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Intramolecular Association of Viologen Dimer and Trimer Radical Cations. An Electrochemical and Spectroscopic Study

Shin-ichiro IMABAYASHI, Noboru KITAMURA, Koichi TOKUDA,[†]
and Shigeo TAZUKE[*]
Research Laboratory of Resources Utilization, Tokyo Institute of
Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227
[†]The Graduate School at Nagatsuta, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227

Viologen dimer and trimer model compounds were prepared and their reduced forms(i.e., radical cation) were investigated electrochemically as well as spectroscopically. Intramolecular association between two viologen radical cations takes place efficiently, which brings about changes in the electrode reduction processes of these compounds.

N,N'-Dialkyl-4,4'-bipyridinium salts represented by methylviologen have been extensively investigated with particular reference to electron transfer sensitization, electrochemical display and so forth.[1,2] A peculiar feature of the cation radical produced by one electron reduction of viologen is the tendency of dimer formation. This phenomenon has been observed in polymeric systems in which viologen groups either constitute the polymer main chain or are bonded to the side group.[3] However, it is difficult to obtain quantitative information on electrochemical and spectroscopic properties of the cation radical from such systems containing statistically distributed many functional groups. From the view point of electrochemistry, electrode processes of mutually aggregating viologen groups are of great interest since the dimer formation will influence the reduction processes of polyviologens. In this report, we describe spectroscopic properties of viologen dimer and trimer cation radicals and show how the presence of the second and third viologen group influences the electrode processes.

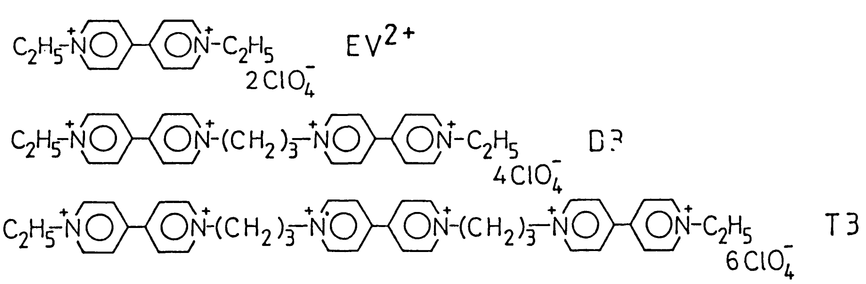

Fig.1. Structures and abbreviations of viologen derivatives.

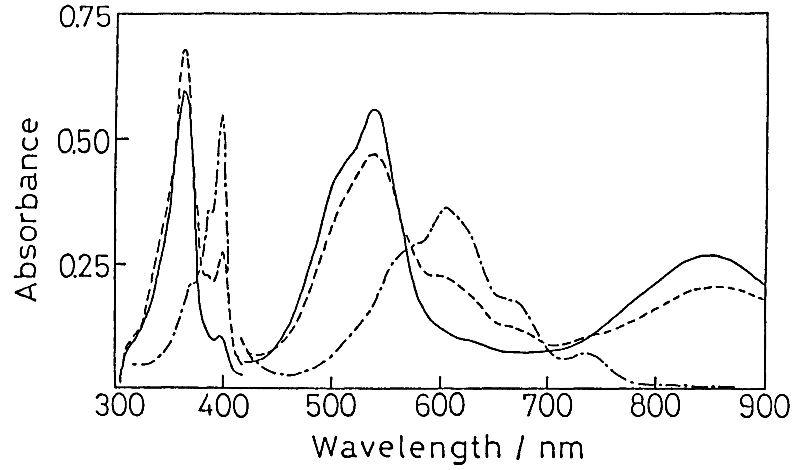

Fig.2. Absorption spectra of EV^{2+} (—·—·—), D3 (———), and T3 (-----) radical cations in DMF. $[EV^{2+}]=1.23\times10^{-3}M$, $[D3]=1.23\times10^{-3}M$, $[T3]=6.59\times10^{-4}M$

Structures and abbreviations of the viologen compounds are shown in Fig.1. Ethylviologen (EV^{2+}) and 1,3-bis(N-ethyl-4,4'-bipyridinium)propane (D3) were synthesized according to literature.4) Synthetic procedures to 1,1'-bis[3-(1'-ethyl-4,4'-bipyridinium)propyl]-4,4'-bipyridinium perchlorate (T3) will be described elsewhere.5) N,N-Dimethylformamide (DMF) was distilled twice over CaH_2 before use. Tetra-n-butyl-ammonium perchlorate (TBAP) as supporting electrolyte was recrystallized 3 times from ethylacetate - n-hexane. Absorption spectra of the viologen radical cations were obtained by thin layer electrochemical cell method.6) Reduction potentials were measured by differential pulse polarography. All experiments were carried out in degassed DMF containing 0.1 M TBAP at 25 °C.

Figure 2 shows the absorption spectra of the viologen radical cations produced by electrolysis at the half wave potential of each compound (vs. Ag wire). The absorption spectrum of ethylviologen radical cation (EV^{+}) has its maxima around 400 nm and 600 nm. The D3 radical cation shows quite different absorption peaking around 360 nm and 533 nm. The absorption spectrum of D3 cation radical agrees well with that of 1,3-bis(N-methyl-4,4'-bipyridinium)propane radical cation which has been assigned to the spectrum of associated viologen radical cations.3a) On the other hand, T3 radical cation has absorption around 600 nm in addition to the spectrum of D3 radical cation suggesting that the absorption is assigned to the superimposed spectrum of associated (533 nm) and unassociated (603 nm) viologen groups. For D3 and T3 radical cations, since the absorption spectra were independent of viologen concentrations, the association between viologen radical cations is concluded to be an intramolecular process.

The fraction of the associated viologen radical cations (F) can be estimated by the following relations. $\mathrm{Abs}_{533} = \varepsilon^{a}_{533}C^{a} + \varepsilon^{ua}_{533}C^{ua}$, $\mathrm{Abs}_{603} = \varepsilon^{a}_{603}C^{a} + \varepsilon^{ua}_{603}C^{ua}$, $F = 2C^{a}/(2C^{a} + C^{ua})$, where Abs_{533} and Abs_{603} are the absorbance of D3 or T3 radical cation at 533 nm and 603 nm, respectively. ε^{a}_{533}(ε^{a}_{603}) and ε^{ua}_{553} (ε^{ua}_{603}) are the molar extinction coefficients of D3 radical cation in water at 533 nm (603 nm) and of EV^{+} in DMF at 533 nm (603 nm), respectively. C^{a} and C^{ua} represent the concentrations of the associated and unassociated viologen radical cations, respectively. F is calculated to be 0.9 and 0.7 for D3 and T3, respectively, indicating that most of the radical cations from D3 and two-third of those from T3 are in associated form. The above figures indicate that two viologen radical cations linked by three methylene groups associate completely whereas an additional radical cations in T3 remains free.

The association between two viologen radical cations strongly influences the electrode processes of D3 and T3 as shown in Fig. 3. D3 exhibits a symmetrical polarogram with full width at half maximum (FWHM) of 56mV while that of T3 is unsymmetrical with FWHM of 52.4 mV. For D3 or T3, each viologen is reduced reversively from 2+ to 1+ so that the reduction processes consist of two (D3) or three (T3) consecutive one-electron transfer reactions, each has a formal potential of E_i (i=1,2,3). We estimated the E_i values from the differential pulse polarograms by curve fitting method proposed by Matsuda et al.[7)] as shown in Table 1. E_1, E_2, and E_3, however, include a symmetrical factor. Namely, in D3, the product of the first reduction has two possible forms, V^{2+}-V^{+} and V^{+}-V^{2+}, so that the first step of the reduction becomes entropically more favorable than the second one by a factor of ln2. As a consequence, the E_i values do not represent the microscopic formal potentials (e_1, e_2, and e_3) corresponding to the first, second, and third step of reducing D3 or T3, respectively. We calculated e_1, e_2, and e_3 by correcting the symmetrical factor on the E_i values as shown in Table 1 assuming that the interaction of viologen groups is equivalent.[8)] For D3 and T3, e_2 shifts towards positive as compared with e_1. This implies that the reduction of the second viologen group is much easier than that of the first one, so that simultaneous two-electron reduction takes place in D3 and T3. The large positive shift in e_2 for D3 and T3 is ascribable to the intramolecular association between two viologen radical cations. The exothermic dimer formation is certainly a favorable condition to introduce the second electron to D3 or T3.[5] On the other hand, the third reduction step of T3 is naturally independent from the effect of dimer formation so that e_3 is identical with e_1 for T3. The results obtained by electrochemical measurements are consistent with those derived by absorption spectroscopy (Fig. 2).

Further discussion on electrode processes of a series of viologen dimer and trimer model compounds will be presented elsewhere.

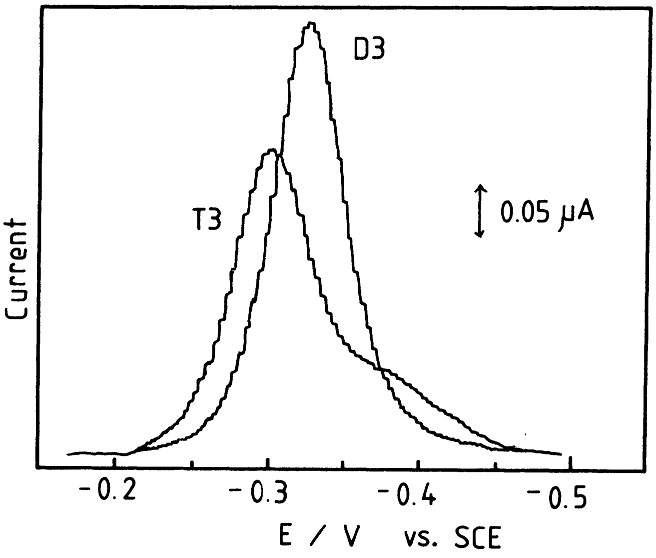

Fig.3. Differential pulse polarograms of D3 and T3 in DMF. [D3]=6.54×10^{-4}M, [T3]=4.47×10^{-4}M

Table 1. Formal potentials of D3 and T3 in DMF (V vs. SCE)

Formal potential[a)]	D3	T3
E_1	-0.336	-0.323
E_2	-0.315	-0.282
E_3	———	-0.368
e_1	-0.353	-0.351
e_2	-0.297	-0.271
e_3	———	-0.351

a) E_i and e_i are the formal potential and microscopic formal potential, respectively.

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