

THE REACTION OF OZONE WITH DIMETHYLLAURYLAMINE¹

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Received April 13, 1965

ABSTRACT

In the oxidation of dimethylaurylamine in chloroform solution by ozone, increase in temperature results in decreased yields of amine oxide and amine hydrochloride and increased yields of amide and carboxylic acid. The reaction is first order in amine and first order in ozone and is not affected by light. These data are consistent with a mechanism involving oxidation of an amine-chloroform charge transfer complex stable at low temperatures.

INTRODUCTION

The reaction of tertiary amines with ozone leads almost exclusively to amine oxides when conducted in chloroform solution below -50° (1, 2, 3). At somewhat higher temperatures (-45° to 0°) or in other polar solvents (specifically in methanol), somewhat lower yields, and isolation of amides, aldehydes, acids, and other products of oxidative attack on the alpha carbon have been reported (4, 5, 6). In nonpolar solvents (pentane, cyclohexane, 1-chlorobutane, carbon tetrachloride), amine oxide yields are very low, regardless of temperature.

Maggiolo and Niegowski (4) suggested a mechanism for the reaction involving electrophilic attack on the amine nitrogen by ozone, followed by decomposition of the intermediate zwitterion (I). This mechanism is postulated by analogy with the Criegee mechanism for reaction of olefins with ozone. No experimental data to support the mechanism are presented. Henbest and Stratford (5, 6) have presented a detailed scheme accounting for production of aldehydes, secondary amines, acids, and amides as a result of oxidation at the alpha carbon atom. This investigation was carried out in an attempt to establish experimentally a mechanism for oxidation at the nitrogen atom.

A systematic study covering a temperature range of -75° to 61° in chloroform solution was selected as the approach most likely to lead to better understanding of the reaction. After the observation that oxidation at the alpha carbon atom was negligible at dry ice temperature, experiments to determine the effects of some other variables were conducted. A preliminary kinetic study was also performed.

EXPERIMENTAL

Reaction at Various Temperatures

Vigorously stirred chloroform solutions of dimethylaurylamine in a micro-reaction apparatus (7) were maintained at the desired temperature while ozone was introduced at a rate of 65 ± 10 mg/min (in a 0.02 c.f.m. oxygen stream). At intervals, titrations for unreacted ozone were performed. The reaction was terminated when a 10% excess of ozone had been absorbed, as determined from the area under the absorption vs. time graph. Solvent was removed by evaporation under vacuum at room temperature. The product was analyzed by titration for amine oxide, amine, amide, and acid, and qualitatively by infrared spectrometry and thin-layer chromatography. Assignment of acids as carboxylic or trialkyl ammonium chloride was based on presence of characteristic N—H or C=O absorption bands in the infrared spectrum. Details are given in Table I.

Effect of Other Variables

A 500-ml flask was fitted with a Tru-Bore stirrer, a gas inlet tube, and an outlet connected at regular intervals to a potassium iodide trap. After the initial reaction, the flask was wrapped to exclude light. Reaction in a dry ice bath (-75°) was continued until the desired amount of ozone had been introduced. Nearly quantitative uptake was observed. Results are summarized in Table II.

¹Presented at the Ozone Symposium, American Chemical Society Southwest Regional Meeting, Houston Texas, December 1963.

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TABLE I
Effect of temperature on dimethylaurylamine ozonization

Temp. (°C)	Concentration (g/100 ml)	Yield ^a (%)	Analysis (% of product)				
			Amine oxide	Amine salt	Amide	Acid	Amine
61	5 ^b	40	18	^c	^c	^{c, d}	^c
25	20	95	28	^c	38	^{c, d}	^c
0	10	95	38	^e	32	^e	15
-15	10	—	42	17	25	0	16 ^f
-75	10	91	65	22	^e	0	13 ^f

^a100 × Weight of product/theoretical weight of amine oxide.

^bExtensive evaporation of solvent during reaction.

^cNot determined.

^dStrong carboxyl band in infrared spectrum.

^eTrace (weak infrared absorption).

^fBy difference.

TABLE II
Oxidation of dimethylaurylamine at -75°

Concentration (g/100 ml)	Ozone excess (%)	Additive (g/100 ml)	Analysis (% of product)		
			Amine oxide	Amine hydrochloride	Amine ^a
5	10	Light	48	27	25
10	10	None	64	23	
10	10	NaOMe (10)	45 ^b	36	
5	10	CaCO ₃ (10)	82	16	
5	10	Na ₂ CO ₃ (10)	64	0 ^c	36
10	35	Na ₂ CO ₃ (10)	77	10	13
10	60	Na ₂ CO ₃ (10)	47	16	
5 ^d	10	None	44 ^{b, e}		
5 ^f	10	None	50 ^b		

^aBy difference when t.l.c. and infrared show no other component.

^bStrong amide carbonyl band in infrared.

^cNo N—H bands in infrared.

^dMeOH solvent.

^eAcid carbonyl band in infrared.

^fEtOAc solvent.

Kinetic Studies

Solutions of 10.0 g of dimethylaurylamine in 50.0 ml of chloroform were prepared. Using an oxygen flow rate of 0.05 c.f.m., each solution, in a gas-washing tower, cooled to -75° in a dry ice bath, was treated with a different concentration of ozone with vigorous stirring. The rate of the reaction, expressed as mg/min of ozone consumed, was initially constant. A straight line graph of rate vs. ozone concentration was obtained (see Table III).

Solutions of 1.00 to 4.00 g of amine in 50.0 ml of chloroform were prepared. Each was placed in a 100 ml, three-necked flask with ground glass sealed stirrer, cooled to -75° and ozonized with a stream of 0.02 c.f.m. containing 65.4 mg/min of ozone. Figure 1 shows typical curves at low and high amine concentrations. A graph of initial rate (extrapolated linearly at high amine concentrations) vs. initial amine concentration was linear.

Amide Analysis⁴

A weighed sample (1–2 g) was placed in a Florence flask with 25 ml of 6 N sodium hydroxide. The mixture was distilled into 10.0 ml of standardized 0.5 N hydrochloric acid until most of the water had been removed.⁵ The distillate was titrated with base, to a methyl red end point, giving the amount of

³Pure chloroform freezes at -63.5°. The technical grade of chloroform used in these experiments froze when a solution containing only 10 g/l was employed, but the freezing point was lowered enough by higher concentrations of amine that no difficulty was encountered.

⁴The amides formed are all secondary products of alpha carbon oxidation to carbinolamine. Therefore, total amide, amine oxide, and amine salt are the significant analyses for determining the mechanism of the primary oxidation step.

⁵The decomposition of aliphatic amine oxides in aqueous solution is extremely slow, even in strong base. The analysis is essentially a Kjeldahl determination without a reduction step (8).

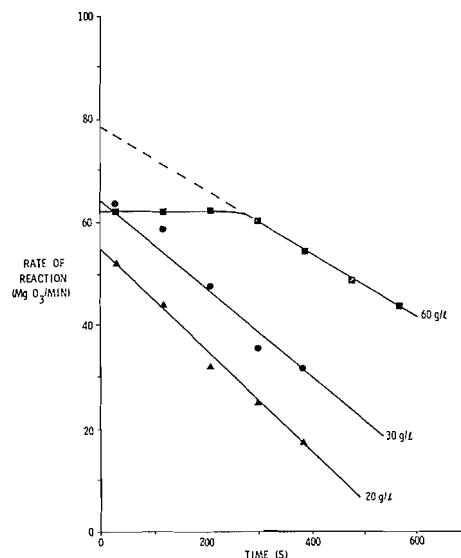


FIG. 1. Typical rates of ozonization.

TABLE III
Rates of dimethylaurylamine oxidation

Ozone input (mg/min)	Initial amine concentration (g/l)	Initial ozone consumption (mg/min)
48.4	166.7	47.2
68.0	166.7	65.6
98.5	166.7	94.0
105	166.7	101.2
65.4	19.6	54.4
65.4	29.1	64.2
65.4	38.5	67.0
65.4	56.6	77.5 ^a
65.4	74.1	86.0 ^a

^aExtrapolated.

dimethylamine (from dimethylauramide and dimethylformamide). The residue was extracted three times with 25 ml of chloroform, then the combined extracts were washed twice with 150 ml of water, mixed with toluene - isopropyl alcohol - bromphenol blue solution, and titrated to determine methylaurylamine (from *N*-methyl-*N*-laurylformamide) and unreacted dimethylaurylamine.⁶ A second sample was titrated without prior treatment, determining the dimethylaurylamine, which was then subtracted from the sum of the other titrations.

Amine Hydrochloride Analysis

A standard titrimetric method⁷ for determination of acids or ammonium salts was employed.

Amine and Amine Oxide Analysis

A nonaqueous acidimetric titration was used for determination of amine and amine oxide (9). Details of the thin-layer chromatography method have also been described previously.

Purification of Dimethylaurylamine Oxide

The mixture obtained from reaction of 50 g of amine in 1 l of chloroform in the presence of 50 g of calcium carbonate at -75° was recrystallized from benzene, yielding 9 g of white powder, m.p. 108-112 $^{\circ}$.

⁶American Oil Chemists' Society Standard Method Nb 2-62.

⁷American Oil Chemists' Society Standard Method Nc 1-62.

Analysis showed that it contained no amine hydrochloride and 89.4% amine oxide. A second recrystallization of a small portion gave anhydrous dimethylaurylamine oxide, m.p. 117–120° (reported m.p. 117–123°) (10).

Oxidation of Dimethylaurylammonium Chloride

A solution of 2.0 g, m.p. 190–194°, in 200 ml of methanol was cooled to -30° and treated with 520 mg of ozone, absorbing 211 mg. Solvent was removed under vacuum. The product, m.p. 146°, contained 7.2% of amine oxide.

DISCUSSION

Synthetic Studies

Conversion of dimethylaurylamine to the oxide increases as the temperature is lowered, while amide formation (Fig. 2) diminishes, until at -75° amide formation is negligible.

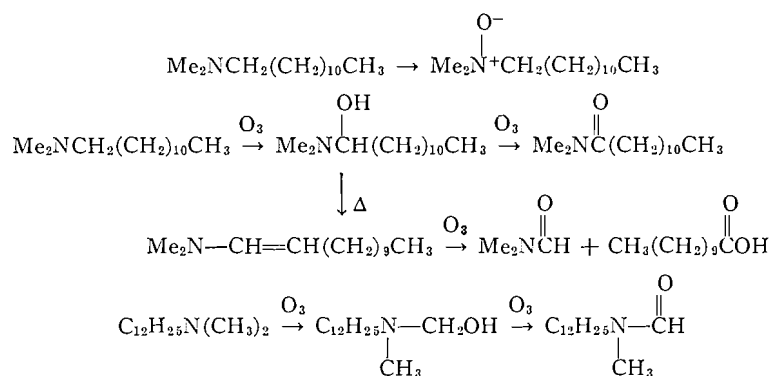


FIG. 2. Reactions of dimethylaurylamine with ozone.

No improvement can be expected at temperatures below -75° , since conversion to the hydrochloride competes, and dimethylaurylammonium chloride does not react rapidly with ozone.⁸ By adding calcium or sodium carbonate, amine hydrochloride formation is minimized (0–10%), and higher yields (64–82%) of amine oxide are attained. Addition of sodium methoxide resulted in a markedly lower yield of amine oxide and extensive formation of by-products. A large (60%) excess of ozone gave a poorer conversion to amine oxide than either 10% or 35% excess. This is probably the result of oxidation of the amine oxide at the alpha carbon. Use of ethyl acetate and methanol as solvents normally leads to slightly lower yields (44 and 50%) of amine oxide than in chloroform carbonate mixtures ($74 \pm 10\%$) but amide formation becomes significant at -75° .

Kinetic Studies

The method employed by Wibaut (11) was used in this investigation. By keeping the oxygen-ozone flow constant and varying discharge voltage, one can measure the dependence of rate on ozone concentration. Absorption of the stream in a potassium iodide trap for 60 s leads to an expression of ozone concentration in mg/min. Similar titration of the off-gas and subtraction from input then gives ozone absorption in mg/min, and is a direct measurement of the rate. Similarly, with constant ozone input and varying concentration of amine, the dependence of rate on amine concentration may be determined. Since the reaction is essentially heterogeneous, no significant rate constants can be obtained.

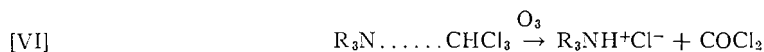
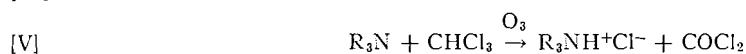
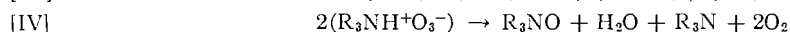
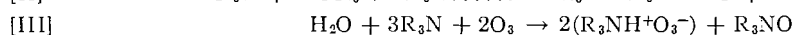
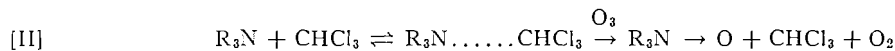
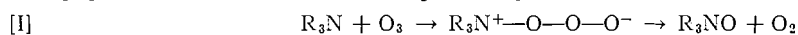
⁸Generally, salt formation stabilizes an amine toward ozone. Because of the marked solvent effects on this reaction, it would have been desirable to verify that reaction of the salt is slow in chloroform, but the amine salt is not appreciably soluble at low temperatures.

Oxidation of dimethylaurylamine to the oxide is first order in ozone and first order in amine at -75° ,

$$d[\text{O}_3]/dt = K[\text{O}_3][\text{R}_3\text{N}].$$

Mechanism of Reaction

There are four likely mechanisms for amine oxide formation: (A) electrophilic attack of ozone [I] (4); (B) preliminary formation of an amine-solvent complex followed by displacement of solvent [II]; (C) formation and decomposition of a trialkylammonium ozonide [III and IV]; and (D) oxidation by a free radical process. Amine hydrochloride (or hydrogen chloride) formation must result from decomposition of chloroform, either free [V] or in an amine-solvent complex [VI].



While it might be possible to propose stepwise mechanisms for oxidation via free radical or trialkylammonium ozonide intermediates which would obey the observed rate expression, the kinetic data strongly suggest either I or II as the actual mechanism. The parallel decrease in conversion to amine oxide and to amine hydrochloride with increasing temperature is consistent with reaction of a low-temperature stable amine-solvent complex, but not with oxidative degradation of chloroform, which would be favored at higher temperatures. The remarkable ability of chloroform to suppress alpha carbon oxidation could be explained if alpha oxidation involves a free radical mechanism. Chloroform would function better as an inhibitor than the other solvents which have been employed.

Spectral evidence for amine-halomethane interaction has been presented (12). The evidence did not clearly differentiate between charge-transfer complexes and contact charge-transfer spectra, but it was suggested that charge-transfer complexes might be the species involved in photochemical reactions leading to amine hydrohalides or enamines (12). Since exclusion of light from the dimethylaurylamine-chloroform-ozone system did not suppress amine hydrochloride formation, one must conclude that the reaction of ozone with an amine-chloroform complex is the principal source of hydrogen chloride. It has also been proposed that the superior yields of amine oxide in chloroform and methanol are due to the hydrogen bonding ability of these solvents (5). Additional work to determine the nature of the amine-solvent complex is needed.

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