Thermal Decomposition of Dimethyllaurylamine Oxide

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Abstract

The principal reaction during thermal decomposition of dimethyllaurylamine oxide is deoxygenation to dimethyllaurylamine; 1-dodecene is also formed. The rates of amine oxide decomposition have been determined in the range of 80–100C. Interpretation of the kinetic data shows that deoxygenation is a primary decomposition process. Comparison of the energy and entropy of activation for olefin formation (36.3 kcal, 12.4 e.u.) and amine formation (20.6 kcal, −30.8 e.u.) shows that these are competing processes with different transition states.

Introduction

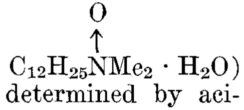
Although the Cope reaction (pyrolysis of tertiary amine oxides to olefin and dialkylhydroxylamine) has been the subject of many papers and reviews (1), no kinetic study had been reported at the time this work was initiated. While the reaction had been presumed (largely from steric considerations) to proceed by a cyclic unimolecular mechanism similar to that generally accepted for ester pyrolysis (1b), it was not until recently that kinetic data in support of such a mechanism became available (2).

The marked effect of solvent on the reaction rate of anhydrous amine oxides suggested that a study of the reaction under conditions approaching those of preparative experiments (1a), i.e., pyrolysis of pure amine oxide hydrates, would be enlightening. Dimethyllaurylamine oxide was chosen because it is a solid, readily available and capable of purification by recrystallization.

Previous analytical methods for amine oxides (3) depended on use of reducing agents (titanium trichloride, etc.) and were not satisfactory for the mixtures obtained from the Cope reaction. Gas chromatographic and acidometric methods were developed and employed.

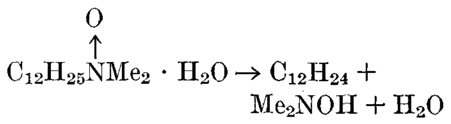
Experimental

Preparation of Amine Oxide. Hydrogen peroxide oxidation of dimethyllaurylamine was used to prepare the amine oxide. The method was essentially as described by Hoh and co-workers (4), using isopropyl alcohol and hydrogen peroxide, then evaporating solvent under vacuum. The amine oxide was recrystallized from benzene, hexane being added to complete precipitation. The materials, mp 90–95C, contained 89.8% amine oxide (as $C_{12}H_{25}\overset{\overset{O}{\uparrow}}{N}Me_2 \cdot H_2O$) and 6.7% dimethyllaurylamine, determined by acidometric titration. The IR spectrum contained a strong O-H absorption band typical of amine oxide hydrates.



Thermal decomposition of dimethyllaurylamine oxide.

A. An approximate 1-g sample dimethyllaurylamine oxide, placed in a test tube and immersed in a constant temp bath was removed, weighed, and returned to the bath at intervals. Linear semilogarithmic plots of wt of amine oxide vs. time resulted from assumption of the stoichiometry:



$$C_{12}H_{25}\overset{\overset{O}{\uparrow}}{N}Me_2 \cdot H_2O \rightarrow C_{12}H_{24} + Me_2NOH + H_2O$$

and calculation of the wt of amine oxide remaining. Residual wt = original wt − wt lost × 247/(61 + 18). It is not known why this should be the case, since analysis showed that this is a minor reaction. Rate constants calculated on this basis show in Table I, but were not used for further calculations. (A reviewer has suggested that rapid loss of water, followed by slow decomposition of the amine oxide would account for these being larger than rate constants determined by method B. This would require that agreement between activation parameters for dodecene formation and those reported by Cram and co-workers be coincidental. Since the pyrolysis of aliphatic amine oxides is much slower than that of phenylbutylamine oxides, it is possible that the rate-determining step is the olefin-forming elimination reaction.) Gas Chromatographic analysis of non-volatile products after 16 hr at 100C showed presence of three components; dimethyllaurylamine oxide (27–35%), dimethyllaurylamine (52–53%), and 1-dodecene (11–21%). Identification was made by comparison of retention times with those of reference materials and by IR spectroscopy of samples purified by gas chromatography.

B. Approximately 1-g samples of amine oxide in test tubes were placed in the constant temp bath, removed at the end of a suitable interval, chilled, and analyzed by acidometric titration. Linear semilogarithmic plots of amine oxide, amine and olefin percentages vs. time (pseudo-first order) were obtained. The rate constants for decomposition to olefin and amine were determined from the equations for parallel first order reactions (5):

$$U/V = [Vi + (K_aA_o/K_t)(1 - e^{-kt})]/[Vi + (K_oA_o/K_t)(1 - e^{-kt})]$$

$$K_a + K_o = K_t$$

U = Amine concn
Ui = Initial amine concn
V = Olefin concn
Vi = Initial olefin concn
A_o = Initial concn of amine oxide
K_a = Rate constant for decomposition to amine
K_o = Rate constant for decomposition to olefin
K_t = Rate constant for amine oxide disappearance

The energy of activation was determined from the slope of the linear plots of log K vs. 1/T, $-Ea/R = \Delta \ln K/\Delta(1/T)$, as 20.6 and 36.3 kcal for amine and olefin formation, re-

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spectively. Entropy of activation was calculated using the equation:

$$\Delta S^{\neq} = [(Ea - RT) + 2.303\,RT \log K_r h/K_b T]/T$$

Data is summarized in Table I.

TABLE I

Thermal Decomposition of Dimethyllaurylamine Oxide

Method	Temp (C)	Rate constant for decomposition [X10(6)]			Entropy of activation	
		Total	To amine	To olefin	Amine	Olefin
A	80.0	3.1				
A	90.0	6.7				
A	100.0	20.6				
B	81.1	1.04	0.74	0.30	−30.8	11.6
B	89.4	3.18	1.41	1.77	−31.0	13.1
B	100.0	10.7	3.8	6.9	−30.6	12.6

Reaction of dimethylhydroxylamine and 1-octene. Vapors from the thermal decomposition of dimethyllaurylamine oxide were passed through a reflux condenser containing hot water in the cooling jacket, then into refluxing 1-octene. When pyrolysis was complete, the octene was titrated with acid, but no amine was found. Gas chromatographic analysis showed less than 5% of a low-boiling impurity in the octene-1, probably dimethylhydroxylamine (identical retention time).

Gas chromatographic analysis of mixtures. The column and operating conditions satisfactory for fatty amines (6) was suitable for analysis of olefin-amine-amine oxide mixtures, using a flow rate of 70 ml/min, column temp 200C, and injection temp 300C. There was slight decomposition of the amine oxide during the analysis.

Determination of amine and amine oxide. The method of Wimer (3b) was modified to permit simultaneous determination of tertiary amine and amine oxide. An 0.1–0.5 g sample was dissolved in 25 ml acetic anhydride and titrated potentiometrically with 0.1 N perchloric acid in dioxane. Two inflections were obtained—the first titrating amine and the second amine oxide. Olefin was determined by difference, since the gas chromatographic analysis (above) showed the presence of only the three components.

Discussion

Aliphatic and alicyclic amine oxides generally decompose to olefins when heated. A small amount of tertiary amine is commonly found in the pyrolysis of other amine oxides (7). In cases where β-hydrogens are inaccessible [N-methylpiperidine oxide (8)] deoxygenation occurs preferentially. The amine might result from an alternate decomposition process, or from reaction of dialkylhydroxylamine and olefins (9) (described amine synthesis by reaction of 2-vinylpyridine with dialkylhydroxyl-amines). Amine formation is a first order process. This requires either very fast reaction of 1-dodecene and dimethylhydroxylamine, or direct formation from amine oxide. Since 1-octene and dimethylhydroxylamine did not react at 120C, the amine must be a primary decomposition product.

The rate constant vs. reciprocal temp plots for amine and olefin formation are straight lines. Since the olefin has a steeper slope, the ratio of products varies with temp. Extrapolation to 120C shows the olefin to amine rate constant ratio would be $95.5 \times 10^{-6} : 15.1 \times 10^{-6}$, or 6.3. This would lead to 86.5% olefin in the product mixture. At higher temp, an even greater ratio of olefin to amine would be expected. Since procedures for preparative experiments call for raising the temp to 120–150C as quickly as possible, it is not surprising that a significant amount of amine is rarely found. Conversely, the lower the reaction temp, the greater the conversion to amine rather than olefin. Thus, extrapolation of the data to 60C gives a ratio of $0.3 \times 10^{-7} : 1.5 \times 10^{-7}$, or 0.20, and a conversion to 16.7% olefin and 83.3% amine.

A previous report (4) describes the gas chromatographic analysis of dimethyllaurylamine oxide, and its pyrolysis in the chromatograph to 1-dodecene and dimethylhydroxylamine. At 300C, the temp of the injection port in both studies, one would not expect to find an amine oxide among the products. Contrary to the previous report, we observed a peak in addition to olefin and amine during analysis of a partially pyrolyzed sample. Comparison of retention time and IR spectrum of a collected sample with those of pure material showed that amine oxide was not extensively pyrolyzed on passage through the chromatograph.

Sahyun and Cram (2) give conclusive evidence that amine oxide dehydrates prior to olefin formation. The energy of activation for dimethyllaurylamine oxide hydrate pyrolysis to 1-dodecene, 36.3 kcal, is in reasonable agreement with the 24.4–34.7 kcal enthalpy of activation for pyrolysis of *threo-* and *erythro-* N, N-dimethyl-3-phenyl-2-butylamine oxide in aqueous tetrahydrofuran or in methanol. The enthalpy of activation for dodecene formation at 373K is calculated (10) ($\Delta H^{\neq} = E_a - RT$) to be 35.6 kcal. One would expect a somewhat higher activation energy for an aliphatic amine oxide, since incipient conjugation with the aromatic system is absent. The entropy of activation, +12.4 ± 0.8 e.u., is within the range of −9.6 to +16 reported by Cram. If olefin formation is rate-determining, the positive entropy of activation can best be explained as resulting from a transition state resembling the fragmented products, i.e., olefin and dimethylhydroxylamine, since one would expect a negative value for the cyclic transition state generally proposed. Alternatively, the positive value is consistent with the fragmentation of hydrate into water and amine oxide in the transition state if dehydration is rate-determining.

Activation parameters for amine formation, activation energy of 20.6 kcal and entropy of −30.8 ± 0.2 e.u., suggest a highly constrained transition state. The activation energy is probably markedly less than the bond dissociation energy for a nitrogen oxygen semipolar bond. It is therefore unlikely that reaction proceeds by dissociation to an amino radical and an oxygen atom. Certainly the large negative entropy of activation does not suggest fragmentation. It seems more likely that deoxygenation would proceed by oxygen transfer from amine oxide to water in a hydrate or dissociated hydrate (This mechanism is presented tentatively, without supporting evidence. It is difficult to conceive of any other simple reaction scheme that would lead to deoxygenation.), a reaction which should require a rigid steric relationship, followed by decomposition of hydrogen peroxide to water and oxygen. Unfortunately, the bond dissociation energy of a semipolar N—O bond is not available. If one assumes it is approximately the same as the N—O bond in nitrogen dioxide, 73 kcal (11) and uses the O—O bond dissociation energy of hydrogen peroxide as 52 kcal (11), and the energy of the hydrate hydrogen bond as 7 kcal (2), the first reaction would be endothermic by 21 kcal. Decomposition of hydrogen peroxide to water and oxygen is exothermic by 23.9 kcal. Considering the uncertainty in the N−O bond energy, this mechanism appears consistent with the activation parameters.

$$R_3N{-}O \ldots HOH \rightarrow R_3N \ldots HOOH \rightarrow R_3N + H_2O + \tfrac{1}{2}O_2$$

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REFERENCES

1. a) Cope, A. C., "Organic Reactions," Vol. 11, John Wiley & Sons, Inc., New York, 1960, p. 317; b) DePuy, C. H. and R. W. King; Chem. Revs. *60*, 431 (1960).
2. a) Cram, D. J., M. R. V. Sahyun, and G. R. Knox, JAOCS *84*, 1734, (1962); b) Sahyun, M. R. V., and D. J. Cram, *Ibid. 85*, 1263 (1963).
3. a) Brooks, R. T., and P. D. Sternglanz, Anal. Chem. *31*, 561 (1959); b) Wimer, D. C., *Ibid. 34*, 873 (1962).
4. Hoh, G. L. K., D. O. Barlow, A. F. Chadwick, D. B. Lake, and S. R. Sheeran, JAOCS *40*, 268–271 (1963).
5. Frost, A. A., and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, 1953, p. 147.
6. Link, W. E., R. A. Morrissette, A. D. Cooper, and C. F. Smullin, JAOCS *37*, 364–366 (1960).
7. Reference 1a, p. 370.
8. Cope, A. C. and N. A. LeBel, J. Am. Chem. Soc., *82*, 4656 (1960).
9. Paquette, L., J. Org. Chem. *27*, 2870 (1962).
10. Reference 5, p. 97.
11. Walling, C., "Free Radicals in Solution," John Wiley and Sons, Inc., New York, 1957, p. 48.

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The Kinetics of Methyl Linoleate Emulsion Autoxidation in the Presence of Polyhydroxy Compounds[1,2]

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Abstract

The kinetics of the autoxidation of methyl linoleate emulsions activated by carbohydrates likely to be present in meat, with special reference to the effects of functional groups, number of carbon atoms and configuration have been investigated by the rate of oxygen uptake. On the basis of equimolar concentrations of aldoses in the system, oxidation rate of methyl linoleate increases as the number of carbon atoms in the sugar molecule decreases, reaching a maximum in the presence of glyceraldehyde. Configuration of the aldose has a slight effect on the oxidation rate of methyl linoleate emulsions.

At comparable molar ratios of hexose to methyl linoleate, the rate of oxidation was found to be: ketohexose > aldohexose > hexahydroxy alcohol.

Replacement of the primary alcohol group in an aldohexose with a methyl group decreases the oxidation rate of methyl linoleate emulsion. An opposite effect is observed when the primary alcohol group is substituted with a carboxyl group, i.e., in the presence of sodium glucuronate.

2-Deoxy-D-glucose and 2-deoxy-D-ribose exhibit a lesser effect on the autoxidation of methyl linoleate emulsion than glucose and ribose, respectively.

Oxidation rates in the presence of reducing disaccharides, maltose, lactose and cellobiose, are more rapid than in the presence of the non-reducing disaccharide sucrose.

Introduction

OF ALMOST A HUNDRED possible monosaccharides containing from two to seven carbon atoms, less than a score have been found in animal cells (6). Glyceraldehyde is found as the phosphate ester in the breakdown product of carbohydrate metabolism. Dihydroxyacetone has been similarly identified. Tetroses have not been found in natural products, but a reduced form, a tetrahydroxy alcohol, erythritol, exists. It has been assumed that the nonexistence of tetroses is due to their extreme reactivities. Most probably tetroses are not synthesized directly but the alcohol is the decarboxylation product of a five-carbon sugar acid. The presence of carbohydrate alcohols in nature may be accounted for by a direct reduction of the reducing sugar or through decarboxylation of the corresponding higher aldonic acid. However, there is no evidence for either mechanism in nature. D-ribose is found in nucleic acids. D-ribulose, D-lyxose, xylulose, glucose, fructose, sedoheptulose and glyceraldehyde are present as phosphoric acid esters in the products of carbohydrate metabolism (17). L-fucose is a constituent of blood group substances which contain galactose, and mannose. By paper chromatography, glucose, fructose, ribose and other unidentified sugars were found in adductor muscle of calves (7). Lilyblade and Peterson (16) identified inositol, glucose, sedoheptulose, mannose, fructose, ribose, ribulose, arabinose and xylose in chicken muscle. During storage under refrigeration, ribose of beef increases from less than 1γ/g to 120γ/g in 16 days, while cold storage at −20C for a month shows 60γ/g (5).

Aliphatic polyhydroxy compounds such as glycerol, sucrose, sorbitol, glucose and fructose act as weak antioxidants (3,13,14,23,25).

Franke (4) reported that autoxidation of linoleic acid is catalyzed by glyceraldehyde and dihydroxyacetone. In a study on the oxidation of tetralin, Robertson and Waters (22) found that ethylene glycol and *tert*-butyl alcohol increased the initial rate of oxidation, while α-tetralol, benzyl alcohol, *n*-butyl alcohol, isopropyl alcohol, cyclohexanol and allyl alcohol inhibited the initial rate. Secondary alcohols are oxidized to ketones in inert solvents by tertiary peroxides (8). Co-oxidation of aliphatic aldehydes and oleic acid gave ca. 20% 9,10-epoxystearic acid and 50–70% aliphatic acid (24). Higher yields of 9,10-epoxystearic acid (70–80%) were obtained by using benzaldehyde. The low yield in the case of aliphatic aldehydes is attributed to preferential oxidation of excess aldehyde.

A close relation to the autoxidation of unsaturated hydrocarbons with the participation of $RO^{\cdot}_2$ is shown by the oxidation of carbohydrates by hydrogen per-

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