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Spectroscopic detection of short-lived anthracene derivative cation radicals using an electron transfer stopped-flow method with the tris(2,4-dibromophenyl)amine cation radical

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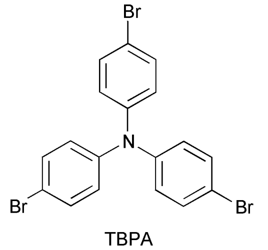
Dynamic transformation profiles of short-lived cation radicals of anthracene derivatives, including 1-methyl, 2-methyl and unsubstituted anthracenes, could be observed using an electron transfer stopped-flow method by adopting the tris(2,4-dibromophenyl)amine cation radical as a reaction initiator.

Because aromatic ion radicals tend to have absorption in the visible region, UV/vis absorption spectrochemical techniques have been applied to the detection of electrochemically generated ion radicals in aprotic solvents, *e.g.*, using optical transparent electrodes.[1] However, the possibility of successful detection depends on the stability of the target ion radicals electrogenerated in solution. If the life-time of the ion radical is a few milliseconds, it is easily expected that the amount of the radical formed on the electrode surface is insufficient for absorption measurements as a limitation in spectroelectrochemical measurements.

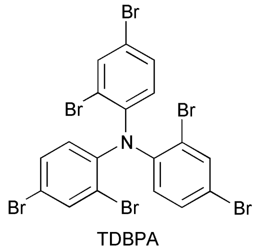
Nevertheless, the spectroscopic detection of short-lived aromatic amine cation radicals has become possible by utilizing the concept of an electron transfer stopped-flow (ETSF) method.[2] In this ETSF method, the spectroscopic detection is carried out by generating unstable cation radicals ($N^{\cdot+}$) *via* electron transfer with another long-lived cation radical ($M^{\cdot+}$) whose formal potential is positive to that of $N^{\cdot+}$, as expressed by eqn. (1)

$$N + M^{\cdot+} \rightarrow N^{\cdot+} + M \qquad (1)$$

Actually, by adopting the tris(4-bromophenyl)amine cation radical (TBPA$^{\cdot+}$) as $M^{\cdot+}$, the dimerization reactions of short-lived methyldiphenylamine and diphenylamine cation radicals could be analysed successfully using this ETSF method.[2,3]



TBPA



TDBPA

An insufficient point of the ETSF method with TBPA$^{\cdot+}$ is that the cation radicals that can be formed ($N^{\cdot+}$) are restricted by the oxidation potential of TBPA$^{\cdot+}$, 0.97 V *vs.* I_3^-,I^-. Due to this restriction, the cation radicals analysed in our previous work were aromatic amine cation radicals.[2–4] If the formal potential of the M/$M^{\cdot+}$ couple is more positive, the number of cation radicals the could be formed would be expanded significantly.

In the present communication, we therefore adopted the tris(2,4-dibromophenyl)amine (TDBPA) cation radical (TDBPA$^{\cdot+}$) as the reaction initiator, $M^{\cdot+}$, to form $N^{\cdot+}$.

It is known that the formal potential of TDBPA$^{\cdot+}$ is 0.44 V positive to that of TBPA$^{\cdot+}$,[5] which permitted us to spectroscopically detect anthracene derivative cation radicals in acetonitrile (AN). When there are no blocking groups on the 9- and 10-positions, anthracene derivative cation radicals are generally short-lived. For example, the anthracene cation radical is so short-lived that the detection was achieved using a fast scan cyclic voltammetry with a scan rate of over 1000 V s^{-1}.[6,7]

In the present paper, it is demonstrated that the measurement of absorption spectra of such short-lived cation radicals can be successfully carried out using the ETSF method with TDBPA$^{\cdot+}$. In addition, it is demonstrated that the reactivity of the anthracene derivative cation radicals toward water can be easily and explicitly compared.

The details of the ETSF method have been described previously.[2,3] As a substrate to form stable cation radicals [$M^{\cdot+}$ in eqn. (1)], tris(2,4-dibromophenyl)amine (TDBPA), which is known to form a very stable cation radical,[5] was used. TDBPA (95%) was synthesized by Wako Pure Chemicals Ltd. after receiving our special order. All the measurements were carried out in AN (Wako chemicals, dehydrated, H_2O < 50 ppm) as a solvent. The AN solutions of TDBPA$^{\cdot+}$ were prepared by a batchwise electrolysis with 0.05 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$, Fluka, puriss. electrochem. grade), and used after diluting to an appropriate concentration by AN. For other chemicals, reagents with as high a grade as possible were purchased mainly from Aldrich and Tokyo Kasei, and used as received.

For the stopped-flow measurements, a rapid-scan stopped-flow spectroscopic system, RSP-601 (Unisoku Co. Ltd., Hirakata, Japan) was used. In this apparatus, dynamic transformation of absorption spectra can be observed with a minimized time interval of 1.0 ms after mixing two solutions.

Fig. 1 shows the cyclic voltammogram (CV) of TDBPA together with those of anthracene, 9-methylanthracene and 9-bromoanthracene in AN recorded at a scan rate of 100 mV s^{-1}.

While the anthracene derivative cation radicals are too unstable to give any reduction waves in the reversed scans, the

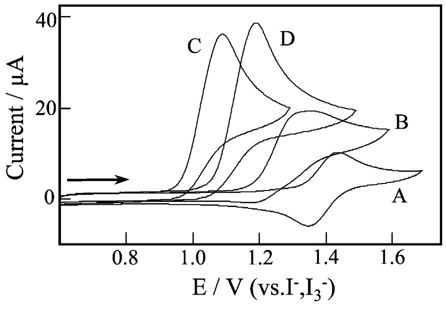


Fig. 1 Cyclic voltammograms of (A) TDBPA, (B) 9-bromoanthracene, (C) 9-methylanthracene and (D) anthracene in AN. Working electrode, Pt disk electrode (diam. 1.6 mm). Scan rate, 100 mV s^{-1}. Substrate concentration, 1.0 mM. Supporting electrolyte, TBAPF$_6$, 0.1 M.

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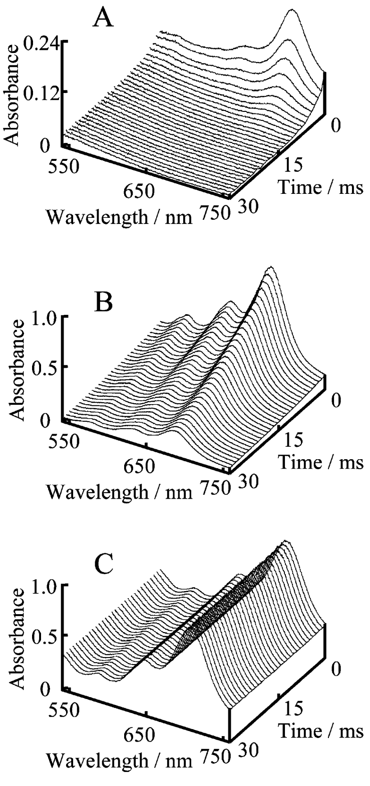

Fig. 2 Dynamic transformation profiles of absorption spectra of (A) anthracene, (B) 9-methylanthracene and (C) 9-bromoanthracene cation radicals measured after mixing of an AN solution of 0.20 mM $\text{TDPBA}^{\cdot+}$ with an AN solution of 0.20 mM neutral anthracene derivatives.

stability of $\text{TDBPA}^{\cdot+}$ in AN can be confirmed from the reversible CV of Fig. 1A. The formal potential of the $\text{TDBPA}^{\cdot+}$/TDBPA couple is 1.41 V *vs.* I_3^-,I^-, which is 0.44 V positive to that of the $\text{TBPA}^{\cdot+}$/TBPA couple.[5]

An AN solution of $\text{TDBPA}^{\cdot+}$ could be prepared by a batchwise electrolysis of TDBPA. The solution of $\text{TDBPA}^{\cdot+}$ had a green color and a broad absorption maximum around 850 nm. The molar absorptivity (ε) was determined by mixing the solutions of $\text{TDBPA}^{\cdot+}$ and TBPA. By observing the absorption spectrum of $\text{TBPA}^{\cdot+}$ obtained after mixing, the ε value of $\text{TDBPA}^{\cdot+}$ was determined to be 1.4×10^4 M^{-1} cm^{-1} at 850 nm from the value of $\text{TBPA}^{\cdot+}$, 3.2×10^4 M^{-1} cm^{-1} at 705 nm.[8]

Judging from the oxidation potentials in Fig.1, it is expected that the anthracene derivative cation radicals can be formed *via* electron transfer with $\text{TDBPA}^{\cdot+}$ using the ETSF method. Fig. 2 shows dynamic transformation profiles of absorption spectra actually obtained by mixing with an AN solution of 0.2 mM $\text{TDPBA}^{\cdot+}$. Even just after mixing, the absorption maximum of $\text{TDPBA}^{\cdot+}$ at 850 nm totally disappears, and the decrease of the absorption of anthracene derivative cation radicals[9] was clearly observed as in Fig. 2.

The decrease of the cation radicals can be attributed to the reaction with a trace amount of water (*ca.* 5 mM) in AN. Thus, the changes in reactivity toward the weak nucleophile, *i.e.* water, due to the substituents on the 9-position can be compared. The 9-methylanthracene cation radical is *ca.* 10 times less reactive than the anthracene cation radical, and the 9-bromoanthracene cation radical is fairly stable compared with the others. This order of reactivity is in agreement with the magnitude of the oxidation currents in Fig. 1, because the increase in the oxidation current is related to the progress of the consecutive reactions with water.

Fig. 3 shows the results for 1-methyl and 2-methylanthracene cation radicals, which are obtained using the same method. A remarkable difference in the rate of decrease can be observed between these two derivative cation radicals. It is of interest that the 2-methylanthracene cation radical is apparently more stable than the 9-methylanthracene cation radical (Fig. 1B). This implies the blocking effect of the reaction site is not a definite determining factor to stabilize the cation radical in these methyl derivatives.

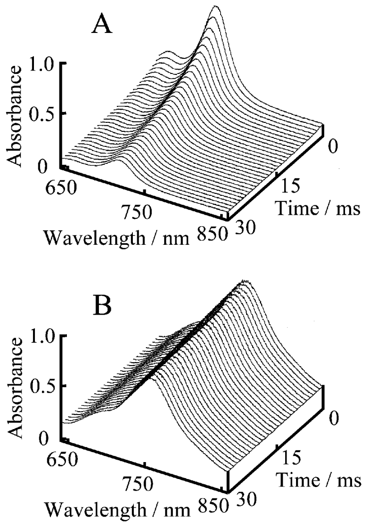

Fig. 3 Dynamic transformation profiles of absorption spectra of (A) 1-methylanthracene and (B) 2-methylanthracene cation radicals measured after mixing of an AN solution of 0.20 mM $\text{TDPBA}^{\cdot+}$ with an AN solution of 0.20 mM neutral anthracene derivatives.

While further studies are necessary to clarify the reactivity differences in detail, it is worthwhile stressing that spectroscopic detection and reactivity analysis of short-lived anthracene derivative cation radicals have become possible using the ETSF method with $\text{TDPBA}^{\cdot+}$. The present approach would be a useful method for evaluating the reactivities of short-lived cation radicals. This method is comparable to fast scan cyclic voltammetry at over 1000 V s^{-1}. Furthermore, it is advantageous that detailed kinetic analysis of the reaction processes should be possible by observing the absorption spectra in a homogeneous solution as in Figs. 2 and 3.

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