

Spectroscopic studies of interaction between Iodine and Benzyloxy ether Derivatives of Calix[4]arene

S. Taghvaei-Ganjali*

Chemistry Department, North Tehran Branch, Islamic Azad University, Tehran, Iran.

M. Khosravi

Chemistry Department, North Tehran Branch , Islamic Azad University , Tehran, Iran.

K. Tahvildari

Chemistry Department, North Tehran Branch, Islamic Azad University, Tehran, Iran.

A. Naderi

Chemistry Department, North Tehran Branch, Islamic Azad University, Tehran, Iran.

Abstract:

Interaction of para-tert-Bu-Calix[4] arene (**1**), di (**2**) and tri(**3**) benzyloxy-para-tert-Bu-Calix[4]arene with iodine have been examined spectrophotometrically in chloroform solution. The observed time dependence of the charge transfer band in solution was investigated. The pseudo first order rate constants at various temperatures for transformation process were evaluated from the absorbance-time data. The activation parameters (E_a , ΔH^\ddagger and ΔS^\ddagger) were obtained from the corresponding Arrhenius plots and the Eyring Transition-State theory.

Keywords: Interaction of Iodine, Charge Transfer Complex, Calix[4]arene, Activation Parameters

* Corresponding author

Introduction:

Calix[4]arenes are emerging as a new class of synthet... interest in several areas of bioorganic and biomimetic chemistry. It is structurally well defined macrocyclic molecule that is readily available in large quantities and easily modified by chemical reactions¹. Calix[4]arenes have attracted considerable interest as building blocks for constructing selective host molecules².

The intense interest in the macrocyclic ligands centers on the extraordinary stability of their cation complexes and their peculiar ability to selectively bind certain cations in preference to other³⁻⁵. However, studies on neutral molecule-Calixarene interactions have been far fewer in number than those on cation-Calixarene complexes⁶. 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, biomimetic receptors and the conversion of chemical reactions into electronic or optical signals.

Iodine has been found to form with a variety of donor charge-transfer complexes whose properties have been thoroughly studied⁷⁻¹⁰. Some papers have been published in respect to the molecular complexes of iodine with various macrocyclics in solvents.¹¹⁻²¹

In this paper we report the results of kinetic and spectral studies of interactions of benzyloxy ether derivatives of Calix[4]arene in solution and the capability of such interaction compare with *p*-tert-buthyl calix[4]arene²²

Results and Discussion:

The calix[4]arene **1-3** (shown in Fig 1.) were synthesised in our synthetic group^{23,24}. The electronic absorption spectra of mixture calixarenes with an excess amount of iodine (I_2 /Calixarene molar ration of 10) were recorded as a function of time at various temperatures. Sample spectra for the I_2 -Calixarene **2** system in chloroform at 25° C is shown in Fig.2. In all cases, the spectrum obtained immediately after mixing iodine with the calixarene derivations resulted in the 220-320 nm region (241 and 279). In order to obtain further information about the kinetics of the interaction of iodine with calixarene derivatives, the absorbance at 279 nm was monitored as a function of time in solutions of chloroform. Sample absorbance- time plots for the I_2 /Calixarene **3** system in chloroform at different temperatures is shown in Fig.3.

All of the resulting rate constants at various temperatures are summarized in Table 1. Using the corresponding Arrhenius plot (Fig.4.) and Eyring transition state theory²⁵, the activation parameters (E_a , ΔH^\ddagger and ΔS^\ddagger) were Calculated. The results are also included in Table 1.

The data given in Table.1 indicate that, the pseudo-first-order rate constants increase with increasing temperature. The influence of temperature on the I_2 /Calixarene **1** system being more pronounced than that of other complexes and this behavior decreases for **2** and **3** in substitution of phenolic proton with benzyloxy groups in calixarene cavities. The activation energy for complex formation is increased

with increasing of benzyloxy substituents at the lower rim. This correlation shows that the Iodie cation is entered from lower rim and recognized at middle rim. The data given in Table 1. shows also that the observed trend in complexation of **1** could be due to its more convenient conformational arrangement for the process of charge transfer system.

Table 1. shows that the entropies of activation for complexation are high and negative. The negative ΔS^\ddagger values are indeed what we should expect in reactions involving the ionization of neutral molecules. Since the complexation involves ionization, the activated complex maybe an ion pair stabilized by solvation to a greater extent than the initial reactants.

Experimental:

The calix[4]arene 1-3 (shown in Fig 1.) were synthesised in our synthetic group^{23,24}. Resublimed iodine of analytical grade (Merck) was used as received. Reagent-grade chloroform (Merck) was used without any further purification.

All UV-VIS spectra were recorded on a Camspec M350 Double Beam spectrophotometer and absorbance measurements were made with a spectrophotometer equipped with a temperature controlled cell holder.

The temperature was kept constant at the desired temperature of $\pm 0.1^\circ\text{C}$ using a MLW-UH thermostat.

Acknowledgement:

We are grateful to the Research Council of Islamic Azad University. Generous kind from Prof Morteza Khosravi is highly acknowledged.

Table 1. Calculated Rate Constant at Various Temperatures and Activation Parameters for Calix[4]aren/s(1-3/I₂) complexes.

Macrocycle	Temp °C	k_1 s ⁻¹	E_a kJ mol ⁻¹	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger J mol ⁻¹ K ⁻¹	ΔG^\ddagger kJ mol ⁻¹
1	25	2.80×10^{-5}	16	14	-282	100.8 \pm 2.1
	30	3.14×10^{-5}				
	35	3.62×10^{-5}				
	40	3.81×10^{-5}				
	45	4.06×10^{-5}				
2	25	1.07×10^{-5}	21.27	18.8	-277	104.0 \pm 2.1
	30	1.21×10^{-5}				
	35	1.49×10^{-5}				
	40	1.54×10^{-5}				
	45	1.70×10^{-5}				
3	25	1.40×10^{-5}	27.68	25.2	-253.5	103.1 \pm 2.1
	30	1.67×10^{-5}				
	35	1.80×10^{-5}				
	40	2.20×10^{-5}				
	45	2.60×10^{-5}				

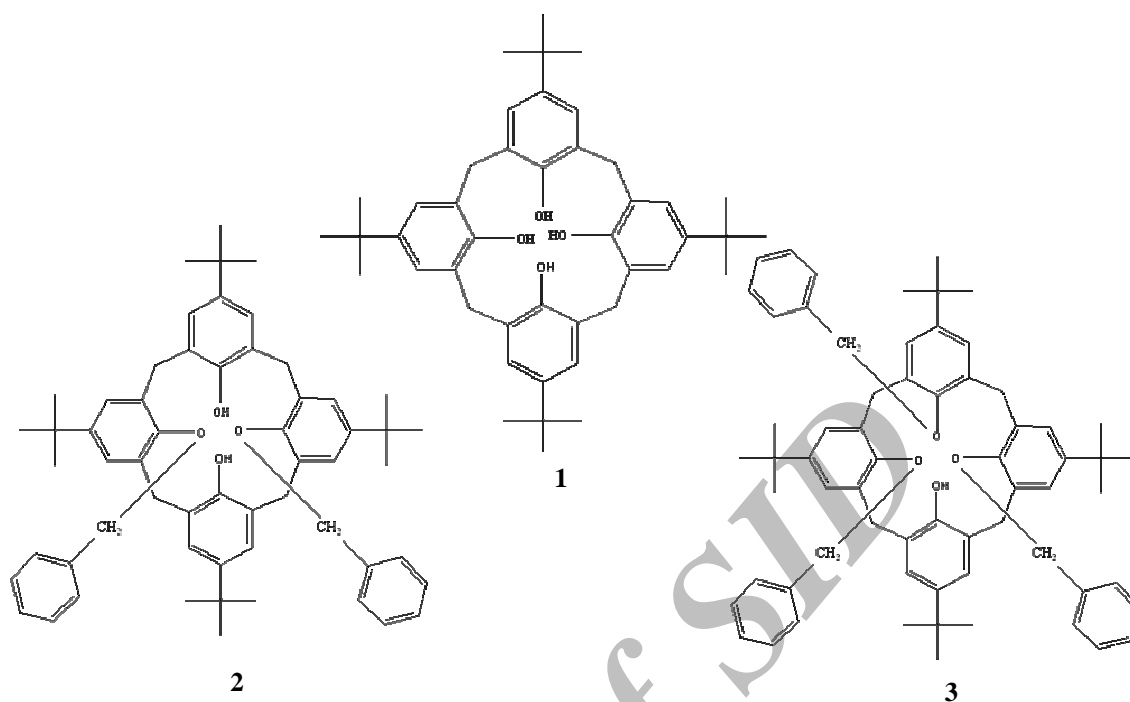


Fig 1. Structure of Calix[4]arene derivatives.

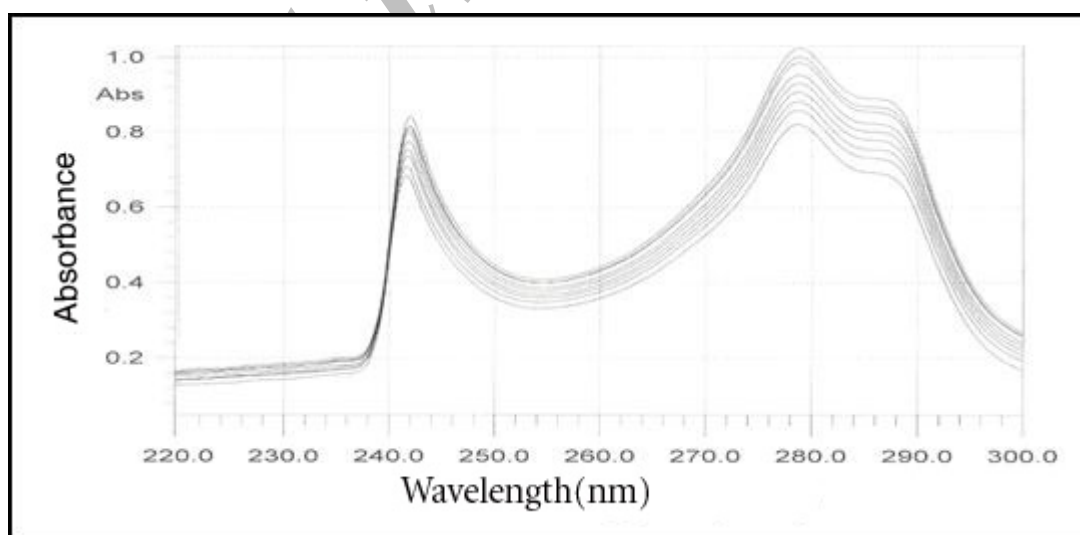


Fig.2. UV-VIS spectra of a mixture of I_2 ($1 \times 10^{-3} \text{ mol dm}^{-3}$) and Calix[4]arene 2 immediately after mixing; time intervals: 15min; 30min; 45min; 60min; 75min; 90min; 105min; 120min.

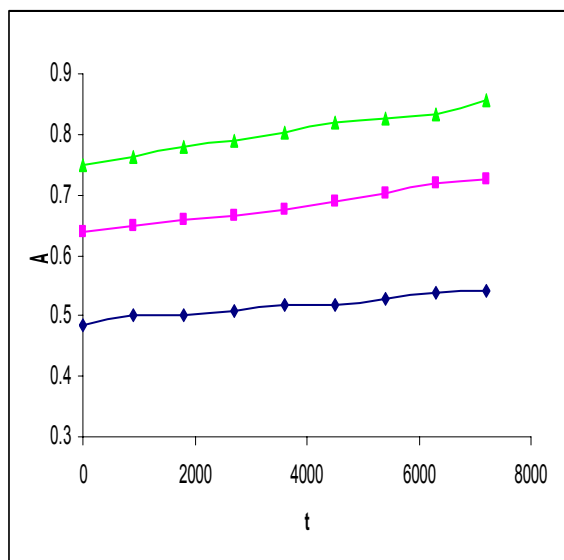


Fig.3. Absorbance-time plots at 282 nm for mix of I_2 ($1 \times 10^{-3} \text{ mol dm}^{-3}$) and Calix[4]arene 3 ($1 \times 10^{-4} \text{ mol dm}^{-3}$) in chloroform at different temperatures: \blacklozenge , 25° C; \blacksquare , 35° C; \blacktriangle , 45° C.

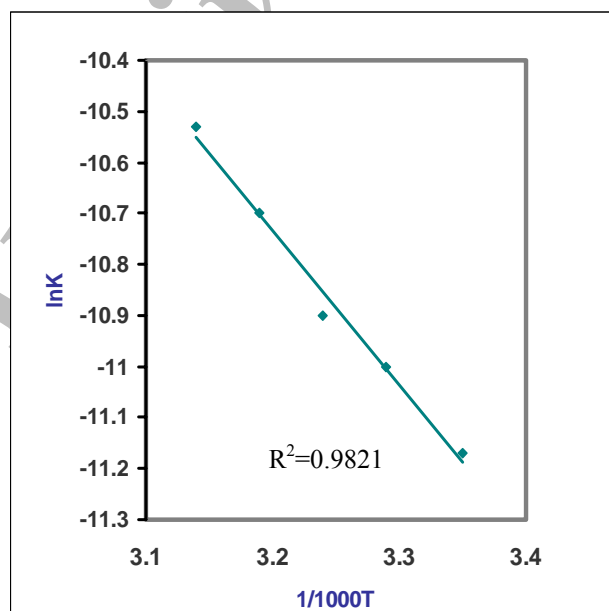


Fig.4. Arrhenius plots of $\ln k$ vs. $1/T$ for Calix [4] arene 3/ I_2 Complex.

References:

- 1- Gustsche, C. D. calixarenes. In stoddart, J. F. (ed.), Monographs in supramolecular chemistry. The Royal Society of chemistry, Cambridge, **1**, 87 (1989)
- 2- Gustsche, C. D.; Levine, *J. Am. Chem. Soc.* **104** , 2652 (1982).
- 3- Izatt, R. M., Bradshaw, J. S., Nielsen, S. A., Lamb, J. D., Christenson, J. J. and Sen, D.; *Chem. Rev.* **85**, 271 (1985).
- 4- Izatt, R. M., Pawlak, K., Bradshaw, J. S., and Bruening, R. L., *Chem. Rev.*, **91**, 1721 (1991).
- 5- Izatt, R. M., Pawlak, K., Bradshaw, J. S., and Bruening, R. L., *Chem. Rev.*, **95**, 2529 (1995).
- 6- Izatt, R. M., Pawlak, K., Bradshaw, Bruening, R. L., and Tarbet, B. J. *Chem. Rev.*, **92**, 1261 (1992).
- 7- Andrews, L. J. and Keefer, R. M.; *Holden-Day, New York* (1964).
- 8- Tamres, M. and Yarwood, J.; *Plenum, New York* (1974).
- 9- Trotter, P. T., and White, P. A., *Appl. Spectrosc.*, **32**, 232(1978).
- 10- Kulevsky, N., and Bultamina, K. N.; *Spectrochim. Acta, Part A*, **46A**, 79 (1991).
- 11- Hopkins, H. P., Jahagirdar, D. V., and Windler, V. E. J.; *J. Phys. Chem*, **82**, 1254(1978).
- 12- Muchova, J., and Holba, V.; *Czech. Chem. Commun.*, **48**, 1158 (1983).
- 13- Andrews, L. J., and Keefer, M. R.; *J. Org. chem.*, **52**, 2690 (1987).
- 14- Nour, E. M., and Shahada, L. A.; *Spectrochim. Acta, Part A*, **44A**, 1277(1988) .
- 15- Nour, E. M., *Spectrochim. Acta, Part A*, **47A**, 473 (1991).
- 16- Hirsch, W., Greenman, J., and Pizer, R.; **Can. J. Chem.**, **71**, 2171(1993).
- 17- Semnani, M., and Shamsipur, M.; *J. Inclusion Phenom.*, **22**, 99 (1995).
- 18- Semnani, M., and Shamsipur, M.; *J. Chem. Soc., Dalton Trans.*, 2215 (1996).
- 19- Semnani, M., and Shamsipur, M.; *Polish J. Chem.*, **71**, 134 (1997).
- 20- Sadeghi, S., and Shamsipur, M.; *Polish J. Chem.*, **71**, 1594 (1997).
- 21- Zolgharnien, J., and Shamsipur, M.; *Polish J. Chem.*, **72**, 2486 (1998).
- 22- Taghvaei-Ganjali, S., Nouri, A., Rahimi, M., and Zare, K. M.; *J. Sci. I. A.U*, **14**, 52, 4384(2004).
- 23- Iwamoto, K., Araki, K., Shinkai, S., *Tetrahedron*; **47**, 4325 (1991).
- 24- Taghvaei, S., Farahzadi, H., *MSc Thesis, IAU, North Tehran Branch*; In Press.
- 25- Lin, S. H., Li, K. P., and Eyring, H.; in "Physical Chemistry, an Advanced Treatise," ed by Eyring, H., Handerson, D., and Yost, Academic Press, New York, **2**, 1(1977).