Kinetics and Preparation of Amine Oxides

C. Joe Toney, F.E. Friedli* and **P.J. Frank**
Witco Corporation, Dublin, Ohio 43017

A kinetic model for the oxidation of dimethyllaurylamine to its amine oxide with hydrogen peroxide was developed. It is a second-order reaction where k = .0250, .0079 and .0037 kg per mol/min at 75, 60 and 50°C, respectively. Amine oxides of *N*-lauryl morpholine, piperidine and 3-methyl piperidine were synthesized, and their rates of formation were determined. Compared to dimethyllaurylamine, the piperidines react slower, while the morpholine reaction is much faster.

KEY WORDS: Amine oxides, dimethyllaurylamine, foam stabilizers, hydrogen peroxide, kinetics, morpholine, piperidine.

The oxidation of a tertiary amine with hydrogen peroxide is a common process used to produce amine oxides. These amine oxides are highly polar with strong hydrogen bonding tendencies (1). Amine oxides find most of their usefulness in shampoo and liquid detergent formulations because of their excellent foam stability, viscosity control, detergency, biodegradability, emolliency and antistatic properties (2).

Surprisingly, not much information is available in the literature on this common reaction. A mechanism for this oxidation is offered by Oswald and Guertin (3). The amine and the hydrogen peroxide initially combine to form an ammonium peroxide. The ammonium peroxide then decomposes to yield the amine oxide with the loss of water (Reaction 1):

$$R_3N + H_2O_2 \xrightarrow{k1} R_3N \cdot H_2O_2 \xrightarrow{k2} R_3NO + H_2O$$

Katritzky and Lagowski (4) in 1971 developed a kinetic model for amine oxide formation from pyridine and perbenzoic acid. They showed this to be second-order reaction. Another group studied the tungsten-catalyzed hydrogen peroxide oxidation of amines (5). A procedure for preparing amine oxides from amines and oxygen has been developed under high pressure (6). It has been the intent of this work to develop a kinetic model for amine oxide formation based upon amine oxides of more commercial interest.

EXPERIMENTAL PROCEDURES

Materials. Dimethyllaurylamine used in these experiments was supplied by Ethyl Corporation (Baton Rouge, LA) and Witco (New York, NY). *N*-laurylpiperidine, *N*-lauryl-3-methylpiperidine and *N*-laurylmorpholine were prepared from lauryl alcohol, and the corresponding tertiary amine by modified known procedures (7).

Morpholine and piperidine were from Aldrich (Milwaukee, WI), while a 3-methyl piperidine was supplied free of charge by DuPont (Boston, MA). The finished tertiary amines were distilled and analyzed as better than 99% pure by gas chromatography.

The hydrogen peroxide used here was a 51% aqueous solution purchased from Fisher Scientific (Fairlawn, NJ). The solvents used were deionized water and 99% isopropyl alcohol purchased from Ashland Chemical (Dublin, OH).

*To whom correspondence should be addressed at Witco Chemical Co., P.O. Box 646, Dublin, OH 43017.

Reaction procedure. The reactions at a 1:1 mole ratio were run by charging solvent (317 g) and 0.657 moles amine (140 g for dimethyllaurylamine) to a 1000-mL jacketed reaction flask, which was connected to a constant-temperature bath. The reaction mixture was heated to reaction temperature, then 43.8 g of 51% aqueous hydrogen peroxide (0.657 moles) was added rapidly. Samples were then taken and analyzed at various times. The reactions at a 2:1 mole ratio and 1:2 were run the same way except for an adjustment in charges for the mole ratios.

Analytical procedure. All of the samples were analyzed by the follow procedure. Into two separate 150-mL beakers, approximately 2 g of sample was weighed to four decimal places, 50 mL of isopropyl alcohol (IPA) was added into beaker "A." Into beaker "B" 50 mL IPA and 10 mL of 99% methyl iodide were added and stirred for about 15 min. The methyl iodide quaternized the free amine in beaker "B," allowing the titration to include only the HCl equivalents needed for the amine oxide. Both samples were titrated to their equivalence points with 0.5n HCl *via* a Sargent Welch automatic titrator (Sargent Welch Scientific Co., Skokie, IL). For dimethyllaurylamine, it is a pH of 3.75, and it is slightly lower for the cyclic amines. The milliequivalents (meq) were calculated as follows:

$$\text{meq} = [\text{titrant (mL)} \times \text{normality}]/\text{sample weight} \quad [1]$$

Then, the percent free amine (fa) was calculated:

$$\text{fa\%} = [(\text{meq}_A - \text{meq}_B) \times \text{MW}_{fa}]/10 \quad [2]$$

where MW is molecular weight. Next, the percent amine oxide (ao) was calculated:

$$\text{ao\%} = (\text{meq}_B \times \text{MW}_{ao})/10 \quad [3]$$

RESULTS AND DISCUSSION

Initially, reactions were run in deionized water with the amine concentration such that the product would be approximately 30% amine oxide. However, it was found that, at a mole ratio where the amine concentration is higher than that of the hydrogen peroxide, the insolubility of the amine in water caused inconsistencies in the experimental measurements of the rate constant (k). Upon this realization, IPA was substituted for the water. It was also found that, for those reactions not being affected by solubility problems, the rate constant for the IPA runs was virtually identical to those run in water (Table 1). However, IPA gave more consistent results.

The mechanism shown in Reaction 1 indicates that the formation of amine oxides is actually two reactions in series. A more accurate description (see Reaction 2 that follows) could be the establishment of an equilibrium between the reactants and the ammonium peroxide with subsequent decomposition of the intermediate to form the amine oxides:

TABLE 1

Kinetics of Oxidation of Dimethyllaurylamine

Temperature (°C)	Mole[a] ratio	Solvent	Rate constant[b]	Index of determination (%)
75	1:1	DI H_2O	0.0233	95
75	1:2	DI H_2O	0.0285	95
75	2:1	IPA	0.0280	95.2
75	1:1	IPA	0.0225	97
75	1:1	IPA	0.0226	96.9
60	1:1	IPA	0.0079	95.4
60	1:1	IPA	0.0079	96.3
50	1:1	IPA	0.0037	96.8

[a]Amine/hydrogen peroxide. IPA, isopropyl alcohol; DI H_2O, deionized water.
[b](kg/mole)/min.

$$R_3N + H_2O_2 \overset{Keq}{\leftrightarrow} R_3N{\cdot}H_2O_2 \overset{k_2}{\rightarrow} R_3NO + H_2O$$

A second-order rate law (Equation 4) can then be derived:

$$d[\text{amine oxide}]/dt = k_2[R_3N{\cdot}H_2O_2] = k_2K_{eq}[R_3N][H_2O_2] = k[R_3N][H_2O_2] \quad [4]$$

Previous work (3) strongly suggests the reversibility of the formation of the ammonium peroxide.

Amine oxide formation is thus similar to fatty amide production from a fatty acid and ammonia, where the intermediate soap is unstable and decomposes both back to reactants and on to amide with loss of a mole of water.

Getting the rate constant (k) from our data involves plotting the natural log of the ratios of reactants at various times during the reaction (8,9). At 75°C, k = 0.0250 kg/mole/min, which held true for mole ratios of 2:1 amine/H_2O_2, 1:2 amine/H_2O_2 and 1:1 equimolar. This supports the assumption that the reaction is second-order. Experimentally, it was found that k = 0.0079 kg/mole/min at 60°C and k = 0.0037 kg/mole/min at 50°C.

Temperature dependence can be demonstrated by using the Arrhenius expression:

$$k = Ae^{-Ea/RT} \quad [5]$$

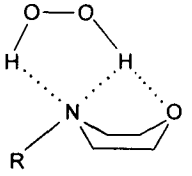
where Ea is the activation energy and A is the preexponential factor. These values can be found by using another form of this expression:

$$\log k = [-Ea/2.303R][1/T] + \log A \quad [6]$$

where −Ea/2.303R is equal to the slope of the line given by a plot of log k vs. 1/T. R is the gas constant equivalent to 1.9872 cal · $mol^{-1}K^{-1}$, and the temperature (T) must be expressed in degrees Kelvin.

The slope was determined to be −3641.263. From this the Ea calculated to be 16,664 cal/mole. By plugging the Ea back into the same expression, A was found to be 691.2 × 10^6. Knowing these values, one can calculate the rate constant at any relevant temperature.

Three cyclic amines (*N*-laurylmorpholine, *N*-laurylpiperidine and *N*-lauryl-3-methylpiperidine) were converted at 75°C and kg/mol/min to their respective amine oxides. The first two have antimicrobial activity (10-13). All three were easily prepared, and their rates of formation were determined as .065, .019 and .018, respectively. The two piperidine versions form slower than dimethyllaurylamine oxide, while laurylmopholine reacts much faster. The piperidines are somewhat more sterically hindered than dimethyllaurylamine. The oxygen in the morpholine ring probably hydrogen-bonds strongly with hydrogen peroxide, thus increasing the K_{eq} for Scheme 1.



SCHEME 1

All the amine oxides at 30% concentration in water remained clear and stable for over 3 mon. Future studies will include foam and foam stability tests.

With the knowledge that the oxidation of a tertiary alkylamine with hydrogen peroxide is a second-order reaction, and knowing the rate constant, one can calculate the rate of reaction by using Equation 4. This information is useful in reactor design to predict reactor size and production rate.

REFERENCES

1. Swern, Daniel, *Bailey's Industrial Oil and Fat Products*, Vol. 1, John Wiley & Sons, New York, 1979, p. 655.
2. Pattison, S.E., *Fatty Acids and Their Industrial Applications*, Marcell Dekker, New York, 1968, p. 133.
3. Oswald, A.A., and D.L. Guertin, *J. Org. Chem. 28*:651 (1963).
4. Katritzky, A.R., and J.M. Lagowski, *Chemistry of the Heterocyclic* N-*Oxides*, Vol. 19, Academic Press, London and New York, 1971, p. 69.
5. Riley, D.P., and P.E. Correa, *J. Org. Chem. 50(9)*:1563 (1985).
6. Ogata, Y., K. Tbmizawa and H. Moeda, *Bull. Chem. Soc. Jpn. 53(1)*:285 (1980).
7. Blackhurst, C.W., U.S. Patent 4,683,336 (1987).
8. Levenspiel, O., *Chemical Reaction Engineering*, John Wiley & Sons, New York, 1962, pp. 49-50.
9. Harris, G.M., *Chemical Kinetics*, D.C. Heath and Company, Boston, 1966, pp. 41-51.
10. Devinsky, F., I. Lacko, A. Nagy and L. Krasnec, *Chem. Zvesti. 32*:106 (1978).
11. Devinsky, F., F. Ferdinand, I. Lacko, D. Mlynarcik, I. Csiba and L. Kracnec, Czech. Patent 182981 (1980).
12. Kuhnen, L., *Chem. Ber. 99(10)*:3384 (1966).
13. Subik, J., G. Takacsova, M. Psenak and F. Devinsky, *Antimicrob. Asents Chemother. 12(2)*:139 (1977).

[Received June 30, 1993; accepted December 9, 1993]