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Complex aspects of reaction kinetics between the 2,3-dichloro-5,6-dicyano-1,4-benzoquinone dianion and alkali metal cations in acetonitrile solution

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The reactions between the electrogenerated 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) dianion (DDQ^{2-}) and the alkali metal cations (M^+: Li^+, Na^+, K^+) in homogeneous acetonitrile solutions were studied using a pulse electrolysis stopped-flow method. Changes in the absorption spectra were observed after the ion pair formation reaction of DDQ^{2-} with Na^+ to form Na_2DDQ. From the decay profile of free DDQ^{2-}, it became clear that the reaction of DDQ^{2-} with Na^+ reached equilibrium through two steps, one fast (several tens of milliseconds) and one slow (several seconds). This complex behavior could be understood by the following two-step mechanism.

$$DDQ^{2-} + Na^+ \xrightarrow{\text{fast}} Na^+\,DDQ^{2-}$$

$$Na^+\,DDQ^{2-} + Na^+\,DDQ^{2-} \xrightarrow{\text{slow}} Na^+{}_2\,DDQ^{2-} + DDQ^{2-}$$

In addition, a difference of the reactivity toward DDQ^{2-} depending on the size of M^+ was evident, though the reaction of DDQ^{2-} and Li^+ was too fast to be followed.

Introduction

Numerous studies have been devoted to the reaction kinetics between electrogenerated cation radicals and nucleophiles,[1–4] and work still continues in this area.[5] By developing a pulse electrolysis stopped-flow method,[6] we have contributed to the kinetic analysis of nucleophilic reactions of electrogenerated cation radicals.[7–10] Using this method, the observation of the decay of the cation radicals can be carried out in homogeneous solution, separated from the electrode phenomena, spectrophotometrically.[6] In this way, kinetic analysis can be performed successfully under the consideration of normal rate laws, such as first-order[7,8,10] and second-order[9,10] in the concentration of the cation radicals.

This method has also been applied to the kinetic analysis of electrophilic reactions of electrogenerated anion radicals,[11–14] in which the alkali and alkaline earth metal cation were adopted as electrophile. As a consequence, the effect of the solvent and metal cations has been clarified in the reactions between the chloranil anion radical and alkaline earth metal cations (M^{2+}).[11,12]

However, it is known for the reactions between electrogenerated species and metal cations that adsorption and deposition of the formed ion pair often affects the electrode reactions significantly. This was the case for the chloranil anion radical;[13] the reversible peak to form the chloranil anion radical was not observed in the presence of M^{2+}.[12,13]

While the reaction kinetics of the chloranil anion radical with M^{2+} could be followed on the basis of an ordinal rate law,[11,12] it is expected that the reaction analyses become difficult due to the complexity of the ion pairing reactions. Depending on the solubility and the magnitude of aggregating interaction of the formed ion pairs, it is expected that the kinetics process does not follow the usual rate laws.

Actually, we found some complexity in the reactions of electrogenerated 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) dianions (DDQ^{2-}) with alkali metal in acetonitrile (AN). Therefore, in the present paper, the complex aspects of the reaction analysis are described in detail, while the observation of the reaction of DDQ^{2-} with Na^+ was reported in an earlier communication.[14]

The complex electrode reactions of DDQ in the presence of Na^+ at platinum electrodes in AN were clarified using various electrochemical measurements under conditions with significant mass transport in our collaborated research with the Compton group, Oxford University, UK.[15] In this case, the presence of Na^+ changed the hydrodynamic voltammogram of DDQ at potentials corresponding to the two-electron, so as to show a spike-like increase and decrease of reductive current. Using diverse electrochemical measurements such as a channel flow EPR measurement and sonovoltammetry, the following complex reduction mechanism was proved.[15]

$$Na^+ + DDQ^{2-} \longrightarrow Na^+\,DDQ^{2-} \qquad (1)$$

$$Na^+\,DDQ^{2-} \longrightarrow Na^+\,DDQ^{2-}{}_{ads} \qquad (2)$$

$$Na^+\,DDQ^{2-}{}_{ads} + Na^+\,DDQ^{2-}{}_{ads} \longrightarrow Na^+{}_2\,DDQ^{2-}{}_{ads} + DDQ^{2-} \qquad (3)$$

This result indicates the complexity of the ion pair interactions on the electrode surface. However, even when the reaction occurred in homogeneous solution, complex aspects of the reactions were apparent in the spectrophotometric results. The aim of the present paper is to discuss the complexity.

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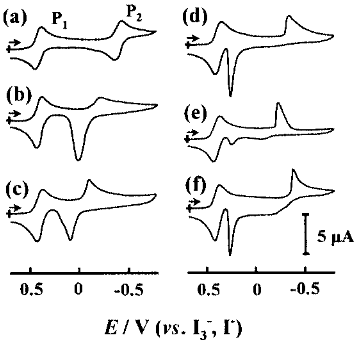

Fig. 1 Changes in cyclic voltammograms of DDQ in AN with the addition of M^+. Working electrode; Pt disk electrode (diam. 1.0 mm). Reference electrode; Pt/(I^-,I_3^-) electrode. Scan rate; 100 mV sec^{-1}. DDQ; 1.0 mM. TBAP; 0.1 mol dm^{-3}. (a) Without M^+. In the presence of (b) $LiClO_4$, 2.0 mmol dm^{-3}, (c) $LiClO_4$, 10 mmol dm^{-3}, (d) $NaClO_4$, 2.0 mmol dm^{-3}, (e) $NaClO_4$, 10 mmol dm^{-3}, (f) $KClO_4$, *ca.* 2.0 mmol dm^{-3} (saturated).

Experimental

Apparatus and procedures

The details of spectroscopic measurements using the pulse electrolysis stopped-flow method have been described previously.[6,12] Controlled potential electrolysis for 10 s, which was long enough for quantitative electrolysis,[6] was performed to generate the electrochemically reduced species. N_2 gas was bubbled into reservoirs to deareate the solutions before each measurement. The temperature was controlled by circulating water at 25 °C.

Cyclic voltammetry (CV) was carried out with a PAR 174 analyzer. A Pt disk electrode of 1.6 mm diameter was used as the working electrode. The reference electrode used was the Pt/(I_3^-, I^-) electrode in AN. All CV experiments were performed in an H-shaped cell at *ca.* 25 °C.

Reagents

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was obtained from Aldrich Co. Ltd., and used after twice-recrystallization from chloroform. As sources of M^+, the perchlorate salts were used. $LiClO_4$ (Wako, GR grade), $NaClO_4$ and $KClO_4$ (Nacalai Tesque, GR grade) were used as received. Acetonitrile (AN) was twice-distilled over P_2O_5. The supporting electrolyte, tetraethylammonium perchlorate (TEAP) or tetrabutylammonium perchlorate (TBAP), was purified by recrystallization four or five times from water or ethanol–water, respectively.

Results and discussion

CVs of DDQ in the presence of Li^+, Na^+ and K^+

The cyclic voltammograms (CVs) of DDQ in acetonitrile (AN) obtained without and in the presence of alkali metal cations (M^+: Li^+, Na^+, K^+) are shown in Fig. 1. The two reversible one-electron redox waves (P_1, P_2), which are attributed to the formation of DDQ anion radicals ($DDQ^{\cdot -}$) and DDQ^{2-} respectively, were observed when the tetrabutylammonium ion of a supporting electrolyte existed as the only cationic species in the solution (Fig. 1a). On the other hand, the reversible response in the second redox wave (P_2) disappeared and new acute peaks, which were attributed to the adsorption or the desorption of the ion pair formed on the Pt electrode, appeared with the presence of M^+ (Fig. 1b–f). By altering the inverting potential of sweep direction, it was ascertained that the changes in the second redox were attributable to the interaction of M^+ with DDQ^{2-}, not with $DDQ^{\cdot -}$.

Compared with the results in the channel flow voltammetry, which reflected the surface reaction rates of formation of $M^+{}_2DDQ^{2-}$ through eqns. (1)–(3),[15] the present CV results indicate only that the ion paring processes between DDQ^{2-} and M^+ involve the adsorption and desorption of the ion pair formed on the Pt electrode surface.

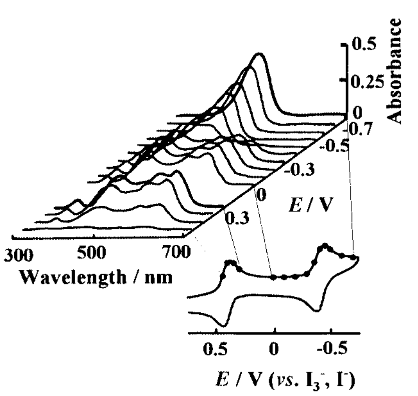

Fig. 2 Changes in absorption spectra depending on the applied potential in the reduction of DDQ in AN with the cyclic voltammogram of DDQ. Each dot on the cyclic voltammogram corresponds to the potential at which each absorption spectrum was observed. Light path; 2.0 mm. [DDQ]; 0.25 mmol dm^{-3}. [TEAP]; 0.1 mol dm^{-3}.

Formation of free DDQ^{2-} in AN using a column electrolysis method

Because a complex response was observed in the electrochemical measurement, we tried to investigate the interaction between DDQ^{2-} and M^+ in homogeneous solution.

At first, the absorption spectrum of DDQ^{2-} in AN was observed in the absence of M^+ using a column-electrolytic continuous-flow method with a controlled-potential electrolysis.[16] Fig. 2 shows the changes in absorption spectra of electrochemically reduced DDQ in AN depending on the applied potential. Both $DDQ^{\cdot -}$ and DDQ^{2-} are so stable in the absence of Na^+, as shown in the CV (Fig. 1a and Fig. 2), that the absorption spectrum of each species can be easily comprehended based on the applied potential. The absorption spectra at 0.30 V and −0.70 V are attributed to those of $DDQ^{\cdot -}$ and DDQ^{2-}, respectively.

Because this method has the advantage that quantitative electrolysis can be achieved instantaneously,[16] there is no interference from a proportionation reaction, which might occur as follows.

$$DDQ + DDQ^{2-} \longrightarrow 2\,DDQ^{\cdot -} \qquad (4)$$

Although the absorption spectrum of $DDQ^{\cdot -}$ is in good agreement with the reported one,[17] the spectrum of DDQ^{2-} is different from the reported spectrum,[17] which was prepared by dissolving Na_2DDQ in ethanol.

To explain this result, we must presume that DDQ^{2-} does not form a contact ion pair with the tetraethylammonium ion (TEA^+) coexisting in the present electrolysis in AN, but that DDQ^{2-} forms a sodium ion pair due to strong interaction.

Changes in absorption spectra in the reaction between DDQ^{2-} and Na^+

To clarify the above assumption, the effect of Na^+ on the absorption spectrum of DDQ^{2-} was observed directly using the pulse electrolysis stopped-flow method. That is, the quantitatively electrolyzed AN solution of DDQ^{2-} was mixed with an AN solution containing Na^+, and then the changes in absorption spectra were observed in an optical flow-cell.

Fig. 3 shows the changes in the absorption spectra caused by mixing with Na^+. The spectrum in Fig. 3b was observed 10 s after mixing free DDQ^{2-} solution with a 10-fold excess of Na^+. While changes in absorption spectra were observed within a second after mixing as a reflection of the kinetic process

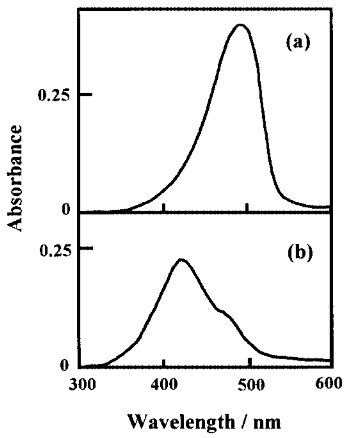

Fig. 3 Absorption spectrum of (a) 0.25 mmol dm^{-3} DDQ^{2-} in AN and (b) 10 s after the mixing of AN solutions of DDQ^{2-} and Na$^+$. In the measurement of (b), a solution of DDQ^{2-} was produced by electrolyzing an AN solution of 0.50 mmol dm^{-3} DDQ containing 0.1 M TEAP with an applied potential of 0.8 V for 10 s, and it was then mixed with a solution of 5.0 mmol dm^{-3} Na$^+$. Light path; 2.0 mm.

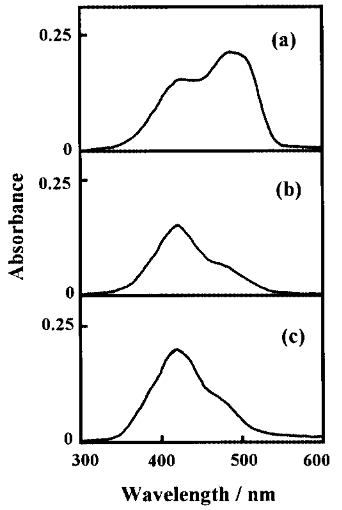

Fig. 4 Absorption spectra obtained 10 s after mixing of AN solutions of DDQ^{2-} and Na$^+$. A solution of DDQ^{2-} was produced by electrolyzing an AN solution of 0.50 mM DDQ under the same conditions as in Fig. 3, and it was then mixed with a solution of (a) 0.50 mmol dm^{-3} Na$^+$, (b) 1.0 mmol dm^{-3} Na$^+$ and (c) 2.0 mmol dm^{-3} Na$^+$. Light path; 2.0 mm.

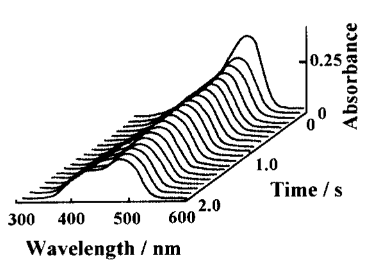

Fig. 5 Dynamic transformation profile of absorption spectra in the reaction of DDQ^{2-} with Na$^+$. A solution of 0.50 mmol dm^{-3} DDQ^{2-} was mixed with a solution of 0.50 mmol dm^{-3} Na$^+$, and then measured at time intervals of 100 ms.

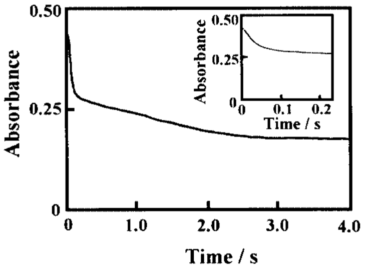

Fig. 6 Time decay curve of free DDQ^{2-} in the reaction of DDQ^{2-} with Na$^+$. A solution of 0.50 mmol dm^{-3} DDQ^{2-} was mixed with a solution of 0.50 mmol dm^{-3} Na$^+$, and then measured. Measurement wavelength; 490 nm. The inserted section is an expanded view of the fast step.

mentioned later, a constant spectrum could be obtained 10 s after mixing. Clearly, the absorption spectrum of the mixed solution (Fig. 3b) is different from that of the free DDQ^{2-} (Fig. 3a), so that the spectrum of Fig. 3b can be attributed to the ion pair formed between DDQ^{2-} and Na$^+$.

Fig. 4 shows the changes in the absorption spectra depending on [Na$^+$] after the mixing. All spectra were observed 10 s after mixing, so as to obtain constant spectra of completely reacted solutions. After mixing with an equimolar solution of Na$^+$, free DDQ^{2-} still remained, as shown in Fig. 4a. On the other hand, when mixed with 1.0 mmol dm $^{-3}$ Na$^+$, *i.e.* two-fold DDQ^{2-}, free DDQ^{2-} almost disappeared, as shown in Fig. 4b. Thus, it was found that the stoichiometry of Na$^+$: DDQ^{2-} seemed to be 2 : 1, *i.e.* the contact ion pair, Na$_2$DDQ, was formed in the reaction.

From the present results, as the reason for the difference from the reported absorption maximum (in ethanol) of DDQ^{2-},[17] it is inferred that the Na$_2$DDQ was not dissociated in ethanol. The slight difference in the wavelength of the absorption maximum between that in Fig. 3b and the reported one (absorption maxima; 398 nm[17]) is presumably attributed to the different solvents. To confirm this, we synthesized the salt of Na$_2$DDQ by the authentic method.[17] Because the absorption spectrum obtained by dissolving the Na$_2$DDQ in AN had an absorption maximum around 420 nm, the existence of DDQ^{2-} as Na$_2$DDQ can be confirmed.

Although slight interaction might be expected with the cation of supporting electrolytes, the absorption spectrum of DDQ^{2-} was identical regardless of the cations, TEA$^+$ or TBA$^+$. Thus, we can call the DDQ^{2-} formed electrochemically free DDQ^{2-}.

From this clear difference with the sodium ion pair, we are able to emphasise one of the advantages of the column-electrolysis method, that the electrogenerated species can be prepared in a free state with little or no interaction with other species.

As for the absorption spectra, a curious increase was observed in the absorption peaks of Na$_2$DDQ with the increase in [Na$^+$] (Fig. 4b,c, and 3b). This is discussed after the results of the kinetic observation.

Kinetic observation of the reaction between DDQ^{2-} and Na$^+$

To analyze the kinetic process of the reaction between DDQ^{2-} and Na$^+$, the changes in absorption spectra were followed just after mixing both the solutions. Fig. 5 shows the changes in absorption spectra with time, after mixing solutions of 0.50 mmol dm^{-3} DDQ^{2-} and 0.50 mmol dm^{-3} Na$^+$. The dynamic transformation profile of the absorption spectra from free DDQ^{2-} to Na$_2$DDQ was clearly observed with this method; *i.e.* the absorption maximum at 490 nm decreased while the absorption maximum around 420 nm increased. The final spectrum at 2.0 s after the mixing was almost the same as that in Fig. 4a, so the reaction is assumed to have reached equilibrium at this time. At equilibrium, it is assumed that the solution contains both free DDQ^{2-} and Na$_2$DDQ, because [Na$^+$] equals [DDQ^{2-}] in this measurement.

To follow the decrease of free DDQ^{2-} more explicitly, the change in absorbance at 490 nm with time was observed using a photomultiplier. The result is shown in Fig. 6. From this decay profile, it is clear that the reaction of DDQ^{2-} with Na$^+$ reaches equilibrium through two steps, one fast (several tens of milliseconds) and one slow (several seconds). The insert is an expanded view of the fast step.

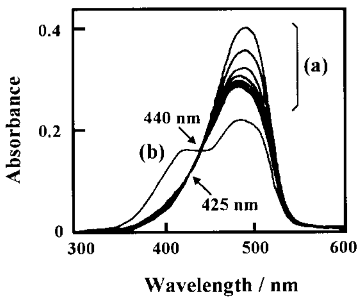

Fig. 7 Transformation profile of absorption spectra in the reaction of DDQ^{2-} with Na^+. A solution of 0.50 mmol dm^{-3} DDQ^{2-} was mixed with a solution of 0.50 mmol dm^{-3} Na^+. (a) Seven spectra in the initial stage of the reaction at time intervals of 35 ms. (b) Absorption spectrum observed after 2.0 s.

For further detailed observation of the fast step, the transformation of the absorption spectra was observed at intervals of 35 ms as shown in Fig. 7a. While significant decay of the free DDQ^{2-} was clearly observed, increase of the peak of Na_2DDQ was less obvious.

Fig. 7b shows the absorption spectrum obtained 2.0 s after mixing, *i.e.* reaction was complete. Assuming that DDQ^{2-} is simply transferred to Na_2DDQ, the isosbestic point should be observed at *ca.* 440 nm. However, the absorption spectra in Fig. 7a show an apparent isosbestic point at 425 nm. In other words, downward deviation of the solution absorbance at 440 nm is observed during the course of the rapid reaction in Fig. 7a, and absorbance at the isosbestic point is expected to return slowly during the ensuing 2.0 s.

These results imply the complex aspects of the present reaction between DDQ^{2-} and Na^+, which cannot be solved under the consideration of normal rate laws, such as being first-order and second-order in the concentration of DDQ^{2-}.

Mechanistic discussion of the reaction between DDQ^{2-} and Na^+

From the above results, the complex aspects of the reaction between DDQ^{2-} and Na^+ can be summarized as follows.

i) Two step decay of DDQ^{2-}, not expressed by ordinal rate laws.

ii) Monotonous decay of DDQ^{2-} in the fast step, with accompanying very slight increases of Na_2DDQ.

iii) Increase of absorption of Na_2DDQ at equilibrium with increase in $[Na^+]$.

Based on these results, the reaction between DDQ^{2-} and Na^+ in homogeneous solution can be discussed.

First, assuming the most simple interaction, a two step mechanism composed of the following two equations is considered.

$$DDQ^{2-} + Na^+ \longrightarrow Na^+\,DDQ^{2-} \qquad (5)$$

$$Na^+\,DDQ^{2-} + Na^+ \longrightarrow Na^+_2\,DDQ^{2-}\ (=Na_2\,DDQ) \qquad (6)$$

If the first step is in equilibrium and the second is the rate determining step, the rate law should be expressed as $-d[DDQ^{2-}]/dt = k[DDQ^{2-}][Na^+]^2$. This is not the case from our results here. Supposing the first step is rate determining, and *e.g.* assuming that eqn. (5) is a much slower reaction than eqn. (6), eqn. (6) cannot take place when $[Na^+]$ equals $[DDQ^{2-}]$ because Na^+ is consumed quantitatively to form $Na^+\,DDQ^{2-}$ in eqn. (5). However, the spectra obtained at equilibrium showed that the stoichiometry of Na^+: DDQ^{2-} was 2 : 1 to form the contact ion pair, Na_2DDQ.

To explain the complexity that is observed in the present reaction as in Fig. 6, it is most reasonable to consider that eqn. (7) is the main reaction to form $Na^+_2DDQ^{2-}$, though eqn. (6) might be concurrent under different concentration conditions.

$$DDQ^{2-} + Na^+ \xrightarrow{\text{fast}} DDQ^{2-} \qquad (5')$$

$$Na^+\,DDQ^{2-} + Na^+\,DDQ^{2-} \xrightarrow{\text{slow}} Na^+_2\,DDQ^{2-} + DDQ^{2-} \qquad (7)$$

On the basis of a mechanism composed of a fast reaction process [eqn. (5′)] and a slow reaction process [eqn. (7)], a two-step decay process would be explained. In addition, the observation concerning the isosbestic point in Fig. 7 is in agreement with this reaction mechanism. That is, the apparent isosbestic point at 425 nm in Fig. 7a can be attributed to that of the rapid reaction between DDQ^{2-} and Na^+ to form Na^+DDQ^{2-}. Furthermore, the downward deviations and the return of the absorbance at 440 nm is evidence of the formation and decay of the proposed intermediate, Na^+DDQ^{2-}.

Of course, in the extreme case that the first reaction is very fast and that the second is very slow, DDQ^{2-} should decrease fast and increase slowly. However, assuming that both the reaction rates are relatively moderate ones, DDQ^{2-} re-generated in eqn. (7) would reasonably participate in eqn. (5′), so that as a consequence the two-step decay should be observed.

Our difficulty in finding the complete solution of both the rate or equilibrium constants is that we could not access the information on the absorption spectrum of the intermediate, Na^+DDQ^{2-}. If the absorption spectrum of Na^+DDQ^{2-} were obtained, numerical analysis would permit us a more rigorous determination of the rate constants. Actually, however, no noticeable increase in absorption was observed in the course of the transformation from DDQ^{2-} to $Na^+_2\,DDQ^{2-}$. Judging from the monotonous decrease of DDQ^{2-} in Fig. 7, it is expected that the molar absorptivity of Na^+DDQ^{2-} is quite small. In addition, because the difference in the absorption spectra of DDQ^{2-} and Na_2DDQ are not so significant compared with that of DDQ and DDQ^{2-}, the absorption of Na^+DDQ^{2-} might reasonably merge into those of DDQ^{2-} and Na_2DDQ.

Under this assumption, the increase of the absorption of Na_2DDQ at equilibrium with the increase in $[Na^+]$ as mentioned in iii) can be accounted for by taking into consideration that $Na^+\,DDQ^{2-}$ remained as a reflection of the equilibrium in the second step [eqn. (7)].

The present results revealed the complex aspects of the interactions of the ion pair formation reaction in homogeneous solution. It is of interest to compare this with the electrode reaction of DDQ in the presence of Na^+, which was fingerprinted by the curious spike-like response in the voltammetry.[15] Based on the many-faceted results under mass transfer conditions, the mechanism given by eqns. (1)–(3) was determined for the electrochemical reduction on the platinum electrode surface.[15]

From the comparison between the results on the electrode surface and in homogeneous solution, it can be concluded that, even in homogeneous solution, the reaction of Na^+DDQ^{2-} with another Na^+DDQ^{2-} takes precedence over the reaction with Na^+.

Although this might be related to the solubility and the aggregating properties of the ion pairs, this would not seem to be the case in the present homogeneous reactions, judging from the homogeneity of the reacted solution within the time domain of the kinetic measurements. On the other hand, however, when the reacted solution was left in a vial for 30 min or longer, an aggregated colored amorphous precipitate was gradually seen to fall down to the bottom part of the vial, and the solution phase became clear.

Effect of alkali metal cations on the reaction rate with DDQ^{2-}

The effect of the identity of M^+ on the reactivity toward DDQ^{2-} can be easily measured using the pulse electrolysis stopped-flow method. Namely, for this purpose, similar measurements were performed by replacing Na^+ with Li^+ or K^+.

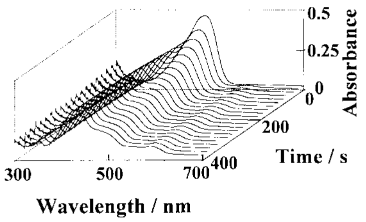

Fig. 8 Dynamic transformation profile of absorption spectra in the reaction of DDQ^{2-} with K^+. A solution of 0.50 mmol dm^{-3} DDQ^{2-} was mixed with a solution of 0.50 mmol dm^{-3} K^+, and then measured at time intervals of 20 s.

However, the decay profile could not be observed in the reaction of DDQ^{2-} with Li^+. This is because the reaction was too fast to be followed in the stopped-flow method (<1 ms), *i.e.* the reaction completed in the mixer before flowing into the optical cell. For this reason, the kinetic process in the reaction between DDQ^{2-} and Li^+ was not accessible in the present work, where merely the absorption spectrum of $Li^+{}_2DDQ^{2-}$ was observed without transforming with time.

On the other hand, the transformation of the absorption spectra could be followed in the reaction of DDQ^{2-} with K^+. The result is shown in Fig. 8. As a remarkable difference from that with Na^+, the reaction is so slow that the observation was sampled over 400 s.

The present results indicate that the difference in reactivity depends on the size of the alkali metal cations directly, something which could not be appreciated from the CVs in Fig. 1, but has been discussed in earlier work by some of us on channel flow voltammetry.[15]

Conclusion

The present work revealed the complex aspects of the electrochemically reduced species and metal cations in homogeneous solution, rather than on the electrode surface, using the pulse electrolysis stopped-flow method.

Our results indicate that reaction between Na^+DDQ^{2-} and Na^+DDQ^{2-} is preferred to that between Na^+DDQ^{2-} and Na^+. In the case of the reactions of chloranil anion radicals and alkaline earth metal cations, the reactions proceeded following a particular rate law. Thus the present case might be an exception to the conventional reactions of the electro-reduced species and metal cations. However, as the nucleation of the product was observed and discriminated in the reduction of TCNQ in the presence of Mg^{2+} and Ba^{2+},[18] specific attention should be paid to this type of reaction, even in homogeneous solution.

Additionally, a difference in reactivity towards DDQ^{2-} could be observed depending on the size of M^+; the reaction of DDQ^{2-} and Li^+ was too fast to be followed. As another example, the reaction between the chloranil dianion and Na^+ was also too fast to be measured using the stopped-flow technique. This indicates that the chloranil dianion is highly reactive compared with DDQ^{2-}.

Despite the restriction that very fast reactions are inaccessible, the present approach allows the elucidation of the homogeneous reactions of electrochemically reduced species. In particular, for the organic dianions, quantitative generation is advantageous over the conventional electrochemical approaches.

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