Absorption Spectra of the Cationic Radical Salt of 3,3′,5,5′-Tetramethylbenzidine in Acetonitrile

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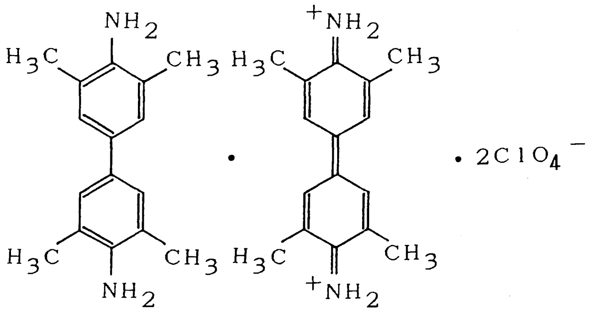
(Received February 2, 1990)

Synopsis. The absorption spectrum of 3,3′,5,5′-tetramethylbenzidine (TMB) perchlorate in acetonitrile strongly depends on both the temperature and concentration. Analyzing the absorption band around 660 nm, which corresponds to the charge transfer from TMB to $(TMB)^{2+}$, the equilibrium constant and the enthalpy change of the charge-transfer complex formation at 25 °C have been obtained as 1.9×10^4 mol^{-1} dm^3 and −66.2 kJ mol^{-1}, respectively.

The absorption spectra of radical salts from aromatic diamines in solution have long been investigated.[1-4] However, no studies have been carried out on the cationic radical salts from a less carcinogenic diamine, 3,3′,5,5′-tetramethylbenzidine (TMB) (TMB had been synthesized by Holland et al.[5]), except for the studies of Josephy et al. on enzyme-catalyzed oxidation of TMB[6,7] and the study of Watanabe et al. on electrolytic oxidation of TMB in aqueous solution.[8] We have obtained, by electrolytic oxidation, a very stable cationic radical salt: TMB perchlorate.[9] We have demonstrated that the salt should be a charge-transfer complex between $(TMB)^{2+}$ and TMB as follows:[10]



In this paper, the absorption spectra of the salt in acetonitrile are reported and the charge-transfer complex formation is discussed.

TMB perchlorate was prepared by a previously reported method.[9] A solution with a concentration of about 3×10^{-4} mol dm^{-3} was prepared followed by diluting the stock solution to the desired concentration just prior to use. The absorbance of the solution in acetonitrile was measured with a Shimadzu MPS-2000 spectrophotometer.

The temperature dependence of the absorption spectrum of TMB perchlorate (1.0×10^{-4} mol dm^{-3}) in acetonitrile is shown in Fig. 1. As the temperature is raised from 15 °C up to 60 °C, the absorption bands around 370 and 660 nm become weaker, whereas the bands around 450 and 800 nm become stronger. Based on the conception that TMB perchlorate is a salt of a charge-transfer complex between $(TMB)^{2+}$ and TMB,[10] it is suggested that the bands around 370 and 660 nm belong to the complex, whereas the bands around 450 and 800 nm belong to $(TMB)^{2+}$. The temperature dependence of the spectrum resembles that for the one-electron oxidation product of TMB generated by horseradish peroxidase in aqueous solution, which has been reported by Josephy et al.[6] They have stated that the complex is composed of the diamine (TMB) and its diimine, where two protons have been dissociated from $(TMB)^{2+}$. We believe, however, that the complex in acetonitrile is composed of TMB and $(TMB)^{2+}$, where no proton is dissociated, since the solvent is not protic.

The apparent molar absorption coefficient, which is defined as the absorbance of the solution divided by the total concentration, becomes smaller at 370 and 660 nm, as the solution is diluted. The dependence of the apparent molar absorption coefficient at 660 nm, $\varepsilon^{660\,\mathrm{nm}}$, on the total concentration of TMB perchlorate, C, is shown in Fig. 2.

Analysis of the concentration dependence can give the equilibrium constant of complex formation, K. In our system, four species are in equilibrium as follows:

$$\mathrm{TMB} + (\mathrm{TMB})^{2+} \rightleftarrows \text{complex} \rightleftarrows 2(\mathrm{TMB})^{+\cdot}. \qquad (1)$$

Let us assume that the second equilibrium in Eq. 1 is negligible. This assumption is reasonable since the reaction in which the complex is formed from the cationic radical $(TMB)^{+\cdot}$ is very slow and, thus, the complex cannot be formed without $(TMB)^{2+}$.[10] K is defined as

$$K = [\text{complex}]/[\mathrm{TMB}][(\mathrm{TMB})^{2+}]. \qquad (2)$$

We introduce the degree of dissociation, α, which is defined as

$$\alpha = \{[\mathrm{TMB}] + [(\mathrm{TMB})^{2+}]\}/C. \qquad (3)$$

From Eqs. 2 and 3 and the relation $[TMB]=[(TMB)^{2+}]$, we obtain

$$1 - \alpha = \{1 + KC - (1 + 2KC)^{1/2}\}/KC. \qquad (4)$$

It we let ε_c be the intrisic molar absorption coefficient of the complex (TMB monomer based quantity) and ε_u be the molar absorption coefficient of the uncomplexed species, we can then write

$$\varepsilon = (1 - \alpha)\varepsilon_c + \alpha\varepsilon_u. \qquad (5)$$

We can thus obtain K, ε_c, and ε_u by a curve-fitting

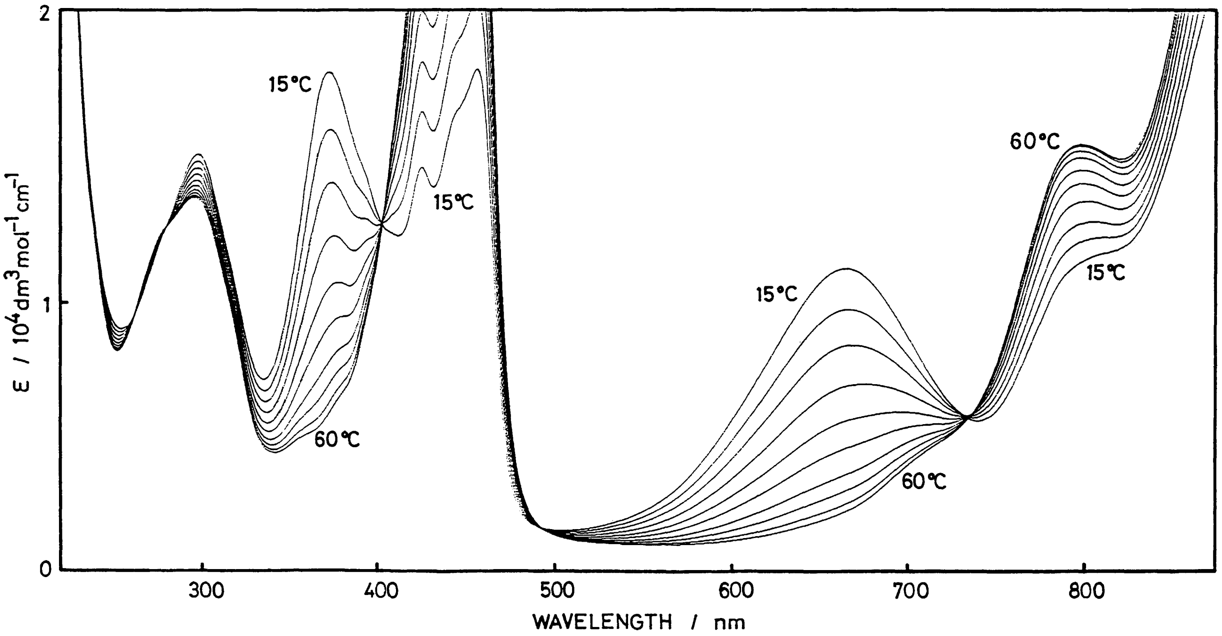


Fig. 1. Temperature dependence of the absorption spectrum of TMB perchlorate in acetonitrile. Concentration: 1.0×10^{-4} mol dm^{-3}. Temperature: 15, 20, 25, 30, 35, 40, 45, 50, 55, 60 °C.

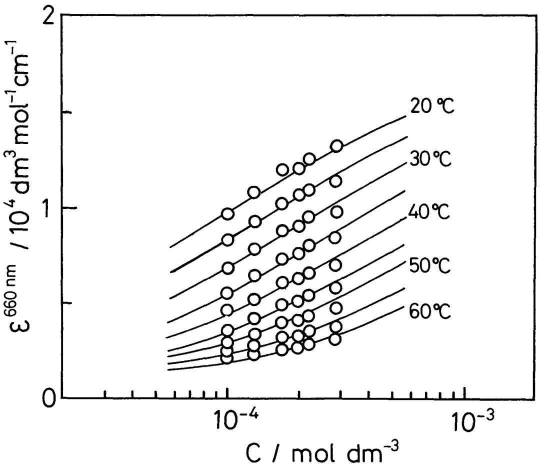


Fig. 2. The dependence of the apparent molar absorption coefficient at 660 nm on the total concentration of TMB perchlorate C from 20 to 60 °C. Open circle: observed value. Solid curve: calculated from Eq. 5.

method. The solid curves in Fig. 2 were obtained thereby. The obtained value for K at 25 °C is 1.9×10^4 dm^3 mol^{-1} and those for ε_c and ε_u at 660 nm are 2.0×10^4 dm^3 mol^{-1} cm^{-1} and 0.1×10^4 dm^3 mol^{-1} cm^{-1}, respectively. Josephy et al.[6] have reported the molar absorption coefficient of the complex in aqueous solution to be 2.0×10^4 dm^3 mol^{-1} (TMB monomer based) at 652 nm. Fortunately, our result in the present work agrees well with this value.

From the temperature dependence of K, shown in Fig. 3, the enthalpy change of complex formation has been estimated as −66.2 kJ mol^{-1}. This value is larger than the value for dimerization of the tetracyanoquinodimethan anion radical, −44 kJ mol^{-1}, which was reported by Boyd and Phillips.[11]

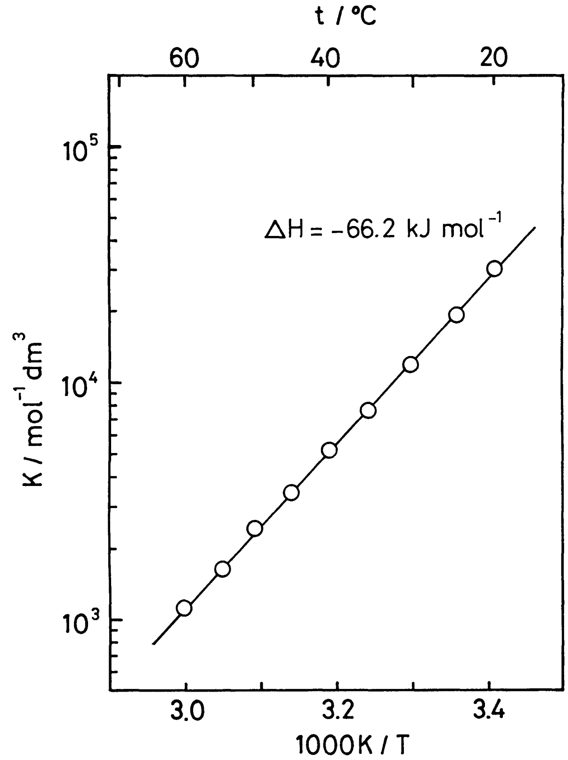


Fig. 3. The temperature dependence of the equilibrium constant K of complex formation for TMB perchlorate.

The absorption spectrum of the cationic radical salt of *N,N,N′,N′*-tetramethylbenzidine (N-TMB) electrochemically synthesized[10)] has been obtained at room temperature. The spectrum has the same shape as the spectrum of the radical in ethanol reported by Takemoto et al.[3)] The spectrum of the N-TMB radical has no absorption bands in the region 500—700 nm. This fact suggests that the charge-transfer force is too weak to analyze complex formation. The reason why the TMB radical makes a stable complex is that the potential difference between the first and second oxidation steps is greater for TMB than for N-TMB by 0.04 V.[10)] In addition, it should be noted that, in the salt of TMB, hydrogen bonding can exist and proton transfer can occur from amino groups to iminium groups, whereas they are impossible in the salt of N-TMB.

More extensive research is now in progress.

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 01604512 from the Ministry of Culture, Science and Education.

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