SPECTROPHOTOMETRIC AND ELECTROCHEMICAL STUDIES OF THE INTERACTION OF CRYPTAND 222 WITH DDQ AND I2 IN ETHANOL SOLUTION

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ABSTRACT. Spectrophotometric and electrochemical studies concerning the interaction of cryptand 222 with DDQ and I_2 have been performed in ethanol solution. In the case of DDQ, the results are indicative of the formation of $C222^+$ and DDQ^- through an equilibrium reaction. The results of I_2 indicate the formation of I_2-ethanol complex and I_3^- in the absence of C222. In the presence of C222, the formation of $C222I^+$ and I_3^- through a non-equilibrium reaction is confirmed. The equilibrium constant of the redox reaction between DDQ and C222 has been calculated from the absorbance mole ratio data, using the nonlinear least square program "KINFIT". The electrochemical reversibility of I^-/I_2 couple and irreversibility of DDQ/DDQ^- is indicated by amperometry. The behavior of DDQ and I_2 has been compared. A comparison with aprotic solvents has also been made.

KEY WORDS: Spectrophotometry, Electrochemistry, Cryptand 222, DDQ, I_2

INTRODUCTION

Benzoquinones such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) are commonly known as electron acceptors used in chemical synthesis. Ubiquinones and plastoquinones are involved in processes of energy storage and utilization and therefore play a vital role in biological systems [1, 2]. Some of these reactions are considered as simple models for biochemical processes [3]. In some photosynthesis redox reactions semiquinones radical anions are produced [4]. Radical anions resulting from electron transfer from nucleophile to quinone molecule form mainly ion pairs – both contact and solvent-separated depending on the system studied [5, 6]. Because, the importance of DDQ as a famous and readily available π-acceptor, its charge-transfer complexes have been the subjects of an extensive study. The related papers have been appeared from 1963 [7] and since then a lot of investigations were performed with different donors [8, 9]. Some of the resulting complexes have been applied for synthetic and analytical purposes [6, 10-12].

One of the interesting branches of the study of charge transfer phenomena is electron donor-acceptor complexes of cyclic polyethers [13] including monocyclic and bicyclic ethers (cryptands) [14-15]. Conventional cryptands possesses two bridgehead nitrogen atoms as characteristic unit which are joined by three oligooxa chain of different length and number of donor atoms [14]. The introduction of this bridge causes a drastic increase in the stabilities of their complexes. This is called cryptate effect [16].

During the past few decades the complexation of iodine with a wide variety of donors has been the subject of extensive research [17]. More recently, some attention has been paid to iodine complexes with macrocyclic crown ethers and their aza derivatives [18]. It has been shown that the substitution of the oxygen atom in macrocycles by nitrogen results in a drastic increase in the stability of the iodine complexes over those of ordinary ones [18]. From this

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point of view, the study of charge-transfer complexes of macrobicyclic cryptands with at least two nitrogen atoms in their tridimentional cavities is of special interest.

To the best of our knowledge, studies of such molecular complexes of cryptand are quite sparse, as compared with those of crown ethers [19]. On the other hand, there is limited published report on the donor-acceptor complexes of cryptands with iodine and DDQ in aprotic solvents [20]. Thus, more study in this field is needed.

We have been currently involved in the study of molecular complexes of crown ethers and cryptands [19, 21-27]. In this paper we report the results of the study of interaction of cryptand 222 with I_2 and DDQ in ethanol solution.

EXPERIMENTAL

4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (C222) from Merck Company (Germany) was recrystallized from reagent grade n-hexane and dried under vacuum over P_2O_5. Reagent grade 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was recrystallised several times from chloroform. Iodine (I_2) (Merck, Germany) was sublimed and stored in a desecator over P_2O_5 before use.

The UV-Vis spectra were recorded on a Perkin Elmer Lambda 2 spectrophotometer (USA) and the absorbance measurements were made with a Philips PU875 spectrophotometer (USA) at 25±1 °C. Conductance measurements were carried out with a Metrohm 660 conductivity meter (Switzerland) in a thermostated cell at 25±1 °C. Biamperometric measurements were made with platinum electrodes, a power supply with direct current and a digital microamperometer in a thermostated cell at 25±1 °C.
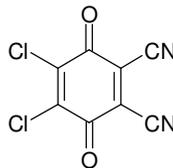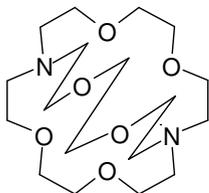
2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane

In order to obtain UV-Vis spectra, 3 mL of 1.65 x 10^{-3} M DDQ or 1.41 x 10^{-3} M of iodine solution was transferred to a 1-cm quartz cell and titrated with a standard C222 solution by a 100-μL Hamilton syringe. The same procedure was followed for obtaining absorbance-mole ratio data of C222-DDQ system. However, 1.98 x 10^{-3} M DDQ was used. Also, the conductance and current-mole ratio data were obtained by titration of 10 mL of 1.65 x 10^{-3} M DDQ or 1.41 x 10^{-3} M iodine solution with C222 standard solution.

RESULTS AND DISCUSSIONS

DDQ interaction. The electronic absorption spectra of 1.65 x 10^{-3} M DDQ in the presence of varying concentrations of C222 are shown in Figure 1. As it can be seen, upon addition of C222, some new bands appear in 375-650 nm regions. The C222 do not have any absorption in this region. So, appearance of these bands can be assigned to the formation of a new product. The existence of an isosbestic point at 375 nm indicates that the adduct forms through an equilibrium reaction [28]. The oxidative property of DDQ has been observed frequently [29-32]. On the other hand, the conductance of pure solvent, 1.65 x 10^{-3} M DDQ, 1.82 x 10^{-3} M C222

and 1.65 x 10^{-3} M DDQ in the presence of 1.82 x 10^{-3} M C222 are 4.2, 6.2, 6.3 and 60.5 µS, respectively. Which means that upon the reaction of C222 and DDQ the conductance is increased considerably. Thus, it is suggested that C222 and DDQ interact through a redox reaction and the new bands are due to DDQ radical anion. The corresponding chemical equation is as follows:

$$C222 + mDDQ \quad \rightleftharpoons \quad C222^{m+} + mDDQ^{-} \tag{1}$$
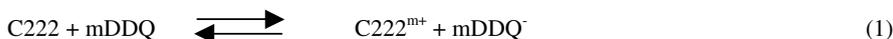
The stoichiometry of the above reaction was determined by plotting absorbance vs. C222/DDQ mole ratio (Figure 2). The plot proves a 1:1 stoichiometry for the reaction of C222 and DDQ [33]. The plot of conductance vs. C222/DDQ mole ratio (Figure 3) shows a good agreement with the spectrophotometric results and further supports the 1:1 stoichiometry.
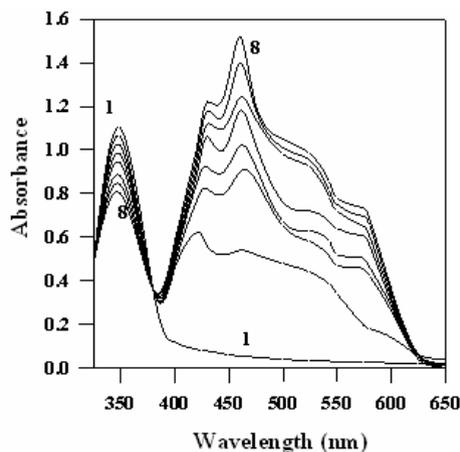
Figure 1. Absorption spectra of 1.65 x 10^{-3} M DDQ in the presence of different concentration of C222 in ethanol solution.
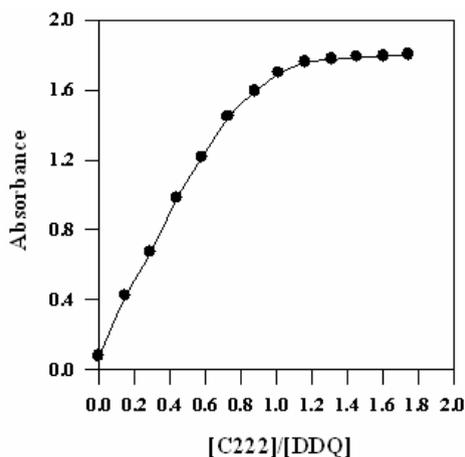
Figure 2. Plot of absorbance vs. C222/DDQ mole ratio in ethanol for a 1.98 x 10^{-3} M DDQ obtained at λ = 460 nm.
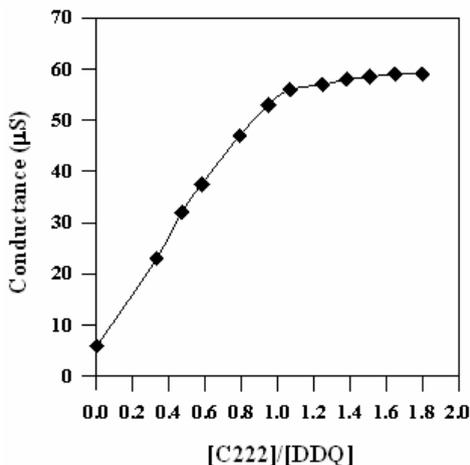
Figure 3. Plot of conductance vs. C222/DDQ mole ratio in ethanol for a 1.65×10^{-3} M DDQ obtained at 25 °C.
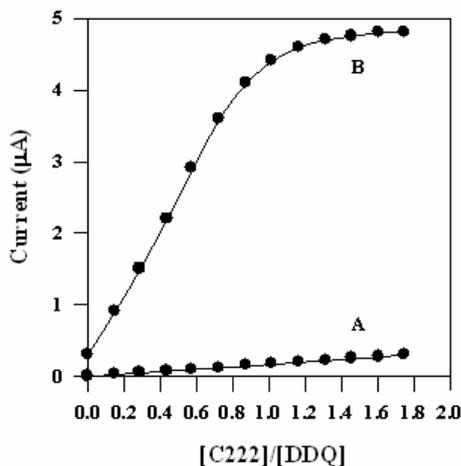
Figure 4. Plot of current vs. C222/DDQ mole ratio for a 1.65×10^{-3} M DDQ obtained at (A) $\Delta E = 0.25$ volt and (B) $\Delta E = 2.00$ volt.

Figure 4A shows the biamperometic titration plot of DDQ with C222 in ethanol solution. The titration has been followed at 0.25 V. As it can be seen, during the titration the current is nearly zero. This means that DDQ⁻/DDQ act as an irreversible couple in ethanol medium [30]. Interestingly, repeating the titration at 2.00 V causes a systematic increase of current, until a 1:1 mole ratio (Figure 4B). Such a behavior clearly shows that the current depends on the amount of DDQ⁻ or C222⁺ production (Eqn. 1). The highly polarizable electrodes and the high employed potential promote the complete concentration polarization [34] (i.e. the conditions in which the

current is proportional to the bulk concentration of electroactive species). So the anodic and cathodic reactions can be formulated as follows:

Anode: DDQ$^-$ $\longrightarrow$ DDQ + e   (2)

Cathode: C222$^+$ + e $\longrightarrow$ C222   (3)

The equilibrium constant, K$_{eq}$, in equation (1) evaluated from the absorbance-mole ratio data and using a non-linear least squares curve fitting program "KINFIT" [35]. The program is based on the interactive adjustment of the calculated values of absorbance to the observed values by either the Wentworth matrix technique [36] or the Powell procedure [37]. Adjustable parameters are K$_{eq}$ and ϵ, where ϵ is the molar absorptivity of DDQ$^-$ radical anion. The observed absorbance of a solution at the λ$_{max}$ of DDQ$^-$ (465 nm) is given by:

$$A_{obs} = \epsilon b[DDQ^-]$$ (4)

The mass balance equations can be written as

$$C_{DDQ} = [DDQ] + [DDQ^-]$$ (5)

$$C_{C222} = [C222] + [C222^+]$$ (6)

$$[C222^+] = [DDQ^-]$$ (7)

The equilibrium constant of the complex is equal to

$$K_{eq} = \frac{[DDQ^-][C222^+]}{[DDQ][C222]}$$ (8)

Substitution of Eqs. (3), (4) and (5) into Eqn. (6) and rearrangement yields

$$(K_{eq} + 1) [DDQ^-]^2 - K_{eq} (C_{C222} + C_{DDQ}) [DDQ^-] + K_{eq} C_{DDQ} C_{C222} = 0$$ (9)

The DDQ$^-$ concentrations, [DDQ$^-$] were calculated from equation (9) by means of a Newton Raphson procedure [38]. Once the value of [DDQ$^-$] 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$_{eq}$ at the current iteration step of the program. Refinement of the parameters is continued until the sum of squares of the residuals between calculated and observed values of absorbances for all experimental points is minimized. The output of the "KINFIT" program comprises the refined parameters, the sum of squares and the standard deviation of the data.

The resulting computer fit of the absorbance-mole ratio is shown in Figure 5. The good agreement between the observed and calculated absorbances further supports the Eqn. (1). The calculated value of stability constant is log K$_{eq}$ = 5.65 ± 0.15. The high value of equilibrium constant is indicative of strong interaction between C222 and DDQ.
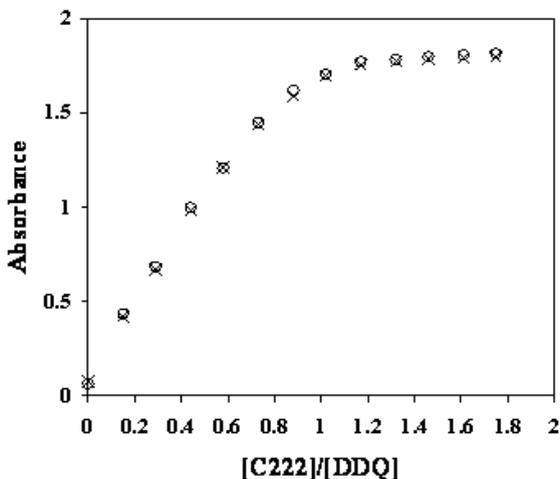
Figure 5. Computer fit of the plot of absorbance vs. C222/DDQ mole ratio obtained at λ = 460 nm and 25 °C: (X) experimental points; (O) calculated points.

Iodine interaction. The electronic absorption spectrum of 1.41 x 10^{-3} M iodine solution in 250-550 nm regions is shown in Figure 6. In this spectrum three bands at 290, 364 and 440 nm can be observed. The 290 and 364 nm bands are well known bands of triiodide ion [39, 40]. On the other hand, the band 440 nm has been observed previously for the mixture of I_2 and ethanol in the n-heptane solution. It has been attributed to the locally excited I_2 band in the I_2-ethanol complex [41]. Infect the λ_{max} of solution of free iodine in n-heptane is equal to 520 nm. Meanwhile upon addition of ethanol a blue shift to 440 nm is observed. This can be assigned to the partial charge transfer from oxygen atom of ethanol to antibonding orbital of iodine. This develops the effective size and increases the excitation energy [42].
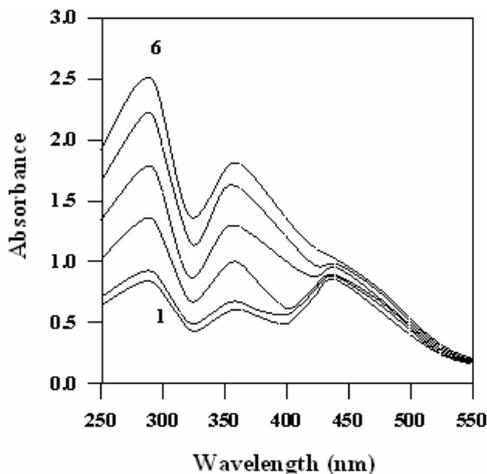
Figure 6. Absorption spectra of 1.41 x 10^{-3} M I_2 in the presence of different concentration of C222 in ethanol solution.

Based on the above discussion, it can be concluded that in solution of I$_2$ in ethanol, both complexed I$_2$ and triiodide exist. The existence of these species can be formulated by the following reactions:

$$nC_2H_5OH + nI_2 \longrightarrow nC_2H_5OH \cdot I_2 \qquad (10)$$

$$nC_2H_5OH \cdot I_2 \ mC_2H_5OH \rightleftharpoons n(C_2H_5OH)_mI^+ + n/3 \ I_3^- \qquad (11)$$
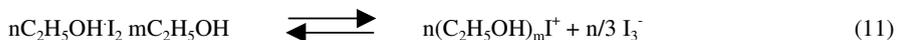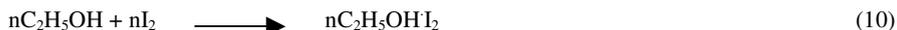
The accuracy of the above reaction (Eqn 11) is further confirmed by the similar reaction of some crown ethers and iodine in inert solvents [19, 23]. It has been proved that through the interaction of macrocycles with iodine, the I$^+$ is located in the cavity of crown ether and coordinated by oxygen atoms of ligand. In a similar fashion, in ethanol, several molecules of solvent coordinate the I$^+$. In addition the higher conductance of 1.41 x 10^{-3} M solution of I$_2$ in ethanol, relative to pure ethanol (the measured values are 4.2 and 10.2 μS, respectively), indicates that the reaction of I$_2$ and solvent is ion producer.

The absence of I$_3^-$ band in the mixture of I$_2$-ethanol in n-heptane and its appearance in the solution of I$_2$ in ethanol is reasonable. It can be attributed to the drastic enhancement of the solvating ability of pure ethanol, relative to the solution of ethanol in n-heptane and the higher dielectric constant of ethanol than that of n-heptane [43]. Both of these effects promote the formation of I$_3^-$.

On the other hand, Figure 6 shows that upon addition of C222 to iodine solution the intensity of triiodide bands (290 and 364 nm) increases. This means that by increasing of C222 to iodine solution, a triiodide formation reaction is occurred. The interaction of C222 with I$_2$ in inert solvents and production of triiodide through the following reaction have been reported [19].

$$C222 + 2I_2 \rightleftharpoons C222I^+I_3^- \qquad (12)$$

A similar reaction will occur in ethanol solution. However, in contrast of inert solvents, instead of free, the complexed iodine will react with C222. Therefore, the following reaction is suggested:

$$C222 + 2C_2H_5OH \cdot I_2 \rightleftharpoons C222I^+ + 2C_2H_5OH + I_3^- \qquad (13)$$
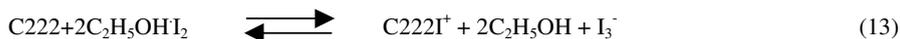
Because of the absence of isosbestic point in the spectra of C222-I$_2$ mixtures, the above reaction is nonequilibrium.

According to the Eqn. 13, upon addition of C222 a decrease in the intensity at 440 nm (λ_{max} of complexed iodine) is expected. However because of simultaneous formation of triiodide and the absorption of this ion in 400-500 nm regions, the reverse is observed. In fact the consumption of iodine causes the 440 nm band to be reduced. In contrast, the production of triiodide results in the increased intensity of this band. The net effect is the initial increase of this band and its final disappearance.

The biamperometric titration curve [34] of 1.41 x 10^{-4} M iodine with C222 is shown in Figure 7 (ΔE = 0.25 V). As it can be seen, in the absence of C222, the current is more than zero. The observed current at C222/I$_2$ = 0 can be related to the presence of triiodide in solution of iodine in ethanol (Eqn. 11). The following half reactions are suggested for the observed current.

$$\text{Anode: } 2I_3^- \rightleftharpoons 3I_2 + 2e \qquad (14)$$

$$\text{Cathode: } I_3^- + 2e \rightleftharpoons 3I^- \qquad (15)$$

On the other hand, increasing of current at $C222/I_2 > 0$ can be assigned to the further production of triiodide during the titration (Eqn. 13). Finally, the level up of the curve is a result of completeness of the reaction [34].
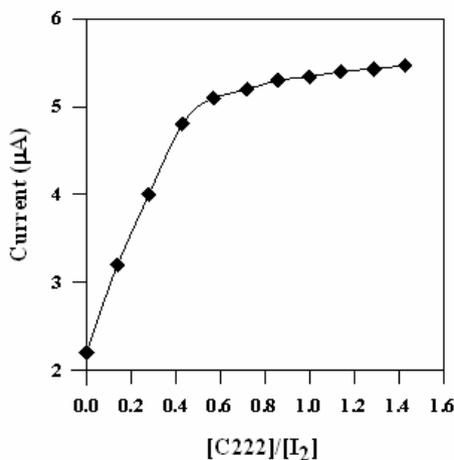
Figure 7. Plot of current vs. $C222/I_2$ in ethanol for a 1.41×10^{-3} M obtained at 25°C ($\Delta E = 0.25$ volt).

It is interesting to note that the biamperometric curve (Figure 7) is indicative of 0.8:2 C222 to I_2 stoichiometry. However, the production of triiodie involves 1:2 ($C222:I_2$) stoichiometry [19]. This ambiguity will clear if we consider that some of iodine molecules had already been converted to triiodide (Eqn.11). Consequently, less than one mole C222 will react with two moles of iodine.
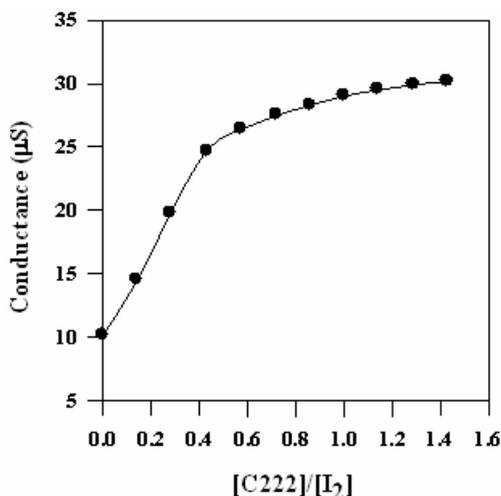
Figure 8. Plot of conductance vs. $C222/I_2$ mole ratio for a 1.41×10^{-3} M iodine obtained at 25°C.

The plot of conductance vs. C222/I$_2$ mole ratio (Figure 8) also proves a 0.8:2 stoichiometry and shows an agreement with the amperometric results. This plot further supports the existence of triiodide in a solution of iodine in ethanol.

The fixation of conductance at the completeness of C222-DDQ (Figure 3) or C222-I$_2$ (Figure 6) reactions (Figures 3 and 8) indicate that acid-base interactions [44] between C222 (as a Lewis base) and C$_2$H$_5$OH (as a Lewis acid) are of minor importance (Eqn. 16). In fact, if such interactions were strong, a further increase of conductance would be anticipated at higher C222/DDQ or C222/I$_2$ mole ratios.

$$C222 + C_2H_5OH \longrightarrow C222H^+ + C_2H_5O^- \tag{16}$$

Comparison of DDQ and I$_2$ in interaction with C222. According to the previous discussion it can be said that:

1) The reaction of C222 and DDQ follows from equilibrium pathway while the reverse is observed for the C222 and I$_2$.
2) DDQ does not have any special reaction with the solvent but I$_2$ reacts with the solvent.
3) DDQ/DDQ$^-$ acts as an irreversible couple. However I$_2$/I$^-$ act as a reversible couple.
4) The high value of K$_{eq}$ (Eqn. 8) and high curvature of current or conductance vs. C222/I$_2$ plots (Figures 7 and 8) indicate that both I$_2$ and DDQ have strong interactions with C222.
5) The interaction of both I$_2$ and DDQ produces the free ions.

Comparison with aprotic solvents. The results of the studies of C222 and other nitrogen containing macrocycles with I$_2$ in aprotic solvents are indicative of the formation of the macrocycleI$^+$I$_3^-$ through equilibrium reaction in one step and nonequilibrium conversion to macrocycleI$^+$ and I$_3^-$ in another step [19, 45]. In macrocycles with only one nitrogen atom the formation of (macrocycle)$_2$I$^+$I$_3^-$ is observed [19, 45]. This study showed that the reaction of iodine follows through nonequilibrium pathway. Also, the ionic products are formed directly. On the other hand, in aprotic solvents the competition with macrocycle is not observed. But, in ethanol, the solvent competes with macrocycle.

In the case of DDQ, equilibrium formation of macrocycleDDQ in one step and nonequilibrium conversion to macrocyle$^+$DDQ$^-$ in another step is reported [26, 46]. In this study direct formation of macrocycle$^+$ and DDQ$^-$ through equilibrium pathway is observed. Both in aprotic and ethanol (as protic solvent) the competition of solvent does not exit. This is in contrast to the behavior of iodine in different solvents.

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