

Kinetics of the Tungstate-catalyzed H_2O_2 Oxidation of Amines in Aqueous Methanol. Acidity Effect¹⁾

Yoshiro OGATA,* Kohtaro TOMIZAWA, and Hirokazu MAEDA

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464

(Received June 13, 1979)

Synopsis. Oxidation of *N,N*-dimethylaniline and benzylamine with H_2O_2 catalyzed by Na_2WO_4 has been kinetically studied in buffered 50% aqueous methanol at 25 °C. The rates with a catalytic amount of Na_2WO_4 fit Eq.: $v = k[\text{amine}]_t[\text{Na}_2\text{WO}_4]_t[\text{H}_2\text{O}_2]^0$ and the pH profile of rate constant shows no dissociation of peroxotungstate at pH 5–10. *N,N*-Dimethylaniline gives *N*-oxide (73%) and benzylamine gives benzaldehyde oxime (65%) under the present kinetic conditions.

The oxidation reactions with hydrogen peroxide catalyzed by metallic salts (*e.g.*, molybdate, tungstate and vanadate) have been reported with epoxidation of fumaric²⁾ and maleic³⁾ acids and allyl alcohol⁴⁾ and also oxidation of amines.^{5,6)} The tungstate-catalyzed oxidation of primary and secondary amines gives the corresponding oximes, hydroxylamines and hydroxamic acids, while the same oxidation of tertiary amines gives the corresponding *N*-oxides. Russian workers reported that the rate expression was shown as: $k_{\text{obsd}} = k[\text{amine}]^1[\text{WO}_4^{2-}]^1[\text{H}_2\text{O}_2]^0$, which was discussed mainly as to the steric effect of amines.^{5,6)} The present paper summarizes our kinetic data and probable mechanisms based on the acidity effect on the oxidation of *N,N*-dimethylaniline forming *N*-oxide and that of benzylamine forming benzaldehyde oxime in aqueous methanol.

Results and Discussion

The Na_2WO_4 -catalyzed H_2O_2 oxidation of *N,N*-dimethylaniline gave *N*-oxide in a yield of 73%. The same reaction of benzylamine gave benzaldehyde oxime in a yield of 65%. These reactions do not occur without the catalyst, hence the active oxidant, peroxotungstate, may be formed by the reaction of Na_2WO_4 and H_2O_2 .

The rates were measured with various initial concentrations of amines and H_2O_2 (*i.e.*, $[\text{PhMe}_2\text{N}]_0 = 3.95\text{--}7.89 \times 10^{-3} \text{ M}$, $[\text{H}_2\text{O}_2]_0 = 9.21\text{--}18.6 \times 10^{-3} \text{ M}$, $[\text{Na}_2\text{WO}_4]_0 = 1.00 \times 10^{-3} \text{ M}$ at pH 5.80 and $[\text{PhCH}_2\text{NH}_2]_0 = 4.53\text{--}18.3 \times 10^{-3} \text{ M}$, $[\text{H}_2\text{O}_2]_0 = 9.10\text{--}17.8 \times 10^{-3} \text{ M}$, $[\text{Na}_2\text{WO}_4]_0 = 1.00 \times 10^{-3} \text{ M}$ at pH 9.40; all data for definite molar ratio of reactants fit the rate equation (1) previously reported,⁵⁾ where $[\]_t$ means the stoichiometric concentration.

$$v = k_{\text{obsd}}[\text{amine}]_t[\text{Na}_2\text{WO}_4]_t \quad (1)$$

The values of k_{obsd} were $1.20 \pm 0.1 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ for PhMe_2N and $5.90 \pm 0.2 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ for PhCH_2NH_2 in 50% aq MeOH at 25 °C.

The rates were measured at various initial concentrations of Na_2WO_4 and H_2O_2 for the oxidation of *N,N*-dimethylaniline and thus the rate is practically independent of the concentration ($4.60\text{--}27.6 \times 10^{-3} \text{ M}$) of H_2O_2 in this range of $0.20\text{--}3.20 \times 10^{-3} \text{ M}$ Na_2WO_4 ; *i.e.*, at initial molar ratio $[\text{Na}_2\text{WO}_4]_0/[\text{H}_2\text{O}_2]_0$ below

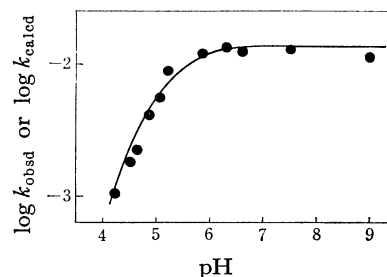


Fig. 1. pH profile for the Na_2WO_4 -catalyzed H_2O_2 oxidation of *N,N*-dimethylaniline in 50% aq MeOH at 25 °C. $[\text{PhMe}_2\text{N}] = 7.00 \times 10^{-3} \text{ M}$, $[\text{H}_2\text{O}_2] = 18.1 \times 10^{-3} \text{ M}$, $[\text{Na}_2\text{WO}_4] = 1.00 \times 10^{-3} \text{ M}$.

● $\log k_{\text{obsd}}$, — $\log k_{\text{calcd}}$.

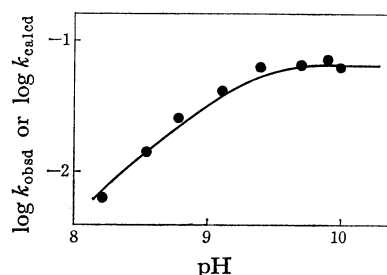


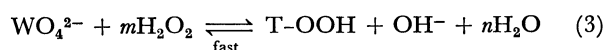
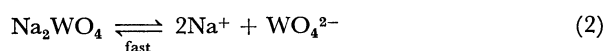
Fig. 2. pH profile for the Na_2WO_4 -catalyzed H_2O_2 oxidation of benzylamine in 50% aq MeOH at 25 °C. $[\text{PhCH}_2\text{NH}_2] = 9.61 \times 10^{-3} \text{ M}$, $[\text{H}_2\text{O}_2] = 13.5 \times 10^{-3} \text{ M}$, $[\text{Na}_2\text{WO}_4] = 1.00 \times 10^{-3} \text{ M}$.

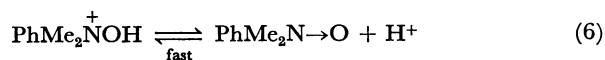
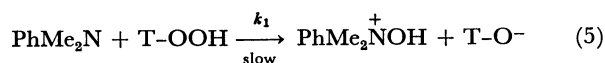
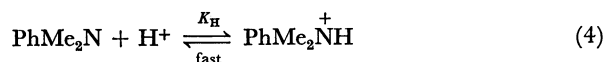
● $\log k_{\text{obsd}}$, — $\log k_{\text{calcd}}$.

1/9; but as the ratio approaches to unity, the rate deviates from the first-order dependence on $[\text{Na}_2\text{WO}_4]_0$. The similar result was obtained for the oxidation of benzylamine. This deviation may be attributed to the decrease of rate of reproducing peroxotungstate with decreasing concentration of H_2O_2 .

The effects of acidity of solution on the second-order rate constant k_{obsd} are shown in Figs. 1 and 2. As apparent from the figures, the rate constants decrease with increasing acidity at pH below 5 for *N,N*-dimethylaniline and at pH below 9 for benzylamine. Since the basicity constants, $K_{\text{H}} = [\text{BH}^+]/([\text{B}][\text{H}^+])$, are 1.15×10^5 for *N,N*-dimethylaniline⁷⁾ and 2.19×10^9 for benzylamine,⁷⁾ the decrease of k_{obsd} is ascribed to the deactivation of amines by protonation of amino nitrogen.

These results suggest a mechanism for *N,N*-dimethylaniline oxidation, where T means WO_3^- , WO_4^- , or WO_6^- . ($m=1, 2, 4$, $n=0, 1, 3$)⁸⁾





Since the rate is determined by step 5 as in the case of analogous oxidation of amines, the rate is expressed as

$$v = k_1[\text{PhMe}_2\text{N}][\text{T-OOH}]. \quad (7)$$

Here,

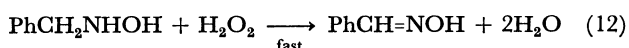
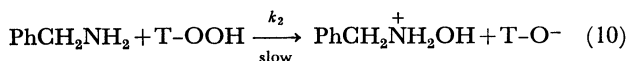
$$[\text{PhMe}_2\text{N}] = [\text{PhMe}_2\text{N}]_t / (1 + K_H[\text{H}^+]). \quad (8)$$

$[\text{PhMe}_2\text{N}]_t$ means stoichiometric or total concentration, *i.e.*, $[\text{PhMe}_2\text{N}]_t = [\text{PhMe}_2\text{N}] + [\text{PhMe}_2\text{NH}^+]$. Sodium tungstate reacts rapidly with excess H_2O_2 giving quantitatively peroxotungstate, T-OOH , whose structure is still ambiguous, *i.e.*, T-OOH may be HWO_5^- , HWO_6^- , HWO_8^- , *etc.*⁸⁾ Hence, Eq. 7 can be transformed into

$$v = \frac{k_1}{1 + K_H[\text{H}^+]} [\text{PhMe}_2\text{N}]_t [\text{Na}_2\text{WO}_4]_t. \quad (9)$$

Introduction of the value of $K_H = 1.15 \times 10^5 \text{ M}^{-1}$ and an average observed value of $k_1 = 1.25 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ at pH independent region ($6 \leq \text{pH} \leq 8$) gave the value of $k_1/(1 + K_H[\text{H}^+])$ or k_{caled} . A plot of $\log k_{\text{caled}}$ *vs.* pH is shown as a solid line in Fig. 1, on which lies the values of $\log k_{\text{obsd}}$ and this supports the mechanism.

Analogously, a mechanism for benzylamine is proposed as follows:



Although benzylhydroxylamine cannot be isolated in the oxidation of benzylamine, the rapid uncatalyzed oxidation of prepared benzylhydroxylamine to benzaldehyde oxime with rate constant $k_{\text{obsd}} \approx 10^{-2} \text{ s}^{-1}$ at 25°C was confirmed. Therefore, the rate for the rate-determining step is expressed as

$$v = \frac{k_2}{1 + K_H[\text{H}^+]} [\text{PhCH}_2\text{NH}_2]_t [\text{Na}_2\text{WO}_4]_t. \quad (13)$$

Here, K_H is $1.2 \times 10^9 \text{ M}^{-1}$ and an average k_2 value was calculated to be $7.24 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$, which is comparable to that in water ($8.4 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$).⁵⁾ By the similar treatments as above, it was found that the observed values of k_{obsd} lie on the calculated solid line in Fig. 2, hence the above mechanism is supported.

In conclusion, the present reaction involves a rate-determining electrophilic attack of HO-O (or $\begin{array}{c} \text{O} \\ | \\ \text{HO-O} \end{array}$) from peroxotungstate on neutral amino nitrogen of amine. The rate for *N,N*-dimethylaniline ($\log k_{\text{obsd}} = -1.9$) is smaller than the rate with H_2SO_5 oxidation ($\log k_{\text{obsd}}$

$= -1.5$)⁹⁾ and the rate with H_3PO_5 ($\log k_{\text{obsd}} = -0.7$).¹⁰⁾ *N,N*-Dimethylaniline is less reactive than benzylamine, which is expected from the lower basicity of *N,N*-dimethylaniline ($K_H = 1.15 \times 10^5 \text{ M}^{-1}$) compared with that of benzylamine ($K_H = 2.19 \times 10^9 \text{ M}^{-1}$).

Experimental

Materials. *N,N*-Dimethylaniline, bp $192-194^\circ\text{C}$, and benzylamine, bp 185°C , used were of guaranteed grade. Sodium tungstate was also of guaranteed grade. Benzylhydroxylamine was prepared by the reaction of benzyl chloride with hydroxylamine hydrochloride in alkaline aqueous ethanol, mp $54-56^\circ\text{C}$ (lit,¹¹⁾ 57°C).

Aqueous hydrogen peroxide for kinetic experiments was prepared by dilution of guaranteed 90% H_2O_2 purchased from Mitsubishi Gas Chem. Co.

Products. *N,N*-Dimethylaniline was oxidized with 3 equivalents of 90% H_2O_2 in the presence of catalytic amount of Na_2WO_4 in 50% aqueous MeOH to yield *N,N*-dimethylaniline *N*-oxide, $\lambda_{\text{max}}^{\text{MeOH}}$ 254 nm ($\log \epsilon$ 2.40), mp $150-152^\circ\text{C}$ (lit,¹²⁾ mp $151-152^\circ\text{C}$). Benzylamine, $\lambda_{\text{max}}^{\text{MeOH}}$ 253 nm ($\log \epsilon$ 2.38) was oxidized with 3 equivalents of 90% H_2O_2 in the presence of Na_2WO_4 at below 20°C , yielding benzaldehyde oxime, bp $78-79^\circ\text{C}/1 \text{ mmHg}$ (lit,⁵⁾ $104^\circ\text{C}/5 \text{ mmHg}$). Benzylhydroxylamine was oxidized analogously to give quantitative yield of benzaldehyde oxime, bp $78-79^\circ\text{C}/1 \text{ mmHg}$. These products were identified by comparison of NMR peaks with those of authentic specimen.

Kinetics. The kinetic experiments were conducted in buffered 50% aqueous MeOH at 25°C . The reaction was started by the addition of aqueous methanol solution of H_2O_2 (5 ml) to thermostated aqueous methanol Na_2WO_4 solution (45 ml). The rate was followed by iodometric titration of H_2O_2 and also by UV spectrophotometry of the pipetted out aliquots. The rates observed by both methods agreed satisfactorily. In the UV spectrophotometry, the decrease of absorption of *N,N*-dimethylaniline at $\lambda_{\text{max}}^{\text{MeOH}}$ 251 nm ($\log \epsilon$ 4.10) and the increase of absorption of benzaldehyde oxime at $\lambda_{\text{max}}^{\text{MeOH}}$ 250 nm ($\log \epsilon$ 4.14) were measured. The buffer solutions were made of AcONa-HCl , AcONa-AcOH , or $\text{KH}_2\text{PO}_4\text{-Na}_2\text{HPO}_4$.

References

- 1) Contribution No. 264.
- 2) M. A. Beg and I. Ahmad, *J. Catal.*, **39**, 260 (1975).
- 3) G. G. Allan and A. N. Neogi, *J. Catal.*, **16**, 197 (1970).
- 4) Z. Raciszewski, *J. Am. Chem. Soc.*, **82**, 1267 (1960).
- 5) K. Kahr and C. Berther, *Chem. Ber.*, **93**, 132 (1960).
- 6) O. L. Lebedev and S. N. Kazarnoski, *Zh. Obshch. Khim.*, **30**, 1631, 3105 (1960).
- 7) N. F. Hall and M. R. Sprinkle, *J. Am. Chem. Soc.*, **54**, 1928 (1932).
- 8) K. F. Jahr and E. Lothar, *Ber.*, **71**, 894, 903, 1127 (1938).
- 9) Y. Ogata and I. Tabushi, *Bull. Chem. Soc. Jpn.*, **31**, 969 (1958).
- 10) Y. Ogata, K. Tomizawa, and T. Morikawa, *J. Org. Chem.*, **44**, 352 (1979).
- 11) L. W. Jones and M. C. Sneed, *J. Am. Chem. Soc.*, **39**, 674 (1917).
- 12) A. C. Cope and P. H. Towle, *J. Am. Chem. Soc.*, **71**, 3423 (1949).