tial integral signals, has been used successfully to measure fat (1–6%) in spent corn germ flake containing 4–11% moisture (2).

The results of the present investigation indicate that NMR procedures can be used to determine oil in plant seeds at the rate of one sample in about 3 min, with an accuracy comparable to present extraction procedures. We believe the instrumental method may be more accurate in certain applications, e.g., oil-rich samples difficult to grind for extraction, "oil-free" meals, and processed meals containing oil bound by excessive heating.

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Hydrogen Peroxide Oxidation of Tertiary Amines[1]

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Abstract

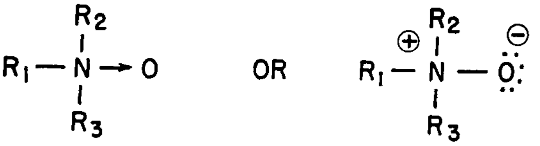
Oxides of tertiary amines, such as dimethyldodecylamine oxide, are known to be useful as detergents and foam stabilizers, and are now in commercial use. The results of an investigation leading to the selection of optimum conditions for producing these compounds are reported. A variety of hydrogen peroxide-derived systems for amine oxidation were investigated. These included hydrogen peroxide in water and in nonaqueous solvents, and peroxy acids under various reaction conditions. Reductometric, acidimetric, and gas chromatographic procedures were used for analysis of reaction mixtures. The preferred reaction uses hydrogen peroxide as oxidant and water as the reaction medium. The product of this reaction is a 30–40% solution of the amine oxide. Other factors affecting the rate and extent of conversion, such as amine purity, are discussed.

Introduction

THE FIRST STUDIES on amine oxides were made in the last decade of the 19th century. Dunstan and Goulding (1), who carried out many studies in this field, called these compounds "oxamines." Recent interest in amine oxides stems from the finding that certain of these compounds are useful as detergents and foam stabilizers. The fatty amine oxides, which show good surface active properties, are in addition biodegradable (2). This is of interest in view of the current demand for "soft" detergents.

Since the turn of the century, few articles have been published on the oxidation of aliphatic amines, although there has been much interest in the oxidation of heterocyclic amines. Cope and co-workers (3) and Cram and co-workers (4) have been active in amine oxidation. Their primary interest, however, has been in stereospecific olefin formation by pyrolysis of amine oxides. A detailed review of amine oxide chemistry was published by Culvenor (5) in 1953. A bibliography of recent amine oxide literature is available (6).

Only tertiary amines form amine oxides. Their structure is as follows:



$$R_1-\overset{\overset{R_2}{|}}{\underset{\underset{R_3}{|}}{N}}\rightarrow O \quad \text{OR} \quad R_1-\overset{\overset{R_2}{|}}{\underset{\underset{R_3}{|}}{\overset{\oplus}{N}}}-\ddot{\underset{\cdot\cdot}{O}}{:}^{\ominus}$$

The oxygen atom is bonded to the nitrogen atom with a polar bond, the electron density being greater on the oxygen atom. The dipolar nature of this bond imparts salt-like properties to the molecule.

It is well known that oxidation of amines can be brought about by the action of a peroxyacid. Aliphatic tertiary amines substituted by C_1 to C_3 alkyl groups have also been oxidized with hydrogen peroxide (3). However, no data have been available on the oxidation of fatty-substituted amines. In order to determine the preferred reaction conditions for oxidizing these amines, we have carried out the studies reported here.

Experimental Procedures

Distillation of Commercial Dimethyldodecylamine. Commercial grade dimethyldodecylamine ("Armeen" DM12D, Armour Industrial Chemical Co.) was vacuum-distilled using conventional apparatus. The column length was 30 cm, and distillate boiling in the range 93–103C was collected at 1–2 mm Hg. The n_D^{25} of the distillate fractions ranged from 1.4347–1.4357. The n_D^{25} of the residue was 1.4415. The yield of distillate was 95.3%.

Apparatus for Oxidation Experiments. The reaction apparatus used in all oxidation experiments was a creased 500 ml three-necked flask fitted with a water condenser, stirrer, and dropping funnel. A thermometer was inserted through the bore of the condenser into the reaction mixture. The flask was placed in a bath equipped to heat or cool.

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[1] Presented at the AOCS meeting in Toronto, Ontario, 1962.

Oxidation of Dimethyldodecylamine by 35% Hydrogen Peroxide in Water Solution. The quantity of dimethyldodecylamine, redistilled or as received from various sources, required to provide 0.40 moles amine was placed in the reaction flask and 42.7 g (0.44 mole) of 35% hydrogen peroxide was added. To correct for differences in amine purity, the weight of each amine to be used was calculated from an average molecular weight determined by potentiometric titration with 0.1 *N* aqueous hydrochloric acid. The amount of dilution water to be added was calculated to give a 30% solution of the amine oxide by weight at 100% conversion. The hydrogen peroxide was added dropwise with stirring over a 1 hr period, the temperature of the reaction mixture being maintained at 60–65C. Unless dilution water was added during this period, the reaction mixture gelled. Gelation was prevented by adding water from time to time in amounts just sufficient to keep the mixture fluid. At the end of peroxide addition, the remaining dilution water was added, and the reaction mixture was heated to 75C. Analyses of reaction mixtures by the acidimetric method showed conversions of 87.2–99.2%, depending on the source and purity of the starting amine.

Drying of Dimethyldodecylamine Oxide. Dimethyldodecylamine oxide, 30% by weight in water, was placed in a crystallizing dish in the hood and allowed to evaporate. When the amine oxide had reached a very thick consistency and no more water appeared to evaporate, the product was placed in a vacuum desiccator over phosphorus pentoxide, and the desiccator evacuated. Care was taken that the product did not foam over the sides of the container during the evacuation. Lumps of the product were broken up and the phosphorus pentoxide was renewed when necessary. Drying was assumed to be essentially complete when the surface of the phosphorus pentoxide desiccant did not change appreciably in appearance after several hours. The product was then subjected to full pump vacuum overnight. The melting point range of the product (Fisher-Johns hot stage) was 117–123C (d). The dried product is extremely hygroscopic.

Oxidation of Dimethyldodecylamine by Hydrogen Peroxide Without Added Solvent. Three experiments were carried out using respectively 35%, 70%, and 90% aqueous hydrogen peroxide in the absence of added solvent. The weight of aqueous hydrogen peroxide required to provide 0.44 mole of peroxide was added to 87.8 g (0.40 mole) of redistilled amine with stirring over a ½ hr period. In the experiment using 70% hydrogen peroxide, 0.40 mole was added to the amine. Reaction mixtures were analyzed reductometrically for amine oxide content. The reaction in which 90% hydrogen peroxide was used was not carried to maximum conversion because of darkening of the reaction mixture. In the experiments using 35% and 70% hydrogen peroxide, the final reaction mixtures were gels which could not be agitated using a conventional laboratory stirrer.

Oxidation of Dimethyldodecylamine by 70% Hydrogen Peroxide in Nonaqueous Solvents. Redistilled dimethyldodecylamine, 87.8 g (0.40 mole), was placed in the reaction flask and the nonaqueous solvent, 44.0 g, was added to the amine. This weight of solvent was sufficient to give a 60% solution of the amine oxide by weight at 100% conversion. Seventy percent hydrogen peroxide, 21.4 g (0.44 mole), was added dropwise, with stirring over a 1 hr period, keeping the temperature of the reaction mixture at 60C. After peroxide addition had been completed, the temperature of the reaction mixture was either kept at 60C or raised to 70C. The reductometric method was used to analyze reaction mixtures.

Oxidation of Dimethyldodecylamine with Preformed Peroxyacetic Acid. Preformed 40% peroxyacetic acid in acetic acid, 83.6 g (0.44 mole), was added dropwise with stirring to redistilled dimethyldodecylamine, 87.8 g (0.40 mole). The addition was made over a 1-hr period. The temperature of the reaction mixture, initially 45C, was allowed to increase to 60C. Cooling was used to maintain this temperature. After addition of the peroxyacetic acid had been completed the reaction mixture was held at 60C. After 2 hr, a sample was withdrawn and analyzed by the reductometric method. It contained 50.6% dimethyldodecylamine oxide (94.3% conversion).

Oxidation of Dimethyldodecylamine by Peroxyformic Acid. Oxidations using peroxyformic acid formed *in situ* were carried out under various reaction conditions, as shown in Table III. In a typical experiment, redistilled dimethyldodecylamine, 110.5 g (0.50 mole), was placed in the reaction flask with 110.5 g dioxane and 2.65 g (0.11 mole) 88–90% formic acid. Seventy percent hydrogen peroxide, 26.7 g (0.55 mole), was added dropwise to the stirred reaction mixture over a 25 min period. The temperature of the reaction mixture, which had been heated initially to 50C, rose to 59C over the course of the addition. After all of the hydrogen peroxide had been added, the reaction mixture was held at 65C. Reaction products were analyzed reductometrically for amine oxide content.

Analytical Methods

Reductometric Method. The reductometric procedure used to determine the amine oxide content of reaction mixtures is a modification of the method developed by Brooks and Sternglanz (7). The amine oxide sample is dissolved in 30 ml of glacial acetic acid containing an additional 25 ml. of 1:4 sulfuric acid. A nitrogen blanket is maintained over the solution while a measured excess of 0.2 *N* titanium trichloride solution is added with stirring. Five ml of 3 *M* ammonium thiocyanate solution is then added to act as catalyst for the reduction. After a 5 min reaction time, the excess titanium (III) is back-titrated with standard ferric sulfate solution. A blank is run to determine the consumption of titanium (III) by the solution of glacial acetic and sulfuric acids, and a correction is made in the calculation of amine oxide content. A correction is also made for the hydrogen peroxide content of the sample.

Acidimetric Method. The acidimetric method used in analysis of amine oxide solutions is a modification of a procedure developed by Armour Industrial Chemical Co. (14). In this procedure, one 2.000 g sample of the amine oxide is dissolved in 50 ml of isopropyl alcohol and titrated potentiometrically with 0.1 *N* hydrochloric acid in isopropyl alcohol. This titration gives the milliequivalents of total basicity in the sample. A second 2.000 g sample is also dissolved in 50 ml of isopropyl alcohol, and 2.0 ml of methyl iodide is added to the solution with stirring. After a 60 min reaction period at room temperature, this solution is titrated potentiometrically with 0.1 *N* hydrochloric acid in isopropyl alcohol. Calculation of the number of milliequivalents of acid required in the second titration gives the milliequivalents of amine oxide in the sample. The difference in milliequivalents between the first

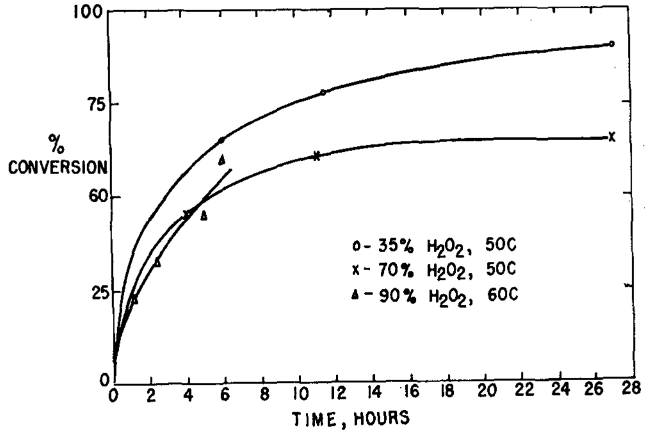


FIG. 1. Oxidation of dimethyldodecylamine without added solvent.

and second titrations gives the milliequivalents of amine in the sample. In practice, it is more convenient to weigh out samples close to 2 g and calculate the titer for the exact weight.

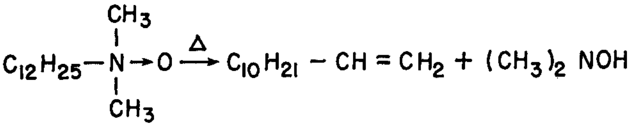
Gas Chromatography of Amines and Amine Oxide Solutions. Gas chromatographic analyses of amines were carried out using an F&M Scientific Co. Model 500 gas chromatograph. The column was ¼ in. in diameter and 6 ft long. The column packing was 60–80 mesh "Chromosorb" W, treated first with 10% (w/w) of potassium hydroxide and then coated with 5.5% (w/w) of "Apiezon" L. Helium flow rate was maintained at 60 ml/min. The injection port temperature was 300C, and the column was maintained at 225C. A 10 μl sample size was used. Under these conditions, the major peak, that for dimethyldodecylamine, appeared in 5.6 min.

Solutions of dimethyldodecylamine oxide in an alcohol solvent were chromatographed under identical conditions. The major peak appeared at 1.5–2.0 min and had the same retention time as that for an authentic sample of 1-dodecene. On pyrolysis, dimethyldodecylamine oxide would be expected to give 1-dodecene by the Cope elimination reaction (3). The injection port temperature is sufficiently high to pyrolyze the amine oxide. Since the peaks for dimethyldodecylamine and 1-dodecene are well separated on the chromatogram, it should be possible to employ gas chromatography as a method for analyzing mixtures of the amine and amine oxide.

Active Oxygen Analyses. Conventional methods of analyzing for hydrogen peroxide and peroxyacids were used (8). Iodometry was employed for hydrogen peroxide analysis, and a combination of iodometry and cerimetry was employed to analyze mixtures of peroxyacids and hydrogen peroxide.

Results and Discussion

Our studies have been concerned primarily with the oxidation of fatty tertiary amines, especially with dimethyldodecylamine. The N-oxide of this compound is known to be useful as a detergent. It is readily soluble in water, alcohols, and polar organic solvents, but only sparingly soluble in hydrocarbon solvents. On pyrolysis, the N-oxide undergoes the Cope elimination reaction (3) to give 1-dodecene and dimethylhydroxylamine, as shown in the equation below. The dried amine oxide is a white, amorphous, hygroscopic solid melting at 117–123C with decomposition.



$$C_{12}H_{25}-\underset{CH_3}{\overset{CH_3}{N}}\rightarrow O \xrightarrow{\Delta} C_{10}H_{21}-CH=CH_2+(CH_3)_2NOH$$

It has been proposed that amine oxidation by hydrogen peroxide proceeds by formation of an amine perhydrate (9,10), and that this perhydrate rearranges to give the N-oxide and water. A mechanism for the oxidation of aniline by peroxyacetic acid has been proposed (11) which involves a molecule of water in the transition state for the oxidation; the rate of oxidation in water is 25 times that in ethanol as reaction solvent. Apparently, water is a unique solvent in amine oxidation, enhancing the rate of formation of the amine oxide and minimizing the decomposition of the N-oxide formed (4,11). We have verified this in our studies.

The objective of this study was to develop a process for the oxidation of dimethyldodecylamine which would yield a high conversion under practical reaction conditions. The most obvious procedure is the direct oxidation of the amine with concentrated hydrogen peroxide. It has been found, however, that direct oxidation of the amine proceeds at a slow rate and does not give complete conversion. The results of experiments using 35%, 70%, and 90% aqueous hydrogen peroxide are shown graphically in Figure 1. The reaction mixtures in these experiments formed gels which became increasingly difficult to agitate properly as the reaction proceeded. The gels did not become fluid on raising the temperature.

The preferred method found for oxidizing dimethyldodecylamine produces the amine oxide as a 30–40% aqueous solution. This concentration range was selected because gelatinous material tends to form at the surface of more concentrated solutions. In the preferred process, 35% hydrogen peroxide is added to the amine with stirring over a 1 hr period during which the reaction mixture becomes gelatinous. Water is added in small portions just sufficient to keep the reaction mixture fluid. When all of the peroxide has been added, the remaining water required to give a final amine oxide concentration of 30–40% is added, and the reaction temperature is raised to 75C. When the water is added in increments in this manner, the oxidation proceeds rapidly to a high conversion. In a typical reaction, a conversion approaching 100% can be realized in 2 hr. The product of the reaction is a colorless solution of the amine oxide.

If all of the dilution water is added at the start of the reaction, amine oxide formation is retarded. The reaction rate is extremely low initially because of immiscibility of the amine with the dilute hydrogen peroxide. While the rate improves as amine oxide is formed to solubilize the amine, excessive reaction times are required to reach high conversions.

The optimum temperature of the reaction mixture

TABLE I

Oxidation of Dimethyldodecylamine by 35% Hydrogen Peroxide in Water Solution at 75C

Amine[a]	Amine oxide, % conversion		Time to max conversion, hr	H_2O_2, % unreacted
	2 hr	Maximum		
Redistilled	99.2	99.2	2	9.2
A	84.4	87.2	4	1.3
B	75.3	88.2	3	3.9
C	93.8	97.7	4	5.0
D	92.3	97.1	4	4.8

[a] Dimethyldodecylamine from various sources.

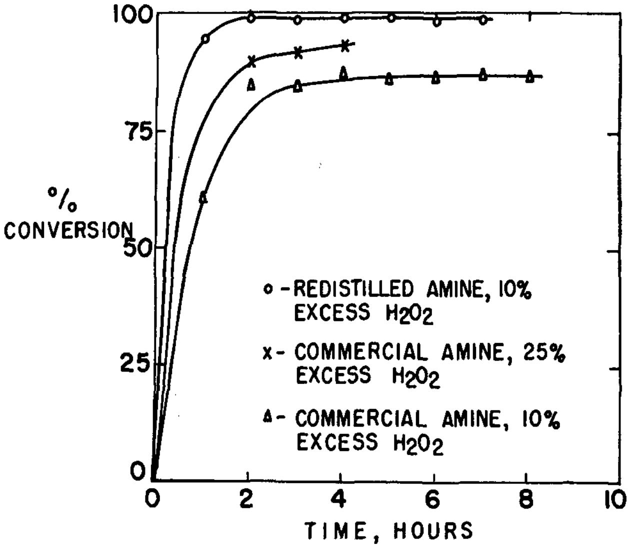


FIG. 2. Oxidation of dimethyldodecylamine by 35% hydrogen peroxide at 75C.

during addition of hydrogen peroxide is 60–65C. At higher temperatures, a yellow color develops; at lower temperatures, the reaction rate decreases. After all of the hydrogen peroxide and water have been added, the temperature can be raised to 70–80C without discoloration. However, the temperature should not be allowed to exceed 90C. Prolonged heating above 60C after completion of the reaction should also be avoided.

About 10% more than the theoretical quantity of hydrogen peroxide is required for complete conversion. At the end of the reaction period a small quantity of unreacted peroxide remains. This can be destroyed by adding the calculated quantity of sodium sulfite.

The purity of the amine affects both the rate and extent of conversion to the N-oxide. This is illustrated in Table I and Figure 2, which compare results obtained on oxidation of amine as received from various sources and after redistillation, eliminating a 5% heel. It was noted that the hydrogen peroxide was consumed more rapidly by the commercial amine samples than by redistilled amine. Therefore, the interfering impurity either consumes or decomposes peroxide. This was proved by experiments using a larger excess of hydrogen peroxide. In an experiment in which the excess was increased from 10–25%, conversion to amine oxide was increased from 87–94%. The nature of the interfering impurity is now being studied.

TABLE II

Oxidation of Dimethyldodecylamine by 70% Hydrogen Peroxide in Nonaqueous Solvents

Solvent[a]	Temp, C	Time, hr	Amine oxide, % conversion	H_2O_2, % unreacted
Methanol	60	20	85.4	6.1
Dimethyl formamide	70	6	78.0	2.8
n-Propanol	70	18	88.7	5.1
Ethyl acetate	60	6	57.8	24.7
Tetrahydrofuran	60	5.5	42.2	31.4
t-Butanol	70	10	83.3	22.0

[a] Sufficient to form a 60% solution of amine oxide at 100% conversion.

TABLE III

In Situ Oxidation of Dimethyldodecylamine by Peroxyformic Acid

Mole ratio formic acid: H_2O_2	Temp, C	Time, hr	Amine oxide, % conversion	H_2O_2, % unreacted
0.1:1	65	6	90	7.8
0.2:1	65	5	91	8.8
0.4:1	65	6	98	8.8
2:1	50	3	57	0.1

In an attempt to obtain a more concentrated product, the use of high-strength hydrogen peroxide in organic solvent systems was investigated. It was found that the rate of oxidation was too slow to be of practical value. Of the solvents evaluated, the best appeared to be t-butanol, but even in this solvent, only 83% conversion was obtained in 10 hr. Data comparing oxidations in various solvents appear in Table II. Only methanol, t-butanol, and tetrahydrofuran gave colorless solutions of the product; other solutions turned yellow during the course of the reaction. At 60% conversion, a gel separated from the tetrahydrofuran and ethyl acetate solutions. With solvents other than alcohols, excessive decomposition of amine oxide product appears to limit conversion. This has been verified in a recent publication by Cram and co-workers (4), who showed that the rate of decomposition by Cope elimination is markedly affected by the nature of the solvent. In tetrahydrofuran, decomposition was $\sim 10^6$ times more rapid than in water. Hydroxylic solvents capable of hydrogen bonding, such as alcohols and water, stabilize the amine oxide.

The use of aliphatic peroxyacids has also been studied. The oxidation of dimethyldodecylamine can be carried out efficiently with peroxyacetic acid. This oxidant can be preformed using either sulfuric acid or a sulfonic acid cation-exchange resin to catalyze the reaction between hydrogen peroxide and acetic acid (12,13). It is also possible to use an *in situ* technique, in which the formation of peroxyacetic acid is accomplished in the reaction mixture by sulfuric acid catalysis. This latter method gives a lower conversion than procedures using preformed peroxyacetic acid. Table III shows that oxidation of the amine can also be brought about by an *in situ* peroxyformic acid procedure.

While peroxyacids are efficient in converting dimethyldodecylamine to the N-oxide, no satisfactory method has been found for obtaining the product in a useable form. In preliminary experiments using vacuum stripping techniques to remove the by-product acid and solvent, the acid was held tenaciously by the amine oxide. This behavior is not surprising, since the amine oxide is a weak base. In contrast to the peroxyacids, hydrogen peroxide in an aqueous system produces the amine oxide in a form suitable for use without further processing.

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