

Two-electron oxidation of *N,N,N',N'*-tetramethylphenylenediamine with a chromium(v) salen complex

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Received 1st July 2008, Accepted 15th September 2008

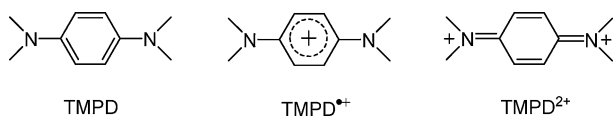
First published as an Advance Article on the web 5th November 2008

DOI: 10.1039/b811140e

The oxidation of tetramethylphenylenediamine (TMPD) with (salen)Cr^VO⁺ generates initially the 2-electron product TMPD²⁺, followed by the reaction with excess TMPD to yield the radical cation, TMPD^{•+}. The kinetics of both TMPD/(salen)Cr^VO⁺ and TMPD/TMPD²⁺ reactions are acid-dependent, with TMPD being the most reactive form, and the doubly protonated TMPDH₂²⁺ exhibiting no discernible reactivity toward either (salen)Cr^VO⁺ or TMPD²⁺. The specific rate constants for the individual reactions are: TMPD/(salen)Cr^VO⁺, $k = (6.28 \pm 0.50) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, TMPDH⁺/(salen)Cr^VO⁺, $(3.89 \pm 0.31) \times 10^5$, TMPD/TMPD²⁺, $(7.61 \pm 0.42) \times 10^8$, and TMPDH⁺/TMPD²⁺, $(3.46 \pm 0.22) \times 10^4$.

Introduction

Tetramethylphenylenediamine (TMPD) and related amines have been the focus of a large number of mechanistic studies. TMPD itself is water-soluble and easily oxidized to the intense blue radical cation TMPD^{•+} ($E = 0.12 \text{ V vs SCE}$).¹ In mechanistic work, the role of TMPD has been that of an electron transfer reagent in thermal^{1–4} and photochemical^{5,6} reactions, kinetic probe,⁷ mediator for generation of non-thermodynamic products,^{8,9} and hole acceptor in quantum dots.¹⁰ In zeolites, TMPD was shown to undergo spontaneous charge separation,¹¹ while photoexcitation in solutions leads to electron transfer to solvent.¹²



Reactions with organic and inorganic radicals and with some metal complexes are clearly 1-e processes, either taking place by outer-sphere electron transfer or requiring preassociation.^{7,13} Reactions with potential 2-e oxidants, on the other hand, may proceed in single 2-e steps or in a sequences of 1-e steps. The latter would appear more likely in view of the pronounced preference of TMPD for 1-e chemistry. Among numerous studies^{14–18} on electrochemistry of TMPD, we found no reports on a successful one-step 2-e oxidation.¹⁵ It appears that in all of the solvents and under all of the conditions, the oxidation took place in distinct 1-e steps. We found only one reliable example of a single-step 2-e chemical oxidation, which was observed in the reaction with I₂.¹⁹ The final product, TMPD^{•+}, was generated in the follow-up reduction of TMPD²⁺ with unreacted TMPD.

In other cases of overall 2-e oxidation,^{20–22} it either has been shown or can be reasonably assumed that the reactions proceeded in two 1-e steps involving TMPD^{•+} as an intermediate. Although we have no evidence that any of the reported mechanistic

assignments are incorrect, the results reported here demonstrate how a 2-e oxidation followed by TMPD²⁺/TMPD comproportionation could be easily disguised as 1-e chemistry unless specific experiments are designed to search for the 2-e pathway.

The oxidant employed in this work, (salen)Cr^VO⁺, ($E(\text{Cr}^{\text{V}}/\text{Cr}^{\text{IV}}) = 0.47 \text{ V vs SCE}$)²³ has ample potential to oxidize tmpd to the radical cation by single electron transfer. Such a path might appear preferable mechanistically, but 2-electron oxidations by (salen)Cr^VO⁺, typically by oxygen atom transfer,^{23,24} are also common. An overall 2-electron oxidation of TMPD should be therefore a realistic possibility, either because the chemistry might involve a genuine 2-e step, or the products of 1-e reaction, {TMPD^{•+} + (salen)Cr^{IV}}, could engage in second electron transfer within the solvent cage prior to diffusing into bulk solution. In both cases, the initial product of TMPD oxidation would be the rarely observed TMPD²⁺. The results are presented herein.

Experimental

The complex salt [(salen)Cr^V(O)](CF₃SO₃) was prepared by oxidizing [(salen)Cr^{III}(H₂O)](CF₃SO₃)²⁵ with iodosobenzene following a literature procedure.^{23,26} Commercial (Aldrich) *N,N,N',N'*-tetramethylphenylenediamine (TMPD) was used as received. The concentrations of (salen)Cr(O)⁺ in aqueous or acetonitrile solutions ($\epsilon_{600} = 2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$),²⁶ and of TMPD^{•+} ($\epsilon_{600} = 8600 \text{ M}^{-1} \text{ cm}^{-1}$)¹³ were determined spectrophotometrically.

The kinetics of the (salen)Cr(O)⁺/TMPD reaction in homogeneous aqueous solution were measured with an Olis RSM-1000 rapid-scan stopped-flow instrument (2 cm pathlength). The data were collected under pseudo-first order conditions using either of the two reagents in large excess, and fitted to an expression for first-order kinetics,

$$\text{Abs}_t = \text{Abs}_\infty + (\text{Abs}_0 - \text{Abs}_\infty)e^{-k_{\text{obs}}t}$$

where Abs_t, Abs_∞, and Abs₀ stand for absorbance at times *t*, zero, and infinity, respectively. To ensure that the acid/base equilibria of organic amines do not alter the concentration of [H⁺] in the course of the kinetic experiments, the concentration of H⁺ was always at least 50 times greater than the concentration of the amines. The

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ionic strength was kept constant at 0.10 M ($\text{HClO}_4 + \text{NaClO}_4$). All of the kinetic data were obtained at $25 \pm 0.02^\circ\text{C}$.

All the UV-Vis spectral data were acquired with a Shimadzu 3101 PC instrument. In-house distilled and ion-exchanged water was further purified by passage through a Millipore Milli-Q water purification system. The fitting of the kinetic data was done with the program Kaleidagraph 3.6.

Results

The reaction between $(\text{salen})\text{Cr}^{\text{VO}}+$ and TMPD generated the blue radical cation, $\text{TMPD}^{\bullet+}$, which was easily recognized by its characteristic and intense spectrum in the 550–600-nm region. The rising absorbance in the stopped-flow kinetic traces obtained in the presence of a large excess of TMPD at 600–610 nm were exponential, Fig. 1, and yielded pseudo-first order rate constants that increased with $[\text{TMPD}]$ at constant $[\text{H}^+]$. The reaction produced two equivalents of $\text{TMPD}^{\bullet+}$ per mole of $(\text{salen})\text{Cr}^{\text{VO}}+$, eqn (1).

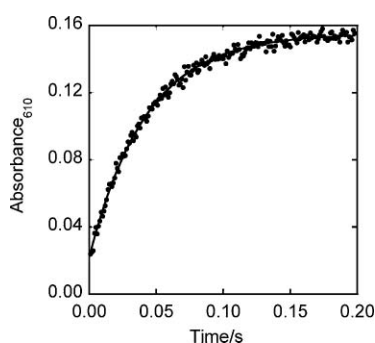
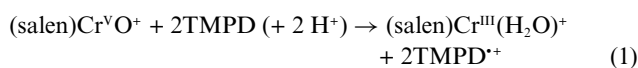


Fig. 1 Kinetic plot at 610 nm for the reaction of $(\text{salen})\text{Cr}^{\text{VO}}+$ ($4\ \mu\text{M}$) with excess TMPD ($2.1\ \text{mM}$) in $0.0242\ \text{M}\ \text{HClO}_4$.

When the conditions were reversed, and $(\text{salen})\text{Cr}^{\text{VO}}+$ was used in large excess over TMPD, the absorbance at 600 nm decreased signaling the loss of $(\text{salen})\text{Cr}^{\text{VO}}+$ without the accompanying formation of $\text{TMPD}^{\bullet+}$, Fig. 2. Kinetic traces were exponential, but the observed rate constants were about ten times larger than those measured with excess TMPD at comparable acid concentrations.

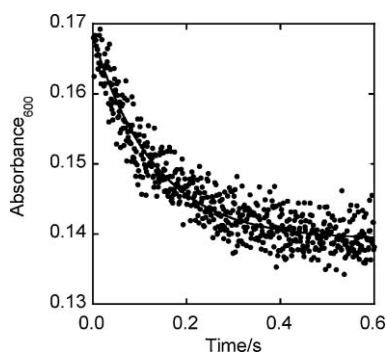
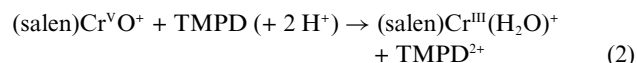


Fig. 2 Kinetic plot at 600 nm for the reaction of TMPD ($6.5\ \mu\text{M}$) with excess $(\text{salen})\text{Cr}^{\text{VO}}+$ ($58\ \mu\text{M}$) in $0.0181\ \text{M}\ \text{HClO}_4$.

Clearly, different reactions are observed under the two sets of conditions. A reasonable explanation for the delayed formation of $\text{TMPD}^{\bullet+}$ is shown in eqn (2–3), according to which the initial step is a two-electron reaction generating $(\text{salen})\text{Cr}^{\text{III}}(\text{H}_2\text{O})^+$ and the doubly oxidized amine. No further reaction occurs when $(\text{salen})\text{Cr}^{\text{VO}}+$ is in excess, but under the reversed conditions, the initially generated TMPD^{2+} is reduced to $\text{TMPD}^{\bullet+}$ in the comproportionation step of eqn (3). It is this step that is experimentally observed with TMPD as excess reagent.



According to this scheme, it should be possible to detect reaction 2 even in experiments with excess TMPD, although the large absorbance increase in the follow-up reaction 3 ($\Delta\epsilon_{610} = 8600\ \text{M}^{-1}\ \text{cm}^{-1}$) may overshadow the small absorbance decrease caused by reaction 2. This absorbance decrease is made even smaller by the stoichiometric factor of 2 in eqn (1). None the less, convincing evidence for reaction 2 was observed in the early stages of an experiment with a 7-fold excess of TMPD, Fig. 3. The reasonably large concentration of $(\text{salen})\text{Cr}^{\text{VO}}+$ ($24\ \mu\text{M}$) was necessary to increase the signal to noise ratio in the crucial initial stages (shown), and the high $[\text{H}^+]$ ($0.0604\ \text{M}$) slowed the reaction sufficiently to bring it into a measurable range at the high $[\text{TMPD}]$ used. The initial absorbance decrease in Fig. 3 was small, but clearly detectable before the onset of the $\text{TMPD}^{\bullet+}$ build-up.

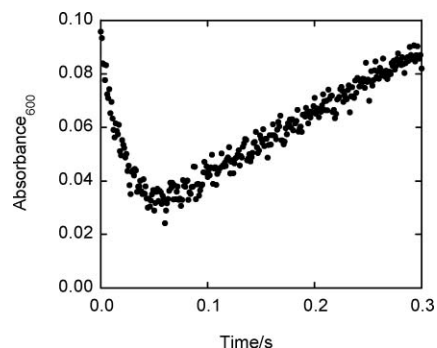


Fig. 3 Initial stages of a reaction between $(\text{salen})\text{Cr}^{\text{VO}}+$ ($24\ \mu\text{M}$) and excess TMPD ($0.17\ \text{mM}$) in $0.0604\ \text{M}\ \text{HClO}_4$.

Kinetics of $(\text{salen})\text{Cr}^{\text{VO}}+/\text{TMPD}$ reaction

At a constant acid concentration, the reaction is first-order in TMPD, as evidenced by excellent fits of the kinetic traces to the first-order rate equation. The reaction is also first-order in $(\text{salen})\text{Cr}^{\text{VO}}+$. The plots of k_{obs} against the concentration of $(\text{salen})\text{Cr}^{\text{VO}}+$ are linear with zero intercept, and yield second-order rate constants at a given $[\text{H}^+]$. The dependence on $[\text{H}^+]$, studied in the range $0.005\ \text{M} < [\text{H}^+] < 0.10\ \text{M}$, is displayed in Fig. 4.

The data were fitted to eqn (4), which takes into account the two acid/base equilibria for TMPD and different reactivities for the three protonation levels of TMPD, eqn (5–9). The acidity constants were fixed at their known values,² $K_{a1} = 6.3 \times 10^{-3}\ \text{M}$, and $K_{a2} = 4.7 \times 10^{-7}\ \text{M}$. The fit yielded the rate constants $k_1 = (6.28 \pm 0.74) \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}$, $k_2 = (3.88 \pm 0.58) \times 10^5$, and

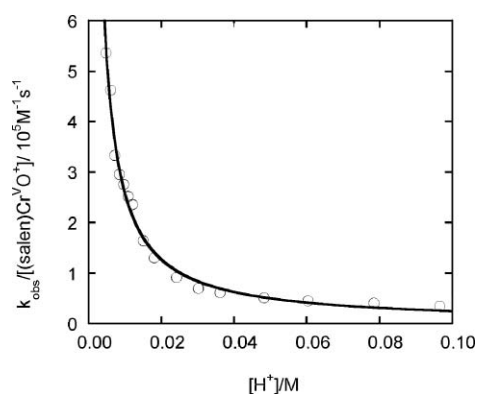
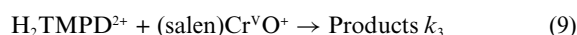
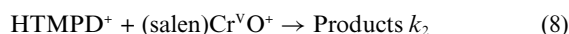
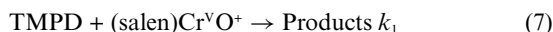


Fig. 4 Acid-dependence of the second-order rate constant for the oxidation of TMPD (3.5–7 μM) with excess (salen) Cr^{VO^+} (33–53 μM).

$k_3 = 89 \pm 11000$. Obviously, the reactivity of TMPDH_2^{2+} is negligible and subject to large error. Fixing k_3 at zero had almost no effect on the calculated values of k_1 , $(6.28 \pm 0.50) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, and k_2 , $(3.89 \pm 0.31) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, and even the standard deviations decreased only moderately compared to those obtained in the three-parameter fitting.

$$k_{\text{obs}} = \frac{k_1 K_{\text{a}1} K_{\text{a}2} + k_2 K_{\text{a}1} [\text{H}^+] + k_3 [\text{H}^+]^2}{[\text{H}^+]^2 + K_{\text{a}1} [\text{H}^+] + K_{\text{a}1} K_{\text{a}2}} \quad (4)$$



Kinetics of the $\text{TMPD}^{2+}/\text{TMPD}$ reaction

These experiments required an excess of $[\text{TMPD}]$ over $[(\text{salen})\text{Cr}^{\text{VO}^+}]$, as described in the previous section. Since both reactions 2 and 3 are first order in $[\text{TMPD}]$, the formation of TMPD^{2+} in reaction 2 was about 10 times faster than reaction 3 under all of the conditions, so that there was no interference from reaction 2 in kinetic measurements. The reaction was first order in the limiting reagent and in $[\text{TMPD}]$. The form of the $[\text{H}^+]$ dependence, shown in Fig. 5, closely mimics that observed in the $(\text{salen})\text{Cr}^{\text{VO}^+}/\text{TMPD}$ reaction, but values of the derived rate constants are smaller, *i. e.* $k_1' = (6.80 \pm 0.60) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ($\text{TMPD}/\text{TMPD}^{2+}$ reaction), $k_2' = (4.08 \pm 0.40) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ($\text{HTMPD}^+/\text{TMPD}^{2+}$), and $k_3' = -1110 \pm 60 \text{ M}^{-1} \text{ s}^{-1}$ ($\text{H}_2\text{TMPD}^{2+}/\text{TMPD}^{2+}$). Setting $k_3' = 0$, yielded $k_1' = (7.61 \pm 0.42) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $k_2' = (3.46 \pm 0.22) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$.

To confirm that the $\text{TMPD}/\text{TMPD}^{2+}$ reaction was indeed the source of the absorbance increase at 600 nm, we looked for alternative ways to generate TMPD^{2+} in solution.^{27,28} The oxidation of TMPD with a two-fold excess of Ce(IV) was successful. Upon mixing, the solution developed a dark blue color typical for $\text{TMPD}^{\bullet+}$, followed by the fading of the color as $\text{TMPD}^{\bullet+}$ was further oxidized by Ce(IV) to the colorless TMPD^{2+} . This

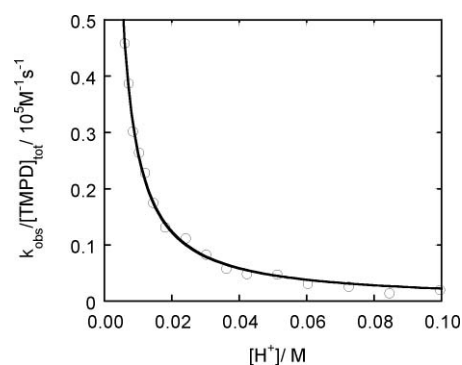
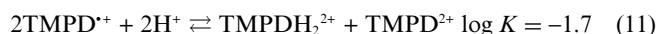


Fig. 5 Acid-dependence of the second-order rate constant for the reaction of TMPD^{2+} with excess TMPD (0.4–2.6 mM).

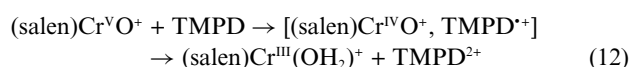
material was quickly loaded into a stopped flow and mixed with TMPD. The formation of $\text{TMPD}^{\bullet+}$ followed the same kinetic profile as that shown in Fig. 5, and yielded $k_1 = (3.77 \pm 0.21) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $k_2 = (0.80 \pm 0.06) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. These values are somewhat lower than those derived from $(\text{salen})\text{Cr}^{\text{VO}^+}$ reactions, but the overall picture strongly supports our reaction scheme for the $\text{TMPD}/(\text{salen})\text{Cr}^{\text{VO}^+}$ reaction in eqn (2–3).²⁹

Discussion

The combination of the reduction potentials ($E_1 = 0.12 \text{ V}$ vs SCE for $\text{TMPD}^{\bullet+}/\text{TMPD}$,¹ $E_2 = 0.72 \text{ V}$ for $\text{TMPD}^{2+}/\text{TMPD}^{\bullet+}$, *i. e.* 0.6 V greater than E_1)³⁰ and the acidity constants² for TMPDH_2^{2+} and TMPDH^+ yields the equilibrium constant for disproportionation of $\text{TMPD}^{\bullet+}$, $\log K_{10} = -10$. The reaction yielding TMPDH_2^{2+} and TMPD^{2+} , eqn (11), has $\log K_{11} = -1.7$. Disproportionation is thus unfavorable in both acidic and neutral solutions, which makes the radical the thermodynamic product, as experimentally observed.



Based on this analysis, one might have expected the reaction to adopt a direct 1-e path, but the 2-e reduction potential for $(\text{salen})\text{Cr}^{\text{VO}^+}$ is obviously large enough to generate TMPD^{2+} . This may be accomplished in a single 2-e step (by initial electron or oxygen atom transfer), although the large structural changes accompanying the oxidation of TMPD to TMPD^{2+} may favor a rebound mechanism as in eqn (12), or formation of 1-e products, $(\text{salen})\text{Cr}^{\text{IV}}\text{O}^+$ and $\text{TMPD}^{\bullet+}$ within the solvent cage followed by rapid second electron transfer. In a related reaction between a high-valent oxo-iron porphyrin complex and dimethylaniline, oxygen atom transfer has been demonstrated recently in the gas phase, although this path seems to be significant only when formation of the radical becomes endothermic.³¹



In any case, $\{(\text{salen})\text{Cr}^{\text{III}}(\text{OH}_2)^+ + \text{TMPD}^{2+}\}$ are generated. These products are thermodynamically greatly disfavored (by about 0.6 V)³⁰ over the alternative, $\{(\text{salen})\text{Cr}^{\text{III}}(\text{OH}_2)^+ + 2\text{TMPD}^{\bullet+}\}$, into which they are transformed in a separate, follow-up step. The extra energy stored in TMPD^{2+} relative to $\text{TMPD}^{\bullet+}$

decreases at higher $[H^+]$ as TMPD is protonated, eqn (10–11), but even in 1 M H^+ , reaction 11 still generates products that are 0.1 V uphill of 2 TMPD $^{2+}$.

In summary, a complementary 2-e reaction between (salen)-Cr $^{VO^+}$ + TMPD generates products that are significantly higher in energy than the thermodynamically more favorable alternative. Quantitative formation of the kinetic products, {(salen)-Cr $^{III}(OH_2)^+ + 2TMPD^{2+}$ }, requires either that the initial reaction takes place in a single two-electron step, or that the second of two one-electron steps within the solvent cage be extremely rapid so as to prevent any cage escape.

Acknowledgements

This manuscript has been authored under Contract No. DE-AC02-07CH11358 with the U.S. Department of Energy.

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