methanol was stirred for 95 hr. and then treated with 1.9 g. (7 mmoles) of barium acetate. The resulting mixture was filtered and the residue was washed with methanol. The combined filtrates were acidified with hydrochloric acid, saturated with sodium chloride, and repeatedly extracted with ether. After the ethereal extracts had been washed with aqueous sodium bicarbonate, dried, and concentrated under a 75-cm. Vigreux column, the concentrate was added to a boiling ethanolic solution of 1.41 g. (9.13 mmoles) of 2, 4-dinitrophenylhydrazine and 0.2 ml. of concentrated hydrochloric acid. The resulting solution was concentrated to dryness under reduced pressure and the residue was chromatographed on Silica-Gel. The 2, 4-dinitrophenylhydrazone of cyclohexanone, eluted with carbon tetrachloride-ether mixtures, was recrystallized from ethanol to separate 48.5 mg. (3.3%) of the pure derivative as orange plates, m.p. 159.5–160.3°, which was identified with an authentic sample by a mixed melting-point determination, comparison of infrared spectra and comparison of R_f values on thin-layer chromatography.[24]

Hydrogenation of the Methyl Ether 3.—A solution of 17.9 g. (0.0681 mole) of the methyl ether **3** in 325 ml. of methylcyclohexane was hydrogenated over 59.6 g. of a copper chromite catalyst employing an initial temperature of 27° and 1900 p.s.i. and a final temperature of 250° and 2790 p.s.i. After the resulting mixture had been filtered and the catalyst washed with ether, the combined organic solutions were washed successively with aqueous hydrochloric acid and aqueous sodium hydroxide. The basic fraction, isolated in the usual way, afforded 1.3228 g. (8.7%) of the amino alcohol **7**, m.p. 164.2–166°. The organic solution of the neutral products was dried and concentrated and the residue distilled in a short-path still to separate 190.1 mg. (2.7%) of a lower-boiling liquid, and 972.1 mg. of a higher-boiling solid fraction, m.p. 62–63°. The lower-boiling liquid, $n^{24}D$ 1.4638 (lit.,[25] $n^{25}D$ 1.4628), was identified with an authentic sample of cyclohexylcarbinol (**14**) by comparison of infrared and mass spectra.

The solid higher-boiling fraction, was chromatographed on Silica-Gel to separate, after elution with a pentane–ether mixture and sublimation (56° at 0.01 mm.), 754.8 mg. (5.65%), of dicyclohexylcarbinol (**13**) as white rosettes, m.p. 63.4–64.3°, and 35 mg. of the starting ether **3**, m.p. 94.5–96°. The dicyclohexylcarbinol (**13**) has infrared absorption[16] at 3605 and 3450 cm.$^{-1}$ (unassoc. and assoc. O—H) with a broad n.m.r. peak[17] at 6.99 τ (1H, half band width *ca.* 9 c.p.s., >CH—OH) as well as broad, complex absorption (23H) in the region 8.0–9.1 τ.

Anal. Calcd. for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.29; H, 12.30.

An authentic sample of the carbinol **13**, as white cubes from ether m.p. 62.8–64° (lit.,[26,27] 63°), was prepared in 22% yield by reaction of ethereal cyclohexylmagnesium bromide with methyl formate following the previously described procedure.[27] The product was identified with the previously described sample by comparison of infrared spectra, R_f values on thin-layer chromatography,[24] and a mixed melting-point determination.

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[24] A silica gel coating was employed.

[25] W. J. Bailey, J. J. Hewitt, and C. King, *J. Am. Chem. Soc.*, **77**, 357 (1955).

[26] O. Neunhoeffer, *Ann.*, **509**, 115 (1934).

[27] P. Sabatier and A. Mailhe, *Bull. soc. chim. France*, [3] **33**, 74 (1905).

Organic Nitrogen Compounds. I. Peroxide Intermediates of Tertiary Alkylamine Oxidation by Hydrogen Peroxide

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The primary products of the reaction of tertiary alkylamines and hydrogen peroxide are trialkylammonium peroxides which decompose to yield trialkylamine oxides. The latter have a great tendency to form addition compounds with hydrogen peroxide. The course of the reaction can be best followed in the case of triethylenediamine which gives a well defined, crystalline diammonium diperoxide. On heating, this yields the corresponding diamine dioxide which can be converted to a dihydrogen peroxide adduct. Infrared spectra of the compounds support the proposed reaction route and indicate strong and characteristic hydrogen bondings in the trialkylamine– and trialkylamine oxide–hydrogen peroxide adducts.

The oxidation of tertiary aliphatic amines by aqueous hydrogen peroxide to yield amine oxides is a well known reaction. The first studies of the reaction were carried out at the end of the 19th century by Wolffenstein[1,2] in Germany and Dunstan[3] in England. The course of such oxidations was first discussed by Wieland.[4] He assumed that the hydrogen peroxide first adds to the amine to form an ammonium peroxide which on decomposition yields the amine oxide with the loss of water:

$$R_3N + H_2O_2 \longrightarrow R_3N\cdot H_2O_2 \longrightarrow R_3NO + H_2O$$

Another formulation of the reaction is also possible[5]:

$$R_3N + H_2O_2 \longrightarrow R_3{}^+NOH\ [{}^-OH] \longrightarrow R_3NO + H_2O$$

It was felt that the formation of alkylammonium peroxides from alkylamines and alkyl hydroperoxides in our earlier work[6,7] and the formation of ammonium peroxide from ammonia and hydrogen peroxide[8,9] supported the reaction route proposed by Wieland.

$$R_3N + R'O_2H \longrightarrow R_3N\cdot HO_2R'$$

$$NH_3 + H_2O_2 \longrightarrow NH_3\cdot H_2O_2$$

In the work reported here the reactions of trialkylamines with hydrogen peroxide to form amine oxides were studied. Using highly concentrated hydrogen peroxide reactant, ammonium peroxide intermediates of the reaction were isolated and converted to the corresponding amine oxides and their hydrogen peroxide adducts.

Trialkylamine–Hydrogen Peroxide Adducts.—Trialkylamine–hydrogen peroxide adducts (trialkylammonium peroxides) were formed on treating simple tertiary aliphatic amines with highly concentrated (90% +) hydrogen peroxide at low temperatures (about −50°). These trialkylammonium peroxides are unstable, color-

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[1] W. Wernick and R. Wolffenstein, *Ber.*, **31**, 1553 (1898).

[2] L. Mamlock and R. Wolffenstein, *ibid.*, **33**, 159 (1900).

[3] W. R. Dunstan and E. Goulding, *J. Chem. Soc.*, **75**, 1004 (1899).

[4] H. Wieland, *Ber.*, **54**, 2353 (1921).

[5] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 595.

[6] A. A. Oswald, F. Noel, and A. J. Stephenson, *J. Org. Chem.*, **26**, 3969 (1961).

[7] A. A. Oswald, F. Noel, and G. Fisk, *ibid.*, **26**, 3974 (1961).

[8] J. D'Ans and O. Wedig, *Ber.*, **66**, 3075 (1913).

[9] O. Maass and W. H. Hatcher, *J. Am. Chem. Soc.*, **44**, 2472 (1922).

less liquids at room temperature, although they solidify at higher temperatures than the original amines on cooling. Their peroxide character is indicated by their positive reaction with sodium iodide.[10] However, trialkylamine oxides may also oxidize the iodide. In our work aromatic thiols—*e.g.*, 2-naphthalenethiol—were found to be selective reagents for the peroxide adducts. The trialkylamine–hydrogen peroxide adducts reacted quantitatively with 2-naphthalenethiol as did hydrogen peroxide in the presence of trialkylamine catalyst:

$$R_3N \cdot H_2O_2 + 2ArSH \longrightarrow R_3N + 2H_2O + ArSSAr$$

$$H_2O_2 + 2ArSH \xrightarrow[(R_3N)]{} 2H_2O + ArSSAr$$

The reactions of triethylenediamine [1,4-diazabicyclo[2.2.2]octane] were studied in detail because, unlike simpler trialkylamines, triethylenediamine yielded well defined products with hydrogen peroxide.

It was found that a crystalline alkylammonium peroxide, triethylenediammonium diperoxide can be readily isolated from an instantaneous, exothermic reaction of triethylenediamine with concentrated (30% +) aqueous hydrogen peroxide at low temperatures.

$$N(CH_2CH_2)_2N + 2\ H_2O_2 \longrightarrow H_2O_2 \cdot N(CH_2CH_2)_3N \cdot H_2O_2$$

Triethylenediammonium diperoxide is a colorless crystalline solid. It is very soluble in water or alcohol; rather insoluble in hydrocarbons or ether. Some physical and analytical data of the compound are given in Table I. The diperchlorate and the dihydrochloride of triethylenediamine, which were previously known but not sufficiently characterized,[11] were also prepared in connection with comparative spectral studies. Their data are recorded in Table I.

The triethylenediamine–dihydrogen peroxide adduct reacted quantitatively with 2-naphthalenethiol in a manner analogous to other trialkylamine–hydrogen peroxide adducts:

$$H_2O_2 \cdot N(CH_2CH_2)_3N \cdot H_2O_2 + 4ArSH \longrightarrow N(CH_2CH_2)_3N + 4\ H_2O + 2ArSSAr$$

The infrared spectra of the hydrogen peroxide adducts of trialkylamines were also examined to obtain more information about their structure (Table II). The spectra of the perchloric acid and hydrogen chloride adducts of trialkylamines were also studied in comparison with the hydrogen peroxide adducts. Spectra of numerous amine hydrohalides in the hydrogen bonding region have been studied by Sandorfy and coworkers.[13,14] However, no comparative study of halide and hydrate hydrogen bonds was made.

In the present study it was found that, in the hydrogen bonding region, the hydrochlorides and perchlorates of trialkylamines have more numerous absorption peaks at higher wave lengths than the hydrogen peroxide adducts. This indicates a stronger type of hydrogen bonding which is probably due to the more polar character of these salts. Characteristic differences were also observed in the methylene bending region. These are illustrated by the spectra of triethylenediamine adducts in Fig. 1.

A comparison of the spectra of the water, hydrogen peroxide, and perchloric acid adducts show the increasing polar character of these adducts in that order.

The hydrate exhibits one broad band in the hydrogen bonding region (2.5–4 μ) at 2.95 μ. The hydrogen peroxide adduct has two additional strong bands at higher wave lengths 3.27 and 3.63 μ. In the case of the diperchlorate and dihydrogen chloride, the CH absorption bands at 3.40 and 3.45 are masked by the strong hydrogen bonding and absorption occurs at wave lengths as high as 3.85 μ.

In the region between 6.5 and 7.5 μ, both the diperchlorate and the dihydrochloride show a characteristic triplet with bands at 6.8, 7.0, and 7.1 μ. Triethylenediamine hydrate and dihydrogen peroxide show only one absorption peak at 6.8 μ in this region. It is believed that the appearance of strong absorption peaks at 7.0 and 7.1 μ is associated with the quaternerization of the nitrogen.

In the region between 11 and 12 μ there is another characteristic triplet at 11.25, 11.65, and 11.80 μ for both the diperchlorate and the dihydrochloride. This triplet is absent in both the hydrate and the dihydrogen peroxide adduct. It is probably due to the appearance of the triethylenediammonium group in the diperchlorate and the dihydrochloride.

On the basis of the infrared studies, it can be concluded that the liquid trialkylamine hydrogen peroxide adducts and the solid triethylenediamine–hydrogen peroxide adduct (triethylenediammonium diperoxide) are hydrogen bonded polar complexes,

$$\overset{\delta+}{R_3N} \ldots H{-}\overset{\delta-}{O}{-}O{-}H,$$

$$H{-}\overset{\delta-}{O}{-}O{-}H \ldots \overset{\delta+}{N}(CH_2CH_2)_3\overset{\delta+}{N} \ldots H{-}\overset{\delta-}{O}{-}O{-}H,$$

and not ionic ammonium salts. This is in contrast with the conclusions of Simon and co-workers[15,16] with regard to the structure of ammonium peroxide. On the basis of its Raman spectrum, solid ammonium peroxide was assigned an ionic structure:

$$[NH_4^+]\ [^-O_2H]$$

Trialkylammonium peroxides are thermally unstable compounds; on decomposition they yield trialkylamine oxides, either as hydrates or as anhydrous compounds.

$$R_3N \cdot H_2O_2 \longrightarrow R_3NO \cdot H_2O$$

The decomposition of trialkylammonium peroxides is quite rapid at 50° and effective cooling is necessary to keep the decomposition under control. During the course of the reaction, the trialkylammonium peroxide is partly dissociated:

$$R_3N \cdot H_2O_2 \rightleftarrows R_3N + H_2O_2$$

The resulting free amine (triethyl-, tri-*n*-propyl-, tri-*n*-butylamine) separates as an upper phase. On prolonged heating with effective stirring the larger part of the amine phase disappears and is converted to the amine oxide.

The decomposition of trialkylammonium peroxides could be best followed using triethylenediammonium diperoxide as a model compound. Triethylenedi-

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[10] C. C. J. Culvenor, *Rev. Pure Appl. Chem.* **3**, 83 (1953).

[11] O. Hromatka, *Ber.*, **75**, 1302 (1942).

[12] A. C. Cope and H. H. Lee, *J. Am. Chem. Soc.*, **79**, 964 (1957).

[13] B. Chenon and C. Sandorfy, *Can. J. Chem.*, **36**, 1181 (1958).

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[15] A. Simon and U. Uhlig, *Ber.*, **85**, 977 (1952).

[16] A. Simon and H. Kriegsmann, *Naturwissenschaften*, **42**, 14 (1955).

Table I

Derivatives of Trialkylamine-Hydrogen Peroxide Reactions. I. Physical and Analytical Data

No.	Components: Base (1 mole)	Components: Acid, moles	Formula	M.p.,[a] °C.	Yield, %	Calcd. C	Calcd. H	Calcd. N	Calcd. O	Calcd. Cl	Found C	Found H	Found N	Found O	Found Cl	Peroxide,[i] %
I	Triethylenediamine	H_2O_2, 2	$C_6H_{16}N_2O_4$	112 dec.	86	39.99	8.95	15.54	35.5	...	40.28	9.06	15.38	35.2	...	98
II		$HClO_4$,[b] 2	$C_6H_{14}N_2O_8Cl_2$	300	98	23.02	4.50	8.95	40.9	22.65	22.79	4.76	9.08	39.7	22.60	...
III		HCl, 2	$C_6H_{14}N_2Cl_2$	290 dec.[c]	90	38.93	7.62	15.14	...	38.31	38.85	7.76	15.06	...	38.69	...
IV		Picric acid, 2	$C_{18}H_{18}N_8O_{14}$	295 dec.[d]	97											
V	Triethylenediamine dioxide	H_2O, 1	$C_6H_{14}N_2O_3$	70 dec.	95	44.43	8.70	17.27	29.6	...	44.75	8.88	17.11	29.2	...	...
VI		H_2O, 2	$C_6H_{16}N_2O_4$	52–54	99	39.99	8.95	15.54	35.5	...	40.25	9.22	15.64	34.0	...	...
VII		H_2O_2, 2	$C_6H_{16}N_2O_6$	124 dec.[d]	70.5	33.96	7.60	13.20	45.2	...	34.10	7.82	13.13	45.0	...	100
VIII		$HClO_4$, 2	$C_6H_{14}N_2O_{10}Cl_2$	290 dec.	96	20.88	4.09	8.12	46.4	20.55	20.52	4.09	8.46	46.7	20.30	...
IX		HCl, 2	$C_6H_{14}N_2O_2Cl_2$	195 dec.	91	33.20	6.50	12.90	14.7	32.66	33.18	6.76	12.87	14.7	32.91	...
X		Picric acid, 2	$C_{18}H_{18}N_8O_{16}$	125 dec.	95 (97)[h]	35.89	3.01	18.60	42.5	...						...
XI	Trimethylamine oxide	H_2O_2, 1	$C_3H_{11}NO_3$	87 dec.[d]	64	33.02	10.16	12.83	44.0	...	32.82	9.95	14.11	43.7	...	93
XII	Triethylamine oxide	H_2O_2, 1	$C_6H_{17}NO_3$	98 dec.[d]	73	47.66	11.33	9.26	31.7	...	47.67	11.33	9.17	32.0	...	102
XIII		Picric acid, 1	$C_{12}H_{18}N_4O_8$	184 dec.[e]	95 (95)[h]	41.62	5.24	16.18	37.0	...	41.58	5.17	16.32	36.8	...	...
XIV	Tripropylamine oxide	Picric acid, 1	$C_{15}H_{24}N_4O_8$	131–133[f]	87 (85)[h]	46.39	6.23	14.42	32.9	...	46.30	6.16	14.31	32.5	...	...
XV	Tributylamine oxide	Picric acid, 1	$C_{18}H_{30}N_4O_8$	108–110[g]	83 (80)[h]	50.23	7.02	13.01	29.7	...	50.22	7.00	13.03	29.6	...	...

[a] Melting point determinations were carried out between glass slides on a Koffler block. After the first determination the substance was heated fast to its expected melting (decomposition) point. The results are uncorrected. [b] The perchlorate of triethylenediamine was first prepared by Hromatka[11] but was not analyzed because it explodes on heating. [c] Hromatka[11] notes that his compound does not melt at 280°. [d] Melts with sudden, very violent gas evolution (bubbling and frothing). [e] Dunstan and Goulding[3] give a m.p. of 164°. [f] Dunstan and Goulding record a m.p. of 129°. [g] Cope and Lee[12] give a m.p. of 110–111°. [h] Yields recorded in brackets were obtained starting from the hydrogen peroxide adduct. [i] Peroxide contents were determined by the oxidation of 2-naphthalenethiol in the presence of 1,1,3,3-tetramethylbutylamine. They are listed as per cent of the calculated value.

Table II

Derivatives of Trialkylamine–Hydrogen Peroxide Reactions. II. Characteristic Absorptions in the Infrared

No.	Compound: Base (1 mole)	Compound: Acid, moles	Concn.,[a] %	Absorption peaks (μ, w = weak): Hydrogen bonding	Methylene and associated	Amine oxide and other
...	Triethylenediamine	H_2O 1	0.1		6.85	11.05 11.28 12.85
I		H_2O_2 2	0.1	3.27 3.63	6.85	10.68 w 11.0 w 11.6 w 12.85, 14.38
II		$HClO_4$ 2	0.1	3.35–3.46 3.60 3.87	6.8 7.0 7.1	10.68 w 11.26 11.67 11.8 12.65 w
III		HCl 2	0.5	3.33–3.44 3.56 3.71 3.85	6.8 7.0 7.1	
VI	Triethylenediamine dioxide	H_2O 2	0.1	Inflections only	6.82	10.69 11.2 11.85 12.55 14.39
VII		H_2O_2 2	0.1	3.20 3.58	6.85 6.95 w	10.65 11.7 12.5 14.31
VIII		$HClO_4$ 2	0.5	3.27 3.38 3.55 3.71	6.8 7.13 7.28	10.68 10.94 11.72 12.52 14.35
IX		HCl 2	0.5	3.33 3.51 3.66	6.8 7.27	10.75 w 10.95 11.70 12.55 14.45
...	Trimethylamine	$HClO_4$ 1	0.5	3.40 3.75 4.0 w 4.09	6.76 7.02 7.16	10.68 w
...		HCl 1	0.5	3.41 3.75 4.0 w 4.09	6.76 7.02 7.16	
...	Trimethylamine oxide	H_2O 1	0.5	Inflections only	6.86 7.17	10.60
XI		H_2O_2 1	0.5	Inflections only	6.86 7.24	10.60
...	Triethylamine	$HClO_4$ 1	0.5	3.4 3.5 w 3.7 3.83 4.0	6.8 6.85 7.0 7.2 w 7.3 w	10.69 w
...		HCl 1	0.5	3.42 3.67 3.77 4.05	6.78 7.0 7.18 7.25 w 7.35 w	
...	Triethylamine oxide	H_2O 1	0.1	Inflections only	6.86 7.26	10.60
XII		H_2O_2 1	0.1	3.20 3.35 3.68	6.86 7.24	10.60
...		$HClO_4$ 1	0.5	3.3 3.44 3.54 3.64	6.75 7.04 7.25	10.69 w
...		HCl 1	0.5	3.36 3.52 3.67	6.83 6.97 w 7.22 7.38	10.66

[a] In KBr pellet.

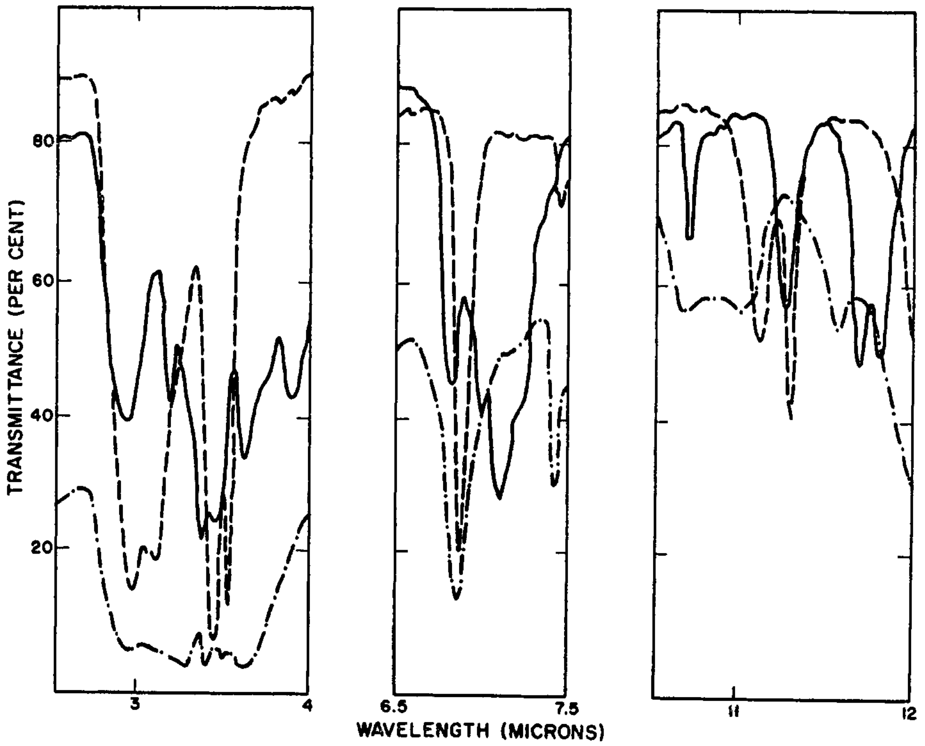

Fig. 1.—Infrared absorption spectra of triethylenediamine hydrate (- - - -), triethylenediammonium diperoxide (–. – . –), and triethylenediammonium diperchlorate (———) at 0.5% concentration in KBr pellets.

ammonium diperoxide starts to decompose at 60°. The exothermic decomposition can be conveniently carried out portionwise at 100°. The decomposition product solidifies on standing at room temperature to a crystal mass melting at 52–54°. These crystals are not able to oxidize mercaptans. It is suggested that this product is the dihydrate of triethylenediamine dioxide and the main decomposition reaction takes place according to the following reaction equation:

$$H_2O_2 \cdot N(CH_2CH_2)_3N \cdot H_2O_2 \longrightarrow H_2O \cdot ON(CH_2CH_2)_3NO \cdot H_2O$$

In vacuo at about 60°, triethylenediamine dioxide dihydrate loses one of the crystal waters to form the hygroscopic monohydrate.

Crystalline perchloric, hydrochloric, and picric acid derivatives of triethylenediamine dioxide (Table I) were prepared for its better characterization according to the following reaction equation:

$$ON(CH_2CH_2)_3NO \cdot 2H_2O + 2HAc \longrightarrow ON(CH_2CH_2)_3NO \cdot 2HAc$$

$$Ac = ClO_4,\ Cl,\ OC_6H_2(NO_2)_3$$

Trialkylamine Oxide–Hydrogen Peroxide Adducts.—It has been mentioned several times in the literature[10,17–20] that some amine oxides crystallize with hydrogen peroxide in the crystal lattice. In this study it has been found that trialkylamine oxides generally react with hydrogen peroxide yielding well defined adducts:

$$R_3NO + H_2O_2 \longrightarrow R_3NO \cdot H_2O_2$$

Because of the reaction, the amine oxides obtained from trialkylamine–hydrogen peroxide reactions were usually peroxidic according to the mercaptan method.

The hydrogen peroxide adducts of trialkylamines could be simply prepared by adding an equimolar amount of hydrogen peroxide to the amine oxide. The hydrogen peroxide adducts of trimethylamine oxide and triethylamine oxide were isolated as well defined crystalline compounds. The adducts of tri-*n*-propylamine oxide and tri-*n*-butylamine oxide were viscous liquids at room temperature and could not be crystallized.

The hydrogen peroxide adducts of amine oxides could be also prepared in a one step reaction from trialkylamines. When two moles of hydrogen peroxide were added per mole of trialkyl (-ethyl, -*n*-propyl,-*n*-butyl)-amine, trialkylamine oxide–hydrogen peroxide adducts were again the main products after prolonged stirring of the reaction mixture at 50°.

When equimolar amounts of trimethylamine and hydrogen peroxide were mixed at 50° and the mixture was allowed to come to room temperature, spontaneous exothermic decomposition started. At 38°, the mixture released half of the trimethylamine. The remaining mixture crystallized to yield the adduct of trimethylamine oxide–hydrogen peroxide. It is proposed that the following reactions took place:

$$(CH_3)_3N + H_2O_2 \longrightarrow (CH_3)_3N \cdot H_2O_2 \longrightarrow (CH_3)_3NO \cdot H_2O$$

$$(CH_3)_3NO \cdot H_2O + (CH_3)_3N \cdot H_2O_2 \longrightarrow (CH_3)_3NO \cdot H_2O_2 + (CH_3)_3N + H_2O$$

Also from an equimolar mixture of triethylamine and hydrogen peroxide, the corresponding amine oxide–hydrogen peroxide adduct precipitated on concentration.

The hydrogen peroxide adduct of triethylenediamine oxide which readily crystallized, was the easiest to isolate. It could be obtained in an almost quantitative

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(17) A. C. Cope and P. H. Towle, *J. Am. Chem. Soc.*, **71**, 3423 (1949).

(18) M. Polonowski and M. Polonowski, *Bull. Soc. Chim.*, **39**, 1147 (1926).

(19) M. Oesterlin, *Ber.*, **76**, 224 (1943).

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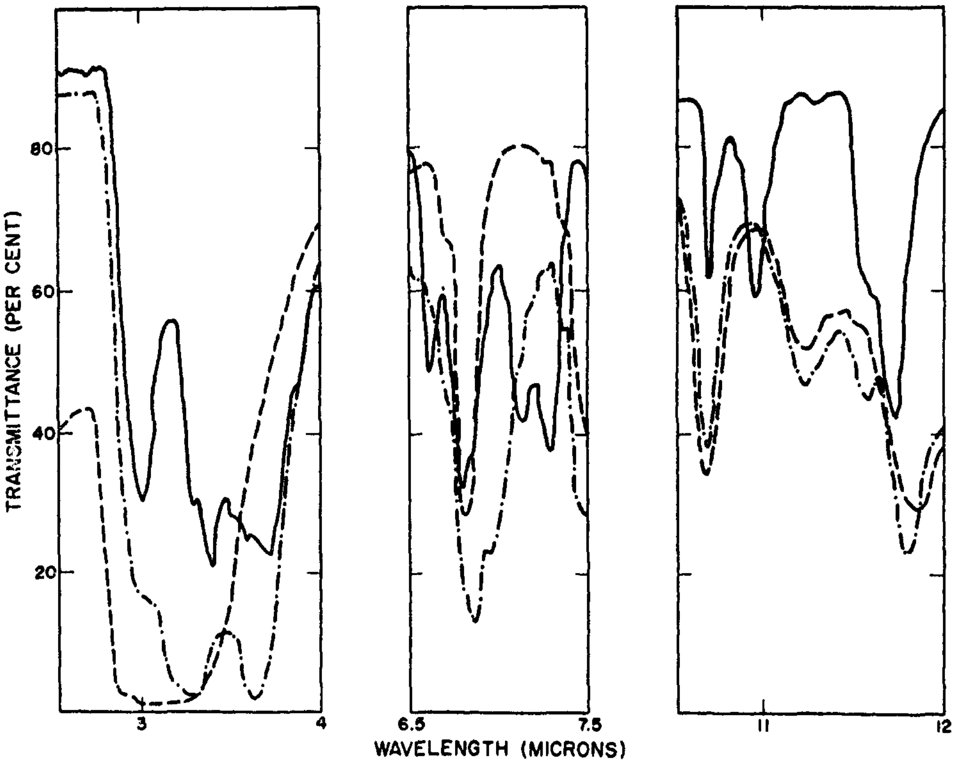

Fig. 2.—Infrared absorption spectra of triethylenediamine dioxide hydrate (– – – –), triethylenediamine dioxide dihydrogen peroxide (– . – . –), and triethylenediamine dioxide diperchloric acid (———) at 0.5% concentration in KBr pellets.

yield by reacting triethylenediamine dioxide hydrate with a slight excess of hydrogen peroxide:

$$ON(CH_2CH_2)_3NO + 2H_2O_2 \longrightarrow H_2O_2 \cdot ON(CH_2CH_2)_3NO \cdot H_2O_2$$

Triethylenediamine could be converted directly to the diamine dioxide dihydrogen peroxide, by simply adding four moles of hydrogen peroxide to a methanol solution of one mole of the diamine at 60°. The product crystallized on subsequent cooling.

The solubility characteristics of trialkylamine oxide–hydrogen peroxide adducts are similar to that of trialkylamine oxides. They are highly soluble in water and alcohol, and only slightly soluble in ether, acetone, and benzene. The latter solvents can be used for the precipitation of the crystalline hydrogen peroxide adducts from very concentrated water solutions. The crystalline hydrogen peroxide adducts do not show the strong hygroscopicity characteristic of the lower molecular weight anhydrous trialkylamine oxides. They decompose with gas evolution on heating. Some of their physical and analytical data are shown in Table I.

One mole of these adducts quantitatively oxidizes two moles of an aromatic thiol:

$$R_3NO \cdot H_2O_2 + 2ArSH \longrightarrow R_3NO + 2H_2O + ArSSAr$$

The hydrogen peroxide adducts of tripropylamine oxide and tributylamine oxide, which contained water, also oxidized the amounts of thiol expected on the basis of the above equation. This is an indirect support for the structure of the trialkylamine oxide–hydrogen peroxide adducts in general.

Picric acid adducts are generally used for the characterization of amine oxides which are usually difficult to isolate. In our work it has been found that the hydrogen peroxide adducts of amine oxides also give peroxide free amine oxide picrates.

$$R_3NO \cdot H_2O_2 + HOC_6H_2(NO_2)_3 \longrightarrow R_3N \cdot HOC_6H_2(NO_2)_3 + H_2O_2$$

The reaction was especially useful for the characterization of the liquid hydrogen peroxide–tri-*n*-propylamine oxide and -tri-*n*-butylamine oxide adducts. Physical and analytical data of some of the picrates prepared are given in Tables I and II.

The infrared spectra of trialkylamine oxides and their derivatives were also studied to obtain more information about their structures (Table II). The water and hydrogen peroxide adducts of trialkylamine oxides have nearly identical infrared spectra except in the hydrogen bonding region. The broader hydrogen bonding absorption of the hydrogen peroxide adducts indicated the existence of stronger types of hydrogen bonds. The similarity of the rest of the spectra of the two types of adducts indicated that they have basically the same hydrate-like character. The perchloric acid and hydrogen chloride adducts of amine oxides, on the other hand, both had very similar spectra, very different from those of the water and hydrogen peroxide adducts. They show additional hydrogen bonding absorption bands between 3–4 μ, and a decreased absorption at 10.7 μ, where the $\equiv N \rightarrow O$ group absorbs.[22] These observations indicate that they are quaternary ammonium salts:

$$\left[\overset{\delta+}{R_3NOH}\right]\left[\overset{\delta-}{Ac}\right];\ Ac = ClO_4, Cl$$

The characteristic differences between the various types of adducts of amine oxides are illustrated by the spectra of triethylenediamine dioxide adducts in Fig. 2.

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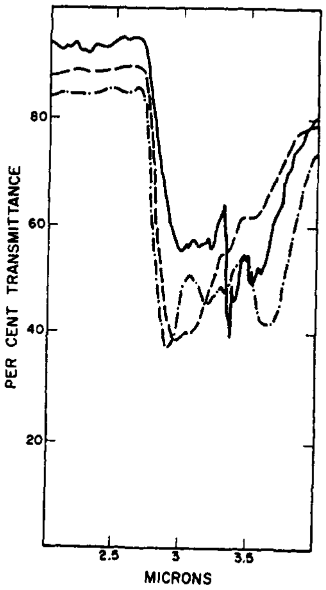

Fig. 3.—Infrared absorption spectra of an equimolar mixture of *triethylamine and 90% hydrogen peroxide [initially (triethylammonium peroxide* ———) and after 90 min. (triethylamine oxide – – – –) as such between NaCl plates] and of triethylamine oxide–hydrogen peroxide (–.–.–) at 0.1% concentration in KBr pellet.

The almost equally strong NO absorption at 10.7 μ in the hydrate and the dihydrogen peroxide shows that the proposed formation of an ionic amine oxide hydrate intermediate having a quaternary ammonium cation with a covalent hydroxyl group[5] in tertiary amine oxidation is very unlikely.

In addition to the absorptions discussed in general, the diperchlorate and dihydrogen chloride of triethylenediamine dioxide show absorption peaks at 7.2 and 10.95 μ which are absent in the dihydrate and the diperoxide. These gave additional support to a quaternary ammonium salt structure for these adducts.

$$[Ac^-]\ [HON^+(CH_2CH_2)_3{}^+NOH][Ac^-];\ Ac = ClO_4,\ Cl$$

A comparison of the spectra of the corresponding adducts of trialkylamine oxides with those of trialkylamines shows that the former have less ionic character than the latter. This is expected on the basis of the reduced basicity of the amine oxides in general in comparison to the corresponding amines.

On the basis of comparative spectral study it can be concluded that the order of increasing ionic character of trialkylamine derivatives is the following: oxide–hydrate, –hydrate, oxide–hydrogen peroxide, –hydrogen peroxide, oxide–perchloric (hydrochloric) acid, – perchloric (hydrochloric) acid.

Investigation of the change of the infrared spectrum of a triethylamine hydrogen peroxide mixture with time (Fig. 3) supported the proposed course of trialkylamine–hydrogen peroxide reactions. The initial mixture had a spectrum in the 2.5–7-μ region which is characteristic of the trialkylammonium peroxide. After 90 minutes the spectrum was typical of a trialkylamine oxide. After two days' standing, triethylamine oxide–hydrogen peroxide adduct crystallized out from the reaction mixture, which also showed a typical spectrum.

Experimental

Materials.—The hydrogen peroxide used in most of these experiments was an industrial 90 wt. % aqueous solution supplied by the du Pont de Nemours & Company. According to our determination by 2-naphthalenethiol in the presence of 1,1,3,3-tetramethylbutylamine, it contained 91% hydrogen peroxide. Triethylenediamine was supplied by the Houdry Process Corporation and contained less than 2% water. The trialkylamines were C. P. reagents.

Spectral Studies.—The infrared absorption spectra of adducts of trialkylamines and trialkylamine oxides with hydrogen peroxide and various acids were obtained using a Baird Model 4–55 spectrophotometer. The spectra were recorded in potassium bromide pellets. This technique was employed because no interfering absorption bands are introduced. Spectra using this technique (Table II, Fig. 1–3) showed the same bands as those obtained with mulls using either Nujol (paraffinic oil) or perfluorokerosene.

Trialkylammonium Peroxides.—To 0.1 mole of trialkyl-*(methyl-, ethyl-, propyl-, butyl-)amine, 0.1 mole of* 90% hydrogen peroxide was added at −50°. An instantaneous slightly exothermic reaction took place and a colorless mixture was obtained. This mixture is a very viscous liquid at −50° while the amine component is a mobile liquid. At 0° the mixture is a clear liquid. At room temperature, it is unstable and exothermically decomposes.

Triethylenediammonium Diperoxide. In Ether.—To a solution of 11.2 g. (0.1 mole) of triethylenediamine, 1,4-diazabicyclo-[2.2.2]octane, in 200 ml. of diethyl ether, 7.9 g. of 90% aqueous hydrogen peroxide (0.2 mole) was added portionwise with stirring. The temperature of the reaction mixture was kept below 20° with occasional ice–water cooling during the addition. A slightly exothermic reaction resulting in the instantaneous precipitation of the colorless diperoxide took place. The precipitate was filtered with suction, washed with ether, and dried *in vacuo* at room temperature to yield 15.5 g. (86%) of triethylenediammonium diperoxide. Some physical, analytical, and spectral data of the the compound are shown in Tables I and II.

In Alcohol.—To a solution of 11.2 g. (0.1 mole) of triethylenediamine in 20 ml. of methanol 4 g. of 90% hydrogen peroxide (0.1 mole) was added slowly with stirring and cooling. The resulting crystal slurry was diluted with 80 ml. of benzene and filtered with suction. The temperature of the mixture was kept below 5° during all these operations. The resulting crystal cake was washed with benzene and dried *in vacuo* to yield 85.5 g. (91.6%) of diethylenediammonium dioxide. An infrared spectrum of this compound in a 0.1% potassium bromide pellet is identical with that of the compound precipitated from ether.

Triethylenediammonium diperoxide can be synthesized with analogous methods in water, alcohol, and benzene. Even in cases where less than equivalent amount of hydrogen peroxide is added, *the diperoxide precipitates. To avoid the decomposition* of the diperoxide, it is advisable to remove fast all the water and alcohol from the precipitate by solvent washing or vacuum drying.

Determination of Hydrogen Peroxide Adducts by the Mercaptan Method.—Hydrogen peroxide or its adduct (about 0.001 mole) was dissolved in about 5 ml. of methanol and 10 ml. of 0.2 *M* naphthalenethiol solution in toluene and 0.3 ml. of 1,1,3,3-tetramethylbutylamine were added to it. The mixture was allowed to stand for 30 min. If precipitation (bis-2-naphthyl disulfide) was observed during this period, additional toluene was added to the mixture until it became a clear solution. After 0.5 hr. the solution was diluted with 100 ml. of alcoholic sodium acetate and titrated potentiometrically for thiol content with 0.1 *N* silver nitrate *solution in isopropyl alcohol in the usual manner.*[23]

Trialkylamine Oxides.—When the liquid unstable trialkylammonium peroxides were allowed to come to room temperature, an exothermic decomposition took place. The temperature rose spontaneously to 50°. At this temperatue effective cooling—*e.g.*, with solid carbon dioxide–alcohol mixture—was necessary to keep the decomposition under control. After the exothermic reaction subsided, the resulting mixtures were stirred for an additional hour at 60–100° to complete the reaction. The temperature used was directly proportional with the molecular weight of the amine from trimethyl to tributylamine. The amount of the separate top phase, triethyl-, tripropyl-, and tributylamine, was subtracted from the amount of the starting amine and amine

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(23) E. R. H. Davies and J. W. Armstrong, *J. Inst. Petrol.*, **29**, 323 (1943).

oxide yields were calculated on the basis of their picrates formed on mixing the bottom phase with a saturated solution of picric acid. The amount of the picric acid reactant used was equivalent to a pure amine oxide bottom phase. Yields and some physical and analytical data of the picrates are shown in Table I.

Triethylenediamine Dioxide from Triethylenediammonium Diperoxide.—About 3 g. of the 60 g. (0.33 mole) of diperoxide starting material was placed into a large test tube and was stirred with a thermometer while it was slowly heated up using a water bath. At about 60° the temperature of the dry finely divided powder started to rise. Although solid carbon dioxide–alcohol cooling was used above 100°, the temperature shot up to 140° and an almost colorless liquid resulted. With the increasing decomposition temperature an increasing rate of gas evolution was observed.

The rest of the diperoxide was decomposed at about 100° by adding it to the stirred decomposition mixture in portions. After all the diperoxide has been added and the exothermic decomposition has subsided, the mixture was heated at 100° for 1 hr. to complete the decomposition. The resulting liquid solidified to a crystal mass on standing at room temperature. This was dried to yield 5.7 g. (95%) of triethylenediamine dioxide dihydrate, m.p. 52–54°. Some characteristic physical, analytical and spectral data of the compound are given in Tables I and II.

When the dihydrate was melted and dried for 6 hr. at 60°, it lost 1 mole of water and formed the amorphous, colorless, hydroscopic monohydrate. Analytical data of this latter compound are also given in Table I.

Trialkylamine Oxide–Hydrogen Peroxide Adduct. From Trialkylamine Oxide.—A 90% aqueous solution of 0.11 mole of hydrogen peroxide was added to 0.1 mole of trialkylamine oxide or its hydrate at room temperature and the mixture was stirred until a homogeneous liquid resulted. The hydrogen peroxide adducts of trimethylamine oxide and triethylamine oxide were then crystallized from the corresponding solutions by concentrating them *in vacuo* or by dilution with acetone and subsequent cooling by solid carbon dioxide–alcohol mixture. The yields and some analytical and physical data of these products are shown in Tables I and II. The raw hydrogen peroxide adducts of tri-*n*-propylamine oxide and tri-*n*-butylamine oxide could not be crystallized. The peroxide character of the adducts was checked by reacting them with 2-naphthalenethiol. One mole of the adduct oxidized 2 moles (±4%) of thiol.

From Trialkylamine.—A 90% aqueous solution of 0.21 mole of hydrogen peroxide was added to 0.1 mole of trialkylamine at −50° with stirring. The resulting mixture was allowed to come to room temperature, where a spontaneous, exothermic reaction started. The temperature was kept below 50° with cooling until the reaction subsided. In the case of triethyl, tri-*n*-propyl-, and tri-*n*-butylamine oxides, heterogeneous liquid mixtures with some free amine on the top resulted temporarily. These were stirred for an additional hour at 50° to form a homogeneous mixture. On concentration or on dilution with acetone and cooling, the hydrogen peroxide adducts of trimethylamine oxide and triethylamine oxide crystallized from the corresponding reaction mixtures in 52 and 69% yield, respectively.

From Trialkylammonium Peroxide.—Trimethylammonium peroxide (0.1 mole) started to decompose exothermically at room temperature. The temperature of the liquid peroxide rose to 38° where a strong evolution of trimethylamine gas started. By the end of the exothermic decomposition the mixture lost 2.7 g. weight. The liquid residue partly solidified on standing and yielded 3.2 g. (59%) of trimethylamine oxide–hydrogen peroxide, which decomposed on fast heating at 87° with strong gas evolution and the formation of a liquid. Physical and analytical data of the compound are given in Tables I and II.

Triethylamine oxide–hydrogen peroxide adduct also crystallized in 40% yield from an equimolar mixture of triethylamine and 90% hydrogen peroxide after 2 days' standing on a watchglass.

Triethylenediamine Dioxide Dihydrogen Peroxide Adduct. From Triethylenediamine Dioxide.—To 9 g. (0.05 mole) of liquid triethylenediamine dioxide dihydrate 4.4 g. (0.12 mole) of 90% hydrogen peroxide was added dropwise at 70° with stirring and cooling. The reaction mixture was allowed to cool to room temperature and crystallize at 0°. By filtration and subsequent drying *in vacuo*, 7.5 g. (70.5%) of triethylenediamine dioxide dihydrogen peroxide was obtained in the form of colorless crystals. Physical and analytical data of the compound are given in Tables I and II.

Triethylene diamine dioxide dihydrogen peroxide can be also prepared in the heterogeneous phase by stirring solid triethylenediamine dioxide hydrate in 90% hydrogen peroxide at room temperature.

From Triethylenediamine.—To a solution of 5.6 g. (0.05 mole) of triethylenediamine in 15 ml. of methanol 8.3 g. (0.22 mole) of 90% hydrogen peroxide was added slowly at about 60° in the course of an hour with stirring. Then the mixture was slowly cooled to −40° and filtered to yield 6.8 g. (64%) triethylenediamine dioxide dihydrogen peroxide.

Triethylenediamine Dioxide Derivatives.—**Triethylenediamine dioxide diperchlorate** was prepared by adding 70% aqueous perchloric acid to a methanolic solution of the dioxide with solid carbon dioxide–alcohol cooling and stirring. After filtration of the cold reaction mixture, the crude product was purified by recrystallization from methanol. Physical and analytical data of the compound are given in Tables I and II.

Triethylenediamine dioxide dihydrogen chloride was precipitated by introducing anhydrous hydrogen chloride into a solution of triethylenediamine monohydrate in ether alcohol mixture. The product was filtered off, washed with ether, and analyzed. Data are given in Tables I and II.

Triethylenediamine dioxide dipicrate was precipitated by mixing saturated methanolic solutions of triethylenediamine dioxide monohydrate and picric acid. Data are given in Tables I and II.

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