Encapsulating Property of a p-t-Butylcalix[6]arene Derivative: Formation of Charge-Transfer Complexes of Alkadienes with Iodine in the Presence of Octopus-Type Calix[6]arene

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Abstract. This paper deals with the ability of p-*tert*-butylcalix[6]arene derivative **1**, which has six 3,6,9-trioxadecyl substituents at the phenolic oxygens, to encapsulate CT complexes of alkadienes with iodine. By adding I_2 to alkadienes in CH_2Cl_2 in the presence of **1**, the absorbance at 363 nm, which was ascribed to I_3^- ion, increased in the order: 1,5-hexadiene < 1,9-decadiene ≪ 1,7-octadiene. The reactivity features of the CT complexes in the presence of **1** are discussed.

Key words: Encapsulating property of p-t-butylcalix[6]arene derivative, charge-transfer complex, iodine, diene.

1. Introduction

Calixarenes represent a new class of synthetic receptors in host–guest chemistry [1]. Various functionalized calixarene derivatives have been synthesized and have found widespread chemical applications. However, the major focus of research in this field has so far been on the chemistry of calix[4]arenes, the conformation of which can be readily identified. The chemistry of calix[6]arenes, however, remains unexplored, mainly because of their conformational complexity.

Previously, we reported that the calix[6]arene derivative **1** serves as a catalyst for a variety of organic transformations [2–6]. An important structural feature of **1** is that this molecule contains both a hydrophobic functionality, which is composed of six aromatic groups, and a hydrophilic functionality, which is composed of six trioxadecyl groups. We also demonstrated that **1** has a 1,4-*anti*-conformation (Fig. 1) [4,7] and its ability to catalyze organic reactions strongly depends on the nature of the solvents used, which govern a variation in the binding ability toward alkali metal ions [4]. Interestingly, when **1** was employed as a catalyst for the generation of dichlorocarbene from $CHCl_3$ and solid KOH in CH_2Cl_2 in the presence of alkadienes having isolated double bonds, mixtures of mono-

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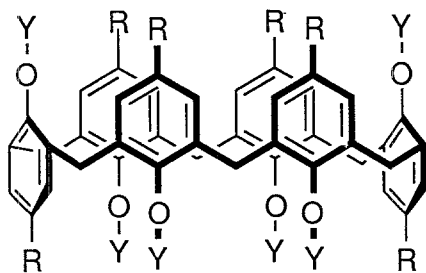1 : Y = (CH$_2$CH$_2$O)$_3$CH$_3$
2 : Y = H
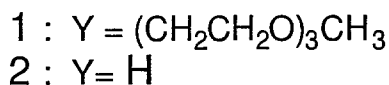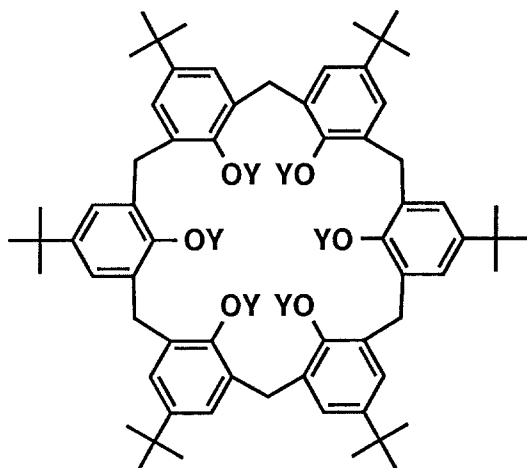
Formula 1.

and bis(dichlorocarbene) adducts were obtained with the predominant formation of monoadducts [6]. It has been suggested that the reaction occurs within the cavity of the calixarene with the results of kinetic measurements being used to support the suggestion. However, no direct evidence for the uptake of substrate molecules in the cavity has yet been obtained. Recently, fluorescence measurements have shown that a water-soluble p-tert-butylcalix[8]arene bearing polyoxyethylene chains includes such organic molecules as 1-anilino-8-naphthalenesulfonate (ANS) in its hydrophobic cavity [8]. The present paper examines the encapsulating feature of 1 through the formation of alkadiene–iodine charge transfer (CT) complexes.

2. Experimental

2.1. MATERIALS

Calix[6]arene 1 was prepared from p-tert-butylcalix[6]arene (2) [9] and 3,6,9-trioxadecyl-p-toluenesulfonate by the method reported previously [2,4]. 1-(p-tert-Butylphenyl)-1,4,7,10-tetraoxaundecane (3) was prepared from p-tert-butylphenol and 3,6,9-trioxadecyl-p-toluenesulfonate [4]. Other organic compounds were purchased and purified by distillation. Spectral grade organic solvents were used for electronic spectral measurements.

R = *tert*-butyl

$$Y = (CH_2CH_2O)_3CH_3$$

Fig. 1. 1,4-*anti* Conformation of calixarene **1**.

$$O(CH_2CH_2O)_3CH_3$$

3
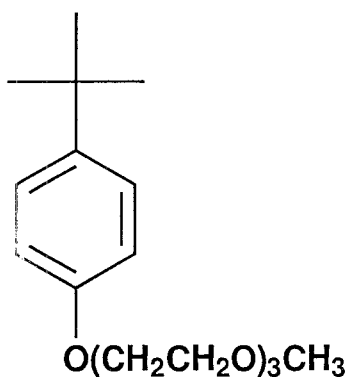
Formula 2.

2.2. MEASUREMENTS OF ELECTRONIC SPECTRA

Electronic spectra were recorded with a Shimadzu UV-260 spectrophotometer equipped with a variable temperature cell holder. The cell holder was maintained at 20 ± 0.1 °C.

A stock solution of iodine (5.0×10^{-3} mol dm^{-3}) in CH_2Cl_2 was prepared and stored in the dark. The concentration of iodine in the solution was determined by electronic spectral measurement before use. A sample solution was prepared by adding a given amount of the I_2–CH_2Cl_2 solution to a CH_2Cl_2 solution containing
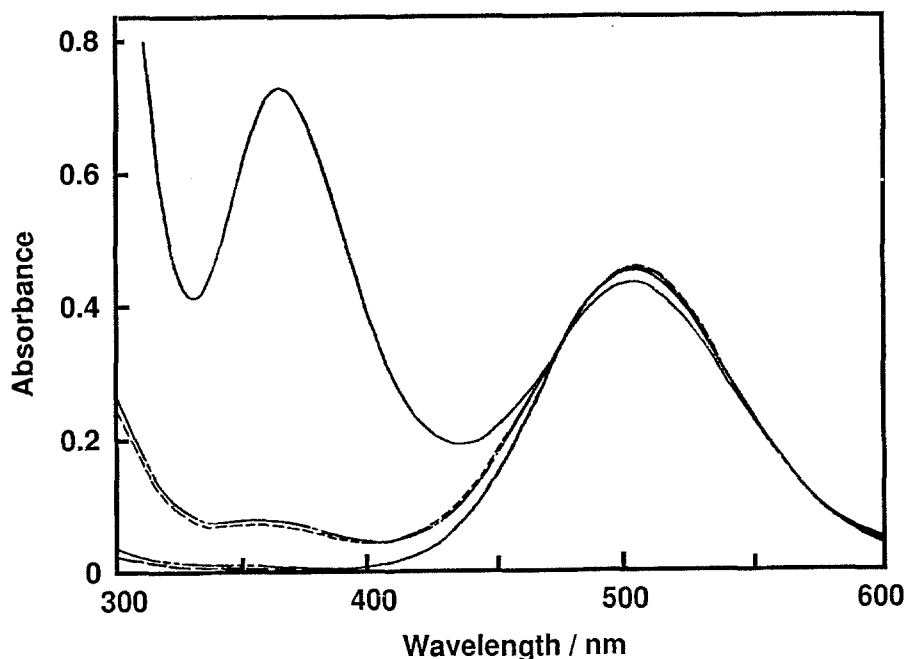
Fig. 2. Absorption spectra of the CH_2Cl_2 solutions of the complex in the presence of **1**: I_2 + 1,7-octadiene + **1**, —; I_2 + 1,7-octadiene + **3**, - - -; I_2 + **1**, - - - -; I_2 + 1,7-octadiene, - - - - - -; I_2, - - -; $[I_2]$ = 5.0 × 10^{-4} mol dm^{-3}, [1,7-octadiene] = 4.0 × 10^{-2} mol dm^{-3}, $[\mathbf{1}]$ = 1.0 × 10^{-4} mol dm^{-3}, $[\mathbf{3}]$ = 6.0 × 10^{-4} mol dm^{-3}.

a given amount of an alkene or an alkadiene and **1**, and maintaining the solution at 20 °C in a water bath. After holding at this temperature for 10 min, the electronic spectrum of the sample solution was recorded.

2.3. DETERMINATION OF STOICHIOMETRY OF I_2-DIENE COMPLEXES

The sum of the concentrations of I_2 and alkadiene was kept constant at 5.0 × 10^{-3} mol dm^{-3}, while the molar ratio of the alkadiene to I_2 was varied (the continuous variation method). The CT band of the complex appeared in the 300–320 nm region in CH_2Cl_2 and was measured at 20 °C. The absorbance (A^{CT}) of the CT complex was calculated from the following equation:

$$A^{CT} = A_{obs} - \epsilon_D[\text{alkadiene}] - \epsilon_{I_2}[I_2]$$

where A_{obs} is the observed absorbance of the CT absorption at 310 nm for the 1,7-octadiene–I_2 complex, and ϵ_D and ϵ_{I_2} and the molar absorption coefficients for the alkadiene and I_2, respectively, at the same wavelength.
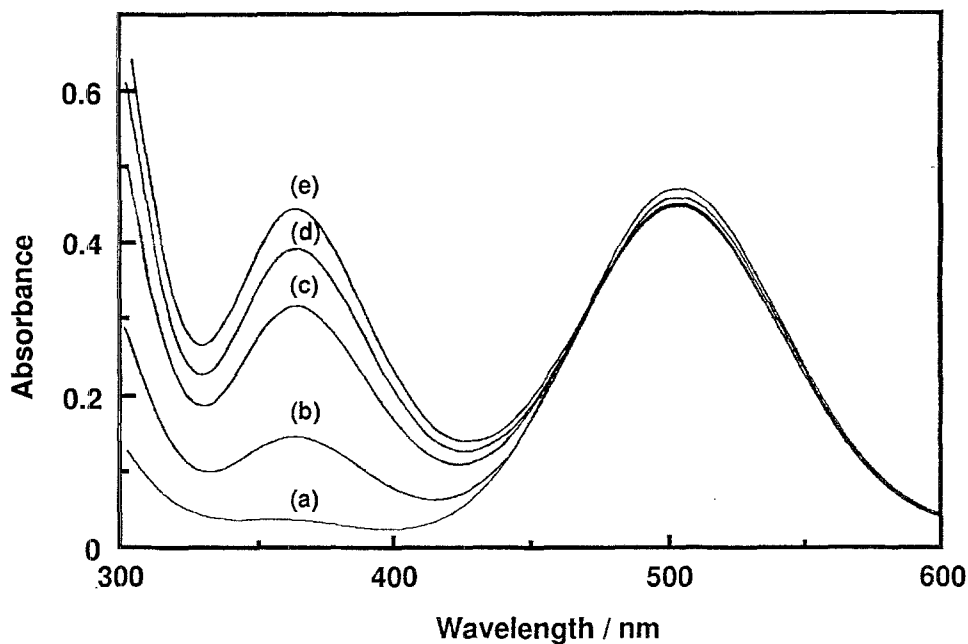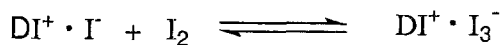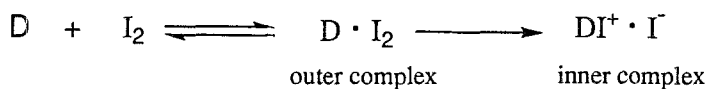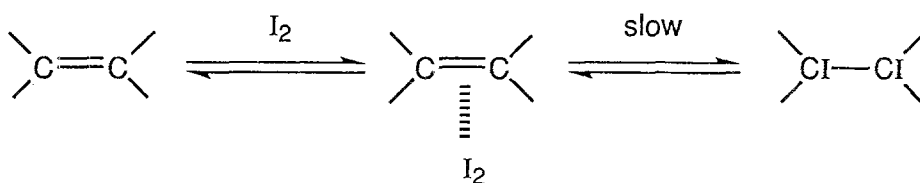
Fig. 3.   Effect of the concentration of the added calixarene on the absorption spectra of the iodine/1,7-octadiene/calixarene system in CH_2Cl_2: $[I_2] = 5.24 \times 10^{-4}$ mol dm^{-3}, $[1,7$-octadiene$] = 2.0 \times 10^{-2}$ mol dm^{-3}, $[1] = 0$ (a), 5.0×10^{-6} (b), 2.5×10^{-5} (c), 5.0×10^{-4} (d), 2.5×10^{-3} (e) mol dm^{-3}.

Scheme 1.

Scheme 2.
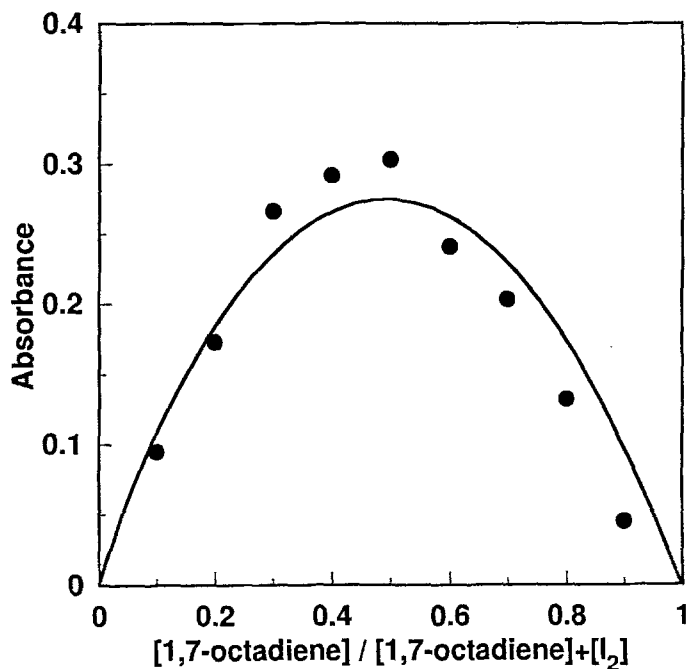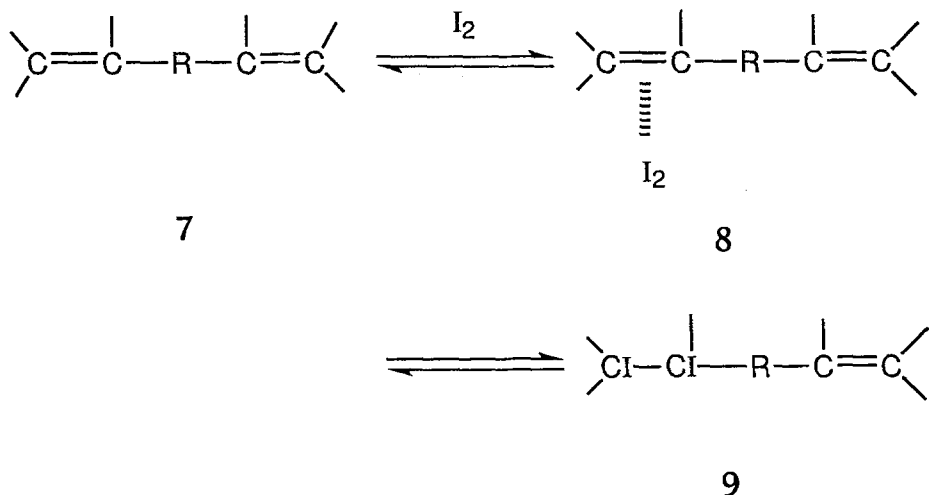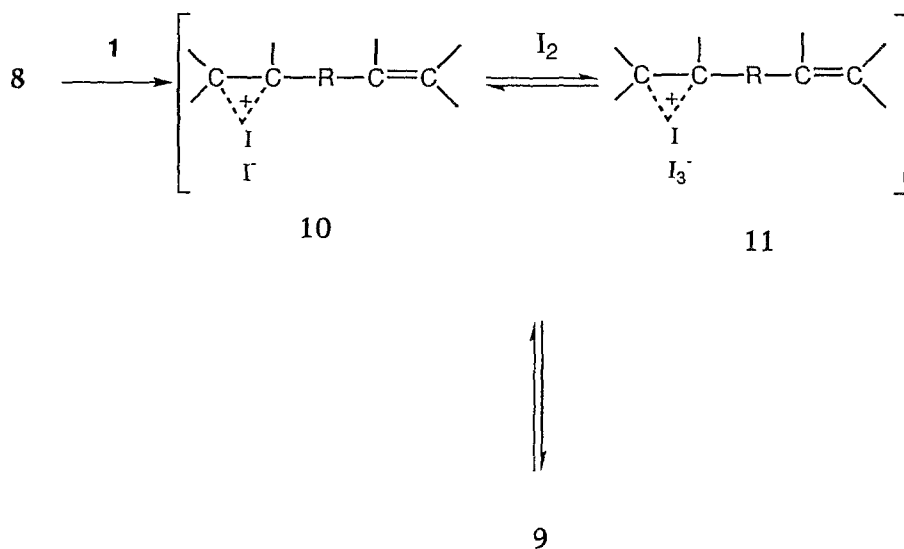
Fig. 4.   Continuous variation study of the alkadiene/iodine system in CH_2Cl_2 at 20 °C. [1,7-octadiene] + [I_2] = 5.0×10^{-3} mol dm^{-3}.

Scheme 3.

3. Results and Discussion

Figure 2 shows the effect of **1** and the monomer model **3** on the electronic spectrum of a CH_2Cl_2 solution of 1,7-octadiene and I_2. In the presence of **1**, a strong absorp-
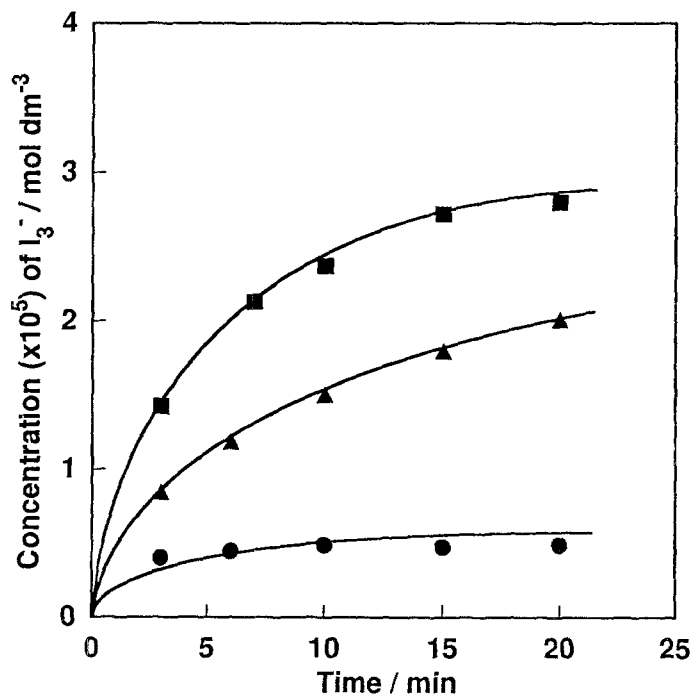
Scheme 4.

Fig. 5. Time course of the formation of I_3^- ion in the 1,7-octadiene/I_2/1 system in three solvents: CH_2Cl_2; ■, CH_2ClCH_2Cl; ▲, CH_3Cl; ●, [1,7-octadiene] = 3.00×10^{-2} mol dm^{-3}, [I_2] = 4.92×10^{-4} mol dm^{-3}, [1] = 1.01×10^{-4} mol dm^{-3}.

tion band appeared at 363 nm. This absorption band was also observed when another alkadiene, such as 4-vinylcyclohexene or (+)-1-methyl-4-(1-methylethenyl)cyclohexene (d-limonene) was added to the solution in place of 1,7-octadiene. However, the 363 nm absorption band was weakened in the absence of **1** and also even in the presence of **3**, and the band was not observed in the absence of the alkadiene (Figure 2). Furthermore, the absorbance of this band increased with increasing concentration of **1** (Figure 3).

σ-Electron donating compounds, such as triphenylarsine [10], dimethylsulfoxide [11], and pyridine [12], are known to form 1 : 1 dissociative inner CT complexes with I_2 via associative outer complexes. Triiodide ion I_3^-, which exhibits an absorption band at 363 nm, is then produced by the reaction of the inner CT complexes with I_2 (Scheme 1) [10–12]. The spectral data shown in Figure 2 strongly suggest that I_3^- ion can also be formed by the reaction of alkadiene with I_2 in the presence of **1**. On the other hand, it is known that alkene **4** reacts with I_2 to give *vic*-diiodoalkane **6** via the alkene–I_2 complex **5** (Scheme 2) [13]. In the case of alkadienes, however, there is a possibility that the reaction with I_2 produces both 1 : 1 and 1 : 2 complexes. Hence, the stoichiometry of the 1,7-octadiene–I_2 complex formation was studied spectroscopically by examining the absorption band in the 300–320 nm region, which is associated with the CT complex formation. The results for the 1,7-octadiene–I_2 complex are shown in Figure 4. These results clearly show that 1,7-octadiene forms predominantly a 1 : 1 CT complex with I_2 under the above conditions. Similar experiments indicated that 1,5-hexadiene, 1,9-decadiene, and 4-vinylcyclohexene also form 1 : 1 complexes with I_2 (Scheme 3). The equilibrium constants (K_c) for the alkadiene–I_2 complex formation were evaluated from spectral measurements using the Benesi–Hildebrand equation [14]. The K_c values for 1,9 -decadiene, 1,7-octadiene, and 1,5-hexadiene were 5.4, 1.7, and 0.2 $dm^3\ mol^{-1}$, respectively.

In the presence of **1**, the alkadiene–I_2 complex **8** was converted into inner complex **10**, which subsequently reacted with I_2 to give I_3^- ion **11** (Scheme 4). The conformation of **1** shown in Figure 1 suggests that the formation of I_3^- ion may occur within the cavity, which is made up of four trioxadecyl groups: it would be reasonable to suppose that the complexes **10** and **11**, especially their cationic part, can be stabilized in the cavity by an electrostatic interaction with four trioxadecyl groups. This supposition was partly supported by the fact that I_3^- ion was not formed by the reaction of 1,7-octadiene with I_2 in CH_2Cl_2 in the presence of **2**, which does not form such a cavity.

In order to clarify the mechanistic and reactivity features of the alkadiene–I_2 complex formation, as well as I_3^- ion formation, the solvent effects on these reactions were examined. Kinetic measurements were performed in three solvents for the reaction of 1,7-octadiene with I_2 at 20 °C. Figure 5 shows the formation of I_3^- ion over time. This result indicates that the rate of the formation of I_3^- ion is greatly affected by the nature of the solvents used and decreases in the order:
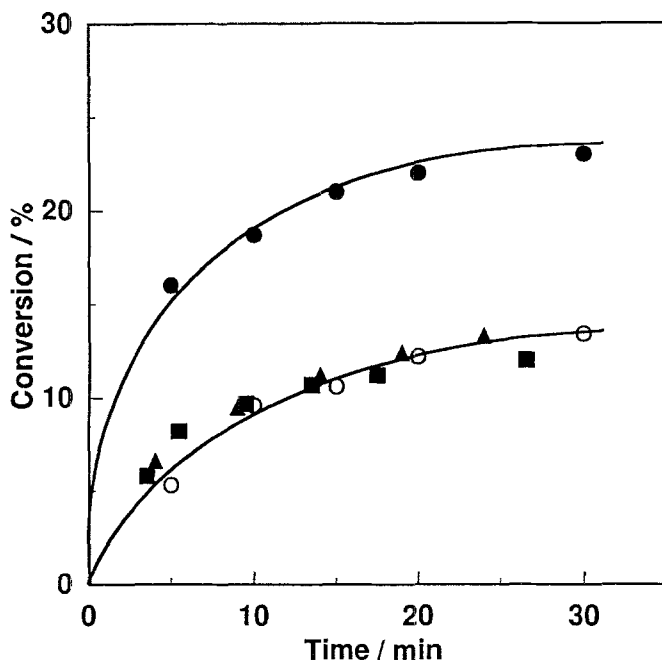
Fig. 6. Time course of the conversion of the olefinic proton to the halogenated methine and methylene protons in the reaction of 1,7-octadiene and I_2 in $CDCl_3$ at 25 °C in the presence of **1** (●), **2** (▲), and **3** (■) and in the absence of these additives (○). [1,7-octadiene] = 3.62 $\times 10^{-1}$ mol dm^{-3}, $[I_2] = 1.21 \times 10^{-1}$ mol dm^{-3}, [**1**] and [**2**] = 3.62 $\times 10^{-2}$ mol dm^{-3}, [**3**] = 2.17 $\times 10^{-1}$ mol dm^{-3}.

$CH_2Cl_2 > ClCH_2CH_2Cl > CHCl_3$. A similar solvent effect has been observed in the binding ability of **1** toward alkali-metal cations in organic solvents [4].

The addition reaction of I_2 to 1,7-octadiene was also studied by ^{1}H-NMR measurements. The spectra of the $CDCl_3$ solutions containing 1,7-octadiene and I_2 in the presence of **1, 2**, or **3** and in the absence of these additives were recorded at 25 °C at given time intervals. New signals, which were assigned to the halogenated methine and methylene protons of **9**, appeared in the 3.6–4.4 ppm region, their intensities increasing with time. Figure 6 shows the time-course of the conversion of the olefinic protons to the halogenated methine and methylene protons. The percentage conversions were calculated from the following equation:

% Conversion=

$$\frac{\text{Integrated intensity of the signals of halogenated methine and methylene protons}}{\text{Integrated intensity of the signals of olefinic protons in the absence of } I_2}$$

$\times 100$

The rate of formation of **9** in the presence of **1** was faster than that in the presence of **2** or **3** and in the absence of these additives. This result indicates that **1** accelerates
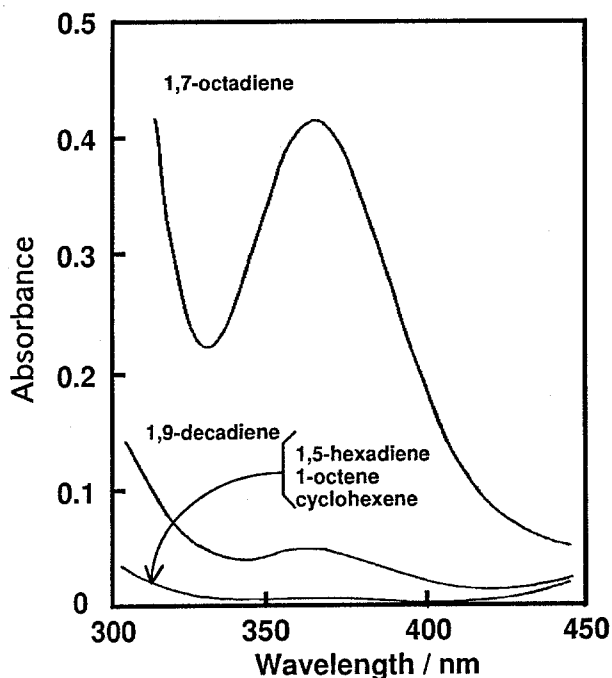
Fig. 7.   Absorption spectra of the I_3^- ion in the presence of alkadienes, iodine, and 1. Solvent: CH_2Cl_2, [1] = 1.0×10^{-4} mol dm^{-3}, [diene] or [monoene] = 1.0×10^{-1} mol dm^{-3}, [I_2] = 9.0×10^{-5} mol dm^{-3}, measured at 20 °C.

the I_2 addition reaction to 1,7-octadiene through the formation of complex 10 or 11 and suggests that the activation energy for the I_2 addition reaction would be decreased by the formation of a cationically polarized π-complex such as 10 or 11.

The rate of formation of I_3^- ion depended upon the alkadiene structure. The electronic spectra of CH_2Cl_2 solutions containing I_2 and various alkadienes in the presence of 1 at 20 °C are shown in Figure 7. In these experiments, the sample solutions were kept at 20 °C for 10 min after adding I_2 to the CH_2Cl_2 solutions containing alkadienes and 1. The variation of absorbance at 360 nm show that the ability to form I_3^- ion decreases in the order 1,7-octadiene $\gg$ 1,9-decadiene > 1,5-hexadiene. Alkenes such as 1-octene and cyclohexene have little or no ability to produce I_3^- ion.

All the above results are consistent with the mechanistic route shown in Scheme 4. An alkadiene having two isolated double bonds produces the alkadiene–I$^+$ species 10 and 11 via 1 : 1 CT complex 8. The cationic part of 10 and 11 may be stabilized by encapsulating with 1. A striking feature of this reaction is that alkenes do not form such complexes, and hence they do not lead to the production of I_3^- ion. This may be explained by assuming that the cationic part of 11 is surrounded by four trioxadecyl groups and stabilized by the electrostatic interaction between

them. In addition, **1** has aromatic groups. The olefinic group of **11** that remained intact in the iodination reaction may be stabilized by a π–π^* interaction with aromatic rings. CPK molecular models suggest that 1,7-octadiene has the most suitable chain length to be captured inside **1** through the above two interactions. The distances between the two terminal carbons of 1,5-hexadiene, 1,7-octadiene, and 1,9-decadiene are approximately 62, 86, and 110 Å, respectively. The distance between the center of the aromatic ring and the middle point of the trioxadecyl group in **1** is about 80 Å. Therefore, 1,7-octadiene has a suitable molecular structure for capture by **1**.

Acknowledgment

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