

MOLECULAR COMPLEXES OF IODINE WITH CYCLIC POLYETHERS IN CHLOROFORM: KINETICS OF FORMATION

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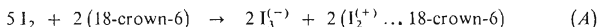
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Received February 26th, 1982

Absorbance changes of solutions of iodine and 15-crown-5, 18-crown-6 and dibenzo-18-crown-6 in chloroform were studied. Absorption maxima due to the triiodide anion were observed. The obtained rate constants and their temperature dependence indicate formation of molecular complexes (cyclic polyether ... I₂) and (cyclic polyether ... I₂⁺) I⁽⁻⁾.

Iodine forms with many compounds charge transfer complexes whose properties have been thoroughly studied¹. Less attention, however, has been paid to molecular complexes of iodine with cyclic polyethers. Although complexes of iodine with 12-crown-4, 15-crown-5 and 18-crown-6 in various solvents are described^{2,3}, the corresponding equilibrium constants and thermodynamic parameters are known only for cyclohexane solutions. According to absorption spectra it was concluded^{2,3} that solutions of mixtures of iodine and cyclic polyethers contain, in addition to the molecular complex, also triiodide anion which is formed³ according to Scheme (A).



The presence of the triiodide anion was proved also in formation of molecular complexes of iodine with other compounds⁴. Neither of the cited studies describes the kinetics of complex formation. Upon mixing together chloroform solutions of iodine and 18-crown-6 we observed significant absorbance changes with time in the whole spectral region studied (16 000–40 000 cm⁻¹). In our present work we investigate absorbance changes of solutions of iodine and 15-crown-5, 18-crown-6 and dibenzo-18-crown-6 in chloroform with the aim to obtain kinetic parameters of the reactions and contribute thus to the knowledge of interactions between the components.

EXPERIMENTAL

18-Crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) was prepared according to ref.⁵. 15-Crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) was synthesized from diethylene glycol and 1,8-dichloro-

-3,6-dioxaoctane as described in ref.⁶. Dibenzo-18-crown-6 (2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene) was prepared at the Institute of Polymers, Slovak Academy of Sciences, Bratislava, according to ref.⁷.

All the spectrophotometric measurements were performed in a 3 cm cell on a Specord UV-VIS (Carl Zeiss, Jena) instrument. The temperature accuracy was $\pm 0.1^\circ\text{C}$. The reaction components, the constant amount of iodine in chloroform (0.1 ml of a $4.5 \cdot 10^{-3} \text{ mol dm}^{-3}$ solution) and chloroform, containing the dissolved cyclic polyether, were pipetted directly into the cell, the final volume being 4.5 ml. Chloroform was dried over molecular sieves.

RESULTS AND DISCUSSION

The time dependences of absorption spectra of mixtures of iodine with 18-crown-6, 15-crown-5 or dibenzo-18-crown-6 in chloroform at constant temperature are depicted in Fig. 1. The absorption maxima at $33\,980 \text{ cm}^{-1}$ and $27\,360 \text{ cm}^{-1}$ belong to triiodide anion (*cf.*³), absorption maxima at $20\,000 \text{ cm}^{-1}$ are due to solution of iodine in chloroform. In the case of dibenzo-18-crown-6 the absorption maximum at $33\,980 \text{ cm}^{-1}$ is overlapped by a maximum of the cyclic polyether in chloroform. The absorption spectra of solutions containing 15-crown-5 or 18-crown-6 are practically identical.

We measured changes of absorbance of systems iodine – 15-crown-5, iodine – 18-crown-6, and iodine – dibenzo-18-crown-6 in chloroform at various temperatures and concentrations of the cyclic polyethers. The absorbance changes at $27\,360 \text{ cm}^{-1}$ were in accord with a first-order kinetics. The rate constants were calculated by the Guggenheim method using the relationship $-\ln \Delta A = k \cdot t + \text{const.}$, where ΔA is the difference between absorbances at the time t and t' ; the difference $t - t'$ was invariably greater than two half-lives of the reaction. The rate constants are given in Table I.

The plot of the rate constant logarithm against the reciprocal temperature was linear in all the studied cases, the temperature coefficients $d \ln k/d(1/T)$ being negative and amounting to $-38.1 \text{ kJ mol}^{-1}$, $-41.0 \text{ kJ mol}^{-1}$ and $-39.7 \text{ kJ mol}^{-1}$ for the respective reactions with 15-crown-5, 18-crown-6 and dibenzo-18-crown-6. Molar absorption coefficient for the triiodide anion in chloroform at $27\,360 \text{ cm}^{-1}$ was found to be $a = 2.4 \cdot 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and for iodine in chloroform at $19\,550 \text{ cm}^{-1}$ $a = 7.8 \cdot 10^2 \text{ cm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (*cf.*³); from the difference between absorbances at the mentioned wavenumbers it follows that in the presence of all the studied cyclic polyethers $0.53\text{--}0.55 \text{ mol}$ of $\text{I}_3^{(-)}$ was formed. The uncertainty in the estimation of moles of the formed $\text{I}_3^{(-)}$ is caused by the great difference between the molar absorption coefficients of $\text{I}_3^{(-)}$ and I_2 in chloroform (Fig. 1). The formation of the triiodide anion can be explained by formation of a molecular complex (cyclic polyether ... $\text{I}^{(+)}$) $\text{I}_3^{(-)}$. The existence of molecular complex of this type has been assumed² on the basis of conductivity measurements of iodine solution in dichloroethane.

The found negative temperature coefficient indicates a mechanism according to which iodine with the cyclic polyether in chloroform gives primarily a molecular complex which is further decomposed as described by Scheme (B).

TABLE I

Rate constants of reaction of iodine (10^{-4} mol dm $^{-3}$) with cyclic polyethers in chloroform

Polyether	10^2 c/mol dm $^{-3}$	T/K	10^3 k/s $^{-1}$
15-Crown-5	0.83	289.15	1.42
15-Crown-5	0.83	298.15	0.88
15-Crown-5	0.83	305.15	0.64
15-Crown-5	1.90	298.15	1.25
15-Crown-5	5.02	298.15	1.59
15-Crown-5	7.14	289.15	4.73
15-Crown-5	7.14	298.15	3.17
15-Crown-5	7.14	313.15	1.22
18-Crown-6	0.83	298.15	1.04
18-Crown-6	7.14	298.15	3.57
18-Crown-6	7.14	305.15	2.53
18-Crown-6	7.14	313.15	1.56
Dibenzo-18-crown-6	0.83	289.15	0.57
Dibenzo-18-crown-6	0.83	298.15	0.38
Dibenzo-18-crown-6	0.83	313.15	0.16

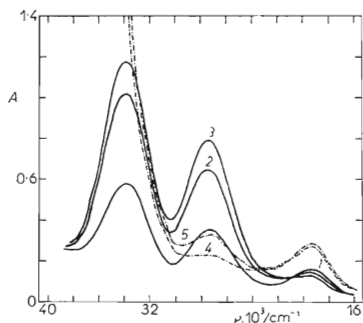
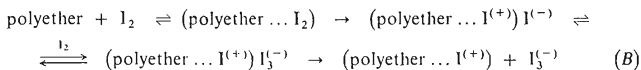


FIG. 1

Absorption spectrum of iodine in chloroform ($1 \cdot 10^{-4}$ mol dm $^{-3}$); concentration of cyclic polyethers: 15-crown-5, $1.9 \cdot 10^{-2}$ mol dm $^{-3}$ 298.1 K: 1 2.5 min after mixing the solutions, 2 69 min, 3 147 min; dibenzo-18-crown-6, $8.3 \cdot 10^{-3}$ mol dm $^{-3}$, 289.1 K: 4 1 min, 5 93 min. Cell thickness 3.00 cm



The experimental rate constant is obviously a product of the actual rate constant and the equilibrium constants of the mentioned equilibria. With increasing temperature the equilibrium concentration of one or the other molecular complex, or both, decreases. The observed relatively large negative value of $d \ln k/d(1/T)$ shows that changes of the equilibrium constant with temperature are connected with decomposition of an unstable complex. Of complexes, shown in Scheme B, the most likely one is the complex (polyether ... I₂) in which iodine is bonded to the polyether by a weak van der Waals bond. As the rate-determining step we can consider either the slow decomposition of the molecular complex (polyether ... I₂) or the slow dissociation of the complex (polyether ... I⁽⁺⁾) I₃⁽⁻⁾.

REFERENCES

1. Andrews L. J., Keefer R. M.: *Molecular Complexes in Organic Chemistry*, Russian translation, p. 27. MIR, Moscow 1967.
2. Serguchev Yu. A., Petrenko T. I.: *Teor. Eksp. Khim.* 13, 705 (1977).
3. Hopkins P. H., Jagahirdar D. V., Windler F. J.: *J. Phys. Chem.* 82, 1254 (1978).
4. Lang R. P.: *J. Phys. Chem.* 78, 1657 (1974).
5. Gokel W., Cram D. J.: *J. Org. Chem.* 39, 2445 (1974).
6. Cook L., Caruso T. C., Byrne M. P., Bowera Ch. W., Speak D. H., Liotta Ch. I.: *Tetrahedron Lett.* 1974, 4029.
7. Pedersen C. J.: *J. Amer. Chem. Soc.* 89, 7017 (1967).

Translated by M. Tichý.