The Rate Constant of Dimer Cation Formation of Triphenylamine and Substituent Effects

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The pulse radiolysis studies of triphenylamine and methyl substituted triphenylamines in 1,2-dichloroethane have indicated that the dimer cation formation is the main process and coupling at the *para* sites is predominant. The spectrum of transient dimer cations with λ_{max} at 400 and 850 nm, and the dimerization rate constant of k = 1.3 x 10^8 dm^3 mol^{-1} s^{-1} were obtained.

The reactions of cation radicals of triphenylamine (TPA) and substituted triphenylamines were studied extensively by means of chemical[1-3] and electrochemical[4-10] oxidation methods. In the electrochemical oxidation of TPA in acetonitrile solutions, the over-all reaction scheme is suggested as follows.

$$\mathrm{TPA} \longrightarrow \mathrm{TPA}^{+\cdot} + e^- \qquad (1)$$

$$2\mathrm{TPA}^{+\cdot} \longrightarrow \mathrm{TPB} + 2\mathrm{H}^+ \qquad (2)$$

$$\mathrm{TPB} \longrightarrow \mathrm{TPB}^{+\cdot} + e^- \qquad (3)$$

$$\mathrm{TPB}^{+\cdot} \longrightarrow \mathrm{TPB}^{2+} + e^- \qquad (4)$$

It has been proposed that the initially formed TPA cation radicals couple exclusively, then dimerization of the cation radical is followed by rapid deprotonation yielding tetraphenylbenzidine (TPB). In the case of substituted TPA, generation of the corresponding benzidines was verified by electrochemical and spectroscopic methods, as well as by chemical isolation.[4,5,8] The second order coupling rate constants were evaluated to be 1.1 x 10^3-3 x 10^3 dm^3 mol^{-1} s^{-1} for TPA.[3,5-10] However, direct observation of dimerization and deprotonation process was not reported due to the limited time resolution of electrochemical methods. On the other hand, time resolved pulse radiolysis studies of TPA the subsequent reactions of TPA cation radicals were not reported so far.[11-13] The direct kinetic studies of TPA cation radicals using the pulse radiolysis technique are reported in this paper.

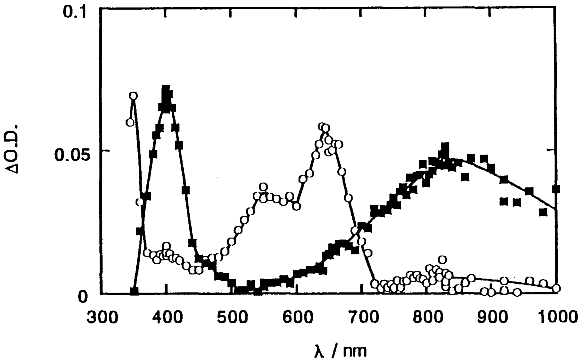

Figure 1. Transient absorption spectra of 1.03 x 10^{-3} mol dm^{-3} triphenylamine in 1,2-dichloroethane obtained immediately (○) and 40μs (■) after pulse radiolysis.

Figure 1 shows the transient absorption spectra obtained immediately and 40 μs after irradiation of deaerated TPA (1.03 x 10^{-3} mol dm^{-3}) in 1,2-dichloroethane with a 10 ns, 45 MeV electron pulse at room temperature.[14] The absorption maxima at 350, 550, and 650 nm are characteristic bands of triphenylamine cation radical.[15] After 40 μs, these bands disappeared and the new bands at 400 and 850 nm were formed. These bands are due to neither TPB nor a TPB radical cation which has the absorption maximum at 480 nm. The apparent first order decay rate constants at 350 and 550 nm and the grow-in rate constants at 400 nm and 820 nm were in good consistent. The apparent first order rate constants depended on the TPA concentrations but not on absorbed doses. These results evidenced the reaction of the TPA cation radical with the parent molecule (reaction 5).

$$\mathrm{TPA}^{+\cdot} + \mathrm{TPA} \longrightarrow (\mathrm{TPA})_2^{+\cdot} \qquad (5)$$

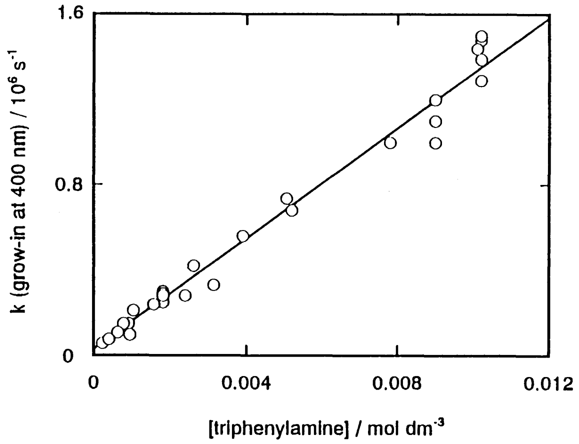

Figure 2. Apparent first order rate constants of the formation of the absorption at 400 nm as a function of the triphenylamine concentration.

Figure 2 shows concentration dependence of the grow-in rate constant at 400 nm. From the slope of the straight line the dimer cation formation rate constant was obtained as k_5 = 1.3 x 10^8 dm^3 mol^{-1} s^{-1}. This value is *ca.* 10^5 times larger than that of coupling of TPA cation radicals (reaction 2) reported previously.

The coupling position was investigated by blocking with methyl groups at *ortho*, *meta*, and *para* positions.[16] Figure 3 shows effects of *para*-substitution on the decay rates of parent cation radicals observed at 550 nm (a) and the grow-in rates of the dimer cation at 400 nm (b). Rate constants of dimerization were estimated in similar way for TPA and given in Table 1. Substitution by methy groups caused considerable decrease of the dimerization rate constant. The marked decrease in the grow-in rate constants was observed for *para*-substituted triphenylamines as the number of methyl groups increased, especially a negligible value was obtained in the case of tri-*p*-tolylamine. On the contrary, in the cases of the *ortho* and *meta* substitution the increase of blocked positions did not have any effect on the dimerization rate constants.

In the present pulse radiolysis studies the spectrum of triphenylamine dimer cations was reported for the first time, and the *para-para* coupling between the TPA cation radical and the parent TPA was found to be the predominant process which leads to formation of the triphenylamine dimer cation.

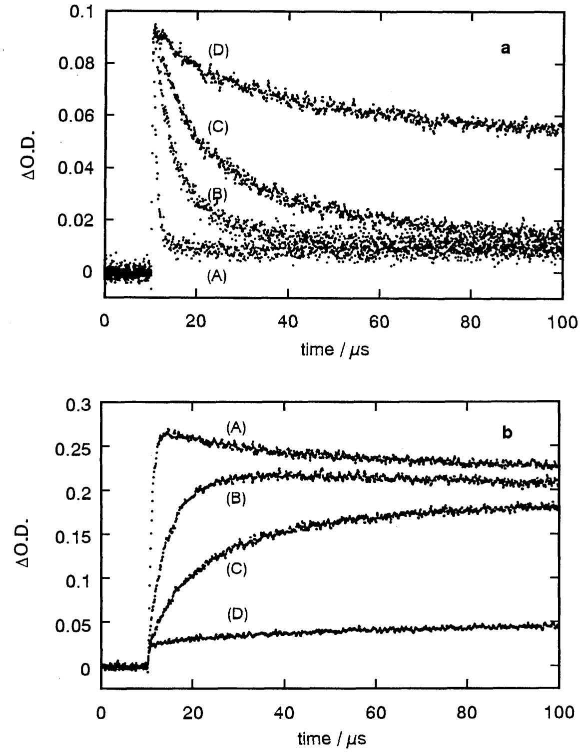

Figure 3. Pulse radiolysis of 1.0 x 10^{-2} mol dm^{-3} triphenylamines in 1,2-dichloroethane. a) Decay kinetic traces of *para*-methylsubstituted triphenylamine cation radicals at 550 nm. b) Grow-in kinetic traces of the dimer cation at 400 nm.
(A): triphenylamine, (B): 4-methyltriphenylamine, (C): 4,4'-dimethyltriphenylamine, (D): tri-*p*-tolylamine.

Table 1. Rate constants of dimer cation formation of substituted triphenylamines in 1,2-dichloroethane

Substrate	k / 10^7 dm^3 mol^{-1} s^{-1}
triphenylamine	13.0
2-methyltriphenylamine	2.7
2,2'-dimethyltriphenylamine	2.3
tri-*o*-tolylamine	2.1
3-methyltriphenylamine	4.7
3,3'-dimethyltriphenylamine	7.7
tri-*m*-tolylamine	3.2
4-methyltriphenylamine	2.2
4,4'-dimethyltriphenylamine	0.63
tri-*p*-tolylamine	—[a]

[a] Difficult to measure owing to a very small change of absorption.

References and Notes

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