Chemistry of Singlet Oxygen. 37. One-Electron Oxidation of Tetramethylphenylenediamine by Singlet Oxygen[†]

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Tetramethylphenylenediamine (TMPD) undergoes a one-electron transfer to ${}^{1}O_{2}$ in H₂O; the formation of TMPD⁺· (Würsters blue) is detected by laser flash spectroscopy. The formation of TMPD⁺· is competitively quenched by known ${}^{1}O_{2}$ quenchers. Furthermore, there is a large increase in TMPD⁺ formation in D₂O, relative to H₂O, as would be anticipated for a ${}^{1}O_{2}$ reaction. The rate (k_{r}) of electron transfer to ${}^{1}O_{2}$ is shown to be (3.3) \pm 1.5) \times 10⁹ M⁻¹ s⁻¹, close to the diffusion-controlled limit. The formation of observable ions does not take place in any solvent other than $H_2O(D_2O)$, or with any other of the electron-rich aromatic amines studied. It is suggested that the formation of observable radical ions depends on the ease of ionization of the substrate and on the solvation of the resulting ions.

Electron-transfer-initiated photooxygenations have been of interest to our group and others for some time.^{1,2} We have noted both similarities¹ and differences^{3,4} between the electron-transfer-initiated and ${}^{1}O_{2}$ reactions. The possibility of direct electron transfer from substrate to ${}^{1}O_{2}$, yielding substrate radical cation and superoxide, was first suggested by Mazur and Foote.^{5,6} However, direct evidence for the formation of either substrate radical cation or O_2^- in these reactions has been lacking. Recently, indirect chemical evidence for the formation of O_2^{-} (~1%) in the reaction between ${}^{1}O_{2}$ and N,N-dimethyl-p-anisidine in aqueous media has been reported.⁷ It has also been suggested that some electron transfer occurs between NADH and ${}^{1}O_{2}$, the O_{2}^{-} formation being detected by monitoring benzoquinone reduction in a laser flash experiment.⁸ Direct observation of either superoxide or the concomitant cation from these reactions has not been reported.

We now report direct evidence that one of the major modes of interaction between ¹O₂ and tetramethylphenylenediamine (TMPD) in aqueous medium is electron transfer, yielding TMPD⁺ (Würster's blue), as shown by laser flash photolysis.9,10 The frequency-doubled 530-nm beam of a Nd:YAG laser was used to excite erythrosine $(4 \times 10^{-5} \text{ M})$ with $1 \times 10^{-4} \text{ M}$ TMPD in O₂-saturated (1 atm) water. The species thus formed is long-lived, showing no decay after 50 μ s. The absorption spectrum measured 15 μ s after the flash is shown in Figure 1, along with a spectrum of TMPD⁺. The spectra match very well, confirming that the species is TMPD⁺.

If we exclude contributions from dye-dye interactions,^{11,12} there are four major pathways which could lead to TMPD+ formation (Scheme I). TMPD exhibits a weak absorption at 530 nm, $\epsilon = 313$,¹³ and path A (direct ejection of an electron) is a known reaction for electron-rich aromatic compounds.¹⁴ Path A can be excluded here because a solution photolyzed without erythrosine gave no evidence of TMPD⁺ formation. Path B, direct reaction with singlet dye, is unlikely at the concentration of TMPD used because of the short fluorescence lifetime of erythrosine in H_2O , 120 ps.¹⁵ We confirmed that path C (reaction of substrate with triplet) is not a major pathway by showing that, under oxygen (where $[O_2] > 10[TMPD]$), the amount of TMPD⁺ formed is greater than in a helium-saturated

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Scheme I



solution. (However, the fact that TMPD⁺ is still formed under He-saturated conditions indicates that path C can occur in the absence of O_2 .) By exclusion, pathway D (1O_2) is the major route for oxidation of TMPD. We confirmed the ${}^{1}O_{2}$ pathway by several different kinetic tests.

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PATH D

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(10) Transient absorptions were detected by a United Detector Technology Inc. PIN silicon photodiode (Pin-020A). The diode had a 13-V bias and its signal was amplified by a National Semiconductor high-speed op-amp. This signal was amplified further by a second op-amp (overall gain > 10 V/W). The diode is sensitive from 400 to 1050 mm. The remainder of the laser apparatus has been described previously. TMPD was purified as described previously.²¹

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(12) Dye-dye interactions can be ignored at the low dye concentration used in this experiment.

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Figure 1. Absorption spectrum of species formed by laser flash of TMPD+. (a) Spectra taken on Beckman Model 25 spectrophotometer after Hg2Cl2 oxidation of TMPD and millipore filtration. (b) Spectra taken 15 μ s after laser flash (see ref 10).

The rate of electron transfer from TMPD to ${}^{1}O_{2}$, k_{r} , can be determined approximately by calculation from the amount of ${}^{1}\text{O}_{2}$ produced and the final amount of TMPD⁺.¹⁶ We find $k_{\rm r} \sim (3.3 \pm 1.5) \times 10^{9} \,\text{M}^{-1} \,\text{s}^{-1}$, close to the diffusion-controlled value for H₂O, 6.4×10^9 M⁻¹ $s^{-1,20}$ This value for k_r is somewhat higher than the rate of quenching of ${}^{1}O_{2}$ by TMPD in methanol, reported to be $1 \times 10^9 \ M^{-1} \ s^{-1}$.²¹

Confirming that ${}^{1}O_{2}$ is the major pathway is the fact that compounds known to react with ${}^{1}O_{2}$ competitively inhibit TMPD⁺ formation. The quenching rate (k_{α}) for these acceptors can be determined from

$$A_0/A = 1 + k_0[Q]/(k_r[TMPD] + k_d)$$
 (1)

where $k_d = 3.3 \times 10^5 \text{ s}^{-1}$ in H₂O,²² $k_r = 3.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (see above), A and A_0 are the amount of TMPD oxidized 15 μ s after the laser flash in the presence and absence of Q, respectively, [TMPD] is the initial concentration of TMPD (eq 1 assumes [TMPD] >> A), and [Q] is the concentration of added inhibitor. The rates thus determined for dimethylfuran, 1.1×10^9 M⁻¹ s⁻¹, and anthracene-9-carboxylate, $2.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, compare well with the known rates for these acceptors of 1.5×10^9 M⁻¹ s^{-1 23a} and $4.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$,^{23b} respectively.

The lifetime of ${}^{1}O_{2}$ is known to increase dramatically when solvent is changed from H_2O to D_2O .^{24,25} Path D dictates a corresponding increase in the amount of TMPD⁺. if k_d limits the lifetime of ${}^{1}O_2$.²⁶ Figure 2 shows

(25) (a) whilehold, F.; Brummer, J. G. Submitted to J. Phys. Chem. Ref. Data. (b) The value quoted is for anthracene-9-sulfonate. (24) Lindig, B. A.; Rodgers, M. A. J. J. Phys. Chem. 1979, 83, 1683. (25) Merkel, P. B.; Kearns, D. R. J. Am. Chem. Soc. 1972, 94, 1029. (26) For this to be true, the condition $k_{\rm s}[{\rm TMPD}] < k_{\rm d}$ must hold; under these conditions (where $[{\rm TMPD}] = 4.4 \times 10^{-6}$ M) the terms are 1.5×10^{5} and 3.3×10^{5} (ref 22), respectively.



Figure 2. Effect of solvent deuteration on TMPD⁺ appearance: (D) absorbance in H_2O , (Δ) absorbance in D_2O ; solid lines are the theoretical curves.

that this is indeed the case. Also drawn in Figure 2 are theoretical curves for appearance of TMPD+, due to reaction of TMPD with ${}^{1}O_{2}$, in H₂O and D₂O. The curves were calculated according to the method of Young et al.²⁷ (see Appendix A). The excellent fit observed confirms the mechanistic pathway suggested.

We have studied the $TMPD^{-1}O_2$ reaction in a variety of solvents (MeOH, $(CF_3)_2$ CHOH, and HCONH₂). The formation of TMPD⁺ from ${}^{1}O_{2}$ is not observed in any solvent other than $H_2O(D_2O)$ although some TMPD⁺ is formed in these solvents by other mechanisms. We have also looked at several other electron-rich aromatic amines which could in principle give radical cations absorbing in the visible (tetramethylbenzidine, tetramethylbenzidine-3-sulfonic acid, N,N-dimethyl-p-anisidine). We have not observed electron transfer to ${}^{1}O_{2}$ for any of these compounds even though the process should be exothermic in H₂O for all of the compounds studied.²⁸ Consistent with these results is the report by Inoue et al.³¹ that the yield of O_2^{-} with TMPD is 6.5%, but with N,N-dimethyl-panisidine it is only about 1.1%, probably too low to be detected by our apparatus. It is likely that the initial charge-transfer complex between ${}^{1}O_{2}$ and these substrates decays to ground state at a rate which is competitive with dissociation to free ions.³²

We assume the O_2^{-} is the initially formed coproduct in the electron-transfer process; however, we have no direct evidence that this is the case. As mentioned previously, some O_2 has been noted in both N,N-dimethyl-panisidine⁷ and NADH⁸ reactions with ${}^{1}O_{2}$ in H₂O.

It should be noted that the dismutation of O_2^{-} . (presumably formed by electron transfer to ${}^{1}O_{2}$ or by direct 3 erythrosine-O₂ interaction)³⁴ in H₂O would create strong oxidizing agents which certainly could oxidize TMPD under the reaction conditions. These effects can be ignored because the disproportionation of O_2 should be slow (on our timescale) under the reaction conditions.³⁵ Further-

(28) Assuming $E_{1/2}$ (red. O₂) in H₂O = -0.33 V vs. SCE²⁹ and E_{00} (¹O₂) $= 1 \text{ eV}.^{30}$

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⁽¹⁶⁾ $[\text{TMPD}^+]_{\text{final}} = [k_r[\text{TMPD}]/(k_r[\text{TMPD}] + k_d)][^1O_2]_{\text{initial}}$ $[^1O_2]_{\text{initial}}$ can be calculated from $\Phi(^1O_2)$ with erythrosine (0.68)¹⁷ and the amount of erythrosine excited by the laser flash. The amount of erythrosine excited by laser is determined from the change in optical density at 475 nm immediately after the flash (assuming ϵ for ³erythrosine is similar dye, eosin).¹⁸ Since ϵ_{475nm} (erythrosine) = 1.73 × 10⁴ M⁻¹ cm⁻¹, Δ [erythrosine] = Δ OD_{475nm}/(1.73 × 10⁴). [TMPD⁺·]_{final} can be determined from its extinction coefficient at 605 nm, 11 000 M⁻¹ cm⁻¹.¹⁹

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⁽³²⁾ An attempt to trap O_2^{-1} (before possible back-electron transfer) by superoxide dismutase failed for N_rN -dimethyl-*p*-anisidine. [SOD] =

more, formation of O_2^{-} by ³erythrosine- O_2 interaction is a very inefficient process, accounting for <0.1% of the ³erythrosine- O_2 interaction.³⁴

The results show that path D is the major mechanism of photooxidation of TMPD under our conditions. The formation of the radical ions seems to depend on the ease of ionization of the substrate and solvation of the resulting ions. If both factors are not favorable, no separation to observable ions appears to occur.

Appendix A

The parameters used to obtain the theoretical lines in Figure 2 were the following:

$$\ln \left([\text{TMPD}] / [\text{TMPD}]_{\infty} \right) = k_{\text{r}} [{}^{1}\text{O}_{2}]_{0} e^{-\alpha t} / \alpha$$

where $\alpha = k_r [\text{TMPD}]_{av} + k_d$; $k_r = 2.0 \times 10^9$; $[{}^{1}\text{O}_2]_0 = 1.7$

× 10⁻⁵ M in both H₂O and D₂O; $k_d^{H_2O} = 3.3 \times 10^5 \text{ s}^{-1,22}$ $k_d^{D_2O} = 1.9 \times 10^4 \text{ s}^{-1,24} [\text{TMPD}]_{\infty}^{H_2O} = 4.0 \times 10^{-5} \text{ M},$ $[\text{TMPD}]_{\infty}^{D_2O} = 3.06 \times 10^{-5} \text{ M}; [\text{TMPD}]_{av} = [\text{TMPD}]_0 - [\text{TMPD}^+]_{\infty}/2.$

The value of $[TMPD]_{\infty}^{H_2O}$ can be read directly from the curve

$$\begin{split} [\text{TMPD}]_{\omega}^{\text{H}_{2}\text{O}} &= [\text{TMPD}]_{0} - [\text{TMPD}^{+}\cdot]_{\omega}^{\text{H}_{2}\text{O}} = \\ & 4.38 \times 10^{-5} \text{ M} - \frac{0.038 \text{ A}}{11000 \text{ cm}^{-1} \text{ M}^{-1}} \\ [^{1}\text{O}_{2}]_{0}^{\text{H}_{2}\text{O}} &= \frac{k_{r}[\text{TMPD}] + k_{d}}{k_{r}[\text{TMPD}]} [\text{TMPD}^{+}\cdot]_{\omega}^{\text{H}_{2}\text{O}} \\ [\text{TMPD}^{+}\cdot]_{\omega}^{\text{D}_{2}\text{O}} &= \frac{k_{r}[\text{TMPD}]_{av}}{k_{r}[\text{TMPD}]_{av}} [^{1}\text{O}_{2}]_{0} \end{split}$$

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FEATURE ARTICLE

Two-Particle Dynamics: Reflections, Rings, and Reactions

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A microscopic theory of two-particle motion in reacting and nonreacting fluids is presented. The emphasis of the description is on the correlated collision events which are responsible for a coupling of the motions of the particles and, in the reactive case, give rise to the coupling between particle diffusion and reaction. In addition, some phenomenological approaches are examined from the perspective of the microscopic theory.

1. Introduction

A number of dynamical processes of chemical interest involve the correlated motion of pairs of particles in solution. Consider, for instance, the frictional properties (viscosity, friction, and diffusion coefficients) of colloidal suspensions.¹ Here the system of interest is a collection of large colloidal particles dispersed in a medium composed of small molecules. In this circumstance it is sensible to treat the fluid as a continuum and apply the methods of hydrodynamics to the problem. Provided the concentration (volume fraction) of the suspended particles is small then, in most cases, first corrections to the frictional properties (like the Huggins coefficient for viscosity) depend on the interactions between pairs of particles. The resulting two-particle hydrodynamic problem is difficult but tractable. However, there are situations where one is interested in the frictional properties of solute molecules whose size is not large compared to that of the solvent, such as those that arise in the discussion of various correlation functions of interest in nuclear magnetic relaxation or collision-induced light-scattering studies.²

Another example is the study of chemical reactions in the condensed phase.³ The (bimolecular) reaction process involves the correlated motion of pairs of reactant molecules in a dense solvent. Often the reactants are not large compared to the solvent molecules, in fact, it is not difficult to realize situations where the solvent is larger than the solute. One of the most studied examples, that of iodine

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