SHORT COMMUNICATION

Kinetics of Hydrogen Peroxide Oxidation of Alkyl Dimethyl Amines

J.C. Gee* and R.C. Williamson

Chevron Chemical Company, Kingwood, Texas 77339

ABSTRACT: We measured the absolute rate constants for the hydrogen peroxide oxidation of two different octyl dimethyl amines in isopropanol/water mixtures at 23°C. The amines were 1-octyl dimethyl amine (**1**) and 2-ethylhexyl dimethyl amine (**2**); their structures were analogous to those most often encountered in commercial alkyl dimethyl amine oxide production. The observed first-order rate constants for the disappearance of amine across a range of H_2O_2 concentrations (0.5–8 M) indicated that the overall rate was first-order in amine and 3/2-order in H_2O_2. Calculations showed $k_1 = 0.16\ M^{-1}h^{-1}$, $k_2 = 0.046\ M^{-1}h^{-1}$, and $k_1/k_2 = 3.5$. The rates appeared to decrease with increasing steric hindrance around the nitrogen atom. We also investigated the effect of water on the reaction rates. When $[H_2O] < \sim4.5$ M in isopropanol, the rates increased with increasing $[H_2O]$; for $[H_2O] > \sim4.5$ M, the rates were insensitive to $[H_2O]$.
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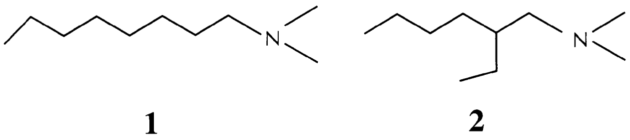
KEY WORDS: Alkyl dimethyl amine, amine oxide, hydrogen peroxide, kinetics, oxidation, tertiary amine.

Hydrogen peroxide oxidation of tertiary amines yields amine oxides. Many amine oxides, particularly those with at least one long alkyl side chain, are of industrial importance. Linear 1-alkyl dimethyl amine oxides, for example, find widespread use as foam stabilizers, antistatic agents, biocides, and viscosity builders. They are therefore common ingredients in shampoos and detergent formulations, hair conditioners, bathroom cleaners, and various cosmetic formulations (1).

The precursors to these amines oxides are linear 1-alkyl dimethyl amines (ADMA). These amines generally contain traces of linear 2- or 3-alkyl dimethyl amines and up to a few percentage of branched ADMA, which derive from the internal and branched olefins present with the 1-alkenes used to manufacture them. We were interested in the relative oxidation rates of these different ADMA and report here results of our kinetic investigations.

Our study centered on the oxidation rates of two different octene-derived ADMA: 1-octyl dimethyl amine (**1**) and 2-ethylhexyl dimethyl amine (**2**). The structures of these amines were analogous to the most common ADMA structures encountered in commercial amine oxide production. Furthermore, the C_8 chains were short enough to provide good solubility of the amines in isopropanol/water mixtures, but they were long enough to model adequately the C_{12} and longer chains normally used for commercial surfactants. The isopropanol/water mixture was chosen as the solvent, because it allowed the formulation of homogeneous solutions with the ADMA and H_2O_2 (Scheme 1).



SCHEME 1

EXPERIMENTAL PROCEDURES

Materials. 1-Octyl dimethyl amine was purchased from Aldrich Chemical Company (Milwaukee, WI) and used as received. Hydrogen peroxide was purchased from Interox (Houston, TX) as a 70% solution of H_2O_2 in water and used as received. Isopropanol was purchased from Mallinckrodt Chemical (Paris, KY) and used as received. Water was distilled and then filtered through a Barnstead (Dubuque, IA) NANOpure ultrapure water system.

2-Ethylhexyl dimethyl amine was synthesized as follows: About 25 mL 2-ethylhexyl bromide (Aldrich) was combined with 40 mL isopropanol and 40 mL of 40% aqueous dimethyl amine (Aldrich) in a round-bottom flask. The mixture was stirred at 70°C for about 23 h; then, it was combined with 8.6 g NaOH, 60 mL water, and 60 mL hexane in a separatory funnel. After agitation, the organic phase was collected, and the aqueous phase was extracted twice more with 60-mL portions of hexanes. The combined organic portions were dried for 20 min over anhydrous Na_2SO_4 and then filtered. Solvents were removed under reduced pressure at temperatures as high as 70°C, and the remaining liquid was dried for 25 min over anhydrous NaOH. The solids and a trace of brown oil were removed by filtration. The product was 16.0 g of a clear, slightly beige liquid that was 94% ADMA by gas chromatography (GC) flame-ionization detection (FID) (73% yield).

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*To whom correspondence should be addressed at Chevron Chemical Company, 1862 Kingwood Dr., Kingwood, TX 77339.

The mass spectrum of the product showed a molecular ion peak at *m/z* 157, as well as a base peak at *m/z* 58 for $C_3H_8N^+$, the expected fragment after typical α-β cleavage in this ADMA structure. The ^{13}C nuclear magnetic resonance spectrum (75 MHz, neat) showed nine peaks, with shifts at 10.8(*q*), 14.2(*q*), 23.5(*t*), 24.7(*t*), 29.3(*t*), 31.7(*t*), 37.5(*d*), 46.0(*q*, 2C), and 64.5(*t*) ppm from tetramethylsilane.

Hydrogen peroxide standardization. Commercial-grade 70% aqueous H_2O_2 was standardized by iodimetric titration. About 0.5 g of the 70% solution was added to about 137 g of distilled water to prepare a dilute peroxide solution suitable for titration. Excess KI was added to 1–2 g of the dilute peroxide solution in 50 mL isopropanol, along with 1–5 mL glacial acetic acid, and this solution was heated to its boiling point for 1–3 min to reduce all peroxide. The resulting yellow solution was titrated to a colorless endpoint with standardized aqueous sodium thiosulfate (Aldrich). The percentage H_2O_2 in the commercial sample was given by:

$$\%\ H_2O_2 = 1.7 \times (\text{mL } Na_2S_2O_3 \text{ soln.}) \times (\text{conc. } Na_2S_2O_3) \times D/(T \times C) \quad [1]$$

where D = grams of dilute H_2O_2 made; T = grams of dilute H_2O_2 titrated; C = grams of commercial H_2O_2 used to make the dilute solution (soln.); and the concentration (conc.) of $Na_2S_2O_3$ was in moles/liter. The solution used was 69.50% H_2O_2.

Kinetic procedure. GC/FID was used to monitor the disappearance of the ADMA during the course of reaction. Our instrument was a Hewlett-Packard (Wilmington, DE) 5890 Series II Plus gas chromatograph with a 12 m HP Ultra 1 column (0.20 mm i.d., 0.33 µm film thickness) operating at an initial pressure of 150 kPa. The temperature program began at 100°C and was increased 20°C/min to ≥180°C. The retention times were 1.23 min for **1** and 0.97 min for **2**.

In a typical experiment, 0.1–0.25 g of ADMA was combined with 0.12 g of *n*-tridecane (internal standard), 0-6 mL distilled water, < 8 g 69.50% aqueous H_2O_2, and isopropanol in a 25-mL volumetric flask. The molar ratio of H_2O_2 to ADMA was always ≥20. After the solution had thermally equilibrated, 0.5-mL aliquots of the solution were distributed into 25 separate GC vials; the vials were each sealed with a crimp cap and equilibrated at 23 ± 0.1°C on an autosampler rack, held at constant temperature by circulating fluid from a constant temperature bath. The autosampler periodically injected 0.1–0.3-µL samples from the vials for analysis. Reaction progress was monitored for 3–5 half-lives, with ≥6 points/half-life. The peak integral for each ADMA relative to the peak integral for *n*-tridecane was used to represent [ADMA] in subsequent calculations. Ambient temperature in the laboratory was 23°C. Because the vials were out of the autosampler rack for brief periods during transport to the injector, we minimized possible minor temperature fluctuations by maintaining the samples at 23°C throughout each experiment. Investigations at temperatures substantially different from ambient would preclude the use of the autosampler.

RESULTS AND DISCUSSION

A number of papers have reported that the oxidation of tertiary amines by hydrogen peroxide follows first-order kinetics in each reactant, making the reaction second-order overall (2,3). Evidence indicates that there is an initial pre-equilibrium, in which the amine and peroxide form an ammonium peroxide complex that decomposes with rate k to give the amine oxide and water (4) (Scheme 2).

According to this scenario, the observed rate would then be:

$$\frac{-d[\text{ADMA}]}{dt} = k'[\text{ADMA}]\text{H}_2\text{O}_2] \quad [2]$$

And when $[H_2O_2] >> [\text{ADMA}]$:

$$\frac{-d[\text{ADMA}]}{dt} = k_{\text{obs}}[\text{ADMA}] \quad [3]$$

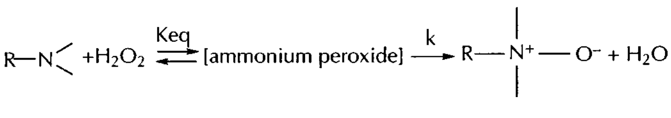
where $k_{\text{obs}} = k'[H_2O_2]$, and the observed reaction would be first-order in ADMA. The slope of a plot of $\ln[\text{ADMA}]_t$ vs. time would then give k_{obs} for the oxidation of ADMA (5,6). Alternatively, because

$$[\text{ADMA}]_t = [\text{ADMA}]_0 e^{-kt} + [\text{ADMA}]_\infty \quad [4]$$

a nonlinear least-squares fit of the raw data to this form also gives k_{obs}, and we used this approach.

Following this protocol, we set out to determine the absolute (and relative) rate constants for oxidation of **1** and **2** by H_2O_2 at 23°C. In a preliminary set of experiments, we combined **1**, *n*-tridecane, aqueous H_2O_2, and isopropanol, and then determined the observed first-order rate constants at several different concentrations of H_2O_2 (0.5–3 M). Disappearance of the amine showed excellent first-order behavior beyond five half-lives: The absolute values of the correlation coefficients for plots of $\ln[\text{ADMA}]_t$ vs. time were ≥0.99. But the plot of k_{obs} vs. $[H_2O_2]$ was not linear; instead, it showed nonlinear upward curvature with increasing $[H_2O_2]$.

Noting that the addition of each gram of H_2O_2 also meant the addition of 0.44 g of H_2O to these solutions (because the H_2O_2 was in an aqueous solution), we decided to investigate the effect of water concentration on the oxidation rate. Re-



SCHEME 2

sults showed that the rate increased with increasing water content when $[H_2O] < \sim 4.5$ M, but increasing $[H_2O]$ beyond this point had no effect on the reaction rate. The results appeared consistent with water stabilization of a charged intermediate. We postulate that, up to a point, increasing $[H_2O]$ in isopropanol increases K_{eq} in favor of the proposed ammonium peroxide intermediate, thereby increasing the observed rate of oxidation, but water clearly is not a reactant in the transformation.

In a separate set of experiments, we added additional distilled water to each sample and determined k_{obs} for essentially the same range of $[H_2O_2]$ as before. We kept $[H_2O_2] + [H_2O] = 14.1$ M for this entire set of samples, attempting to maintain a similar solvent system in each; the resulting water concentrations were 11–14 M. The plot of k_{obs} vs. $[H_2O_2]$ was still nonlinear. However, the plot of $\ln(k_{obs})$ vs. $\ln[H_2O_2]$ showed a best-fit linear least-squares slope of 1.4 with a correlation coefficient of 0.998. This result suggested that $k_{obs} = k_1[H_2O_2]^{3/2}$, and that $-d[\text{ADMA}]/dt = k_1[\text{ADMA}][H_2O_2]^{3/2}$. A nonlinear least squares fit of the data to this form gave $k_1 = 0.16\ \text{M}^{-1}\text{h}^{-1}$.

Corresponding work with **2** led to the same rate law. We performed essentially the same experiments with **2** that we had performed with **1**, keeping $[H_2O] > 4.5$ M. However, because **2** oxidized more slowly than did **1**, a broader range of $[H_2O_2]$ was possible with **2** (0.5–8 M) than with **1** (0.5–3 M). The plot of $\ln(k_{obs})$ vs. $\ln[H_2O_2]$ showed a best-fit linear least-squares slope of 1.5 with a correlation coefficient of 0.999. The calculated k_2 was 0.046 $\text{M}^{-1}\text{h}^{-1}$. We included **1** in some of these solutions and, within experimental error, calculated the same k_1 as before. The relative oxidation rate for **1** and **2** was then $k_1/k_2 = 3.5$. Tables 1 and 2 summarize the data.

TABLE 1
Summary of Data for 1-Octyl Dimethyl Amine

g 69.50% H_2O_2	g added H_2O	$[H_2O_2]$ (M)	$[H_2O]$ (M)	k_{obs} (h^{-1})
0.664	0.000	0.543	0.450	0.024
1.583	0.000	1.294	1.072	0.089
2.1513	0.000	1.758	1.456	0.21
2.788	0.000	2.279	1.888	0.38
3.237	0.000	2.646	2.192	0.52
3.466	0.000	2.833	2.347	0.62
3.4661	0.0000	2.833	2.347	0.65
3.4756	0.9691	2.841	4.504	0.78
3.4611	1.5168	2.829	5.710	0.78
3.4700	1.9948	2.836	6.777	0.78
3.4630	2.5578	2.831	8.022	0.72
3.4733	2.9922	2.839	8.993	0.77
3.4645	4.0514	2.832	11.339	0.78
3.4650	5.9291	2.832	15.507	0.80
0.6778	5.8990	0.554	13.553	0.082
1.1237	5.5862	0.919	13.161	0.16
1.5817	5.2877	1.293	12.808	0.26
2.1174	4.9240	1.731	12.364	0.34
2.4475	4.6908	2.001	12.069	0.47
2.7742	4.4747	2.268	11.811	0.54
3.2329	4.1723	2.643	11.450	0.70
3.4628	4.0150	2.831	11.257	0.77

TABLE 2
Summary of Data for 2-Ethylhexyl Dimethyl Amine

g 69.50% H_2O_2	g added H_2O	$[H_2O_2]$ (M)	$[H_2O]$ (M)	k_{obs} (h^{-1})
0.6738	5.6242	0.551	12.94	0.019
1.1247	5.5589	0.919	13.10	0.039
1.5773	5.2843	1.289	12.80	0.064
2.4494	4.6915	2.002	12.07	0.13
3.2327	4.1585	2.642	11.42	0.19
4.8839	3.0663	3.993	10.11	0.35
6.1136	2.2330	4.999	9.096	0.52
7.3355	1.4117	5.998	8.100	0.74
9.4393	0.0000	7.718	6.391	0.96

To our knowledge, ours is the first reported work that has involved the study of this oxidation across such a wide range of hydrogen peroxide concentrations. Earlier reports (2,3) that focused on smaller concentrations of H_2O_2 and narrower concentration ranges of H_2O_2 indicated that the overall reaction was first-order in both amine and H_2O_2. However, when examined across the range of $[H_2O_2]$ that we used, the kinetic data strongly point to the reaction's being first-order in amine and 3/2 rather than first-order in H_2O_2.

Steric interactions between ADMA alkyl groups and incoming H_2O_2 molecules strongly affect the rate of ADMA oxidation. The nitrogen lone pair of electrons is less hindered for the linear 1-alkyl dimethyl amine (**1**) than for the branched 2-ethylhexyl dimethyl amine (**2**). Introduction of an alkyl branch at C_2 appears to create substantial steric hindrance around the nitrogen and retards the rate of oxidation relative to that of the linear amine. Future work will investigate the effect of temperature on the oxidation rate.

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