January, 1980] © *The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, **53**, *285—286 (1980)* 285

Kinetics of the Tungstate-catalyzed H_2O_2 Oxidation of Amines in Aqueous Methanol. Acidity Effect[1)]

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(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.: $v=k[\text{amine}]_t[Na_2WO_4]_t[H_2O_2]^0$ 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 fumaric[2)] and maleic[3)] acids and allyl alcohol[4)] 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: $k_{\text{obsd}}=k[\text{amine}]^1[WO_4^{2-}]^1[H_2O_2]^0$, 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.*, $[PhMe_2N]_0=3.95-7.89\times10^{-3}$ M, $[H_2O_2]_0=9.21-18.6\times10^{-3}$ M, $[Na_2WO_4]_0=1.00\times10^{-3}$ M at pH 5.80 and $[PhCH_2NH_2]_0=4.53-18.3\times10^{-3}$ M, $[H_2O_2]_0=9.10-17.8\times10^{-3}$ M, $[Na_2WO]_0=1.00\times10^{-3}$ M at pH 9.40; all data for difinite molar ratio of reactants fit the rate equation (1) previously reported,[5)] where $[\;]_t$ means the stoichiometric concentration.

$$v=k_{\text{obsd}}[\text{amine}]_t[Na_2WO_4]_t \tag{1}$$

The values of k_{obsd} were $1.20\pm0.1\times10^{-2}\ M^{-1}\ s^{-1}$ for $PhMe_2N$ and $5.90\pm0.2\times10^{-2}\ M^{-1}\ s^{-1}$ 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—27.6×10^{-3} M) of H_2O_2 in this range of 0.20—3.20×10^{-3} M Na_2WO_4; *i.e.*, at initial molar ratio $[Na_2WO_4]_0/[H_2O_2]_0$ below 1/9; but as the ratio approaches to unity, the rate deviates from the first-order dependence on $[Na_2WO_4]_0$. 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.

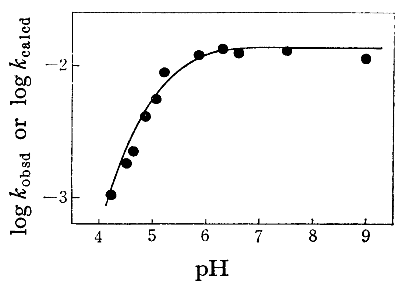

Fig. 1. pH profile for the Na_2WO_4-catalyzed H_2O_2 oxidation of *N,N*-dimethylaniline in 50% aq MeOH at 25 °C. $[PhMe_2N]=7.00\times10^{-3}$ M, $[H_2O_2]=18.1\times10^{-3}$ M, $[Na_2WO_4]=1.00\times10^{-3}$ M.
● log k_{obsd}, —log k_{calcd}.

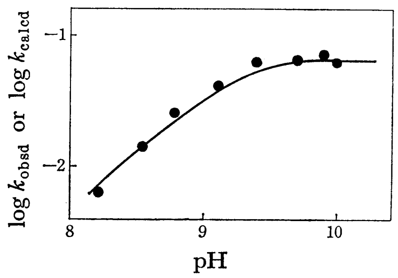

Fig. 2. pH profile for the Na_2WO_4-catalyzed H_2O_2 oxidation of benzylamine in 50% aq MeOH at 25 °C. $[PhCH_2NH_2]=9.61\times10^{-3}$ M, $[H_2O_2]=13.5\times10^{-3}$ M, $[Na_2WO_4]=1.00\times10^{-3}$ M.
● log k_{obsd}, —log k_{calcd}.

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, $K_H=[BH^+]/([B][H^+])$, are 1.15×10^5 for *N,N*-dimethylaniline[7)] 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)]

$$Na_2WO_4 \underset{\text{fast}}{\rightleftharpoons} 2Na^+ + WO_4^{2-} \tag{2}$$

$$WO_4^{2-} + mH_2O_2 \underset{\text{fast}}{\rightleftharpoons} \text{T-OOH} + OH^- + nH_2O \tag{3}$$

$$\mathrm{PhMe_2N + H^+ \underset{fast}{\overset{\mathit{K}_H}{\rightleftharpoons}} PhMe_2\overset{+}{N}H} \tag{4}$$

$$\mathrm{PhMe_2N + T\text{-}OOH \underset{slow}{\xrightarrow{\mathit{k}_1}} PhMe_2\overset{+}{N}OH + T\text{-}O^-} \tag{5}$$

$$\mathrm{PhMe_2\overset{+}{N}OH \underset{fast}{\rightleftharpoons} PhMe_2N{\rightarrow}O + H^+} \tag{6}$$

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

$$v = k_1[\mathrm{PhMe_2N}][\mathrm{T\text{-}OOH}]. \tag{7}$$

Here,

$$[\mathrm{PhMe_2N}] = [\mathrm{PhMe_2N}]_t/(1+K_H[\mathrm{H^+}]). \tag{8}$$

$[\mathrm{PhMe_2N}]_t$ means stoichiometric or total concentration, *i.e.*, $[\mathrm{PhMe_2N}]_t=[\mathrm{PhMe_2N}]+[\mathrm{PhMe_2\overset{+}{N}H}]$. 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

$$v = \frac{k_1}{1+K_H[\mathrm{H^+}]}[\mathrm{PhMe_2N}]_t[\mathrm{Na_2WO_4}]_t. \tag{9}$$

Introduction of the value of $K_H=1.15\times10^5\ \mathrm{M^{-1}}$ and an average observed value of $k_1=1.25\times10^{-2}\ \mathrm{M^{-1}\,s^{-1}}$ at pH independent region ($6\leq\mathrm{pH}\leq8$) gave the value of $k_1/(1+K_H[\mathrm{H^+}])$ or k_{calcd}. A plot of log k_{calcd} *vs.* pH is shown as a solid line in Fig. 1, on which lies the values of log k_{obsd} and this supports the mechanism.

Analogously, a mechanism for benzylamine is proposed as follows:

$$\mathrm{PhCH_2NH_2 + T\text{-}OOH \underset{slow}{\xrightarrow{\mathit{k}_2}} PhCH_2\overset{+}{N}H_2OH + T\text{-}O^-} \tag{10}$$

$$\mathrm{PhCH_2\overset{+}{N}H_2OH \underset{fast}{\rightleftharpoons} PhCH_2NHOH + H^+} \tag{11}$$

$$\mathrm{PhCH_2NHOH + H_2O_2 \underset{fast}{\longrightarrow} PhCH{=}NOH + 2H_2O} \tag{12}$$

Although benzylhydroxylamine cannot be isolated in the oxidation of benzylamine, the rapid uncatalyzed oxidation of prepared benzylhydroxylamine to benzaldehyde oxime with rate constant $k_{\mathrm{obsd}}\approx10^{-2}\ \mathrm{s^{-1}}$ at 25 °C was confirmed. Therefore, the rate for the rate-determining step is expressed as

$$v = \frac{k_2}{1+K_H[\mathrm{H^+}]}[\mathrm{PhCH_2NH_2}]_t[\mathrm{Na_2WO_4}]_t. \tag{13}$$

Here, K_H is $1.2\times10^9\ \mathrm{M^{-1}}$ and an average k_2 value was calculated to be $7.24\times10^{-2}\ \mathrm{M^{-1}\,s^{-1}}$, which is comparable to that in water ($8.4\times10^{-2}\ \mathrm{M^{-1}\,s^{-1}}$).[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– (or $\begin{array}{l}\diagup\mathrm{O}\\ \;|\\ \diagdown\mathrm{O}\end{array}$) from peroxotungstate on neutral amino nitrogen of amine. The rate for *N,N*-dimethylaniline (log $k_{\mathrm{obsd}}=-1.9$) is smaller than the rate with H_2SO_5 oxidation (log $k_{\mathrm{obsd}}=1.5$)[9] and the rate with H_3PO_5 (log $k_{\mathrm{obsd}}=-0.7$).[10] *N,N*-Dimethylaniline is less reactive than benzylamine, which is expected from the lower basicity of *N,N*-dimethylaniline ($K_H=1.15\times10^5\ \mathrm{M^{-1}}$) compared with that of benzylamine ($K_H=2.19\times10^9\ \mathrm{M^{-1}}$).

Experimental

Materials. *N,N*-Dimethylaniline, bp 192—194 °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 °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, $\lambda_{\mathrm{max}}^{\mathrm{MeOH}}$ 254 nm (log ε 2.40), mp 150—152 °C (lit,[12] mp 151—152 °C). Benzylamine, $\lambda_{\mathrm{max}}^{\mathrm{MeOH}}$ 253 nm (log ε 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 °C/1 mmHg (lit,[5] 104 °C/5 mmHg). Benzylhydroxylamine was oxidized analogously to give quantitative yield of benzaldehyde oxime, bp 78—79 °C/1 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 $\lambda_{\mathrm{max}}^{\mathrm{MeOH}}$ 251 nm (log ε 4.10) and the increase of absorption of benzaldehyde oxime at $\lambda_{\mathrm{max}}^{\mathrm{MeOH}}$ 250 nm (log ε 4.14) were measured. The buffer solutions were made of AcONa–HCl, AcONa–AcOH, or KH_2PO_4–Na_2HPO_4.

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