# Stoichiometry, Thermodynamics and Kinetics of Host–Guest Interactions between Cryptand C222 and Iodine in 1,2-Dichloroethane. Formation of a C222.I$^+$ Inclusion Cryptate

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**Abstract.** The host–guest molecular complexation reaction between cryptand C222 and iodine has been studied spectrophotometrically in 1,2-dichloroethane solution. The resulting 1 : 1 and 2 : 1 ($I_2$ to C222) complexes were formulated as $(C222 \ldots I^+)I^-$ and $(C222 \ldots I^+)I_3{}^-$, respectively. The enthalpy and entropy of the complex formation reactions were evaluated from the temperature dependence of the formation constants. The resulting complexes are both enthalpy and entropy stabilized. The spectrophotometric, NMR, conductometric and potentiometric results emphasize that the complexes are positive iodine cryptates. The rate constants for the formation and proton-assisted dissociation of the $(C222 \ldots I^+)I_3^-$ complex at various temperatures and the corresponding activation parameters were evaluated. Based on the results thus obtained, possible pathways for the complexation reaction are proposed.

**Key words:** C222-$I_2$ complexation, spectrophotometry, 1,2-dichloroethane, inclusion cryptate

## 1. Introduction

Although, during the past few decades, the complexation of iodine with a wide variety of donating ligands has been the subject of extensive research [1–3], the complexation of macrocycles with $I_2$ is a relatively young area of research [4]. In 1978, Hopkins *et al.* [5] observed spectroscopic evidence for the formation of molecular complexes between 12-crown-4, 15-crown-5 and 18-crown-6 and iodine in methylene chloride and cyclohexane solutions. Subsequently, the first evidence for the complex formation between iodine and cryptand C222 with $^1$H NMR spectrometry was reported by Pierre *et al.* [6]. More recently, increasing attention has been focused on the study of the interactions of macrocyclic ligands with iodine [7–16]. However, there are only a few reports on the complexation of cryptands with neutral molecules [6, 7, 17].

It has been clearly shown that substitution of the oxygen atoms in a crown ether ring by NH groups results in a drastic increase in the stability of the iodine com-

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plexes [7, 10, 13, 15] over those of ordinary crowns [5, 8, 9, 14]. Moreover, we [7, 13, 15, 16] and others [6, 10, 17] have observed some evidence for the formation of iodine complexes with some aza-substituted crown ethers and cryptands with general formula [macrocycle …$I^+$]$I_3^-$, in which $I^+$ could be included inside the macrocyclic cavity. We have recently commenced a systematic study of the iodine-macrocycle complexation by different spectroscopic methods [7, 13–15]. In this paper we report the stoichiometry, stability and thermodynamic and kinetic parameters for the complexation of $I_2$ with cryptand C222 in 1,2-dichloroethane (DCE) solution. Spectroscopic and electrochemical information revealed the inclusion of $I^+$ inside the cryptand's cavity.

## 2.  Experimental

Cryptand C222 (Merck) was of the highest purity available and used without any further purification except for vacuum drying over $P_2O_5$. Reagent grade iodine, trichloroacetice acid and DCE (all from Merck) were used as received.

All UV-Vis spectra were recorded on a GBC 911 spectrophotometer in a 10 mm quartz cell and the absorbance measurements were made with a Metrohm 662 probe-type photometer at various temperatures ($\pm 0.1$ °C). Conductance measurements were carried out with a Metrohm 712 conductivity meter. Potentiometric titrations were performed at the surface of a platinum electrode using a Model 624 Metrohm pH/mV meter. The proton NMR spectra were recorded on a Jeol JNM-EX90 FTNMR spectrometer operating at a field of 21.15 kG (90 MHz). In all experiments, TMS was used as an internal standard. Specific details are given in the Results and Discussion section.

## 3.  Results and Discussion

A series of solutions containing $1.5 \times 10^{-4}$ M iodine in DCE in the presence of an increasing amount of C222 were prepared and allowed to reach equilibrium. Then, the electronic absorption spectra of the solutions were recorded at 25 °C (Figure 1). While none of the reactants show any measurable absorption in the 250–420 nm spectral region, addition of the cryptand to the iodine solutions results in two absorptions in this region. As seen from Figure 1, the new absorption bands are located at 295 and 363 nm. It should be noted that the resulting spectrum resembles that of a 1 : 1 mixture of tetrabutylammonium iodide and iodine in DCE. These two absorptions are well known to be characteristic of the formation of triiodide ion, $I_3^-$, in the process of complex formation between iodine and different electron-pair donor ligands [3, 7, 10, 13–15]. The existence of a well defined isosbestic point at 470 nm is indicative of a single transformation of iodine to triiodide ion.

However, as it is obvious from Figure 1A, while the intensity of the 295 and 363 nm bands increases with increasing C222/$I_2$ mole ratio up to a value of 0.5, further addition of the macrocycle results in decreased intensity of these bands, so that
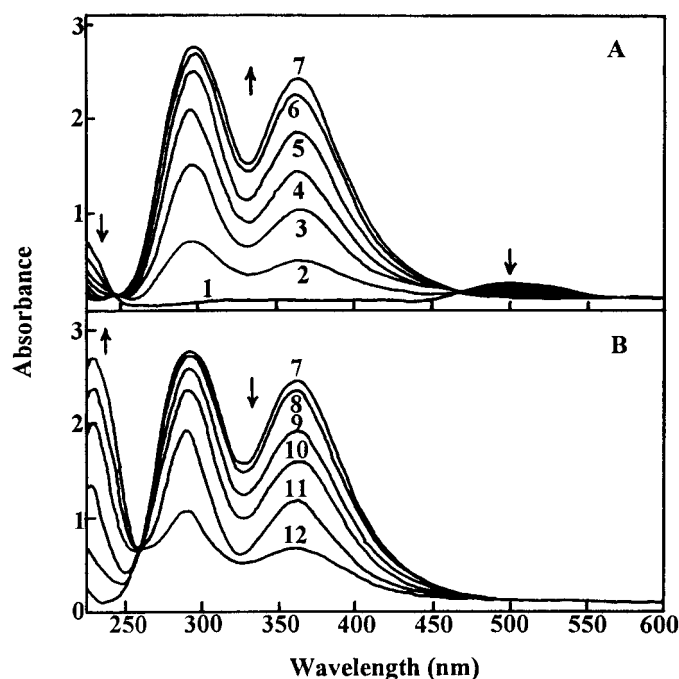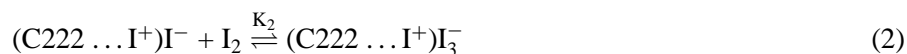
*Figure 1.* Electronic absorption spectra of $1.5 \times 10^{-4}$ M iodine in DCE in the presence of varying concentration of C222. The C222/I$_2$ mole ratios are: (A) 1, 0.00; 2, 0.08; 3, 0.17; 4, 0.25; 5, 0.33; 6, 0.42; 7, 0.50; (B) 8, 0.66; 9, 0.83; 10, 1.00; 11, 1.33; 12, 1.66.

they begin to disappear at relatively high mole ratios (Figure 1B). Simultaneously, after a C222/I$_2$ mole ratio of 0.5, a new band at about 235 nm begins to grow with increasing concentration of the macrocyclic ligand. This is most probably due to the formation of I$^-$ ion in solution at C222/I$_2 > 0.5$. Noteworthy, the 235 nm band was clearly observed for a solution of tetrabutylammomium iodide in DCE solution. The presence of a second isosbestic point at about 270 nm (Figure 1B) confirms a single transformation of triiodide to iodide ion.

The plots of absorbance vs. C222/I$_2$ mole ratio at 510, 363, 295 and 235 nm are shown in Figure 2. It is quite obvious that, while the mole ratio plot at 510 nm ($\lambda_{max}$ of I$_2$ in DCE) shows just a gradual decrease with increasing concentration of C222, the corresponding plots at 363 and 295 nm possess a maximum absorbance at a mole ratio of 0.5 and then begin to decrease gradually with a small inflection at a mole ratio of about 1. Meanwhile, the mole ratio plot at 235 nm shows two distinct breaks at the ligand to iodine mole ratios of 0.5 and 1. Such spectral behavior strongly emphasizes the successive formation of (C222 ... I$^+$)I$_3^-$ and (C222 ... I$^+$)I$^-$ species in DCE as

$$C222 + 2I_2 \overset{K_1}{\rightleftharpoons} (C222 \ldots I^+)I^- \tag{1}$$

$$(C222 \ldots I^+)I^- + I_2 \overset{K_2}{\rightleftharpoons} (C222 \ldots I^+)I_3^- \tag{2}$$
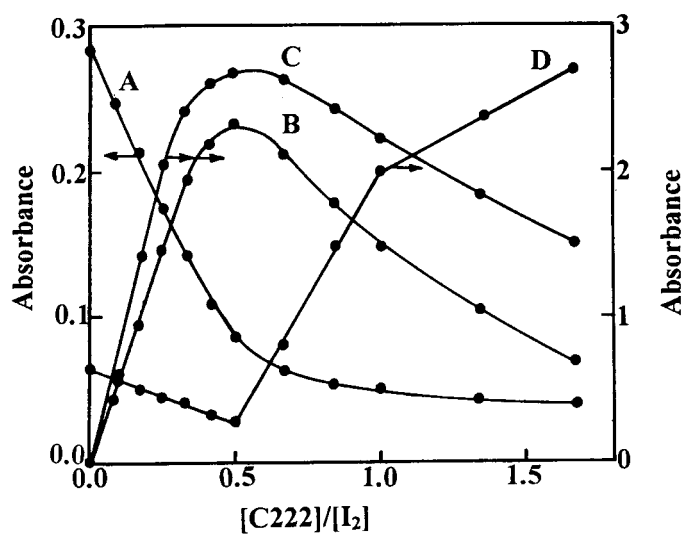
*Figure 2.* Plots of absorbance vs. C222/$I_2$ mole ratio in DCE solution obtained at 510 nm (A), 363 nm (B), 295 nm (C) and 235 nm (D).
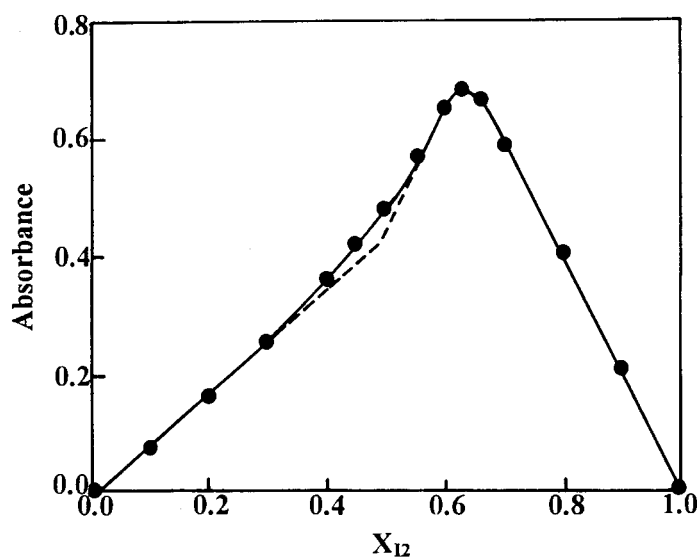


*Figure 3.* Continuous variations plot for the C222-$I_2$ system in DCE solution; $\lambda$ = 363 nm.

The stoichiometry of the resulting molecular complexes was further examined by the method of continuous variations [18] and the resulting plot is shown in Figure 3. As seen, the plot possesses two distinct inflection points at $X_{I_2}$ values of 0.5 and 0.66, clearly supporting the respective formation of (C222 ... $I^+$)$I^-$ and (C222 ... $I^+$)$I_3^-$ species in solution.

*Table I.* ^{1}H NMR spectral data for C222 at different $I_2$/C222 mole ratios in deuterated DCE

| | | $\delta$ (ppm) | | |
|---|---|---|---|---|
| $[I_2]$/[C222] | Species | $-NCH_2-$ | $-OCH_2-$ | $-CH_2CH_2O-$ |
| 0.0 | C222 | 2.66 | 3.56 | 3.67 |
| | | (triplet) | (triplet) | (singlet) |
| 0.5 | C222 + (C222...I$^+$)I$^-$ | 2.68 + 3.02 | 3.65 | 3.65 |
| | | (two broad singlets) | (broad singlet) | (broad singlet) |
| 1.0 | (C222...I$^+$)I$^-$ | 3.04 | 3.68 | 3.68 |
| | | (triplet) | (broad singlet) | (broad singlet) |
| 2.0 | (C222...I$^+$)I$_3^-$ | 3.12 | 3.68 | 3.68 |
| | | (triplet) | (broad singlet) | (broad singlet) |

The proton NMR spectra of C222 were obtained in DCE in the presence of increasing amount of $I_2$ at 25 °C and the results are summarized in Table I. As seen, the formation of 1 : 1 and 2 : 1 ($I_2$ to C222) species result in a pronounced down field shift of about 0.4 ppm in the chemical shift of the $-CH_2N-$ protons, while the shift in the $-CH_2O-$ and $-OCH_2CH_2O-$ proton resonances are negligible. It seems reasonable to assume that such a large shift is due to the charge migration mainly from the n-electrons of the nitrogen atoms of the cryptand to the $b_{2\sigma u}$ antibonding molecular orbital of iodine [19, 20] It is noteworthy that, when the $I_2$/C222 mole ratio in DCE solution is equal to 0.5, two broad singlets of approximately equal intensity are observed at 2.68 and 3.02 ppm corresponding to free and complexed C222 molecules. The large chemical shift difference of the $-CH_2N-$ protons of the free C222 and its iodine complex as well as their very slow exchange kinetics at room temperature would be a good indication for the inclusion of I$^+$ (with ionic size of 1.64 Å) [17] inside the C222 cryptate; the halogen's positive charge is presumably shared by the two cryptand's nitrogens (in an endo-endo conformation), most probably via a sp$^3$d-type hybridization.

The large increase in the electrical conductance of $I_2$ solutions in DCE upon addition of the neutral cryptand reveals an ionic character for the resulting $I_2$-C222 complexes. Noteworthy, while an iodine solution of $1.05 \times 10^{-4}$ M in DCE has a negligible conductivity, the molar conductance of the solution increases to 36.8 and 27.8 S cm$^2$ mol$^{-1}$ for the $I_2$-C222 and $2I_2$-C222 systems, respectively.

Furthermore, a $1.0 \times 10^{-3}$ M solution of iodine in DCE was potentiometrically titrated with a known C222 solution at the surface of a platinum electrode at 25 °C and the resulting titration curve is shown in Figure 4. As seen, the titration curve shows a relatively sharp inflection point at a C222/$I_2$ mole ratio of about 0.5, indicating the occurrence of reaction (1) in solution. As indicated on the potentiometric profile of Figure 4, before the inflection point, the redox system $I_3^-$/$I_2$ is responsible for the observed potential changes, while after the inflection point,
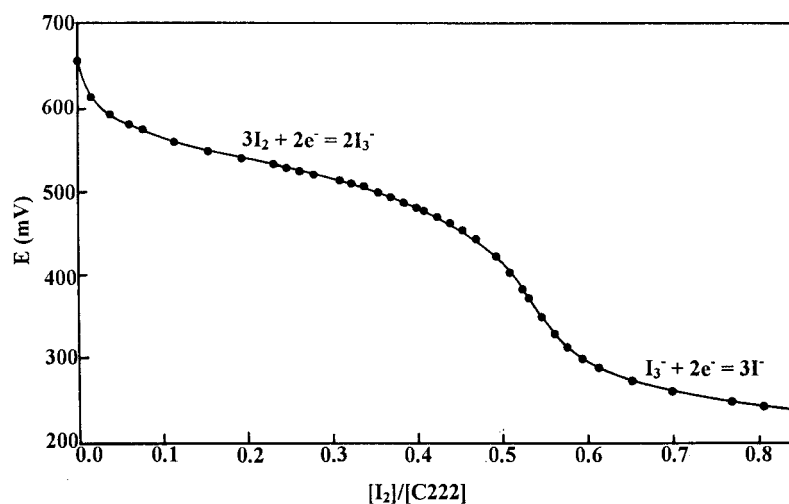
*Figure 4.* Potentiometric profile for titration of 10.0 mL of $1.05 \times 10^{-3}$ M $I_2$ with C222 in DCE.
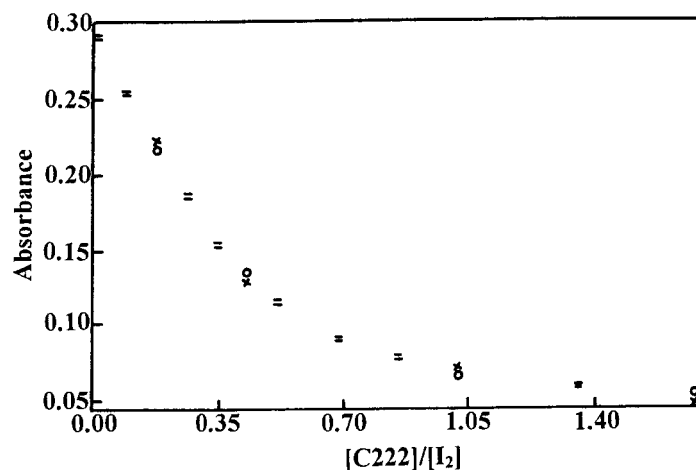


*Figure 5.* Computer fit of the plot of absorbance vs. C222/$I_2$ mole ratio obtained at 510 nm and 25 °C: ($\times$), experimental points; (o) calculated points; (=), experimental and calculated points are the same within the resolution of the plot.

the redox system is $I_3^-/I^-$. Thus, the electrochemical studies carried out in DCE solutions unambiguously confirm the ionic character of the resulting complexed species. Moreover, $I_2$, $I_3^-$ and $I^-$ are the only reactive species detected, as they were also characterized by UV-Vis spectrophotometric measurements.

For the evaluation of the stepwise formation constants of the resulting molecular complexes, $K_1$ and $K_2$, from the absorbance-mole ratio data, a non-linear least-squares curve fitting program KINFIT was used [21]. The program is based on the iterative adjustment of calculated to observed absorbance values. Adjustable

*Table II.* Stepwise formation constants at various temperatures and enthalpy and entropy values for the 1 : 1 and 2 : 1 complexation between iodine and cryptand C222 in DCE

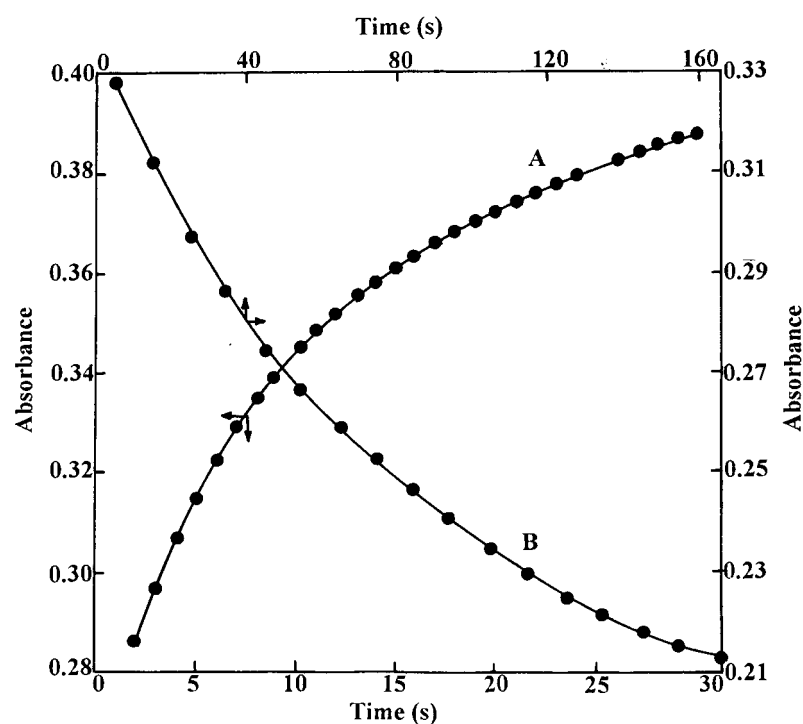| Temperature (°C) | log $K_1$ | log $K_2$ |
|---|---|---|
| 15 | $4.55 \pm 0.03$ | $4.62 \pm 0.03$ |
| 25 | $4.47 \pm 0.02$ | $4.56 \pm 0.03$ |
| 35 | $4.40 \pm 0.04$ | $4.49 \pm 0.02$ |
| 45 | $4.33 \pm 0.04$ | $4.40 \pm 0.03$ |
| | $\Delta H_1 = 12.8 \pm 0.1$ kJ mol$^{-1}$ | $\Delta H_2 = -12.7 \pm 0.8$ kJ mol$^{-1}$ |
| | $\Delta S_1 = 42.6 \pm 0.3$ J mol$^{-1}$K$^{-1}$ | $\Delta S_2 = 44 \pm 2$ J mol$^{-1}$ K$^{-1}$ |



*Figure 6.* Absorbance-time plot at 405 nm at 20 °C for the pseudo-first-order formation (A) and proton-assisted dissociation (B) of the $(C222 \ldots I^+)I_3^-$ complex in DCE solution.

parameters are $K_1$, $K_2$ and $\epsilon_{I_2}$, where $\epsilon_{I_2}$ is the molar absorption coefficient of iodine.

The observed absorbance of an iodine solution in DCE at its $\lambda_{max}$ is given by Equation (3), where $b$ is the thickness of the cell. The mass-balance equations can be written as (4) and (5).

$$A_{obs} = \epsilon_{I_2}[I_2] \tag{3}$$

*Table III.* Rate constants at various temperatures and activation parameters for the formation of $(C222 \ldots I^+)I_3^-$ complex in DCE

| Temperature (°C) | $10^2 \, k_{obs}^f \, (s^{-1})$ |
|---|---|
| 10 | $4.2 \pm 0.2$ |
| 20 | $8.3 \pm 0.2$ |
| 30 | $13.6 \pm 1.0$ |
| 40 | $21.9 \pm 0.6$ |
| $E_{af} = 40 \pm 1 \text{ kJ mol}^{-1}$ | |
| $\Delta H_f^{\ddagger} = 38 \pm 1 \text{ kJ mol}^{-1}$ | |
| $\Delta S_f^{\ddagger} = -137 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$ | |

$$C_I = [I_2] + [(C222 \ldots I^+)I^-] + 2 [(C222 \ldots I^+)I_3^-] \tag{4}$$

$$C_{C222} = [C222] + [(C222 \ldots I^+)I^-] + [(C222 \ldots I^+)I_3^-] \tag{5}$$

Substitution of Equations (4) and (5) in the corresponding $K_1$ and $K_2$ equations and rearrangement yield Equation (6).

$$K_1 K_2 [I_2]^3 + [K_1 K_2 (2C_{C222} - C_I) + K_1][I_2]^2$$
$$+ [1 + K_1(C_{C222} - C_I)][I] - C_I = 0. \tag{6}$$

The free iodine concentrations, $[I_2]$, were calculated by means of a Newton-Raphson procedure [22]. Once the value of $[I_2]$ had been obtained, the concentration of all other species involved were calculated from the corresponding mass-balance equations by using the value of $K_1$ and $K_2$ at the current iteration step of the program. Refinement of the parameters was continued until the sum-of-squares of the residuals between the calculated and observed absorbance values for all experimental points was minimized. The output of the program KINFIT comprises the refined parameters, the sum-of-squares and the standard deviations of the data.

In order to have a better understanding of the thermodynamics of the complexation reactions of iodine with C222, it is useful to consider the enthalpic and entropic contributions to these reactions. The $\Delta H°$ and $\Delta S°$ values were determined by measuring the formation constants as a function of temperature. The $K_1$ and $K_2$ values at various temperatures, obtained by computer fitting of the corresponding absorbance-mole ratio data are listed in Table II. A sample computer fit of the mole ratio data is shown in Figure 5. The fair agreement between the observed and calculated absorbances further supports the occurrence of both 1 : 1 and 1 : 2 complexation between C222 and $I_2$ in DCE solution. Plots of log K vs. 1/T were linear for both $K_1$ and $K_2$ values. The $\Delta H°$ and

*Table IV.* Rate constants at various temperatures and activation parameters for the proton-assisted dissociation of the $(C222\ldots I^+)I_3^-$ complex in DCE

| Temperature (°C) | $10^2\, k_{obs}^d\ (s^{-1})$ |
|---|---|
| 15 | $1.02 \pm 0.04$ |
| 20 | $1.13 \pm 0.04$ |
| 25 | $1.45 \pm 0.03$ |
| 30 | $1.87 \pm 0.09$ |
| 35 | $2.17 \pm 0.09$ |
| $E_{ad} = 30 \pm 2$ kJ mol$^{-1}$ | |
| $\Delta H_d^{\ddagger} = 28 \pm 2$ kJ mol$^{-1}$ | |
| $\Delta H_a^{\ddagger} = -188 \pm 6$ J mol$^{-1}$ K$^{-1}$ | |

$\Delta S°$ values were determined in the usual manner from the slopes and intercepts of the plots, respectively, and the results are also included in Table II. As seen, the formation of 1 : 1 and 2 : 1 ($I_2$/C222) complexed species are both enthalpy and entropy stabilized. A similar trend in $\Delta H°$ and $\Delta S°$ values has also been reported for the complexation of iodine with dibenzopyridino-18-crown-6 [16] and 2,4,6,8-tetraphenyl-2,4,6,8-tetraazabicyclo[3.3.0]octane in chloroform solution [23].

In order to investigate the kinetics of molecular complex formation between iodine and C222, the absorbance (at $\lambda = 405$ nm) of a $1.5 \times 10^{-5}$ M C222 solution in DCE in the presence of a 60 fold excess of iodine was monitored with time at four different temperatures. This was done by interfacing of the probe-type instrument to a personal computer. A sample absorbance-time plot at 20 °C is shown in Figure 6. The absorbance changes were found to be in accord with a pseudo-first-order kinetics. The rate constants were calculated by using the relationship

$$\ln(A_\infty - A_t) = -k(t - t_0) + \ln(A_\infty - A_0), \tag{7}$$

where $A$ is the absorbance of the solution. The resulting rate constants at various temperatures, obtained from the slopes of the corresponding linear $\ln(A_\infty - A_t)$ vs. $(t - t_0)$ plots, are summarized in Table III. Using the corresponding Arrhenius plot of $\ln k$ vs. $1/T$ and the Eyring transition-state theory [24], the activation parameters $E_{af}$, $\Delta H_f^{\ddagger}$ and $\Delta S_f^{\ddagger}$ were calculated. The results are also included in Table III.

The time dependence of the triiodide absorption bands and the large negative $\Delta S_f^{\ddagger}$ value obtained indicate the transformation of an initially formed 1 : 1 C222-$I_2$ outer complex into an inner complex (C222-$I^+$)$I^-$ followed by the fast reaction of the inner complex with iodine to form $I_3^-$ ion [25].

Recent ultrasonic absorption studies of the kinetics of conformational changes of different cryptands in nonaqueous aprotic solvents revealed only one relax-
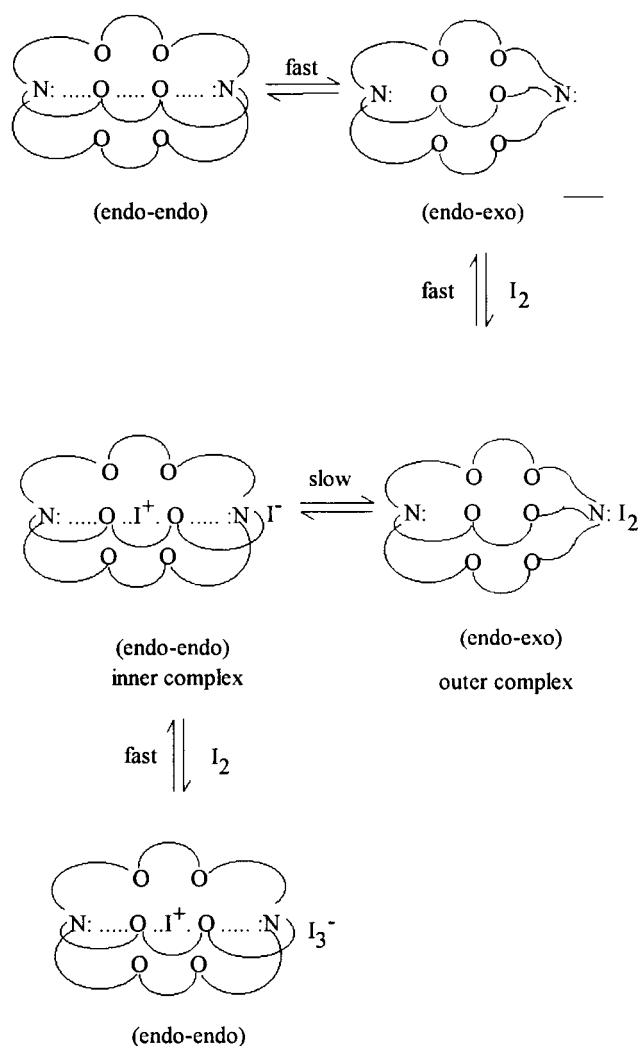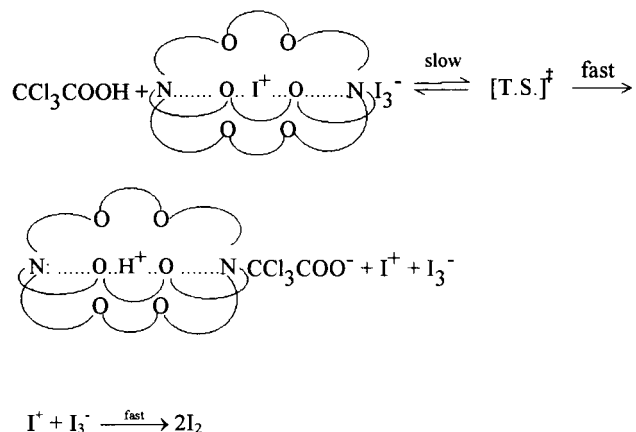
*Scheme 1.*

ation process which was attributed to the conformational equilibrium endo-exo $\rightleftharpoons$ endo-endo [26, 27]. Based on the above mentioned experimental conclusions and considering the fact that the external complexes of cryptands (C222-$I_2$ outer complex in our case) prefer the endo-exo conformation, while the inclusion type cryptates have an endo-endo conformation [28, 29], the pathway shown in Scheme 1 could be proposed for the formation of the $(C222 \ldots I^+)I_3^-$ complex.

The proton-assisted dissociation kinetics of the $(C222 \ldots I^+)I_3^-$ complex was also studied by addition of excess amount of trichloroacetic acid to an equilibrated $1.0 \times 10^{-5}$ M solution of the molecular complex and subsequent monitoring of absorbance (at 405 nm) against time at five different temperatures. A sample absorbance-time plot at 20 °C is also included in Figure 6. The pseudo-first-order

rate constants calculated at various temperatures and the corresponding activation parameters $E_{ad}$, $\Delta H_d^{\ddagger}$ and $\Delta S_d^{\ddagger}$ are summarized in Table IV. In this case, the dissociation of the molecular complex could proceed via the following pathway:



*Scheme 2.*

The positive enthalpy of activation in going from the complex $(C222\ldots I^+)I_3^-$ to the protonated cryptand and free $I^+$ and $I_3^-$ ions reflects a weaker structure, a poorer overlap and a floppy geometry for the transition state when it is compared with the initial iodine cryptate. The large negative $\Delta S_d^{\ddagger}$ (i.e. much more negative than $\Delta S_f^{\ddagger}$) could be due to the penetration of solvent molecules between the charged center of the molecule in the transition state, thus facilitating the release of charged iodine species from the complex [16, 30]. Based on the above mentioned experimental results, it seems reasonable to propose the following transition state for the dissociation pathway:
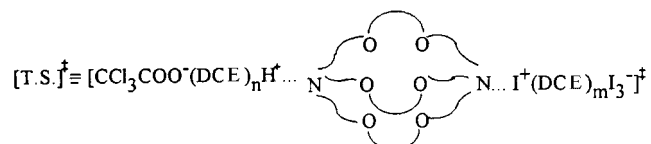


*Scheme 3.*

## Acknowledgements

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