

Electron-Transfer Stopped-Flow Method for the Spectroscopic Detection and Kinetic Analysis of Cation Radicals

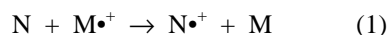
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In the electrochemical oxidation of aromatic molecules in aprotic solvents, the cation radicals are formed as a result of one-electron transfer. If such cation radicals are short-lived, the spectroscopic detection with conventional methods should be very difficult due to the consecutive chemical and/or electrochemical reactions. In addition, the heterogeneous natures of the electrode reaction would hinder the observation of pure absorption spectra of the cation radicals.

To overcome these problems, we have been observing the changes in absorption spectra of cation radicals using an electron-transfer stopped-flow (ETSF) method [1-6]. In this method, for a concrete example, unstable cation radicals ($N^{\bullet+}$) are formed via the electron transfer with stable cation radicals ($M^{\bullet+}$). That is, when the oxidation potential of the $M^{\bullet+}/M$ couple is positive to that of the $N^{\bullet+}/N$ couple, the electron transfer reaction of Eq. 1 should be favorable thermodynamically.



Thus, by mixing the solutions of N and $M^{\bullet+}$, we can form $N^{\bullet+}$ via Eq. 1, initiate the reaction of $N^{\bullet+}$, and observe the changes in absorption spectra of $N^{\bullet+}$.

As apparent from this principle, the ETSF method is not an electrochemical approach. However, the spectrochemical detection of short-lived cation radicals, which are formed in the electrochemical oxidation in aprotic solvents, can be easily carried out using this technique.

In our previous studies, various effects of neutral molecules on the reactions of aromatic amine cation radicals have become apparent [1-6]. In the reactions of the cation radicals of diphenylamine and methyldiphenylamine, the neutral molecules merely change the equilibria of the consecutive electron transfer reactions after the rate determining dimerization reaction [1,2]. The neutral molecule of 1-aminopyrene promotes the reaction of cation radicals in the catalytic manner [3]. Nucleophilic attack of the neutral molecule is significant in some cases, as the case of the reactions of 4-bromo-*N,N*-dimethylaniline cation radical [4]. Stabilization of the triphenylamine cation radical was observed with the presence of a large excess of the neutral molecules [5]. In addition, the acid-base equilibrium between the *N,N*-dimethyl-*p*-toluidine cation radical and the neutral molecule can be a driving force of the reaction [6].

The investigations on the effect of the neutral molecules on the reactions of aromatic amine cation radicals are now in progress for the other systems, i.e., anisidine and methyl-substituted diphenylamine derivatives. Fig. 1 shows the changes in absorption spectra of anisidine derivative cation radicals.

In previous studies, we used tris(4-bromophenyl)amine (TBPA) as a substrate to form stable cation radicals, $M^{\bullet+}$, in Eq. 1. However, the use of tris(2,4-dibromophenyl)amine (TDBPA), which has further higher oxidation potential than TBPA, should be effective to form the cation radicals

Using $TDBPA^{\bullet+}$, the formation of anthracene derivative cation radicals in normal acetonitrile, i.e. with no additives such as acids, was examined. As a result, the observation of the absorption spectrum of anthracene cation radical has become possible using the ETSF method, in spite of the reaction with trace amount of water. Thus, with this approach, the reactivities of 1-methyl-, 2-methyl- and 9-methyl-anthracene cation radicals were compared. Consequently, while 1-methyl-anthracene cation radical was stable as shown in Fig. 2A, 2-methylanthracene was decreased as shown in Fig. 2B, which indicates that the cation radical is less stable than that of 9-methylanthracene. These details are now in investigation, and will be presented at the meeting.

- [1] M. Oyama, T. Higuchi and S. Okazaki, *Electrochem. Commun.*, 2000, **2**, 675.
- [2] M. Oyama, T. Higuchi and S. Okazaki, *J. Chem. Soc., Perkin 2*, 2001, 1287.
- [3] M. Oyama, T. Higuchi and S. Okazaki, *Electrochem. Commun.*, 2001, **3**, 363.
- [4] M. Oyama and T. Higuchi, *J. Electrochem. Soc.*, 2002, in press.
- [5] M. Oyama, T. Higuchi and S. Okazaki, *Electrochem. Solid-State Lett.*, in press.
- [6] M. Oyama, M. Goto and H. Park, *Electrochem. Commun.*, in press.

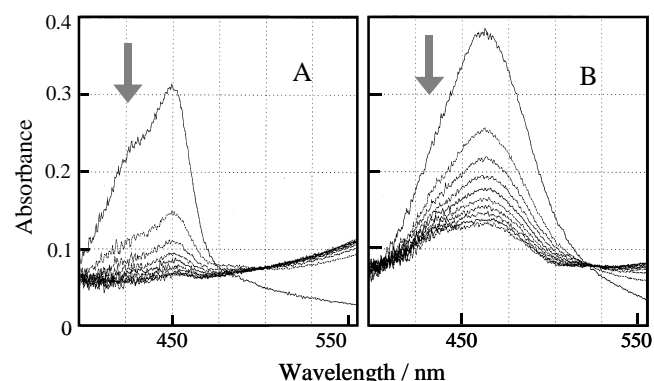


Fig.1. Changes in absorption spectra of the cation radicals of (A) anisidine and (B) *N*-methyl-anisidine, after generating through the electron transfer with $TBPA^{\bullet+}$. Time interval of the measurements was 1.0 s.

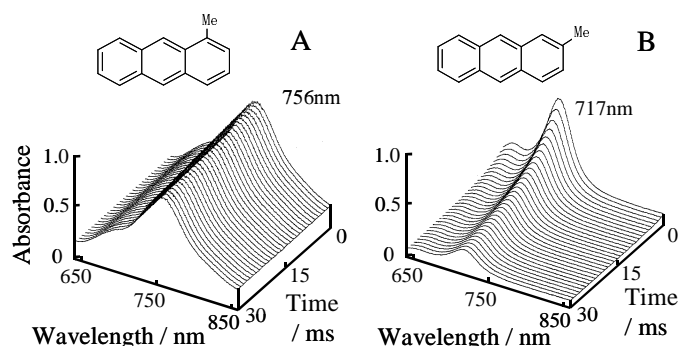


Fig.2. Changes in absorption spectra of (A) 1-methyl- and (B) 2-methyl-anthracene cation radicals, after generating through the electron transfer with $TDBPA^{\bullet+}$.