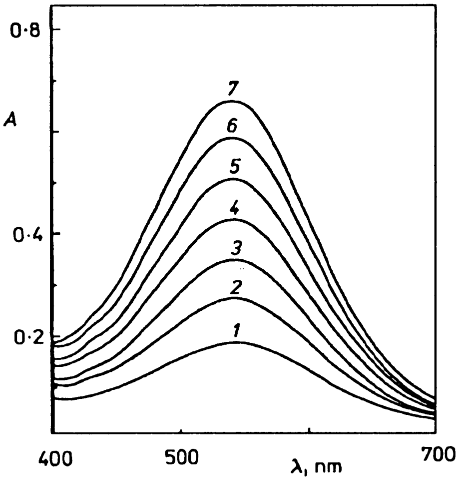

FIG. 1
Electronic absorption spectra of the CT complex solutions of donor *II* with TCNE in CH_2Cl_2 at 20 °C. [II]: 0.01 mol dm^{-3}; [TCNE]: *1* 0.004, *2* 0.006, *3* 0.008, *4* 0.01, *5* 0.12, *6* 0.14, *7* 0.16 mol dm^{-3}

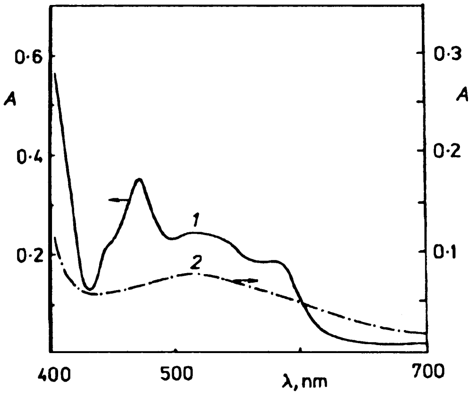

FIG. 2
Electronic absorption spectra of the CT complexes solutions of donor *II* with DDQ and CHL in CH_2Cl_2 at 20 °C. *1* DDQ–*II* CT complex, [DDQ] = [II] = 1 . 10^{-3} mol dm^{-3}; *2* CHL–*II* CT complex, [CHL] = 4 . 10^{-3} mol dm^{-3}, [II] = 5 . 10^{-4} mol dm^{-3}

donor *I* (R^2 = CH_3) compared to that of donor *II* (R^2 = Ph) can be atttributed to the relatively high inductive effect of its methyl group. On the other hand, the observed high donor ability of donor *II* on compared to that of *III* is due to the high electron withdrawing power of pyrimidine moiety *III*. This behavior is consistent with weak base character of the pyrimidine ring ($pK_a = 1.31$) relative to that of the pyridine ring ($pK_a = 5.20$, ref.[20]).

Effect of Solvent on Complex Formation Constants

To study the effect of solvent on the stability of heteroarylthiourea derivatives, the CT complex of donor *I* which TCNE has been investigated in different solvents of various polarities ($C_2H_4Cl_2$, CH_2Cl_2 and $CHCl_3$) at 10 °C. The data for the determination of the stability constants for the *I*–TCNE system in different solvents are presented in Table III and show that the formation constant value of the CT molecular complex increases as dielectric constant of the solvent is decreased. Evidently the formed CT complex is of strong *n*–π type and thus increasing the dielectric constant of medium will result in dissociation of dative structure I^+–$TCNE^-$ into the corresponding radical ions due to the expected high dipole–dipole or dipole–induced dipole interaction in the same direction.

Thermodynamic Properties of CT Complexes

The enthalpy changes (ΔH) connected with the formation of the CT complexes studied were obtained from van't Hoff equation plots and listed in Table II.

According to Mulliken[21,22], the ratio between the coefficient of the dative bond wave function ($\psi_{D^+ - A^-}$) to the nonbond wave function ($\psi_{D - A}$), $(b/a)^2$, was evaluated and recorded in Table II. The results obtained indicate that the magnitude of the interaction between heteroarylthiourea derivatives and TCNE is high.

TABLE III
Spectral characteristics, formation constants (K_{CT}) for the CT complex of donor *I* with TCNE at 10 °C in various solvents as well as the ionization potential of donor *I*

Solvent	Dielectric constant D	λ_{max} nm	E_{CT} eV	IP eV	K_{CT} $dm^3\ mol^{-1}$	ε_{CT} $dm^3\ mol^{-1}\ cm^{-1}$
$C_2H_4Cl_2$	10.65	542	2.278	8.25	15.42 ± 2.70	678.00 ± 188.00
CH_2Cl_2	9.08	540	2.286	8.27	18.90 ± 3.50	492.00 ± 87.00
$CHCl_3$	4.80	535	2.308	8.29	23.82 ± 3.87	683.00 ± 190.00

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