Kinetics of Oxidation and Comproportionation Reactions Involving an Oxammonium Ion, Benzyl Alcohol and Methyltrioxorhenium(VII)

TIMOTHY H. ZAUCHE, JAMES H. ESPENSON
Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011
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ABSTRACT: The reactions of 4-hydroxy-2,2,6,6-tetramethylpiperidinium N-oxide, an oxammonium ion abbreviated R₂NO¹, have been studied. The previously unreported triflate salt was used in this study because the anions of the usual chloride and bromide salts can themselves be oxidized. Reactions between R₂NO¹ and alcohols produce ketones and aldehydes; the rate constant for PhCH₂OH is 4.4 × 10⁻³ L mol⁻¹ s⁻¹ in acetonitrile at 298 K. The immediate product is the hydroxylamine, R₂NOH, but its further comproportionation reaction with R₂NO¹ yields the stable piperidinyl oxyl radical, R₂NO•. The rate constant of this reaction is 1.78 × 10³ L mol⁻¹ s⁻¹ at 298 K. The possibility of using R₂NO¹ and MTO as co-catalysts for the oxidation of alcohols was explored, but the competitive rates are such that the resultant is not particularly attractive. © 1999 John Wiley & Sons, Inc. Int J Chem Kinet 31: 381–385, 1999

INTRODUCTION

Oxammonium ions, such as 4-hydroxy-2,2,6,6-tetramethylpiperidinium N-oxide, R₂NO¹ in Chart 1, are strong oxidizing agents. Alcohols are oxidized by R₂NO¹ stoichiometrically and catalytically. Both electrochemical [1,2] and chemical methods have been used, with a variety of reagents such as HOCl [3–5], MCPBA [6], and Cu(II) [7]. Primary alcohols react preferentially over secondaries, possibly for steric reasons [4,8]; for that reason PhCH₂OH was used in most of these studies. During most oxidations R₂NO¹ is converted to R₂NOH without an intermediate piperidinyl oxyl radical, R₂NO•. The comproportionation equilibrium, R₂NOH + R₂NO¹ ↔ 2 R₂NO + H⁺, favors the radical; thus after the initial stage of the reaction R₂NO¹ predominates.

Correspondence to: J. H. Espenson
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Hydrogen peroxide oxidizes secondary hydroxylamines to nitrates when methyltrioxorhenium (CH₃ReO₃, abbreviated as MTO) [9] or Na₂WO₄ [10] is used as catalyst. α-Tetramethylsubstituted amines are converted to N-oxyl radicals with MTO−H₂O₂ [11], perhaps by the same mechanism (Scheme I). Alcohols are oxidized with MTO−H₂O₂ [12,13], albeit very slowly.

This study reports the kinetics for several steps related to this chemistry: the oxidation of R₂NOH by a peroxorhenium complex derived from MTO, the reaction between R₂NO and benzyl alcohol, and the comproportionation reaction between R₂NHOH and R₂NO. We have also examined the possibility, using alcohol reactions as the test case, that R₂NO⁺ might act in concert with MTO to promote certain oxidations.

EXPERIMENTAL

Some reagents were purchased: 2,2,6,6-tetramethylpiperidinium N-oxide (HTEMPO), 4-hydroxy-2,2,6,6-tetramethyl-1-oxo-piperidine-1,4-diol and 2,2,6,6-tetramethyl-1-oxo-piperidinium trifluoromethanesulfonate, (AgCF₃SO₃), as were HPLC-grade organic solvents. 2,2,6,6-Tetramethylpiperidinium chloride were prepared from HTEMPO acid, in contrast to most cases where a high [H⁺] can be used to stabilize the rhenium catalyst [19]. Thus, conditions were selected to minimize the amount of H⁺ released during any reaction, owing to the involvement of side reactions (to be discussed).

RESULTS AND INTERPRETATION

Peroxides Derived from MTO

Two stepwise equilibrium (but not instantaneous) reactions that take place between MTO and hydrogen peroxide are described later. Because they have received attention previously [20], it suffices here to present reactions (1) and (2) and to show the structural
**Oxidation and Comproportionation Reactions**

**Kinetics of Oxidation of the Hydroxylamine**

The oxidation of R$_2$NHOH by the peroxorhenium compound B, reaction (3), was monitored at 240 nm by recording the buildup of R$_2$NO, $e_1 = 1.85 \times 10^4$ L mol$^{-1}$ cm$^{-1}$. This radical resulted from the second step of the sequence, the rapid comproportionation reaction between R$_2$NO$^-$ and R$_2$NOH, reaction (4).

$$B + R_2N\overset{\cdot}{O} \rightarrow A + R_2\overset{\cdot}{N}O + OH^- \quad (3)$$

$$R_2N\overset{\cdot}{O}^- + R_2N\overset{\cdot}{O}H \rightarrow 2R_2\overset{\cdot}{N}O + H^+ \quad (4)$$

The concentrations employed were 0.6 – 3.0 mM MTO, 200 mM H$_2$O$_2$, and 0.7 – 2.0 mM R$_2$NOH. With this high concentration of hydrogen peroxide, B$_2$ is present at an appreciable concentration, whereas A remains <2% of the total rhenium. The kinetic contribution of A can be neglected. (To verify that point, we showed that the rate constant was independent of [H$_2$O$_2$] in the range 0.1 – 0.4 M.) In this reaction sequence, A is formed as B reacts. Under these conditions B was rapidly regenerated, however, since A reacts with hydrogen peroxide to give B; $k_2$ (Scheme II) is $6.2 \times 10^{-2}$ L mol$^{-1}$ s$^{-1}$ in acetonitrile. That reaction is sufficiently rapid to maintain [B] at its equilibrium concentration.

The second-order rate constant for reaction (3) was evaluated from a plot of $v_i$ against [B], which was taken as [Re], for the reasons previously stated. This plot is displayed in Figure 1. The least-squares slope affords the value $k_3 = 3.0 \pm 0.1$ L mol$^{-1}$ s$^{-1}$ in acetonitrile at 298 K. In comparison, the closely-related reaction of B with N-benzyl-N-tert-butylhydroxylamine has $k_3 = 0.94$ L mol$^{-1}$ s$^{-1}$ in methanol at 298 K [9]. The similarity of these values substantiates that the two independent determinations correspond to the same chemistry.

The reaction sequence found for numerous other secondary hydroxylamines features two steps. Initially and rate controlling is the transfer of an oxygen atom from a peroxorhenium moiety to the electron pair of the nitrogen. Rapidly following is an elimination reaction that creates a C$\equiv$N double bond in the product nitrene, Scheme III.

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**Figure 1** Kinetic data for the oxidation of the hydroxylamine derived from 4-hydroxy-2,2,6,6-tetramethylpiperidinium N-oxide by methyl(oxo)(diperoxo)rhenium(VII), B.

This graph shows that the initial reaction rate, $v_i$, is a linear function of the product of the concentrations of the two reactants.
The first step of the sequence occurs by nucleophilic attack of the nitrogen lone pair on one of the four peroxo oxygen atoms of B. These peroxides have been activated by the inductive effect of the highly electropositive Re(VII) center to which they are coordinated. In effect, the peroxide is activated electrophilically. The transition state for this process can be depicted like this:

![Transition State Diagram]

**Figure 2** The kinetic analysis of the data for reaction (4) in acetonitrile at 298 K. The values of \( k' \), obtained from eq. (7), are shown here as a plot of \( k'(s^2) \) vs. \( D \), the difference in the initial concentrations of the reactants; the slope of this plot is \( k_4 \).

The comproportionation reaction between \( R_2 NOH \) and \( R_2 NO_1 \), reaction (4), was monitored by stopped-flow and conventional UV-Vis methods. The initial conditions were 18–32 \( \mu M \) \( R_2 NO_1 \), 46–416 \( \mu M \) \( R_2 NOH \). A few of these experiments were carried out under pseudo-first-order conditions, but most were not. These data were fit to the form for mixed-second-order kinetics, eq. (5) in terms of concentration and eq. (6) in terms of absorbance.

\[
[R_2 NO] = \frac{[R_2 NO_1]_0}{R} \times \frac{R - 1}{R \times e^{\sigma s} - 1} \tag{5}
\]

\[
\text{Abs}_s = \text{Abs}_0 + \frac{(R - 1) \times (\text{Abs}_s - \text{Abs}_0)}{R \times e^{\sigma s} - 1} \tag{6}
\]

where \( R = [R_2 NOH]/[R_2 NO_1]_0 \) and the rate constant \( k' = k_4 \times \Delta \), where \( \Delta = [R_2 NOH] - [R_2 NO_1]_0 \). Data were obtained in nine experiments. The plot of \( k' \) against \( \Delta \) is depicted in Figure 2; its slope gave \( k_4 = (1.78 \pm 0.05) \times 10^3 \text{ mol}^{-1} \text{ s}^{-1} \) in acetonitrile at 298 K.

The position of the equilibrium in eq. (4) can be shifted by protonation of the hydroxylamine, \( R_2 NHOOH = R_2 NH + H^+ \), but doing so provides no advantage here since the protonated hydroxylammonium ion, lacking an unshared electron pair, does not react with \( B \). [9] The low reactivity of \( R_2 NHOOH^+ \) seems general, which is the reason that catalytic \( R_2 NO^+ \) oxidations are generally performed under neutral or basic conditions.

**Kinetics of Alcohol Oxidation by the Oxammonium Ion**

The reaction between these partners is given by reaction (7).

\[
R_2 NO^+ + R'CHOH \rightarrow R_2 NOH + R'C_1 + H^+ \tag{7}
\]

We chose benzyl alcohol as the prototypical alcohol because, in general, it is often more easily oxidized. The buildup of benzaldehyde was monitored by recording the absorbance at 244 nm, with 1–5 mM \( R_2 NO \) and 60–200 mM \( PhCH_2 OH \). These measurements afforded \( k_8 = (4.4 \pm 0.5) \times 10^3 \text{ mol}^{-1} \text{ s}^{-1} \) in acetonitrile at 298 K. The overall reaction stoichiometry is 2\( R_2 NO^+ : 1\) \( PhCH_2 OH \), because rapid comproportionation, reaction (4), occurs immediately thereafter.

The mechanism just described appears similar to that given for the oxidation of primary and secondary alcohols by the oxammonium ion prepared from TEMPO [21]. The literature on the use of stable organic nitroxyl radicals for the oxidation of primary and secondary radicals has recently been reviewed [22].

**Catalyzed Oxidation of Alcohols**

With the kinetic data for the preceding reactions now at hand, the construction of the catalytic cycle was possible. Scheme IV presents an analysis of the transformations occurring. For the sake of simplicity, steps
interconverting MTO and A are not shown. At the outset, the oxidation of PhCH₂OH by B is negligible relative to its oxidation by the oxammonium ion.

\[ \text{PhCHO} + \text{PhCH₂OH} \overset{k_1}{\rightarrow} \text{PhCHO} + \text{PhCH₂OH} \]

The catalytic cycle cannot be sustained for long, however, because the rapid comproportionation reaction drains off the oxammonium ion. These experiments were run without added H⁺, so that the equilibrium in eq. (4) would lie well to the right. To limit the occurrence of reaction (4), which limits the effectiveness of a catalytic mechanism, [MTO] was increased to 40 mM and [R₂NOH]₀ was decreased to 0.1 mM.

Given the rate constants and these observations, it can be recognized that comproportionation limits the catalytic applicability of this scheme. Hypochlorite, a two-electron acceptor, leads to successful oxidations. It appears that under these conditions the MTO-TEMPO co-catalysts are relatively ineffective. It was difficult to sustain the oxidation of alcohol by R₂NO⁻ since it is being more rapidly consumed by reaction (4). Note that the equilibrium in reaction (4) could be reversed at higher [H⁺]. With that, the oxyl radical would be an intermediate, not a dead end. Conditions of high [H⁺] are, however, incompatible with the need for R₂NOH, not the nonreactive R₂NHOH⁻.

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BIBLIOGRAPHY