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Kinetics and Mechanism of Oxidation of Anilines by Hydrogen Peroxide As Catalyzed by Methylrhenium Trioxide

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The oxidation of anilines by hydrogen peroxide in methanol is catalyzed by methylrhenium trioxide, CH_3ReO_3. The major product of the oxidation of aniline at room temperature is nitrosobenzene. For 4-substituted *N,N*-dimethylanilines, the *N*-oxide is the only product. The rate constants for the oxidation of 4-substituted *N,N*-dimethylanilines follow a linear Hammett relationship with $\varrho = -1.19$. The rate constants for the reaction between $CH_3Re(O)_2(O_2)$, referred to as **A**, and $4\text{-}XC_6H_5\text{-}NMe_2$ are as follows: 4-Me, 24.5; 4-H, 18.4; 4-F, 12.7; 4-Br, 8.7; and 4-NO_2, 1.9 L mol^{-1} s^{-1}. This shows that electron-withdrawing substituents inhibit the reaction. The corresponding rate constant for the oxidation of aniline is 2.04 ± 0.11 L mol^{-1} s^{-1}, whereas it is 178 ± 11 L mol^{-1} s^{-1} for the oxidation of *N*-phenylhydroxylamine to nitrosobenzene. A mechanism has been assigned on the basis of the kinetics and product yields. The data are consistent with the attack of the nucleophilic nitrogen atom on one of the peroxidic oxygen atom of **A**. The kinetics of the reaction of CH_3ReO_3 and hydrogen peroxide in methanol were also investigated. The formation of the 1:1 peroxide compound **A** is characterized by an equilibrium constant $K_1 = 261 \pm 6$ L mol^{-1}. The equilibration occurs rapidly: $k_1 = 1150 \pm 60$ L mol^{-1} s^{-1} and $k_{-1} = 4.4 \pm 0.4$ s^{-1} at 25.0 °C. The bisperoxide compound, $CH_3Re(O)(O_2)_2(H_2O)$, **B**, forms more slowly. The rate constant is $k_2 = 308 \pm 16$ L mol^{-1} s^{-1}, and the equilibrium constant is $K_2 = 814 \pm 14$ L mol^{-1} at 25.0 °C in methanol. **B** reacts with the anilines, but much more slowly than **A**.

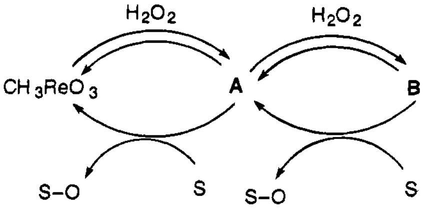
Introduction

Various reagents, including metal compounds, organic peroxides and hydrogen peroxide, have been used to form oxygen-containing derivatives of anilines. Sometimes the reagents are used in combination for greater efficiency. The oxidation of anilines by chromium(VI) compounds leads to benzoquinones.[2] In the presence of manganese dioxide, substituted anilines form symmetrically substituted azobenzenes.[3] Anilines are readily converted to azo compounds by nickel peroxide[4] and are slowly oxidized to azobenzenes by silver carbonate on Celite.[5] The oxidation of *N*-arylhydroxylamines with lead tetraacetate gives the corresponding nitroso compounds.[6] Anilines are oxidized to azoxybenzenes by hydroperoxides, catalyzed by Ti(IV),[7] and to azobenzenes by hydrogen peroxide, catalyzed by cetylpyridinium heteropolyoxometalates.[8]

The current environmental imperatives require the substitution of a "greener" oxidizing agent for those that produce wastes, salts, or other byproducts. Hydrogen peroxide is potentially an important substitute, since its only reduction product is water. This and other advantages have been cited.[9,10]

In general, however, hydrogen peroxide reactions are characterized by high activation energies, which result in slow reactions.[11] For all practical purposes a catalyst is required. In addition to the kinetic acceleration the catalyst will provide, the enhancement of the desired electrophilic activity of peroxide will minimize the importance of free radical pathways which are undesirable owing to the mixture of products.

Scheme 1



Methylrhenium trioxide, CH_3ReO_3, is a homogeneous catalytic activator of hydrogen peroxide in both organic solvents and water. It can also be used heterogeneously on $Al_2O_3-SiO_2$ as a catalyst support.[12] The oxygen is transferred to the substrate from either of the two peroxides that result from CH_3ReO_3 and hydrogen peroxide. This reaction forms rhenium peroxides having 1:1 and 1:2 ratios of metal to peroxide.[13] These compounds are $CH_3Re(O)_2(O_2)$ and $CH_3Re(O)(O_2)_2(H_2O)$, referred to as **A** and **B**.[13] Scheme 1 presents the catalytic cycles for the oxidation of a general substrate **S**, allowing for both **A** and **B** to be effective catalysts.

This general scheme is, for example, representative of the oxidation of thiolatocobalt(III) complexes in aqueous solutions of dilute perchloric acid[14] and of organic sulfides[15] and phosphines[16] in acetonitrile−water. It may also apply to olefin epoxidation in 2-methyl-2-propanol.[17]

[®] Abstract published in *Advance ACS Abstracts,* February 15, 1995.

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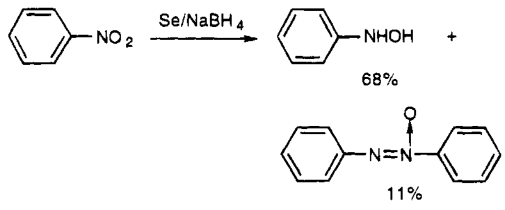
Since the oxidation of amines by methylrhenium trioxide with hydrogen peroxide has not been reported to date, we undertook a study that included both 4-substituted *N,N*-dimethylanilines and some ring-substituted anilines. The tertiary anilines afford the *N*-oxides predominately, whereas aniline itself yields primarily nitrosobenzene. The kinetics of these reactions will give more information about the mechanism by which the rhenium catalyst operates. Since the data suggested that the oxidation of aniline might occur *via* *N*-phenylhydroxylamine, the kinetics of its rhenium-catalyzed oxidation with hydrogen peroxide was also investigated.

Experimental Section

Materials. *N*-Phenylhydroxylamine was synthesized from nitrobenzene.[18] This product was obtained as colorless needles (mp 83−84 °C), and in the process we also obtained another, previously unreported but relatively minor product. It was identified as azoxybenzene [MS 77 (100), 91 (30), 105 (26), 51 (25), 65 (22), 170 (20), 198 (19), 64 (17)] and mp 87−89 °C.



4-Methyl-*N,N*-dimethylaniline and 4-fluoro-*N,N*-dimethylaniline were prepared according to the literature with these minor changes:[19] (1) The system containing the aniline and trimethyl phosphate was heated only gently until the exothermic reaction was completed, before being brought to reflux. (2) The solution containing base was extracted with 1:1 ether−hexane instead of ether only.

Methylrhenium trioxide was prepared from Re_2O_7 and $Sn(CH_3)_4$.[20] The organorhenium peroxide **B**, $CH_3Re(O)(O_2)_2(H_2O)$, was prepared from methylrhenium trioxide.[21] Methanol and hexanes were purified by standard methods.[22] The anilines and other reagents used in this study were obtained commercially.

General Procedure for Synthesis of Nitrosobenzene. A 1.0 mL portion of $ArNH_2$ was dissolved in 10 mL of methanol, mixed with 3.0 mL of 30% hydrogen peroxide, after which 50 mg CH_3ReO_3 was added. The solution was stirred at room temperature for 2 h and then extracted three times with methylene chloride. The combined extracts were dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. The product was purified by column chromatography on silica gel using 1:5−10 ethyl acetate−hexane as the eluent. The product from each aniline was identified spectroscopically by comparison to literature values.[23]

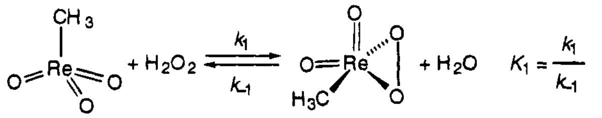
General Procedure for the Synthesis of *N*-Oxides. A mixture of 2−4 g of the 4-substituted *N,N*-dimethylaniline ($ArNMe_2$), 200 mg of CH_3ReO_3, and 10 mL of 30% hydrogen peroxide in 10 mL of methanol was stirred at room temperature for 2−5 h. The product obtained after the solvent had been evaporated under vacuum was recrystallized from methylene chloride. Each product was identified by comparison of its spectra and melting point with those recorded in the literature.[24]

Kinetic Studies. The progress of the reaction was monitored spectrophotometrically, using a Shimadzu UV-2101PC spectrophotometer and a Sequential DX-17MV stopped-flow instrument from Applied Photophysics Ltd., depending on the time scale of a given experiment. Kinetic studies were carried out by monitoring the disappearance of *N,N*-dimethylaniline at 251 nm, the disappearance of 4-bromo-*N,N*-dimethylaniline at 265 nm, the disappearance of 4-fluoro-*N,N*-dimethylaniline at 315 nm, and the accumulation of 4-nitro-*N,N*-dimethylaniline *N*-oxide at 231 nm and 4-methyl-*N,N*-dimethylaniline *N*-oxide at 265 nm. The kinetics with excess *N,N*-dimethylaniline for measurement of the rate constant of the formation of **A** (the 1:1 peroxide of CH_3ReO_3 and hydrogen peroxide) was studied by monitoring the decrease in absorbance at 328 nm.

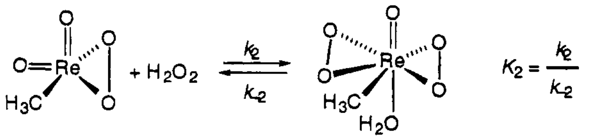
Reaction mixtures were prepared with hydrogen peroxide added last. The order of addition is important, since the steady-state analysis of the kinetic system applied most precisely when the compounds **A** and **B** were not allowed to accumulate prior to the start of the oxidation.

Results

Equilibrium Measurements. It was necessary to measure the equilibrium constants of the reactions between CH_3ReO_3 and hydrogen peroxide in methanol. As cited above, this interaction results in the reversible formation of peroxides with 1:1 and 1:2 ratios rhenium to peroxide, as given in eqs 1−2. Their equilibrium



(1)



(2)

constants K_1 and K_2 were determined from the equilibrium absorbances in the range of 345−400 nm in experiments in which no aniline was present.

The values of the constants K_1 and K_2 were obtained by the nonlinear least-squares fitting of the data to the following equation:[13]

$$\frac{\text{Abs}_\lambda}{[\text{Re}]_T} = \frac{\epsilon_0 + \epsilon_A K_1[H_2O_2] + \epsilon_B K_1 K_2 [H_2O_2]^2}{1 + K_1[H_2O_2] + K_1K_2[H_2O_2]^2} \quad (3)$$

The total concentration of CH_3ReO_3, $[\text{Re}]_T$, was 0.52 mM and the concentration of hydrogen peroxide was varied over a range 1.2−76 mM, using eight concentrations. The equilibrium absorbance was recorded at 345, 360, 380, and 400 nm. The absorbance readings obtained as a function of hydrogen peroxide concentration were fitted to eq 3 by means of the program GraFit that allowed a global fit of all the multiwavelength spectra simultaneously. The data and fitting at one wavelength are shown in Figure 1. The equilibrium constants obtained are $K_1 = 261 \pm 6$ L mol^{-1} and $K_2 = 814 \pm 14$ L

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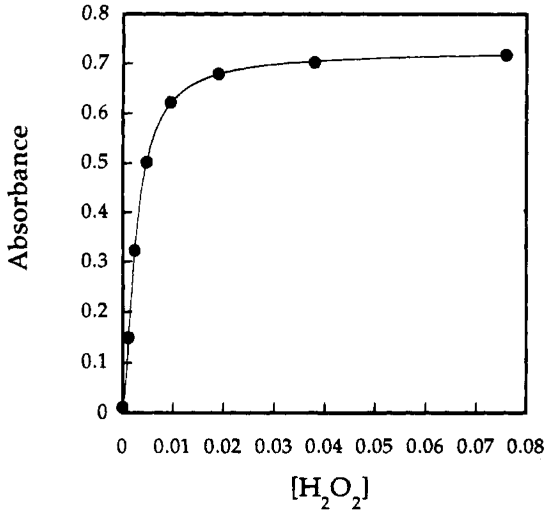

Figure 1. Plot showing the increases in absorbance at 345 nm that result from the formation of two rhenium peroxides in a 0.52 mM solution of CH_3ReO_3 as a function of the concentration of hydrogen peroxide in methanol. This curve and similar ones at other wavelengths were used to evaluate the equilibrium constants K_1 and K_2 for the stepwise binding of peroxide ions.

mol^{-1}. The values are considerably larger than those in water,[13] which are 7.7 L mol^{-1} and 145 L mol^{-1}; the system in methanol is still cooperative (i.e., $K_2 > K_1$), although to a lesser extent than in water.

The initial presence of a small concentration of water in the reaction did not shift the equilibrium, nor did the addition of a small concentration (2–20 mM) of water after the peroxides were formed. This is significant, since it bears on the question of the coordination of solvent to the peroxide **B,** and perhaps to **A.** Were the coordinated solvent methanol, or were the solvent not coordinated at all, then a change in the concentration of water, which itself would then be a reaction product free in solution, would shift the equilibrium position.

Experiments showed that this was not the case under the reaction conditions employed. We take this as evidence that water is the ligand coordinated to rhenium in moist methanol, despite the fact that the activity of methanol is higher than that of water. In other words, the peroxide compounds **A** and **B** are the same species here as they are in water or mixed water–organic solvents. Although the binding of water in **B** could be confirmed in THF by the use of ^{1}H NMR,[21] this was not possible in the hydroxylic solvent CD_3OD, where the formation of D_2O, coordinated or not, eliminates a measurable proton NMR signal.

Rate Constants. The kinetics of reactions 1 and 2 were then examined in methanol. It proved impossible, however, to find conditions where only one of the reactions could be studied. The two were therefore studied together, although the accuracy was less than if each could have been studied separately. The kinetic data consisted of absorbance–time traces that were taken at 300 nm where the absorbance decreases with the reaction progress since CH_3ReO_3 itself has a larger molar absorptivity than **A** or **B** at this wavelength. The concentrations used were $[CH_3ReO_3]_T = 1.6$ mM, and $[H_2O_2]$ was varied in the range 9.8–98 mM.

If we postulate that the equilibrium reactions that produce compounds **A** and **B** also describe the kinetics, the rate equations are

$$\frac{d[\mathbf{A}]}{dt} = k_1[CH_3ReO_3][H_2O_2] - k_{-1}[\mathbf{A}] - k_2[\mathbf{A}][H_2O_2] + k_2[\mathbf{B}] \quad (4)$$

$$\frac{d[\mathbf{B}]}{dt} = k_2[\mathbf{A}][H_2O_2] - k_{-2}[\mathbf{B}] \quad (5)$$

where the possibility that water plays a specific role in the mechanism is ignored for the meantime; we shall return to that point later. These equations were solved for the case $[H_2O_2] \gg [Re]_T$, such that $[H_2O_2]$ remained essentially constant in each experiment. The resulting expressions for [**A**] and [**B**] are the sums of two exponentials, but the two relaxation times are not simply those for the separate reactions in isolation. Rather, both relaxation times are complex functions of the four separate rate constants.[25-27] The buildup of [**B**] is given by

$$[\mathbf{B}]_t = [Re]_T\left[1 + \frac{\lambda_3}{\lambda_2 - \lambda_3}\exp(-\lambda_2 t) - \frac{\lambda_2}{\lambda_2 - \lambda_3}\exp(-\lambda_3 t)\right] \quad (6)$$

where the two observed rate constants are related to the parameters of the kinetic scheme. The approach to the solution is best made through certain combinations of the two rate constants. The expressions for their sum and their product are useful; the equations are as follows:

$$\lambda_2 + \lambda_3 = (k_1 + k_2)[H_2O_2] + k_{-1} + k_{-2} \quad (7)$$

$$\lambda_2\lambda_3 = k_1k_2[H_2O_2]^2 + k_1k_{-2}[H_2O_2] + k_{-1}k_{-2} \quad (8)$$

This pair of equations was used for the analysis of the kinetic data, which consisted of 10 experiments at five concentrations of hydrogen peroxide in the range 0.01–0.10 M. The absorbance buildup followed biexponential kinetics, characterized by the two rate constants λ_2 and λ_3, in accord with this model. The absorbance–time traces were fitted to a double exponential function with a floating endpoint. Figure 2 depicts a typical absorbance–time trace obtained from stopped-flow experiments, and superimposed on it is the biexponential fit. The close fit of the data lends credence to this model.

The analysis of the data according to eqs 7 and 8 is depicted in Figure 3. To obtain numerical results the value of k_{-1} was replaced k_1/K_1 and that of k_{-2} by k_2/K_2, with the equilibrium constants K_1 and K_2 set at their known values. The data fit gave the values of two of the rate constants;[28] the rate constants for the reverse reactions were then calculated from the equilibrium constants. The results are as follows, with the aqueous values shown in parentheses:

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[28] The form of the kinetic equations allows the interchange of k_1 with k_2 and of k_{-1} with k_{-2}. The values were assigned on the basis of other chemical evidence.

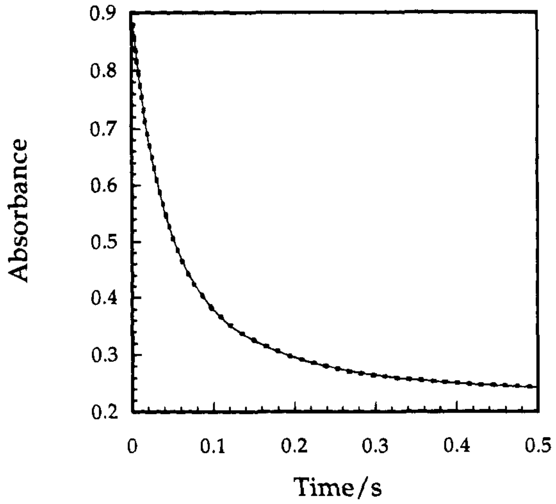


Figure 2. Typical absorbance–time trace at 300 nm from a stopped-flow experiment in methanol, in which 1.6 mM CH_3ReO_3 and 19.6 mM hydrogen peroxide form an equilibrium mixture of the rhenium peroxides **A** and **B**. The smooth curve shows the fitting of the data to a biexponential rate equation.

$$k_1 = 1150 \pm 60 \text{ (aq. 77) L mol}^{-1}\text{ s}^{-1}$$

$$k_{-1} = 4.4 \pm 0.4 \text{ (aq. 9.0) s}^{-1}$$

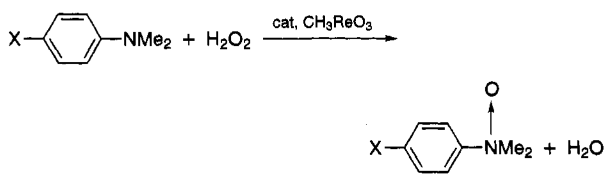
$$k_2 = 308 \pm 16 \text{ (aq. 5.2) L mol}^{-1}\text{ s}^{-1}$$

$$k_{-2} = 0.38 \pm 0.06 \text{ (aq. 0.04) s}^{-1}$$

The addition of up to 10 mM water, when hydrogen peroxide is in excess, did not change the rate in methanol; higher concentrations of water caused the rate to decrease appreciably. A few experiments were also carried out in acetonitrile, where the kinetic retardation of added water was evident even at the lowest concentrations. The "forgiving" nature of methanol with respect to the concentration of water was the major reason for choosing methanol as the solvent. Since water is present in the peroxide solutions, roughly 4–5 mol per mol of hydrogen peroxide, and more is produced in the reaction, its effect on the rates of reaction in solvents where the rate is very sensitive to water would have greatly complicated a quantitative kinetic study.

It should be added that the involvement of water might have been taken into account more explicitly by relating $[H_2O]$ to $[H_2O_2]$ and then including it explicitly in the expressions for the thermodynamic and kinetic data. We opted not to follow this course, however, since to do so would require defining the role of water more precisely than the data allow.

***Para*-Substituted *N,N*-Dimethylanilines.** The oxidation of these anilines with hydrogen peroxide is strongly catalyzed by CH_3ReO_3. In methanol, $ArNMe_2$ forms only the *N*-oxide at room temperature according to eq 9. The individual substrates studied and the yields of the product isolated from each are given in Table 1.



(9)

The yields of this reaction were >85%. This convenient reaction may be used for the preparation of aromatic amine *N*-oxides. The product yields for the compounds with the different *para* substitutents did not differ significantly although it was suggested that electron-withdrawing groups will inhibit the reaction.[29] The catalyzed reactions might, however, be subject to kinetic influences, in that those with electron-withdrawing groups might take longer to reach completion. To explore the kinetic requirements in this practical sense, and also to gain insight into the molecular mechanism, we undertook a study of the reaction kinetics.

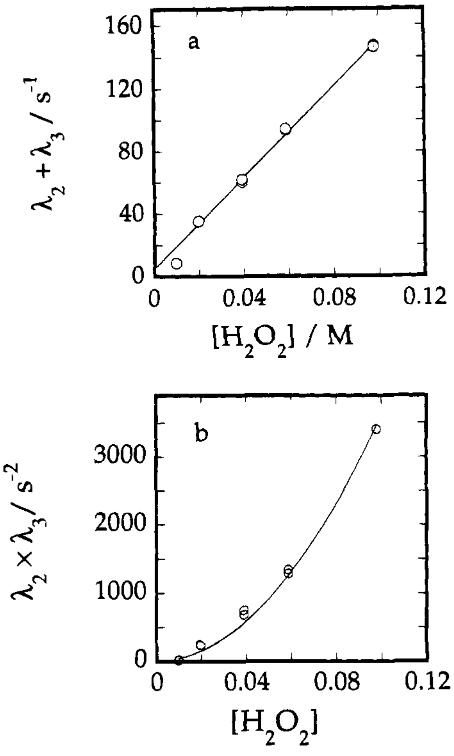


Figure 3. Fit of the kinetic data for the reactions of CH_3ReO_3 with hydrogen peroxide, eqs 1 and 2, is shown in two parts, which depict the variation with the concentration of hydrogen peroxide of (a) the sum of λ_2 and λ_3, the two time constants from the biexponential fitting, and (b) the product $\lambda_2\,\lambda_3$. The smooth lines represent the least-squares fits to eqs 7 and 8.

Table 1. Isolated Yields of the *N*-Oxide from the Oxidation of *Para*–Substituted Dimethylanilines by Hydrogen Peroxide, As Catalyzed by CH_3ReO_3[a]

para substituent	% yield	para substituent	% yield
CH_3	87	Br	89
H	92	NO_2	88
F	85		

[a] In MeOH at room temperature, with an approximate mole ratio of aniline:peroxide:rhenium of 20:50:1.

The Kinetics of the Oxidation of 4-Substituted *N,N*-Dimethylanilines. As the reaction was clean, forming only the *N*-oxide, it was straightforward to study the kinetics. These anilines do not react with hydrogen peroxide without the rhenium catalyst. Figure 4 shows the absorbance changes without and with the catalyst.

The kinetics of the reactions catalyzed by CH_3ReO_3 were evaluated by the initial rate method. The data showed that the reaction is first-order with respect to both CH_3ReO_3 and aniline. Plots were made (see Figure

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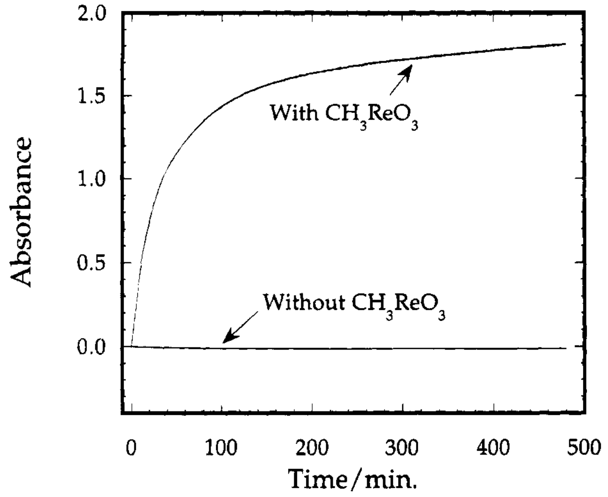


Figure 4. Typical absorbance–time kinetic traces at 251 nm for the oxidation of $PhNMe_2$ in methanol by hydrogen peroxide with and without CH_3ReO_3. The concentrations in MeOH were 13.2 μM CH_3ReO_3, 2.6 mM H_2O_2, and 0.11 mM $PhNMe_2$.

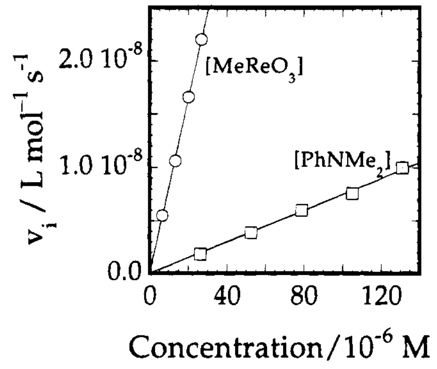


Figure 5. Variation of initial rate of reaction of dimethylaniline with a constant and excess $[H_2O_2]$, 2.76 mM, as a function of $[Re]_T$ at 45 μM $PhNMe_2$ and $[PhNMe_2]$ at 4.15 μM CH_3ReO_3.

5) of $v_i = (-d[\text{aniline}]/dt)_i$ versus $[Re]_T$ at constant $[PhNMe_2]_0$ and of v_i versus $[\text{aniline}]_0$ at constant $[Re]_T$. The rate constants were obtained from the slopes of the plots.

For $PhN(CH_3)_2$ a series of experiments was carried out at five values of $[H_2O_2]$, in the range of 1.6–10.0 mM, with 69 μM $PhN(CH_3)_2$ and 10.6 μM CH_3ReO_3. The values of v_i were constant at $(1.26 \pm 0.01) \times 10^{-8}$ L mol^{-1} s^{-1}, proving the zeroth-order dependence on $[H_2O_2]$ under these conditions.

In a separate series, the rate was determined under conditions where the formation of **A** governed the rate. Thus, this would constitute an independent determination of k_1 and also validate the reaction scheme. So that the kinetic term in k_1 would be the dominant one, an excess of the aniline was used. In the initial stage of the reaction, only **A** was formed. With high $[PhNMe_2]$, however, the subsequent oxidation reaction proceeded more rapidly, and the k_1 step was nearly rate-controlling.

The initial rates from stopped-flow experiments were fit to the equation $v_i = k_1[Re]_T[H_2O_2]$. These determinations were carried out with a constant concentration of CH_3ReO_3 and a varying hydrogen peroxide concentration, the progress of the reaction being monitored at 328 nm where $\Delta\epsilon = 105$ L mol^{-1} cm^{-1}. The plot of v_i vs $[H_2O_2]$ was linear. The slope gave $k_1 = (1.18 \pm 0.06) \times 10^3$ L mol^{-1} s^{-1}. This value agrees well with that obtained from the double exponential curve fitting of the peroxide reactions alone, which gave $k_1 = 1.15 \times 10^3$ L mol^{-1} s^{-1}. On the basis of the above observations, we suggest that the reaction follows the pathway shown in Scheme 2.

Scheme 2

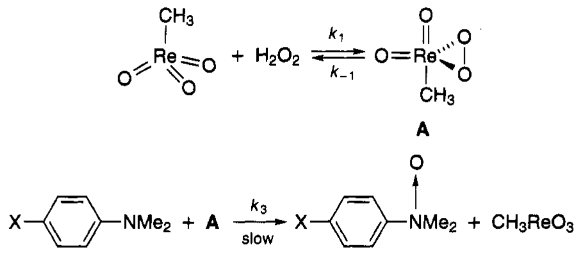


Table 2. Rate Constants for the Oxidation of *Para*-Substituted Dimethylanilines[a,b]

para substituent	k_3/L mol^{-1} s^{-1}	para substituent	k_3/L mol^{-1} s^{-1}
CH_3	24.5	Br	8.7
H	18.4	NO_2	1.9
F	12.7		

[a] In MeOH at 25.0 °C. The rate constants were calculated from initial rate determinations carried out with high concentrations of hydrogen peroxide. [b] The value of k_3 is given by eq 11.

The oxidation of *N,N*-dimethylaniline by **B** was studied with **B** in excess. The reaction was investigated with [**B**] varying in the range of 1.5–7.5 mM, while $[PhNMe_2]$ was kept constant at 11 μM; then [**B**] was kept constant at 1.5 mM, and $[PhNMe_2]$ varied in the range of 5.5–28 μM. The reaction proved to be first-order with respect to [**B**] and $[PhNMe_2]$. The rate constant obtained from the plot of initial rate of the reaction versus [**B**] or $[PhNMe_2]$ is $(1.14 \pm 0.07) \times 10^{-2}$ L mol^{-1} s^{-1}. In comparison, the oxidation of *N,N*-dimethylaniline by **A** has $k_3 = 18.4$ L mol^{-1} s^{-1}. Clearly, the reactivity of **B** toward the oxidation of *N,N*-dimethylanilines is negligible compared to that of **A**.

The steady-state approximation for [**A**] and $[CH_3ReO_3]$ gives the rate equation assuming that Scheme 2 is operative:

$$-\frac{d[\text{aniline}]}{dt} = \frac{k_3[\text{Re}]_T[\text{H}_2\text{O}_2][\text{aniline}]}{\dfrac{k_{-1} + k_3[\text{aniline}]}{k_1} + [\text{H}_2\text{O}_2]} \qquad (10)$$

With excess hydrogen peroxide, such that $(k_{-1} + k_3[\text{aniline}])/k_1 \ll [H_2O_2]$, the equation becomes

$$-\frac{d[\text{aniline}]}{dt} \cong k_3[\text{Re}]_T[\text{aniline}] \qquad (11)$$

This form agrees with the results reported above, in which the orders with respect to catalyst and aniline are unity, whereas that with respect to hydrogen peroxide is zero. From initial rate experiments, we obtained values for the rate constants k_3 for the reactions of 4-methyl-*N,N*-dimethylaniline, 4-fluoro-*N,N*-dimethylaniline, 4-bromo-*N,N*-dimethylaniline, *N,N*-dimethylaniline, and 4-nitro-*N,N*-dimethylaniline at 25.0 °C in methanol. The values are given in Table 2.

Oxidation of *N*-Phenylhydroxylamine. This compound was examined because we came to believe that it might be an intermediate in the reaction of aniline itself. The reaction in the absence of CH_3ReO_3 was examined

Scheme 3

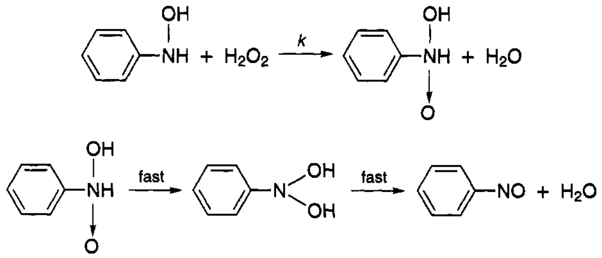


Table 3. Yields of the Nitrosoarenes from the Oxidation of Substituted Anilines by Hydrogen Peroxide, As Catalyzed by CH_3ReO_3[a]

substituent	% yield	substituent	%yield
o-CH_3	78	*p*-OCH_3	89
H	86	*p*-c-hexyl	73
m-CH_3	79	*p*-Cl	52
p-CH_3	82		

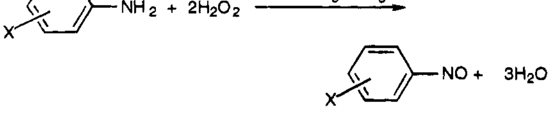
[a] In MeOH at room temperature, with an approximate mole ratio of aniline:peroxide:rhenium of 20:500:1.

with [PhNHOH] = 53–160 μM and $[H_2O_2]$ in the range of 1.04–5.02 mM. The reaction gave nitrosobenzene in about 88% yield. The reaction is first-order with respect to both *N*-phenylhydroxylamine and hydrogen peroxide, as represented by eq 12. The rate constant for the rate-controlling step in Scheme 3 is $k = 0.78 \pm 0.04$ L mol^{-1} s^{-1}.

$$-\frac{d[PhNHOH]}{dt} = k[PhNHOH][H_2O_2] \qquad (12)$$

***N*-Phenylhydroxylamine: Catalysis by CH_3ReO_3.** The catalyzed reaction was investigated with $[Re]_T$ = 14.5–58.4 μM, $[H_2O_2]$ = 1.5–10 mM, and [PhNHOH] in the range of 58.4–233 μM. The reaction with added CH_3ReO_3 proved to be much faster than the uncatalyzed reaction. Under these conditions, with excess hydrogen peroxide, the catalyzed reaction was first-order with respect to both CH_3ReO_3 and phenylhydroxylamine and nearly independent of $[H_2O_2]$. For reasons of simplicity, the initial rate method was used to study the catalyzed reaction. The rate constant for the catalyzed reaction of PhNHOH is $k_3 = 178 \pm 11$ L mol^{-1} s^{-1}. The data suggest that Scheme 2 also applies, with phenylhydroxylamine in place of the aniline. The rate law is the same as that for the oxidation of anilines, as given by eq 10. With a sufficient excess of hydrogen peroxide, such that $[H_2O_2] \gg (k_{-1} + k_3[PhNHON])/k_1$, the expression for the reaction rate reduces to the experimental result expressed by eq 11.

Oxidation of Anilines of the Formula $ArNH_2$. The major product of the oxidation of aniline by hydrogen peroxide catalyzed by CH_3ReO_3 is nitrosobenzene, according to eq 13. The product yields are listed in Table 3. The data suggest that the product yields may be lower for electron-withdrawing substituents.



(13)

The GC–MS results showed that small amounts of the nitroarenes and traces of the azobenzenes were formed as well. The nitroarenes probably come from the further oxidation of nitroso compound. We used nitrosobenzene itself as starting material, and confirmed the occurrence of eq 14, a much slower and therefore minor reaction, under the same conditions.

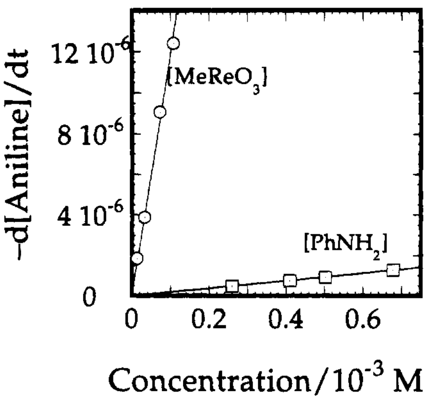
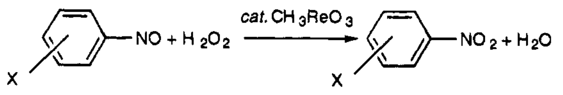
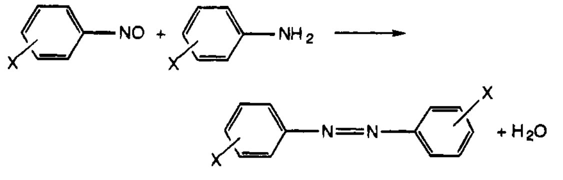


Figure 6. Variation of initial rate of oxidation of $PhNH_2$ at constant $[H_2O_2]$ = 1.96 mM, as a function of $[Re]_T$ at 0.973 mM $PhNH_2$ and as a function of $[PhNH_2]_0$ at $[Re]_T$ = 15 μM.



(14)

The azobenzene may come about from the condensation of nitrosobenzene with aniline. We mixed nitrosobenzene and aniline together in methanol and showed that the major product was azobenzene, which did not require the rhenium catalyst.



(15)

Kinetics of the Catalyzed Oxidation of $PhNH_2$. The reaction was monitored by the buildup of nitrosobenzene at 320 nm where the Δε is 5000 L mol^{-1} cm^{-1}. The initial rate was calculated from the initial slopes of the absorbance–time curves; dAbs/d*t* values were converted to the reaction rates, $-d[PhNH_2]/dt$, by division by $l\Delta\epsilon$ (where l is the pathlength).

The kinetic study was carried out in two parts. In the one, we maintained $[Re]_T$ constant and varied $[PhNH_2]$, and vice-versa; see Figure 6. The results together were used to prove that eq 10 applied here as well.

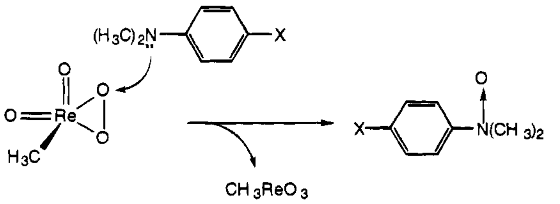
With a large excess of hydrogen peroxide, the reaction became first-order with respect to both $[Re]_T$ and $[PhNH_2]_0$, consistent with the limiting form shown in eq 11. Plots of v_i vs $[Re]_T$ and v_i vs $[aniline]_0$ were linear. The rate constant for $PhNH_2$ was $k_3 = 2.04$ L mol^{-1} s^{-1}.

The oxidation of aniline by **B** was also studied with **B** in excess. The reaction was investigated with [**B**] varying in the range of 2.0–10.0 mM, while [aniline] was kept constant at 12 μM; then [**B**] was kept constant at 2.0 mM and [aniline] varied in the range of 6–30 μM. The reaction proved to be first-order with respect to [**B**] and [aniline]. The rate constant was obtained from the plot of initial rate of the reaction versus [**B**], or [aniline] is $(3.34 \pm 0.15) \times 10^{-4}$ L mol^{-1} s^{-1}. As in the case of *N,N*-dimethylaniline, the reactivity of **B** toward the oxidation of aniline is also negligible compared to that of **A**.

It can be seen from Table 3 that the anilines with an electron-donating group (e.g., *p*-anisidine) gave higher yields. On the basis of the product yields and on the kinetic study of *para*-substituted *N*,*N*-dimethylanilines, *N*-phenylhydroxylamine, and aniline, the assumption that the *N*-phenylhydroxylamine is the intermediate in this MTO-catalyzed oxygen transfer reaction is reasonable. We suggest that this reaction occurs as shown in Scheme 4.

Discussion

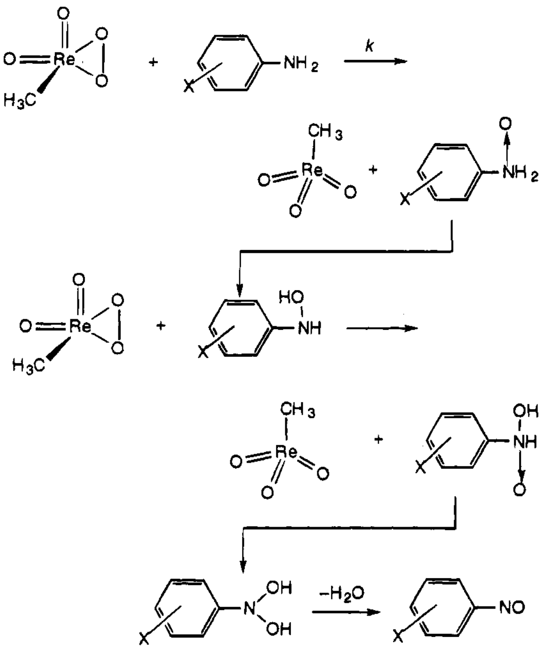
The oxidation of *para*-substituted *N*,*N*-dimethylaniline is inhibited by electron-withdrawing groups. The rate constants from Table 2 follow a linear Hammett relationship. The reaction constant $\varrho = -1.19$, suggesting that the rate-controlling step is the nucleophilic attack of nitrogen lone-pair electrons of anilines on a peroxidic oxygen of **A**.



Electron-donating groups attached to the nitrogen atom of aniline also increase the rate constant. For example, the k_3 for aniline of 2.04 L mol^{-1} s^{-1} increases for $PhNMe_2$ by about 9-fold, to 18.4 L mol^{-1} s^{-1}.

N-Phenylhydroxylamine has an OH group attached to nitrogen. As a result, the rate constant, 178 L mol^{-1} s^{-1}, is about 90 times larger than that of aniline. As it is known that aniline oxidation by peroxy acids proceeds to nitrosobenzene by way of hydroxylamine as intermediates,[30] we suggested that the hydroxylamines may be intermediates in this rhenium-catalyzed oxidation of anilines to the nitrosobenzenes. Since the second step is about 90 times faster than the first, it is difficult to detect the existence of *N*-phenylhydroxylamine directly. The postulate that ArNHOH are intermediates does allow a ready explanation for the formation of the observed products.

Scheme 4



The rate constant for the formation of **A** from CH_3ReO_3 in methanol is much larger than that in pH 1 aqueous media (MeOH: $k_1 = 1150$ L mol^{-1} s^{-1}; H_2O: 77 L mol^{-1} s^{-1}). This suggests that **A** might be stablized in methanol, perhaps because the activity of water is so much lower in methanol. As we mentioned earlier, the addition of more than a trace of water to the reaction of *N*,*N*-dimethylaniline decreased the rate of the formation of the *N*-oxide. The stabilization by methanol can also explain why the equilibrium constant for the reaction of CH_3ReO_3 and H_2O_2, $K_1 = 261$ L mol^{-1} in methanol, is almost 40 times larger than that in water at pH 1, $K_1 = 7.7$.

The oxidations of tertiary amines to *N*-oxides by peroxy acids also show negative ϱ values. For example, $\varrho = -2.35$ for the oxidation of substituted pyridines.[31] It would be interesting to know if the oxygen of peroxy acids is more electrophilic than the oxygen of **A**.

Although anilines $ArNH_2$ can be oxidized to the corresponding nitroso compounds with peroxyacetic acid,[32] they need either long reaction times (48 h) or heating. With the rhenium catalyst, a reaction time of 1 h at room temperature suffices.

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