# A Fast Kinetic Study of the Formation and Decay of N, N, N', N'-Tetramethyl-*p*-phenylenediamine Radical Cation in Aqueous Solution

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The oxidation of N, N, N', N'-tetramethyl-*p*-phenylenediamine (TMPD) by  $S_2O_8^{-}$ , HSO<sub>5</sub>,  $H_2O_2$ , MnO<sub>4</sub>,  $Cr_2O_7^{-}$ ,  $Ce^{IV}$  and molecular bromine and iodine has been studied. The fast kinetics of formation of the diamine radical cation and its further oxidation at a longer time scale, or with a higher concentration of the oxidants at a shorter time scale, were studied by following the absorption and decay of the radical cation, TMPD'<sup>+</sup> at 565 or 615 nm. The reaction was found to be second-order overall, but first-order with respect to [TMPD] and [oxidant]. The values of the second-order rate constants for the formation and decay of the radical cation were found to be in line with the oxidation potentials of the oxidants. Reduction of the radical cation by dithionite was found to regenerate the diamine, and the rate constant for this reaction was also determined.

Oxidation of aromatic amines in solution<sup>1, 2</sup> has been studied by anodic electrochemistry in conjunction with absorption spectrophotometry and e.s.r. to identify the intermediates produced in these organic redox systems. The ease of removal of electrons from the amino function makes it possible to use these amino compounds as sacrificial systems in solar energy conversion.<sup>3</sup> Oxidation of N, N, N', N'-tetramethyl-*p*-phenylenediamine (TMPD) by dioxygen catalysed by Cu<sup>2+</sup> complexes<sup>4</sup> and by singlet oxygen<sup>5</sup> was also reported. The one-electron oxidation products of aromatic p-diamines or Würster's salts<sup>6</sup> are free radicals which may polymerise in a sufficiently concentrated solution and at a low temperature or in the solid state.<sup>7</sup> The photochemistry and radiation chemistry of TMPD centre round the formation of diamine radical cation by direct photolysis<sup>8</sup> and by the reaction with radiolytically generated OH radical.<sup>9</sup> TMPD is quite often used as a one-electron reducing agent with the transient intermediates formed in the reaction of OH with biologically important compounds.<sup>10</sup> The diamine radical cation TMPD<sup>+</sup> formed is stable for more than seven days.<sup>11</sup> At higher concentration of the oxidant, the radical cation is further oxidised, again by one-electron transfer, followed by a hydrolytic cleavage to form benzoquinone and the respective amine.<sup>12</sup> In the present investigation we report the thermal study of one-electron and two-electron oxidation of TMPD by peroxosalts of sulphur, namely peroxomonosulphate (PMS) and peroxodisulphate (PDS),  $H_2O_2$ ,  $MnO_4^-$ ,  $Cr_2O_2^{2-}$ ,  $Ce^{IV}$  and molecular bromine and iodine. The radical cation TMPD<sup>+</sup> is back-reduced to the parent compound by the reaction with dithionite, the rate constant of which has also been measured.

### Experimental

All kinetic measurements were made with the Applied Photophysics 1705 stopped-flow spectrophotometer. Absorption output was digitised with a Datalab 680 transient recorder equipped with a variable input sensitivity and variable sampling interval, and

was monitored by a Trio CS-1562A oscilloscope. Ca. 500-700 data points were collected for each kinetic determination. At least six kinetic determinations were made for each quoted value of  $k_{obs}$ . The data were stored and analysed by a CBM-3032 personal computer. The kinetic plots were plotted on a Hewlett-Packard 7470 graphics plotter. All the measurements were taken at room temperature (25 °C). Doubly distilled water was used to prepare all the reagent solutions. All chemicals used were the best research grade commercially available. TMPD was from Fluka and potassium peroxomonosulphate (PMS) in the form of a triple salt  $(2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4)$  with the trade name Oxone was from Dupont de Nemours & Co., (U.S.A.). Other chemicals such as potassium peroxodisulphate (PDS), KMnO<sub>4</sub>,  $K_2Cr_2O_7$ , Ce (NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> (30%), Br<sub>2</sub> and I<sub>2</sub> were purchased from Sarabhai M. Chemicals and Glaxo Fine Chemicals. Since atmospheric oxygen was found to oxidise TMPD, though at a slower rate than when assisted by stray light,<sup>8</sup> the reaction solution was thoroughly degassed by purified nitrogen and protected from light. The reservoir and the reactant syringes of the stopped-flow apparatus were covered with black cloth. The extent of formation of the diamine radical cation and its decay were monitored at 565 or 615 nm, which correspond to absorbance maxima<sup>11</sup> ( $\varepsilon_{565} = 12500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ;  $\varepsilon_{615} = 12100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ , see fig. 1).

### **Results and Discussion**

The kinetics of oxidation of TMPD by the oxidants mentioned above were carried out under pseudo-first-order conditions.  $[TMPD] = (0.20-1.00) \times 10^{-4} \text{ mol dm}^{-3};$  $[oxidant] = (0.20-5.00) \times 10^{-3} \text{ mol dm}^{-3}$ . The change in concentration of the transient with time was followed in the time scale sampling interval of 0.2–10 ms for the formation of TMPD'+, and in the time scale of 0.5–50 ms for its decay. The plots of  $\ln (A_t - A_\infty)$ against time (where  $A_t$  = absorption at the time t and  $A_\infty$  = absorption at the end of the reaction) were found to be linear up to 50–80% of the reaction (correlation coefficient  $\ge 0.99$ ). The linearity of the assumed first-order relationship establishes that the rate of the reaction is first order with respect to [TMPD] for formation of TMPD'+ and first-order with respect to [TMPD'+] for the decay. The rate of formation or decay of TMPD'+ was also found to be first-order dependent on [oxidant]. The overall second-order rate constants calculated are tabulated (table 1). At high oxidant concentrations and at longer sampling intervals, the product was identified by analysis to be benzoquinone.<sup>13</sup>

For the formation of TMPD<sup>+</sup> the rate law is

$$\frac{\mathrm{d}\left[\mathrm{TMPD}^{\cdot+}\right]}{\mathrm{d}t} = k_{\mathrm{f}}'[\mathrm{TMPD}]$$

where  $k'_{\rm f}$  is the pseudo-first-order rate constant. The second-order formation constant was calculated using the relation

$$k_{2f} = \frac{k_f}{[\text{oxidant}]}.$$

A similar rate law is proposed for the decay process:

$$-\frac{\mathrm{d}\left[\mathrm{TMPD}^{\cdot+}\right]}{\mathrm{d}t} = k'_{\mathrm{d}}[\mathrm{TMPD}^{\cdot+}]$$

where  $k'_{d}$  is the pseudo-first-order decay constant from which the second-order decay constant was calculated using the relation

$$k_{2d} = \frac{k'_d}{[\text{oxidant}]}.$$



Fig. 1. Molar absorption spectrum of TMPD'+.

Table 1. Kinetic data for the formation and decay of TMPD<sup>+</sup> at 25 °C

oxidant	$k_{2\rm f}/{ m dm^3~mol^{-1}~s^{-1}}$	$K_{\rm 2d}/{\rm dm^3\ mol^{-1}\ s^{-1}}$
KMnO₄	$8.60 \times 10^{5}$	$7.18 \times 10^{4}$
Br <sub>2</sub>	$3.40 \times 10^{3}$	$3.70 \times 10^{2}$
PDS	$3.03 \times 10^{3}$	$2.04 \times 10^{2}$
$Ce^{IV}/0.2 \text{ mol } dm^{-3} H_3SO_4$	$1.06 \times 10^{3}$	$1.41 \times 10^{2}$
PMS	$2.80 \times 10^{2}$	3.00
$K_{2}Cr_{2}O_{7}/0.2 \text{ mol } dm^{-3} H_{2}SO_{4}$	3.40	0.55
H <sub>2</sub> O <sub>2</sub>	1.20	0.11

The peroxo compounds, namely peroxomonosulphate (PMS) and peroxodisulphate (PDS), are electron accepting in nature and though they are two-electron oxidants, they behave like a one-electron oxidant. Many reports have appeared concerning the oxidation of organic substrates with these oxidants.<sup>14, 15</sup> They are found to oxidise TMPD to TMPD<sup>+</sup> by one-electron transfer and then further oxidise TMPD<sup>+</sup> to benzoquinone. Comparing the second-order rate constants for the formation of TMPD<sup>+</sup> by PDS and PMS (table 1), it is seen that the rate constant ( $k_{zf}$ ) for PDS is found to be *ca*. one order of magnitude higher than that for PMS. The relative magnitude of the rate constants ( $k_{zd}$ ) of oxidation of TMPD<sup>+</sup> by PDS and PMS is more pronounced than that for the oxidation of TMPD<sup>+</sup> by these oxidants. The oxidation of the radical cation

by PDS occurs more than fifty times faster than that by PMS. In the case of  $H_2O_2$ , the rate constants for the formation of TMPD<sup>+</sup> and its decay are found to be smaller than those of both PDS and PMS. The reactivity trend observed,  $S_2O_8^{2-} > HSO_5^- > H_2O_2$ , is in good agreement with the oxidation potentials of these peroxides.

With the other oxidants it is observed, from the second-order rate constants both for the formation and decay of TMPD<sup>++</sup>, that the rate constants for the decay of TMPD<sup>++</sup> are at least 5–20 times less than the formation rate constants and conform to the following descending reactivity trend:

$$KMnO_4 > Br_2 > PDS > Ce^{1V} > PMS > K_2Cr_2O_2 > H_2O_2$$

The reaction of  $I_2$  with TMPD differs very much from the reactions of the other oxidants. There is a very fast rise in the signal at 565 nm as well as 615 nm (even at the 2 ms time scale and the lowest concentration of  $I_2 = 5.00 \times 10^{-5}$  mol dm<sup>-3</sup>) and the signal intensity remained the same when the concentration of  $I_2$  was equal to that of TMPD. There was no decay of the transient even at the highest concentration of  $I_2$  (2.00 × 10<sup>-3</sup> mol dm<sup>-3</sup>). The observed transient may be a charge-transfer complex between TMPD and  $I_2$ , and not the product of a complete electron-transfer reaction. Iodine is well known to form such charge-transfer complexes.<sup>16, 17</sup> The calculated rate constant for such a process in the present investigation is found to be  $6.28 \times 10^5$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, which is *ca*. two orders of magnitude higher than that for the reaction between TMPD and Br<sub>2</sub>.

The kinetic experiments indicated that the reaction proceeds *via* stepwise one-electron transfer forming TMPD<sup>+</sup> and then quinone. The following mechanism is proposed for the formation and decay of TMPD<sup>+</sup>:

$$(CH_{3})_{2} N \xrightarrow{-e^{-}} N (CH_{3})_{2} + oxidant \xrightarrow{-e^{-}} \left[ (CH_{3})_{2} N \xrightarrow{-(CH_{3})_{2}} N (CH_{3})_{2} \right]^{++}$$

$$\left[ (CH_{3})_{2} N \xrightarrow{-(CH_{3})_{2}} N (CH_{3})_{2} \right]^{++} oxidant \xrightarrow{-e^{-}} H_{2}O \xrightarrow{O} + 2NH (CH_{3})_{2}.$$

The reduction of the TMPD<sup>+</sup> was facilitated by dithionite ion and this separate reaction was monitoried by following the disappearance of TMPD<sup>+</sup> at 565 nm:





The dithionite reduction regenerated TMPD from TMPD<sup>+</sup> alone and not from the product after the two-electron transfer, *i.e.* benzoquinone. The second-order rate constant determined for the above process is  $8.30 \times 10^3$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>.

## Conclusions

Even with the strong oxidants (PDS, PMS and Ce<sup>IV</sup>) at low concentrations, TMPD<sup>+</sup> has a long lifetime (in terms of seconds). The reduction of TMPD<sup>+</sup> by dithionite reveals the reversibility of the reaction TMPD<sup>+</sup>  $\rightleftharpoons$  TMPD as long as TMPD<sup>+</sup> is not oxidised further.

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### References

- 1 R. N. Adams, Acc. Chem. Res., 1969, 2, 175.
- 2 Organic Electrochemistry, ed. M. M. Baizer (Marcel Dekker, New York, 1973).
- 3 A. P. Kohl and A. J. Bard, J. Electrochem. Soc., 1979, 126, 603; T. Ohno, S. Kato, A. Yamada and T. Tanne, J. Phys. Chem., 1983, 87, 775.
- 4 N. Oishi, Y. Nishida and S. Kida, Chem. Lett., 1981, 1031; Inorg. Chim. Acta, 1983, 75, 169.
- 5 E. L. Morning and C. S. Foote, J. Phys. Chem., 1982, 86, 1257.
- 6 R. Willstatter and J. Piccard, Ber., 1908, 41, 1458; L. Michaelis and E. S. Hill, J. Am. Chem. Soc., 1933, 55, 1487.
- 7 J. Piccard, Annalen, 1911, 381, 351; Ber., 1926, 59, 1438.
- 8 G. N. Lewis and D. Lipkin, J. Am. Chem. Soc., 1942, 64, 2801. R. L. Hand and F. Nelson, J. Am. Chem. Soc., 1974, 96, 850; K. Lee and S. Lipsky, J. Phys. Chem., 1984, 88, 4251.
- 9 D. W. Skelly and W. H. Hamill, J. Phys. Chem., 1966, 70, 1636; P. S. Rao and E. Hayon, J. Phys. Chem., 1975, 79, 1063.
- 10 S. Fujita and S. Steenken, J. Am. Chem. Soc., 1981, 103, 2540; D. K. Hazra and S. Steenken, J. Am. Chem. Soc., 1983, 105, 4380.
- 11 L. Michaelis, M. P. Schubert and S. Granick, J. Am. Chem. Soc., 1939, 61, 1981.
- 12 D. W. Leedy, Ph.D. Thesis (Kansas University, 1968).
- 13 A. I. Vogel, A Text Book of Practical Organic Chemistry (Lowe and Braydone, London, 1968), p. 745.
- 14 T. Pandurengan and P. Maruthamuthu, Bull. Chem. Soc. Jpn, 1981, 54, 3551; R. Renganathan, Ph.D. Thesis (University of Madras, 1984).
- 15 D. A. House, Chem. Rev., 1962, 62, 185; W. K. Willmarth and A. Haim in Peroxide Reaction Mechanisms, ed. J. O. Edwards (Interscience, New York, 1962), p. 175.
- 16 R. J. Cvetanovic, F. J. Duncan, W. E. Falconer and W. A. Sunder, J. Am. Chem. Soc., 1966, 88, 1602.
- 17 R. Foster, Organic Charge-transfer Complexes (Academic Press, New York, 1969).

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