



Interaction of Iodine with Hexaaza-18-crown-6 and Tetraaza-14-crown-4 in Chloroform Solution

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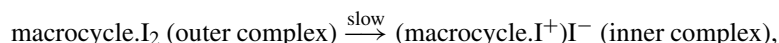
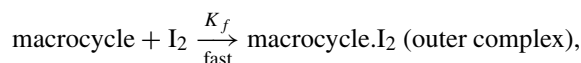
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Abstract

Interactions of hexaaza-18-crown-6 (HA18C6) and tetraaza-14-crown-4 (TA14C4) with iodine have been investigated spectrophotometrically in chloroform solution. The observed time dependence of the charge-transfer band and subsequent formation of I_3^- in solution were related to the slow transformation of the initially formed 1:1 macrocycle. I_2 outer complex to an inner electron donor-acceptor (EDA) complex, followed by fast reaction of the inner complex with iodine to form a triiodide ion, as follows:



The pseudo-first-order rate constants at various temperatures for the transformation process were evaluated from the absorbance-time data. The activation parameters (E_a , ΔH^\ddagger , and ΔS^\ddagger) for the transformation were obtained from the temperature dependence of the rate constants. The stoichiometry and formation constants of the resulting EDA complexes have also been determined. It was found that the $(TA14C4 \cdot I^+) I_3^-$ is more stable than the $(HA18C6 \cdot I^+) I_3^-$ complex in chloroform solution.

Introduction

The formation of molecular complexes between electron donors and electron acceptors has long been recognized as an important phenomenon in many biological processes [1, 2]. Macrocyclic polyethers, a class of compounds first synthesized by Pedersen [3], have been shown to bind cations much more strongly than monofunctional and linear polyfunctional ethers of similar basicity [4, 5]. More recently, the potential of the complexing ability of these macrocycles toward neutral molecules has been investigated [6–10]. Interest in such molecular complexes has been strongly stimulated by the possibility of their applications in such broad areas as separation science, catalysis of chemical reactions and conversion of chemical reactions into electronic or optical signals. Moreover, the charge-transfer involvement in biomolecular interactions can be better demonstrated by

studying simple multi-site donors which would serve as model compounds of biomolecules [11].

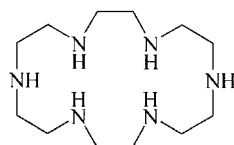
Among different macrocyclic ligands used for molecular complexation, aza substituted crown ethers show very interesting features. It has been clearly shown that the substitution of the oxygen atoms in a crown ether ring by $-NH-$ groups results in a drastic increase in the stability of their complexes with iodine [12–15] and some π -acceptor molecules [16] over those of ordinary crowns [7, 12, 17].

Molecular iodine has been the most studied of halogen acceptors. Although there are many reports on molecular charge-transfer complexes between different aliphatic and aromatic amines and iodine in the literature [18–24], not much work has been done on similar complexes of azacrown ethers (as cyclic amines) [12–15].

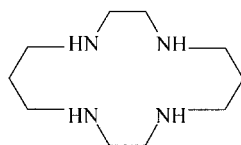
In connection with our previous studies made on the charge-transfer complexes of iodine with macrocyclic crown ethers and their aza derivatives in various solvents [13–17], here we report on the results of kinetic and spectral studies concerning the interaction of iodine with two polyaza-

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crowns, hexaaza-18-crown-6 (HA18C6) and tetraaza-14-crown-4 (TA14C4) in chloroform solution.



HA18C6



TA14C4

Experimental

The macrocycle HA18C6 (Fluka) was of the highest purity available and was used without any further purification. TA14C4 (Merck) was purified by recrystallization from reagent grade benzene and dried under vacuum over P_2O_5 . Resublimed iodine of analytical grade (Merck) was used as received. Reagent grade chloroform (from Fluka) was used without any further purification.

All UV-Vis spectra were recorded on a Philips PUB 700 spectrophotometer and the absorbance measurements as a function of time, at fixed wavelengths, were made with a Philips PU875 spectrophotometer interfaced to a Shimadzu Chromatopac R 3A at various temperatures.

Fresh solutions of iodine and azacrowns were prepared before each series of measurements by dissolving precisely weighed amounts of the components in an appropriate volume of solvent. All solutions were kept in the dark except during sampling.

Results and discussion

The electronic absorption spectra of chloroform solutions of HA18C6 and TA14C4 in the presence of an excess amount of iodine (i.e. $[\text{azacrown}]/[I_2] = 10$) were obtained as a function of time at 25 °C and are shown in Figures 1 and 2.

As it is seen from Figures 1 and 2, while none of the reactants show any considerable absorption in the 250–450 nm range, the spectrum obtained immediately after mixing iodine with the azacrown ethers resulted in two strong absorptions in the 250–450 nm region. The first absorption, located at about 260 nm, corresponds to a charge-transfer band and the second at about 370 nm is the blue-shifted iodine band [25]. Obviously, the spectra recorded for the complexes between azacrowns and iodine are time dependent. As seen, in both cases, the intensity of the charge-transfer band decreased markedly with the elapse of time, while an intensification of new bands at 293 and 364 nm was observed. It should be noted that the bands at 293 and 364 nm are characteristic for the formation of triiodide ion, I_3^- , in the process of complex formation between iodine and different electron pair donor ligands [10, 14, 15, 17, 19, 26–30].

The observed time dependence of the charge-transfer band and the subsequent formation of the I_3^- ion in solution are most probably due to a transformation of the initially

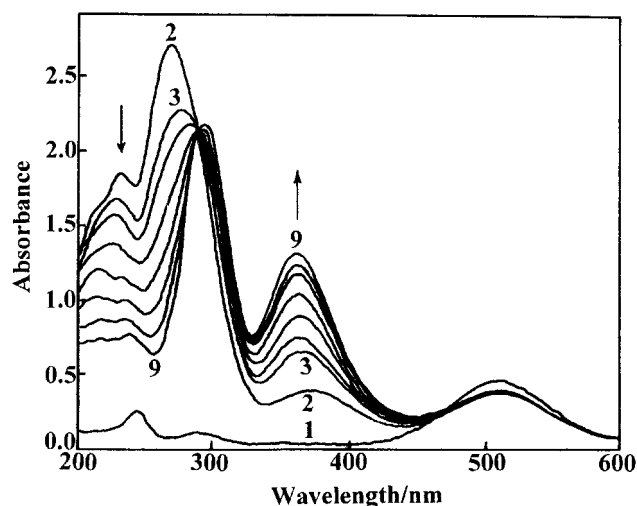


Figure 1. UV-Vis spectra of a mixture of I_2 (5.0×10^{-3} M) and TA14C4 (5.0×10^{-2} M) in chloroform at 25 °C: (1) I_2 alone, (2) immediately after mixing, and at time intervals (3) 10 min, (4) 20 min, (5) 40 min, (6) 60 min, (7) 80 min, (9) 120 min.

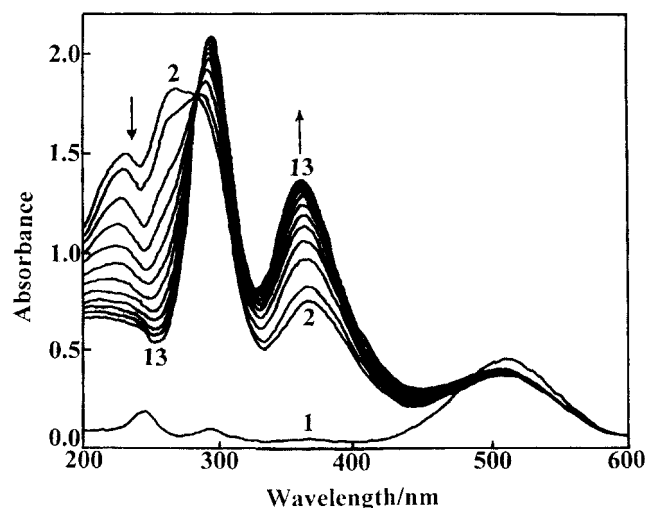
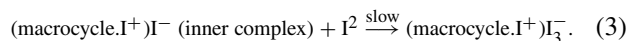
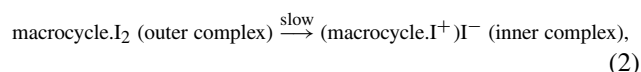
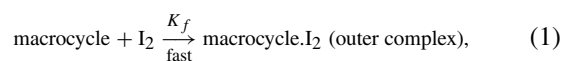


Figure 2. UV-Vis spectra of a mixture of I_2 (5.0×10^{-3} M) and HA18C6 (5.0×10^{-3} M) in chloroform at 25 °C: (1) I_2 alone, (2) immediately after mixing, and at time intervals (3) 2 min, (4) 10 min, (5) 18 min, (6) 26 min, (7) 34 min, (8) 42 min, (9) 50 min (10) 58 min, (11) 66 min, (12) 74 min, (13) 82 min.

formed outer complex into an inner EDA complex followed by a fast reaction of the resulting inner complex with iodine to form a triiodide ion, as follows [31, 32]:



In order to obtain further information about the kinetics and mechanism of the interaction of iodine with HA18C6 and TA14C4, the kinetics of transformation of the outer

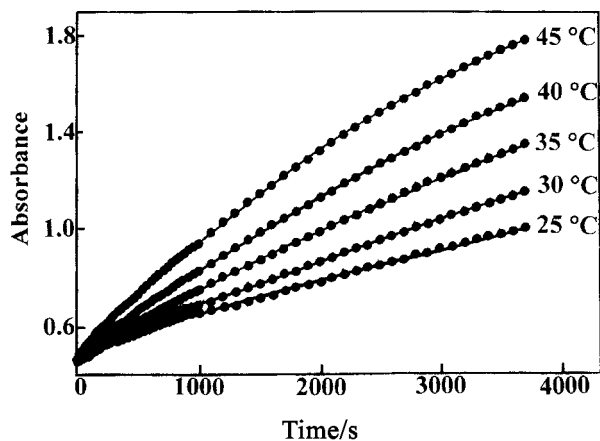


Figure 3. Absorbance-time plots for a mixture of I_2 (3.0×10^{-4} M) and TA14C4 (2.4×10^{-2} M) in chloroform at different temperatures.

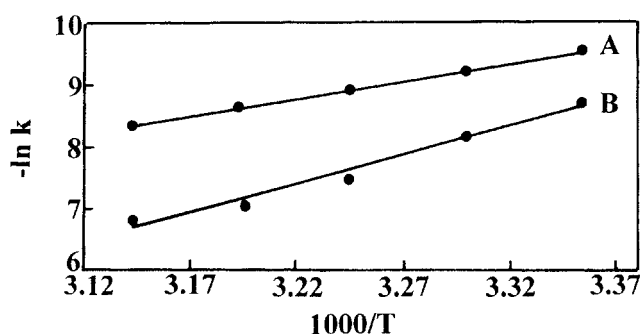


Figure 4. Arrhenius plots for the two azacrown- I_2 systems in chloroform solution: (A) TA14C4, (B) HA18C6.

complexes were followed by the time dependence of I_3^- absorption band at 364 nm. The absorbance of solutions containing reactants at an azacrown-to- I_2 mole ratio of 80:1 in chloroform was monitored as a function of time at 364 nm at various temperatures. Sample absorbance-time plots for TA14C4- I_2 system in chloroform at different temperatures are shown in Figure 3.

The transformation of the outer complexes into the corresponding inner complexes was found to follow a pseudo-first-order kinetic behavior. All of the resulting rate constants at various temperatures are summarized in Table 1. Using the corresponding Arrhenius plots (Figure 4) and the Eyring transition-state theory [33] the activation parameters (E_a , ΔH^\ddagger and ΔS^\ddagger) were calculated and the results are also included in Table 1. The data given in Table 1 indicate that the pseudo-first-order rate constants increase with temperature. It is also obvious that, at each temperature, the rate of transformation of the outer complex to inner complex is in the order HA18C6 > TA14C4. The much faster transformation of HA18C6- I_2 in comparison with the TA14C4- I_2 complex could be related to the increased stability of the latter complex over the former one, as will be discussed later.

The data given in Table 1 indicate that the entropies of activation for the transformation of the outer complexes into the corresponding inner complexes are high and negative. The negative ΔS^\ddagger values are indeed what one should expect in reactions involving the ionization of neutral molecules

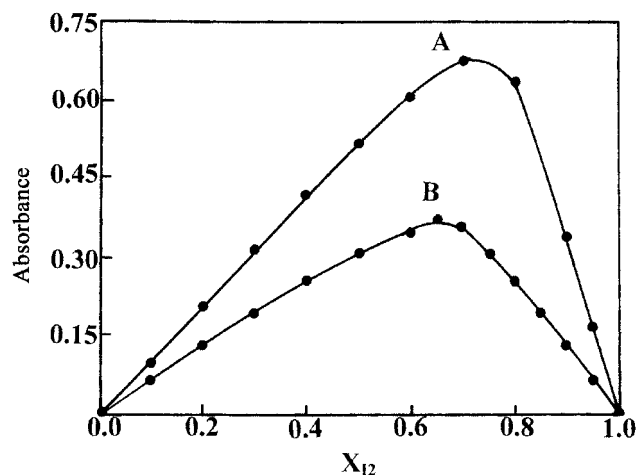


Figure 5. Continuous variations plots for HA18C6- I_2 (A) and TA14C4- I_2 (B) systems in chloroform at 25 °C. Conditions: Varying volumes of equimolar solutions of azacrowns and I_2 (7.5×10^{-3} M) were mixed in a total volume of 2.5 ml; $\lambda = 364$ nm.

[34]. Since the transformation of the outer complex into an inner complex involves ionization, the activated complex may be an ion pair, stabilized by solvation to a greater extent than the initial outer complex. Consequently, the more ordered form of the solvent molecules in the transition state results in a negative ΔS^\ddagger value. On the other hand, the observed positive enthalpy of activation in going from the molecular outer complex to the ionized inner complex reflects a weaker structure, a poorer overlap, and a sloppy geometry for the transition state when it is compared with the initial macrocycle- I_2 complex. Moreover, based on the proposed mechanism, the magnitude of E_a directly determines the facility with which the transformation of outer to inner complex occurs.

It is worth mentioning that the energy of the blue-shifted band of iodine provides a good measure of donor-acceptor interaction, as pointed out by Mulliken [25]. Since the blue shift of the I_2 band arises from an increased separation of the σ and σ^* orbitals occurring when charge is transferred from the donor to the σ^* orbital of I_2 , it is reasonable to conclude that the extent of the blue shift would be dependent on the amount of charge transferred to the iodine molecule. The blue shift observed for the I_2 molecule in the presence of cyclic amines HA18C6 and TA14C4 (from 510 to 370) is much larger than that reported for the ordinary amine- I_2 systems [32]. Therefore, due to the transfer of more charge from the cyclic amines to the iodine molecule, the much more stable charge-transfer complexes between I_2 and cyclic amines are formed in comparison with the ordinary amine- I_2 complexes.

The stoichiometry of the resulting charge-transfer complexes between HA18C6 and TA14C4 and iodine were examined by the method of continuous variations [35]. Plots of absorbance vs. mole fraction of I_2 are shown in Figure 5. The continuous variations plots for the two donors studied exhibited a maximum at value of ~ 0.65 , indicating the formation of 1:2 (macrocycle to iodine) charge transfer complexes in solution.

Table 1. Calculated rate constants at various temperatures and activation parameters for HA18C6-I₂ and TA14C4-I₂ systems in chloroform solution

Ligand	Temperature (°C)	k (s ⁻¹)	E_a (kJ mol ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (J K ⁻¹ mol ⁻¹)
TA14C4 ^a	25	$(7.12 \pm 0.04) \times 10^{-5}$	47 ± 5	45 ± 3	-173 ± 17
	30	$(9.73 \pm 0.03) \times 10^{-5}$			
	35	$(1.34 \pm 0.01) \times 10^{-4}$			
	40	$(1.76 \pm 0.01) \times 10^{-4}$			
	45	$(2.39 \pm 0.01) \times 10^{-4}$			
HA18C6 ^b	25	$(1.60 \pm 0.04) \times 10^{-4}$	77 ± 12	74 ± 12	-68 ± 39
	30	$(2.83 \pm 0.04) \times 10^{-4}$			
	35	$(6.36 \pm 0.09) \times 10^{-4}$			
	45	$(1.1 \pm 0.02) \times 10^{-3}$			

^aInitial concentration of iodine was 1.5×10^{-3} M.

^bInitial concentration of iodine was 9.0×10^{-4} M.

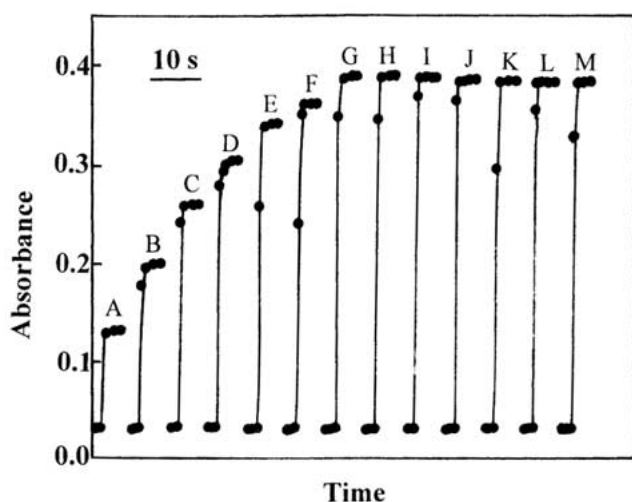


Figure 6. Absorbance vs. time plots for a 1.0×10^{-4} M solution of I₂ in chloroform in the presence of different [TA14C4]/I₂ mole ratios at 25 °C: (A) 0.1, (B) 0.2, (C) 0.3, (D) 0.4, (E) 0.5, (F) 0.6, (G) 0.75, (H) 1.0, (I) 1.2, (J) 1.4, (K) 1.6, (L) 1.8, (M) 2.0.

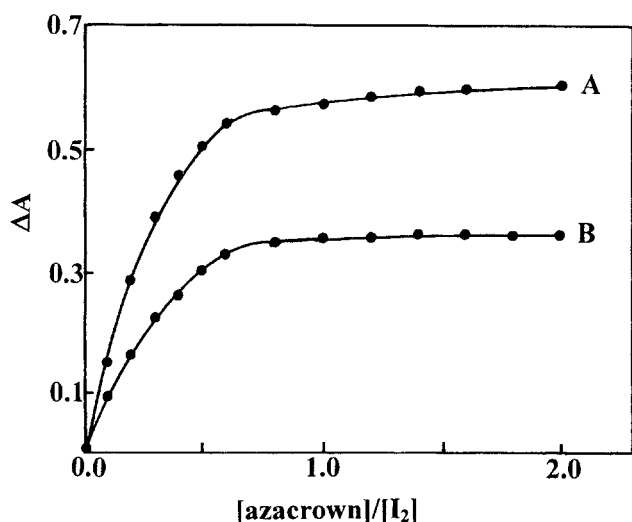


Figure 7. Δ Absorbance vs. [azacrown]/[I₂] plots for HA18C6-I₂ (A) and TA14C6-I₂ (B) systems in chloroform at 25 °C.

For the two azacrowns studied, during the first few seconds after the addition of azacrown to the iodine solution, a rather sharp-functional increase in the absorbance at 364 nm was observed, as was previously reported (Figure 6) [36]. This initial change in the absorbance (ΔA) upon the mixing of the azacrown and I₂ was found to increase along with a rise in the azacrown/I₂ mole ratio to reach a constant value at a mole ratio of (1:2) (see Figure 7). Such a dependence of ΔA on the azacrown/I₂ mole ratio indicates the formation of EDA complexes between the donors and the acceptor used. The corresponding formation constants can be evaluated from ΔA vs. azacrown/I₂ mole ratio as follows.



$$K_f = \frac{[DA_2]}{[D][A]^2}, \quad (5)$$

where D = azacrown and A = I₂,

$$C_D = [D] + [DA_2], \quad (6)$$

$$C_A = [A] + 2[DA_2]. \quad (7)$$

The substitution of Equations (6) and (7) into (5) and rearrangement yields,

$$K_f[A]^3 + K_f(2C_D - C_A)[A]^2 + [A] - C_A = 0. \quad (8)$$

The observed absorbance change of solution is given by

$$\Delta A = \epsilon_{DA_2}[DA_2]. \quad (9)$$

To evaluate the formation constant from the ΔA vs. C_D/C_A mole ratio data, a curve-fitting program KINFIT was used [37]. The free acceptor concentrations [A] were evaluated from Equation (8) by means of a Newton-Raphson procedure. Once the value of [A] (i.e., [I₂]) had been obtained, the concentrations of all other species involved were calculated from the corresponding mass-balance equations by using the estimated value of K_f at the current iteration step of the program. Refinement of the parameters is continued until

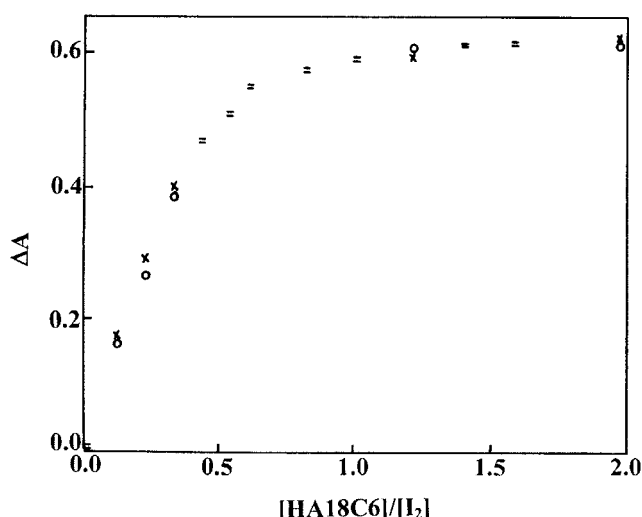


Figure 8. Computer fit of Δ Absorbance vs. [azacrown]/ $[I_2]$ mole ratio for HA18C6- I_2 system in chloroform solution at 25 °C: (x) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plots.

Table 2. Calculated formation constants and molar absorption coefficients for iodine complexes of TA14C4 and HA18C6 in chloroform solution

Ligand	$\log K_f$	ϵ_{DA_2}
TA14C4	9.8 ± 0.1	5004 ± 91
HA18C6	9.3 ± 0.1	8800 ± 262

the sum-of-squares of the residuals between the calculated and observed values of the absorbance change for all experimental points is minimized. The output of the KINFIT program comprises the refined parameters K_f and ϵ_{DA_2} , the sum-of-squares and standard deviation of the data.

A sample computer fit of the ΔA vs. macrocycle/ I_2 data is shown in Figure 8. As can be seen, the fair agreement supports the existence of 1:2 (macrocycle-to-iodine) complexation between the macrocycles and iodine in solution. The $\log K_f$ and ϵ_{DA_2} values obtained by this procedure for the two macrocycle-iodine systems are given in Table 2. The K_f value for the TA14C4- I_2 is larger than that for the HA18C6- I_2 system. The relatively higher stability of the iodine complex of TA14C4 as compared with HA18C6 may be attributed to the more rigid structure of the former ligand which may possibly make the electrons of its donating nitrogens more available for the transfer of charge into the LUMO's of I_2 molecule [38, 39]. Moreover, while the I^+ ion having an ionic size of 1.66 Å [40] is too small for the cavity of HA18C6, it possesses a more suitable fitting condition inside the smaller cavity of TA14C4 [41].

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