ORIGINAL ARTICLE

Kinetic study of charge transfer complexes of ICl_3 with DB18C6 and DC18C6 in some nonaqueous solvents

M. Torabbeigi · T. Madrakian · A. Afkhami

Abstract The spectrophotometric kinetic charge–transfer complex formation of iodine trichloride (ICl_3) with Dibenzo-18-crown-6 (DB18C6), Dicyclohexyl-18-crown-6 (DC18C6) has been studied in chloroform; dichloromethane and propylene carbonate solutions at different temperatures. The results indicated immediate formation of an electron donor–electron acceptor complex; which is followed by two relatively slow consecutive reactions. The pseudo-first-order rate constants for the formation of the ionic intermediate and the final product have been evaluated at various temperatures by computer fitting of the absorbance–time data to appropriate equations. The influences of both the crown's structure and the solvent properties on the formation of donor–electron acceptor complexes and the rates of subsequent reactions are discussed.

Keywords Charge transfer complex · ICl_3 · DB18C6 · DC18C6 · Nonaqueous solvents

Introduction

The macrocyclic polyethers, a class of compounds firstly synthesized by Pedersen [1], were shown to bind much more powerfully that, mono-functional and linear polyfunctional ethers of similar basicity [2–5]. Studies on neutral molecule–macrocycles interaction have been far fewer in number than those on cation–macrocycle interactions. The motivation to study neutral molecule–macrocycle interactions is understandable because the function of neutral molecules is as important as that of charged molecules in many chemical and biochemical processes. In addition, there is increasing interest in molecular complexes of macrocyclic compounds by their possible application in different areas such as separation processes, catalytic chemical reactions, and conversion of chemical reactions to optical or electronic signals and separate certain neutral molecules from environmental system [6–9]. Halogens and interhalogens form donor–acceptor complexes, with a range of Lewis bases. These charge transfer (CT) complexes first proposed by Muliken [10], are now recognized to play a key role in many chemical and biological processes. Consequently, many studies in spectral, thermodynamic, and other aspects of charge transfer complexes have been reported in the literatures [11–13].

We have been recently involved in the spectrophotometric study of interaction between tetraethyleneglycol-bis-(8-quinolyl)ether (TEGQ) as a nitrogen and oxygen containing compound as a donor with ICl_3 as an acceptor in chloroform, acetonitrile and dimethyl sulfoxide at different temperatures [14].

Interactions of diaza-18-crown-6 and diaza-15-crown-5, as electron donors, with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), as an electron acceptor, was investigated spectrophotometrically in acetonitrile and chloroform solutions, was reported in the lecture [15]. The influences of both the azacrown's structure and the solvent properties on the formation of DA complexes and the rates of subsequent reactions were discussed.

The preparation of molecular addition compounds of the type D.ICl and D.ICl_3, where D is a molecule of one of several heterocyclic amines, was reported [16]. Charge

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transfer complexes of iodine trichloride with pyridine, quinoline, and 2,6-lutidine were studied spectrometrically using Job's method of continuous variation [17, 18].

Experimental

Reagents

Reagents with grades of Dibenzo-18-crown-6 (DB18C6), Dicyclohexyl-18-crown-6 (DC18C6) and iodine trichloride (ICl_3), (all from Merck) were of the highest purity available and used without any further purification. Chloroform, dichloromethane and propylene carbonate (all from Merck) were used as solvents. The characters of these solvent are shown in Table 1.

Apparatus

Recording all the electronic spectra and the absorbance measurement at fixed wavelengths were carried out on a Perkin-Elmer Lambda 45 UV–visible spectrophotometer with 1 cm quartz cells. Both sample and blank compartments were kept at a constant temperature by a thermostat, attached to the cell compartment, which allowed the temperature to be maintained constant to ±0.1 °C.

Procedure

The kinetics of complexes of ICl_3 with DB18C6 and DC18C6 in chloroform, propylene carbonate and dichloromethane was investigated in the different temperatures. In all cases crown to ICl_3 mole ratio was 10:1. The spectra for each complex at the certain temperature were recorded at different times. The data were obtained for at least 1 h. The kinetic studies of ICl_3 complexes with DB18C6 and DC18C6 were performed at 342 and 340 nm, respectively. The stock solution of ICl_3 was freshly made on the day of measurements but ligands solutions were stable for a long time.

Table 1 The values of polarity and dielectric constant of chloroform, dichloromethane and propylene carbonate

Solvent	$\varepsilon/\varepsilon_0$[a]	μ[b] (dipole moment)
Chloroform	4.81	1.04
Dichloromethane	9.08	1.55
Propylene carbonate	65.5	4.94

[a] Reference [24]

[b] Reference [25]

Results and discussion

Absorption spectra studies

The electronic absorption spectra of ICl_3 (1.0×10^{-3} mol L^{-1}) in the presence of large excess of DC18C6 and DB18C6 (crown to ICl_3 mole ratio was 10:1) in chloroform, dichloromethane and propylene carbonate solution at different temperature in different time are investigated. Sample spectra of the absorption spectra of ICl_3 (1.0×10^{-3} mol L^{-1}) in the presence of large excess of DB18C6 in dichloromethane solution at 25 °C was monitored as a function of time in the wavelength range 300–600 nm are shown in Fig. 1. As Fig. 1 shows, addition of crown ether to the ICl_3 solution results in some absorption bands in this spectral region, presumably due to the formation of a charge-transfer complex which causes the disappearance of a purple color in solution and increases absorbance in 320 and 360 nm. Obviously, the spectra recorded for the electron donor–acceptor (EDA) complex between DB18C6 and ICl_3 are time dependent. The intensities of the different absorptions increase with time for about 10 min, while the general features of the resulting spectra remain unchanged (Fig. 1). However, after about 10 min, the purple color of solution begins to disappear slowly and the intensity of the absorption bands in the 320–600 nm region decreases with time. This behavior was also show for complexation of ICl_3 with each two ligands in chloroform solution but in the case of propylene carbonate solution, only the decrease of absorption was observed. Figure 2 shows the electronic absorption spectra of DC18C6 with ICl_3 at 25 °C in the different times in propylene carbonate solution.
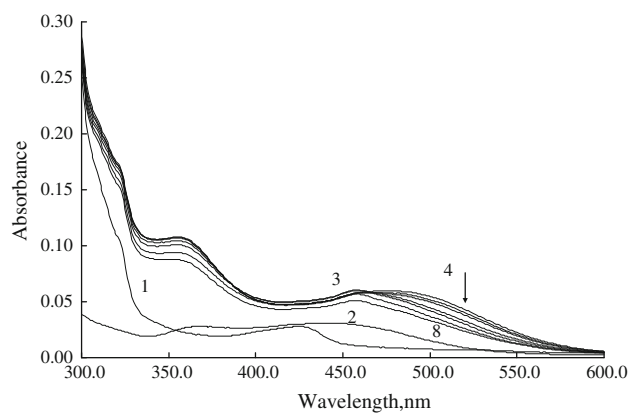

Fig. 1 The UV–Vis spectra of (1) DB18C6 ($C_{DB18C6} = 1.0 \times 10^{-2}$ mol/L), (2) ICl_3 ($C_{ICl_3} = 1.0 \times 10^{-3}$ mol/L), and mixtures of ICl_3 and DB18C6 (ration 1:10) at (3) 0 min, (4) 5 min (5) 15 min, (16) 180 min after mixing in dichloromethane solution at 20 °C
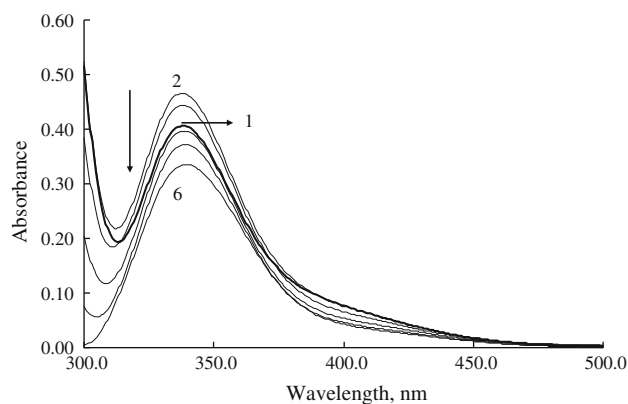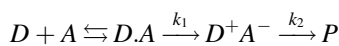
Fig. 2 The UV–Vis spectra of (1) DC18C6 ($C_{DC18C6} = 1.0 \times 10^{-2}$ mol/L), (1) ICl_3 ($C_{ICl_3} = 1.0 \times 10^{-3}$ mol/L), and mixtures of ICl_3 and DC18C6 (ration 1:10) at (2) 0 min, (3) 20 min (4) 30 min, (6) 60 min, (7) 24 h after mixing in propylene carbonate solution at 25 °C

The kinetics studies of formation of ICl_3 complexes with DB18C6 and DC18C6 were carried out in 342 and 340 nm, respectively.

Determination of rate constants of DB18C6 and DC18C6 charge transfer complexes with ICl_3

To obtain the rate constants of charge transfer complexes of ICl_3 with DB18C6 and DC18C6, absorbance values of these complexes were recorded at different times. Figures 3, 4 and 5 show the absorbance–time curves of DB18C6.ICl_3 complexes in different temperatures in dichloromethane, and propylene carbonate solution and DC18C6.ICl_3 complex in chloroform solution.

Both ligands show two steps of complex formation in chloroform and dichloromethane solutions. The above experimental observations seem to be in accord with the following mechanism, which has been proposed before [19–22]. The proposed mechanism for formation of the charge transfer complex as presented at the following:

$$D + A \leftrightarrows D.A \xrightarrow{k_1} D^+A^- \xrightarrow{k_2} P$$

Therefore the increase of absorbance in chloroform and dichloromethane arises from D^+A^- complex formation and the decrease of absorbance results from D^+A^- complex changes to final product. k_1 and k_2 are the rate constants of first and second steps (i.e. formation of D^+A^- complex and resulting product), respectively. In propylene carbonate solution, the first step is too fast; therefore only the second step is observed. For above reaction concentration of DA, D^+A^- and P versus time calculate as the following:
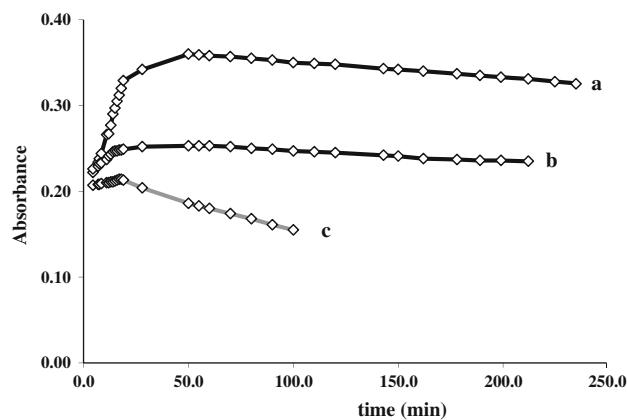
$$[DA] = [DA]_0 \exp(-k_1 t) \tag{1}$$

Fig. 3 Absorbance–time curves of DB18C6.ICl_3 complexes in chloroform solution at (a) 5 °C, (b) 10 °C and (c) 15 °C. Concentration of ICl_3 was 1.0×10^{-3} mol L^{-1}
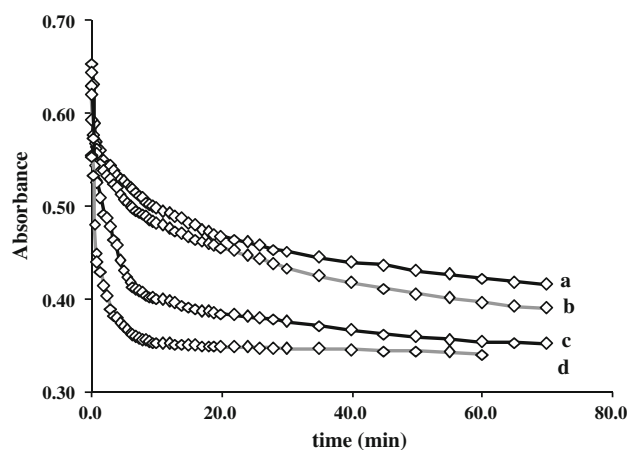

Fig. 4 Absorbance–time curves of DB18C6.ICl_3 complexes in propylene carbonate solution at (a) 10 °C, (b) 15 °C, (c) 20 °C and (d) 25 °C Concentration of ICl_3 was 1.0×10^{-3} mol L^{-1}
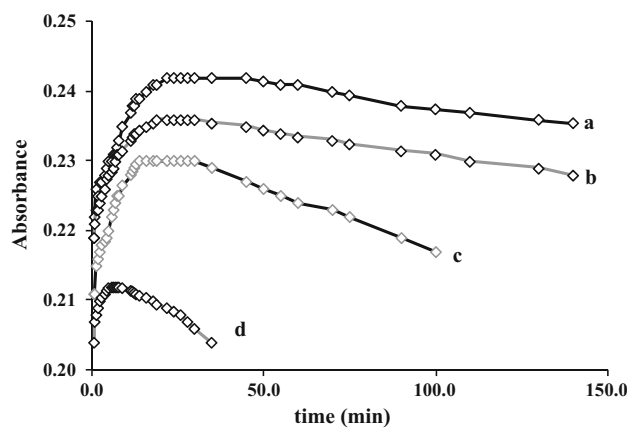

Fig. 5 Absorbance–time curves of DC18C6·ICl_3 complexes in chloroform solution at (a) 5 °C, (b) 10 °C, (c) 15 °C and (d) 20 °C. Concentration of ICl_3 was 1.0×10^{-3} mol L^{-1}

$$[D^+A^-] = \frac{[DA]_0 k_1 [\exp(-k_2 t) - \exp(-k_1 t)]}{(k_1 - k_2)} \quad (2)$$

$$[P] = \frac{[DA]_0 \{1 + k_2 \exp(-k_1 t) - k_2 \exp(-k_1 t)\}}{(k_1 - k_2)} \quad (3)$$

where $[DA]_0$ is the initial concentration of DA at $t = 0$ and $[D^+A^-] = [P] = 0$. The absorbance of the solution is:

$$A_t = \varepsilon_{DA}[DA] + \varepsilon_{D^+A^-}[D^+A^-] + \varepsilon_P[P] \quad (4)$$

where ε_{DA}, $\varepsilon_{D=A^-}$ and ε_P are the molar absorption coefficient of DA, D^+A^- and P, respectively. With replaces them from Eqs. 1–3 and rearranges the Eq. 4, the following equation results:

$$A_t = \frac{[DA]_0 \{(\varepsilon_{DA} - \varepsilon_P) \exp(-k_1 t) + (\varepsilon_{D^+A^-} - \varepsilon_P)[\exp(-k_2 t) - \exp(-k_1 t)]\}}{(k_1 - k_2)} + \varepsilon_P \quad (5)$$

In this reaction if the first step is too fast, the reaction is the quasi first order and then the absorbance of the solution is like the following:

$$A_t = [DA]_0 (\varepsilon_{DA} \exp(-kt) + \varepsilon_P (1 - \exp(-kt))) \quad (6)$$

The first and second step rate constants of charge transfer complexes in chloroform, and dichloromethane were obtained by fitting absorbance–time data in Excel program with (5) equation. And absorbance–time data in propylene carbonate were fitted by (6) equation in excel program and rate constant of charge transfer was obtained throughout. Two samples computer fits of the DB18C6.ICl₃ complex in chloroform solution and propylene carbonate are shown in Figs. 6 and 7, respectively. A fair agreement between the observed and calculated absorbance exists. The fitting of the curves was acceptable and the rate constants of complexes in various temperatures were obtained. The rate
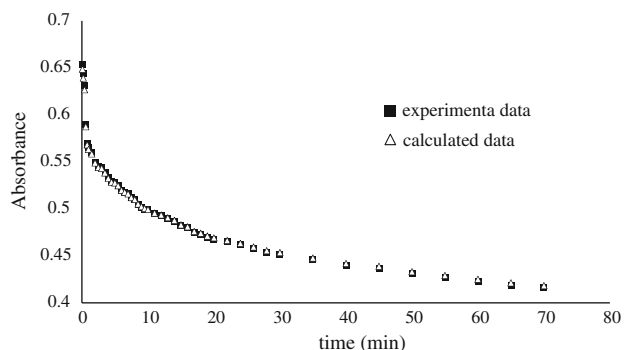
constants of ICl₃ complexes with DB18C6 and DC18C6 in various temperatures in chloroform, dichloromethane and propylene carbonate are listed in Table 2. As Table 2 shows, the values of the rate constants of DB18C6.ICl₃ complex are lower than DC18C6.ICl₃ complex. It is arising of electron-with drawing biphenyl groups of DB18C6 that causes the formation of charge transfer complex to become slow. In both charge transfer complexes, the values of the rate constants in dichloromethane solution are higher than chloroform solution. To be compared with chloroform, dichloromethane has higher polarity and dielectric constant that causes rapid formation of D^+A^- complex and change it in to final product.

Because of the high polarity and dielectric constant of propylene carbonate (shown in Table 1), the first step (formation of D^+A^- complex) in this solution is too fast to be observed. Only the second step is observed and this step of DB18C6 complex is faster than DC18C6.

Determination of ΔH# and ΔS#

The activation parameters ΔH#, and ΔS# were then calculated by using the corresponding Arrhenius plots, and the Eying transition-state theory [23]; the results are given in Table 3. From Table 2 it is obvious that, although the rate of the first step of the reaction is higher than that of the second step, it is associated with higher activation energy as it compared with the value of activation energy for the second step. This may be explained in terms of the compensatory effect of highly negative $\Delta S_1^#$ values on the reaction rate. Thus, the less negative $\Delta S_1^#$ for the production

Fig. 6 The sample of computer fit of the DB18C6.ICl₃ complex in propylene carbonate solution at 10 °C
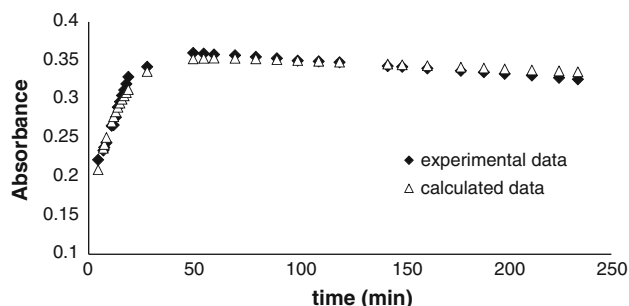

Fig. 7 The sample of computer fit of the DB18C6.ICl₃ complex in chloroform solution at 5 °C

Table 2 The rate constant values of DB18C6.ICl$_3$ and DC18C6.ICl$_3$ complexes in chloroform, dichloromethane and propylene carbonate solvents at different temperatures

Ligand	Solvent	Temperature (°C)	k_1 (s^{-1})[a]	k_2 (s^{-1})[a]
DB18C6	Chloroform	5.0	8.10×10^{-2}	5.48×10^{-4}
		10.0	9.52×10^{-2}	6.51×10^{-4}
		15.0	0.145	9.50×10^{-4}
	Dichloromethane	10.0	0.140	1.50×10^{-3}
		15.0	0.161	2.00×10^{-3}
		20.0	0.240	2.55×10^{-3}
		25.0	0.260	3.01×10^{-3}
	Propylene carbonate	10.0	–	0.117
		15.0	–	0.150
		20.0	–	0.355
		25.0	–	0.726
DC18C6	Chloroform	5.0	0.103	5.62×10^{-4}
		10.0	0.150	7.31×10^{-4}
		15.0	0.194	1.92×10^{-3}
		20.0	0.391	2.80×10^{-3}
	Dichloromethane	5.0	0.180	1.34×10^{-4}
		10.0	0.229	2.11×10^{-3}
		15.0	0.321	3.10×10^{-3}
	Propylene carbonate	10.0	–	1.35×10^{-3}
		15.0	–	8.10×10^{-3}
		25.0	–	3.10×10^{-2}

[a] RSD for all experiments were less than 2%

Table 3 The thermodynamic constant values of DB18C6.ICl$_3$ and DC18C6.ICl$_3$ complexes in chloroform, dichloromethane and propylene carbonate

Ligand	Solvent	$\Delta H_1^{\#}$ (KJ mol^{-1})	$\Delta S_1^{\#}$ (KJ mol^{-1} K^{-1})	$\Delta H_2^{\#}$ (KJ mol^{-1})	$\Delta S_2^{\#}$ (KJ mol^{-1} K^{-1})
DB18C6	Chloroform	37.1	−132.1	34.1	−184.0
	Dichloromethane	29.3	−152.3	30.2	−191.5
	Propylene carbonate	–	–	86.2	40.9
DC18C6	Chloroform	55.0	−65.6	74.1	−40.3
	Dichloromethane	50.9	−77.0	73.2	−38.2
	Propylene carbonate	–	–	135.3	190.7

RSD for all values is less than 2.5%

radical ions may result in the higher rate constants, as it compared with the more negative $\Delta S_2^{\#}$ for its consumption, although from the observed trend in $\Delta H^{\#}$ values an opposite behavior is expected. As the Table 3 shows these kinetic parameter values for both complexes, the values of $\Delta H^{\#}$ in chloroform in both steps, is higher than those of dichloromethane. Therefore according to Eyring's equation, the higher rate constant results in lower $\Delta H^{\#}$ value that it is correspondent with the obtained values. As shown in Table 3, the formation of these complexes in chloroform and dichloromethane solutions is enthalpy and entropy destabilized but the formation of these in propylene carbonate is enthalpy destabilized and entropy stabilized.

Conclusion

Since the formations of some charge transfer complexes were along with kinetic [15, 26], we investigated the kinetic of formation of charge transfer ICl$_3$ complexes with DB18C6 and DC18C6. The kinetic study of formation of these charge transfer complexes show the role of solvent and the substitute groups on the crown ether ring in the reaction rate and the enthalpy of the activated complex. The formation of activated complex in the solvent with high polarity and high dielectric constant occurred fast. The electron with drawing of the ligand can cause the rate constant decrease and the enthalpy value increase.

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