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Kinetic Study of the Interaction Between Some Thiacrown Ethers and Iodine Monobromide

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A spectrophotometric study concerning the interaction between trithia-9-crown-3(TT9C3), tetrathia-12-crown-4 (TT12C4) and hexathia-18-crown-6 (HT18C6) as n-donors with iodine monobromide as σ-acceptor has been followed spectrophotometrically in dichloromethane and trichloromethane solution at 25 ºC. The results are indicative of the formation charge transfer complex in first step followed by the conversion of charge transfer to ionic complex. The rate constants of conversions are obtained from the plot of ln (A_t/A_0) *vs.* t and vary in the order: TT9C3 > TT12C4 > HT18C6. Moreover, the results show the faster reactions in dichloromethane than that of trichloromethane. The possible reasons for such observations are discussed. The conductivity measurements indicate that the free ions are not formed.

Key Words: Spectrophotometry, Iodine monobromide, Thiacrown ethers.

INTRODUCTION

After Pedersen's discovery of macrocyclic crown ethers[1] several hundred of papers have been published on their ionic[2] and molecular complexes[3]. On the other hand, despite the molecular complexes of nitrogen and oxygen containg crown ethers have been studied extensively. The sulphur containing have been less investigated[3]. In continuation to our investigation on molecular complexes of crown ethers[4-6], here we report the results of spectrophotometric study of complexation of some thiacrown ethers and IBr in di- and tri- chloromethane solutions.

EXPERIMENTAL

Reagent grade TT9C3, TT12C4 and HT18C6 from Aldrich company were used as received. Reagent grade iodine monobromide (Ridel) and solvents (Merck) were of the highest purity available and used without any further purification.

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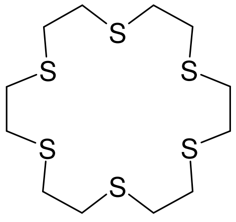
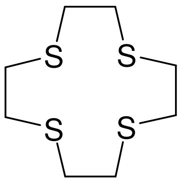
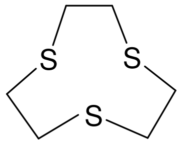


HT18C6



TT12C4



TT9C3

The UV-Vis spectra and the absorbance measurements were made with a UV-Vis Cary spectrophotometer model 150 at 25 ± 0.1 °C. In order to obtain UV-Vis spectra of donors in the presence of acceptor, 3 mL of 10^{-3} M of donor solution was transfered to quartz cell and titrated with a concentrated solution of IBr. For obtaining kinetic spectra and the corresponding data, 3 mL solutions containing 0.05 M of IBr and 10^{-3} M of donor were transfered to quartz cell and the spectra and data were recorded and measured in 5 min intervals.

The conductometric measurements were carried out with a Metrohm 660 conductivity meter in a thermostated cell at 25 ± 1 °C.

RESULTS AND DISCUSSION

Absorption spectra of 10^{-3} M solution of TT9C3 in CH_2Cl_2 in the presence of increasing amounts of IBr are shown in Fig. 1. As seen, upon addition of IBr two new bands are appeared at 300 and 510 nm, respectively. The 300 nm band is due to the formation of charge transfer complex between TT9C3 as n-donor and IBr as σ- acceptor[7]. The appearance of free IBr band at 510 nm indicates that the reaction between IBr and TT9C3 is not complete. Infact, if the reaction would be complete. The free iodine band would not be observed[8].

Similar spectra were observed for the TT12C4-IBr and HT18C6-IBr mixtures in CH_2Cl_2 and $CHCl_3$ solutions. Sample recorded spectra are shown in Figs. 2-4. Such observations indicate that all of the thiacrown ethers do have a charge transfer interaction with IBr.

Interestingly, by passing time the intensity of charge transfer bands were reduced gradually (sample spectra in Fig. 5). This phenomena was not along with the simultaneous intensity increasment of IBr band. So, it can not be assigned to decomposition of complex to initial adducts. Instead it can be attributed to the conversion of colorant charge transfer complex to colourless ionic complex. This is confirmed by the observation of linear relation between ln (A_t/A_0) and time (Figs. 6 and 7)[9]. The linearity can be assigned to the conversion of D:IBr complex to $DI^+{\cdot}Br^-$ or $DBr^+{\cdot}I^-$ complex (D is TT9C3, TT12C4, HT18C6).

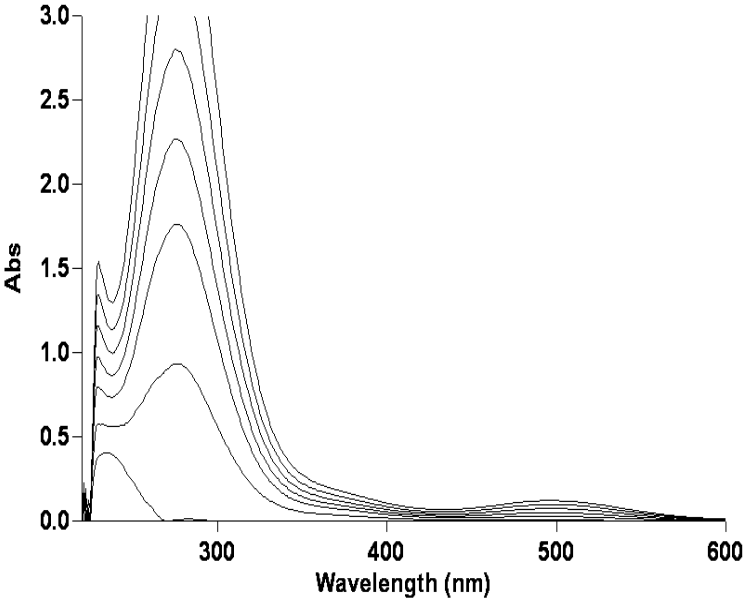


Fig. 1. Absorption spectra of 10^{-3} M solution of TT9C3 in CH_2Cl_2 in the presence of varying quantities of IBr. IBr/TT9C3 mole ratios from bottom to top are: 0.00, 0.18, 0.36, 0.54, 0.72, 0.9 and 1.08

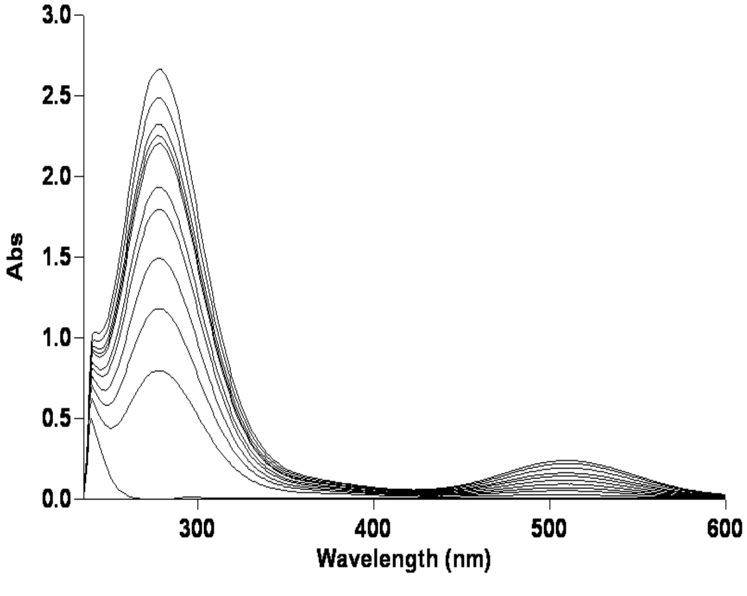


Fig. 2. Absorption spectra of 10^{-3} M solution of HT18C6 in $CHCl_3$ in the presence of varying quantities of IBr. IBr/HT18C6 mole ratios from bottom to top are: 0.00, 0.18, 0.36, 0.54, 0.72, 0.9, 1.08, 1.26, 1.44, 1.62 and 1.80

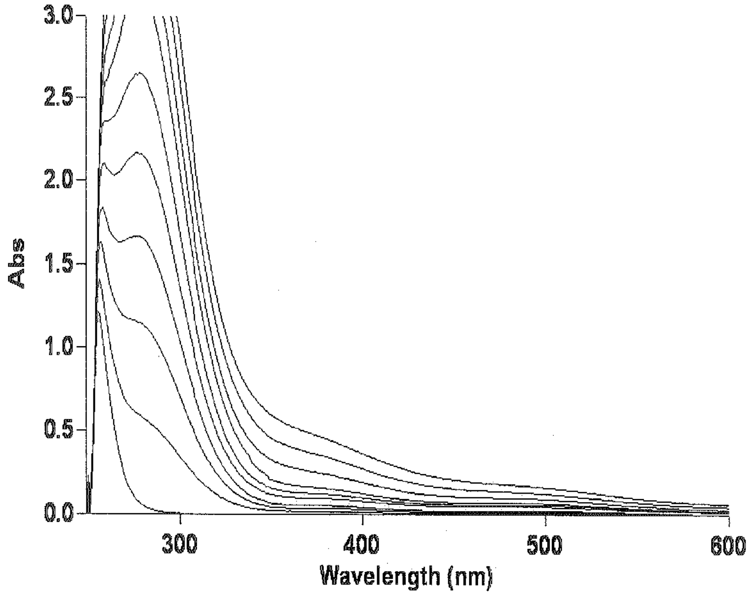


Fig. 3. Absorption spectra of 10^{-3} M solution of HT18C6 in CH_2Cl_2 in the presence of varying quantities of IBr. IBr/HT18C6 mole ratios from bottom to top are: 0.00, 0.18, 0.36, 0.54, 0.72, 0.9, 1.08, 1.26, 1.44 and 1.62

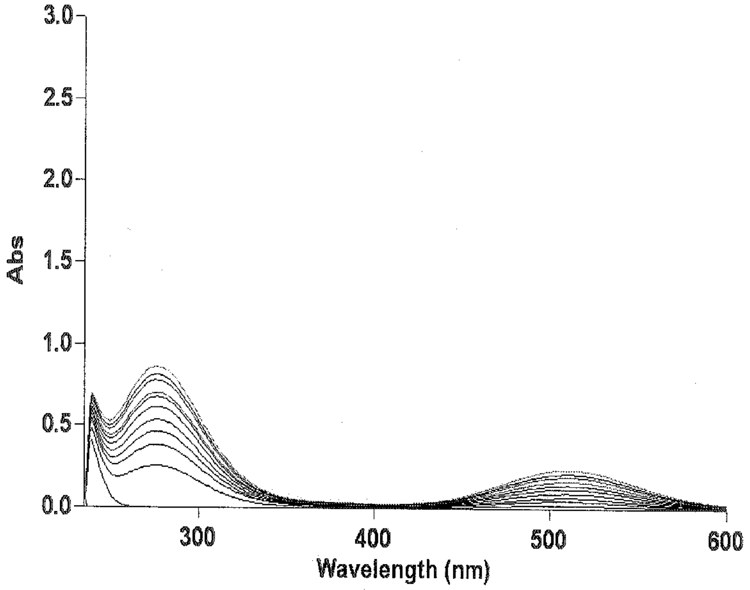


Fig. 4. Absorption spectra of 10^{-3} M solution of TT12C4 in $CHCl_3$ in the presence of varying quantities of IBr. IBr/TT12C4 mole ratios from bottom to top are: 0.00, 0.18, 0.36, 0.54, 0.72, 0.9,1.08,1.26,1.44, 1.62 and 1.80

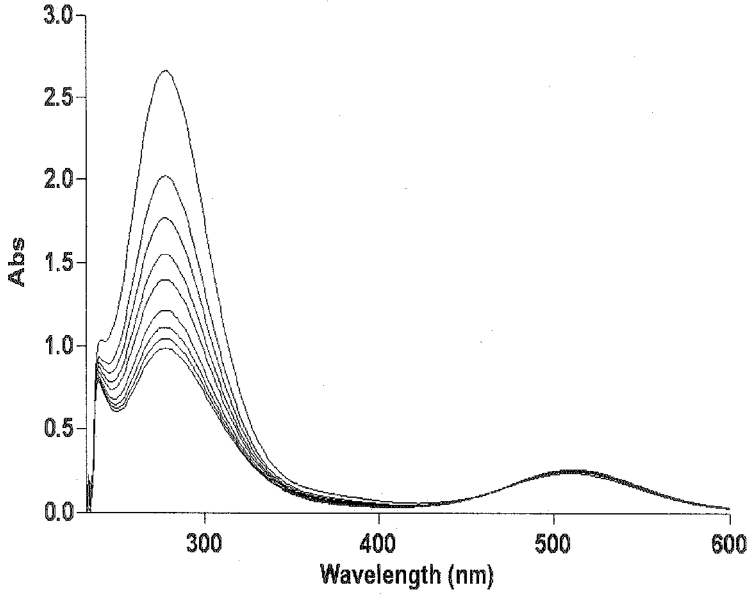


Fig. 5. Absorption spectra of equimolar mixtures of HT18C6 and IBr (10^{-3} M) in $CHCl_3$ in time intervals of 5 min

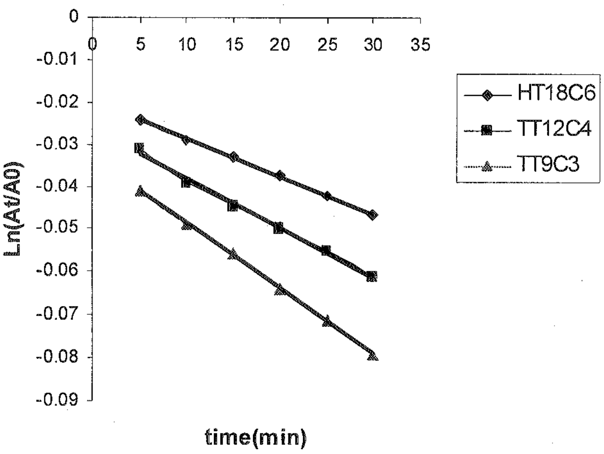


Fig. 6. plot of ln A/A_0 *vs.* t in CH_2Cl_2 solution

The final obtained rate constants are collected in Table-1.The data show that in all cases the CH_2Cl_2 values are more than $CHCl_3$ ones. This is reasonable based on the effect of polarity of solvents on ion pair formation. The polarity of CH_2Cl_2 is more than $CHCl_2$[10]. So, in the former, the ionic products are produced more easily than the later one. In both solvents the k values vary in the order: TT9C3 < TT12C4 < HT18C6.

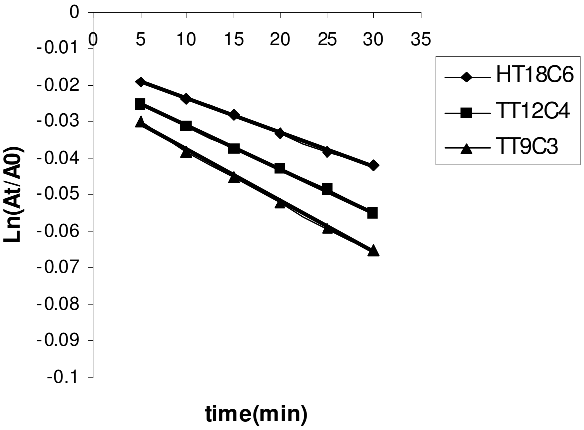


Fig. 7. plot of ln A/A_0 *vs.* t in $CHCl_3$ solution

TABLE-1
THE RATE CONSTANTS OF CONVERSION OF CHARGE TRANSFER TO IONIC COMPLEX IN DI AND TRI CHLOROMETHANE SOLUTION*

Donor	k (min^{-1})	k´ (min^{-1})
TT9C3	0.032 ± 0.001	0.028 ± 0.001
TT12C4	0.025 ± 0.001	0.021 ± 0.001
HT18C6	0.018 ± 0.001	0.011 ± 0.001

*The k and k´ values are the data due to CH_2Cl_2 and $CHCl_3$, respectively.

It is well known that the consistency of the hole radius of metal ions play an important role in the stability of the resulting complexes[11]. On the other hand, the fittness of the Br^+ ionic radious and TT9C3 hole size is more than the other two thiacrown ether[12]. Also, there is not a good fittness between I^+ ionic radius and TT9C3 hole size[12]. So, it can be concluded that in the process of conversion of charge transfer to ionic adduct, the Br^+ ion introduces to the cavity of thiacrown ether. Infact, if the I^+ located in the cavity of macrocycles. It would be anticipated that the most conversion rate to be due to TT12C4 complex.

The usual polarity of IBr is I^+Br^-. However, the experimental evidences show that the polarity of IBr in the complexed form is I^-Br^+. *i.e.*, the complexation reverses the direction of dipole moment of free IBr.

It seems that such a paradox can be attributed to the higher charge density of Br^+ than that of I^+ which will results more electrostatic attraction between Br^+ than that of I^+ and donors. This acts as a strong driving force against the normal polarity and causes the formation of DBr^+I^+ instead of DI^+Br^-.

The conductivity of the pure solvents and the solutions containing donors, acceptors and the equimolar mixtures of donors and acceptors were measured. There was no meaningful difference between the determined values. So, it can be concluded that in none of complexes the free ion is not formed[13].

Conclusion

The interaction of IBr and thiacrown ethers begins with the formation of charge transfer complex and continues with formation of ionic complex. The direction of polarity of IBr in the free and complexed form are in opposite. The higher polarity of CH_2Cl_2 than that of $CHCl_3$ causes that the rate of ion pair formation in the former to be higher than the latter. The fittness of cavity size of macrocycle and ionic radious of Br^+ play an important role in the rate of charge transfer to ionic complex. The final adducts are in the form of ion pair and the free ion is not formed.

REFERENCES

1. C.J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).
2. R.M. Izatt, S.J. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen and D. Sen, *Chem. Rev.*, **85**, 271 (1985).
3. R.M. Izatt, S.J. Bradshaw, K. Pawlak, R.L. Bruening and B.S. Tarbet, *Chem. Rev.*, **92**, 1261 (1992).
4. A. Semnani, A.R. Firooz, H.R. Pouretedal and B. Nazari, *Iran. J. Chem. & Chem. Eng.*, **23**, 57 (2004).
5. A. Semnani, H.R. Pouretedal, B. Nazari and A.R. Firooz, *Scientia Iran.*, **10**, 317 (2003).
6. H.R. Pouretedal, A. Semnani, B. Nazari and A.R. Firooz, *Asian J. Chem.,* **17**, 329 (2005).
7. R.S. Mulliken and W.B. Person, Molecular Complexes, Wiley Inter Science (1969).
8. M.T. Beck and I. Nagypal, Chemistry of Complex Equilibria, John Wiley & Sons (1990).
9. D.A. Skoog, D.M. West and F.J. Holler, Fundamentals of Analytical Chemistry, Saunder College Publishing (1988).
10. CRC Hand Book.
11. C.J. Pedersen and H.K. Frensdorff, *Angew Chem., Int. Ed.*, **11**, 16 (1972).
12. M. Shamsipur, A. Semnani and H.R. Pouretedal, *Iran. J. Sci. Tech.*, **18**, 193 (1994).
13. G.D. Christian and J.E. O'Reilly, Instrumental Analysis, Allyn and Bacon, Inc. (1986).

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