

Direct Observation of Ion Pair Formation between 2,3-Dichloro-5,6-dicyanobenzoquinone Dianion and Sodium Ion

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The dynamic process of ion pair formation was observed through the changes in absorption spectra measured on mixing solutions of 2,3-dichloro-5,6-dicyanobenzoquinone dianion and sodium ion using a pulse-electrolysis stopped-flow method.

In studying the chemical properties of organic anion radicals and dianions, the interaction with cationic species is a significant factor. The ion pairs formed in solution have been extensively studied by preparing them *via* chemical or electrochemical reduction.¹ While the association product and the electronic structure in the equilibrium states have been mainly studied so far, we have developed a method which makes it possible to observe the dynamic processes of ion pair formation by using a pulse-electrolysis stopped-flow method.² We now report the electrochemical generation of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) dianion (DDQ^{2-}) and its reaction with Na^+ . DDQ is known to produce organometallic charge-transfer complexes as an electron acceptor.^{3,4} In particular, DDQ^{2-} was reported to produce unique complexes having a localized ring structure.⁴

We first measured the cyclic voltammograms (CV) of DDQ in acetonitrile (MeCN). Fig. 1 shows the changes in the CV on addition of Na^+ . While two reversible one-electron redox waves (P_1, P_2) were observed when the tetraethylammonium ion of the supporting electrolyte was the only cationic species in the solution [Fig. 1(a)], the reversible response in the second redox wave (P_2) disappeared and a new sharp peak (P_3), which is attributed to the adsorption of the ion pair formed on the Pt electrode, appeared on addition of Na^+ [Fig. 1(b)–(d)]. By altering the inverting potential of the sweep direction, it was ascertained that the changes in the second redox were due to the interaction of Na^+ with DDQ^{2-} , not with DDQ anion radical ($\text{DDQ}^{\cdot-}$).

Since a complex response was observed in these electrochemical measurements, we tried to investigate the interaction between DDQ^{2-} and Na^+ in homogeneous solution. The absorption spectrum of DDQ^{2-} in MeCN was observed in the absence of Na^+ using a column-electrolytic continuous-flow

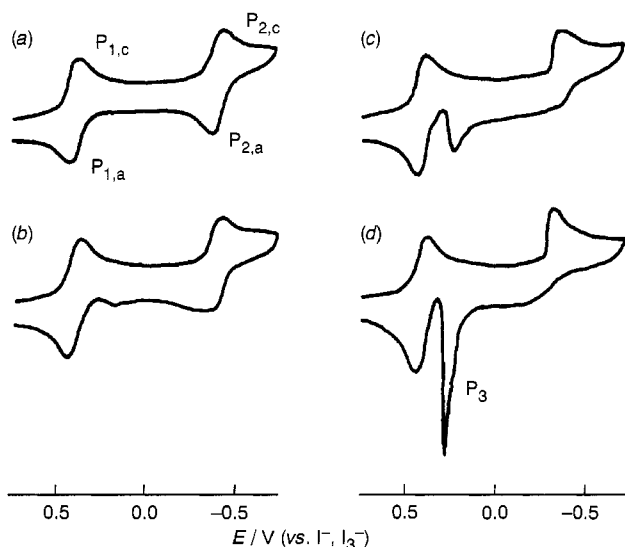


Fig. 1 Changes in cyclic voltammograms of DDQ in MeCN on addition of Na^+ . Working electrode: Pt disk electrode (diam. 1.0 mm); reference electrode: Pt(I^- , I_3^-) electrode; scan rate: 100 mV s^{-1} ; [DDQ] 0.50 mmol l^{-1} ; [Et_4NClO_4] 0.1 mol l^{-1} ; [NaClO_4] (a) 0, (b) 0.25, (c) 0.50, (d) 1.0 mol l^{-1} .

method with controlled-potential electrolysis.⁵ Fig. 2 shows how the absorption spectra of electrochemically reduced DDQ in MeCN changes with applied potential. Both $\text{DDQ}^{\cdot-}$ and DDQ^{2-} are stable in the absence of Na^+ as shown in the CV so that the absorption spectrum of each species can easily be understood on the basis of the applied potential. The absorption spectra at 0.30 V (4) and -0.70 V (14) are attributed to $\text{DDQ}^{\cdot-}$ and DDQ^{2-} , respectively. Since this method has the advantage that quantitative electrolysis can be achieved instantaneously,⁵ there is no interference from a disproportionation reaction, *i.e.* $\text{DDQ} + \text{DDQ}^{2-} \rightarrow 2 \text{DDQ}^{\cdot-}$. Although the absorption spectrum of $\text{DDQ}^{\cdot-}$ is in good agreement with that reported,³ the spectrum of DDQ^{2-} is different from the reported spectrum³ that was recorded for a solution of Na_2DDQ in ethanol. On the basis that DDQ^{2-} exists without the formation of ion pairs in the present electrochemical method, this discrepancy probably results from the difference in the environment of DDQ^{2-} , *i.e.* DDQ^{2-} is in a free state or forms strong ion pairs with Na^+ .

To clarify this assumption, the reaction of DDQ^{2-} with Na^+ was observed directly using the pulse-electrolysis stopped-flow method. The details of this method have been described previously.² In the present work, the quantitatively electrolysed solution of DDQ^{2-} was mixed with a solution containing Na^+ , and then the changes in absorption spectra were observed in an optical flow-cell. Fig. 3 shows the dynamic transformation profile of absorption spectra measured after mixing of solutions of DDQ^{2-} and Na^+ (0.50 mmol l^{-1} each). The changes in the absorption spectra of the solution of DDQ^{2-} were clearly followed with this method; the absorption maximum at 490 nm decreased with an increase in the absorption maximum around 420 nm . From measurements in which the concentration of Na^+ was increased in steps, it was found that the ion pair produced had an absorption maximum at 420 nm , and that the stoichiometry of $\text{Na}^+:\text{DDQ}^{2-}$ was 2:1. Thus, it was clarified that

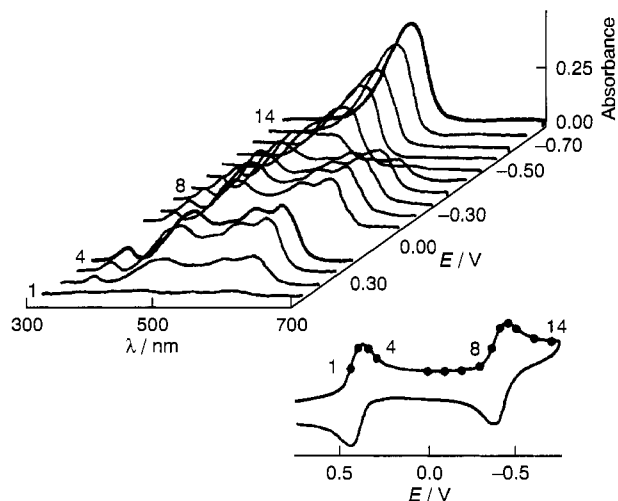


Fig. 2 Changes in absorption spectra with applied potential in the reduction of DDQ in MeCN, with the cyclic voltammogram of DDQ. Each dot (1–14) on the cyclic voltammogram corresponds to the potential at which each absorption spectrum (1–14) was observed. Light-path: 2.0 mm ; [DDQ] 0.50 mmol l^{-1} ; [Et_4NClO_4] 0.1 mol l^{-1} .

DDQ²⁻ existed as Na₂DDQ even in a solution with a large excess of Na⁺, and that the absorption maximum of Na₂DDQ is different from that of the free DDQ²⁻. The spectrum of Na₂DDQ observed with a ten-fold excess of Na⁺ is shown in the graphical abstract. By contrast, the final spectrum at equilibrium in Fig. 3 is composed of free DDQ²⁻ and Na₂DDQ, because [Na⁺] = [DDQ²⁻].

To confirm the interaction of DDQ²⁻ and Na⁺, we synthesized the Na₂DDQ salt by the literature method.³ Since the absorption spectrum obtained by dissolving Na₂DDQ in MeCN had an absorption maximum around 420 nm, the existence of DDQ²⁻ as Na₂DDQ is most probable.

Furthermore, as a result of kinetic analysis of the time-decay curves obtained by following the absorbance of the free DDQ²⁻ at 490 nm, the reaction of DDQ²⁻ and Na⁺ was found to reach in equilibrium through two steps, which consist of fast (several tens of millisecond) and slow (several seconds) reactions. Therefore, reactions (1) and (2) can be assumed for the process.

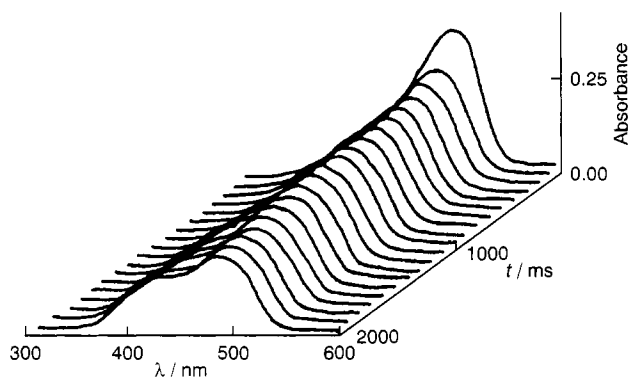
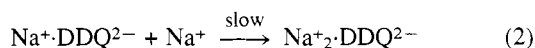
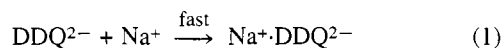


Fig. 3 Dynamic transformation profile of absorption spectra in the reaction of DDQ²⁻ with Na⁺. The solution of DDQ²⁻ was produced by electrolysis a solution in MeCN of 0.50 mmol l⁻¹ DDQ containing 0.1 mol l⁻¹ Et₄NClO₄ with an applied potential of 0.8 V for 10 s, and then it was mixed with a solution of 0.50 mmol l⁻¹ Na⁺. Time interval: 100 ms.

In this manner, the dynamic process of the ion pair formation between DDQ²⁻ and Na⁺ could be observed directly by using the pulse-electrolysis stopped-flow method. It is interesting in this case that the reaction process could be easily followed between the cationic and the anionic species. To investigate the effect of the charge, the reaction of DDQ^{•-} with Na⁺ was observed using the present method. However, no changes in the absorption spectrum of DDQ^{•-} were observed even on mixing with a large excess of Na⁺, which is in good agreement with the CV results.

Similar measurements were also carried out for the reaction of 2,3,5,6-tetrachlorobenzoquinone dianion and Na⁺. The reaction was, however, too fast to be measured with the stopped-flow technique, *i.e.* the reaction was completed within 1 ms. This means that the reactivity of the dianion of quinones towards Na⁺ greatly depends on the quinone substituents.

While the chemical properties of metal salts have been mainly investigated in the static state, the present work has permitted the dynamics of ion pair formation processes between reduced species and metal cations to be observed utilizing the advantages of the flow-electrolysis methods. With this approach the interactions of reduced species with cationic species can be in terms of differences in reaction rates.

The decay curves had a complex appearance probably owing to the occurrence of consecutive reactions and a detailed analysis of the kinetics and mechanism is now in progress.

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