

Substituent Effect on the Cyclization Reactions of Diphenylamine Derivative Cation Radicals in Acetonitrile

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Reactions of aromatic amine cation radicals in aprotic solvents have been studied extensively, e.g. as summarized by Steckhan.¹ Because the oxidative potentials of aromatic amines are relatively negative due to the presence of N atom, electrochemical oxidation is suitable for the generation of the cation radicals, and the follow-up product analysis revealed the complex reaction processes.

Among such reactions of aromatic amine cation radicals, an interesting example of the changes in reaction pathways is the case of diphenylamine derivative cation radicals. For the reactions of 4-substituted-diphenylamine and 4,4'-disubstituted-diphenylamine cation radicals, the different reaction pathways were revealed, i.e., the formation of four different types of dimers having benzidine, dihydrodiphenylphenazine, *p*-phenylenediamine and hydrazine moieties, depending on the bases coexisted in acetonitrile solutions.

While such differences were revealed and identified on the basis of the product analysis in 1970s, kinetic analysis for short-lived aromatic amine cation radicals is now possible due to the methodological developments. Successful kinetic analysis could be performed using fast scan cyclic voltammetry with ultra-microelectrodes, and as a result reaction kinetics have become apparent for some diphenylamine derivative cation radicals.

On the other hand, as an alternative or complementary method for analysing the reaction kinetics of short-lived cation radicals, we are proposing an electron-transfer stopped-flow (ETSF) method, in which objective cation radicals were generated in the stopped-flow operation by mixing with stable cation radicals.²⁻⁶ Although this method is not an electrochemical method, we can analyse the reaction process of cation radicals, which can be usually generated using the electrochemical methods, in homogeneous solutions and under the rigid control of the concentration of precursor molecules. The detection ability of the ETSF method is comparable to the fast scan cyclic voltammetry with the scan rates over 1000 Vs⁻¹.⁵ Using the ETSF method, we observed the decay processes of some methyl-substituted diphenylamine cation radicals in acetonitrile. Consequently, following conclusions were obtained concerning the kinetics of the decay reaction of diphenylamine derivative cation radicals.

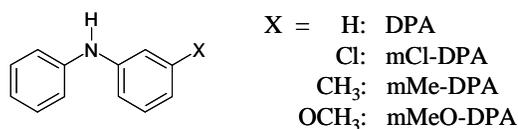
1) For the decay reaction of diphenylamine cation radicals (DPA^{•+}), the reaction rate is not affected by the presence of neutral molecules at all. The rate law was determined to be $-d[\text{DPA}^{\bullet+}]/dt = k [\text{DPA}^{\bullet+}]^2$, where the rate constant, *k*, is $1.0 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$.²

2) Compared with the result of DPA^{•+}, the reaction of 4-methyl-diphenylamine cation radical (pMe-DPA^{•+}) was somewhat complex. While the decay reaction is second order in [pMe-DPA^{•+}] in the absence of pMe-DPA, a slight increase in the decay rate of pMe-DPA^{•+} was observed in the presence of pMe-DPA together with a disappearance of the absorption of the oxidation products

of the benzidine dimer. This change was assigned due to the concurrent cyclization reaction promoted by pMe-DPA as a coexisting base.⁶ The similar behavior was observed in the case of 4,4'-dimethyl-diphenylamine cation radical.⁶

3) Compared with the 4-methyl derivatives, the decay reactions of 3-methyl-diphenylamine and 3,3'-ddimethyl-diphenylamine cation radicals were much faster due to the cyclization reaction. This means that 3-methyl substituent promotes the formation of the dimer having a dihydrodiphenylphenazine moiety, even though the benzidine formation seems to be favorable from the structure.⁶

In addition to the reactions of methyl-substituted DPA^{•+}s including 3-methyl-diphenylamine cation radical (mMe-DPA^{•+}), we observed the reactions of 3-chloro-diphenylamine cation radical (mCl-DPA^{•+}) and 3-methoxy-diphenylamine cation radical (mMeO-DPA^{•+}), whose structures are summarized as below.



Consequently, depending on the nature of the substituents on the 3-position of DPA^{•+}, the different routes of the reactions to form the dimer compounds, i.e., the cyclization or the benzidine dimer formation, were observed through the electrochemical and spectrochemical measurements. The details will be presented at the meeting.

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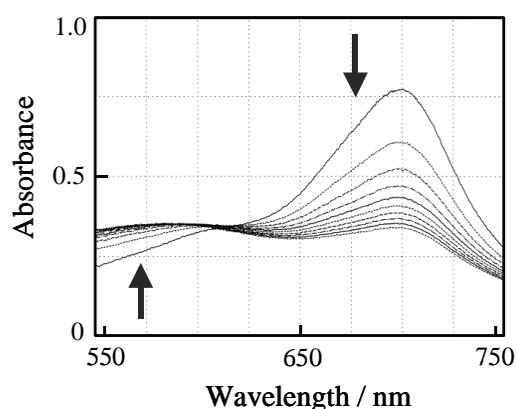


Figure 1. Time resolved absorption spectra recorded after the AN solution of mCl-DPA was mixed with the AN solution of 0.10 mM TBPA^{•+}. Concentration of mCl-DPA: 0.10 mM. Time interval of each spectrum; 10 ms.