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Organic Sulfur Compounds. V. Alkylammonium Thiolate and Peroxide Salts; Possible Intermediates in Amine-Catalyzed Oxidation of Mercaptans by Hydroperoxides

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Aliphatic amines catalyze the reaction of mercaptans and hydroperoxides to yield the corresponding disulfides, alcohols and water. The formation of alkylammonium salts of mercaptans and hydroperoxides was studied as possible explanation of this catalysis. Alkylammonium peroxides form a new class of hydroperoxide salts. They react with aromatic mercaptans at a very fast rate to yield alkylamines plus the same products as the amine-catalyzed mercaptan oxidation by hydroperoxide.

Mercaptans can be oxidized by hydrogen peroxide in a basic aqueous medium according to the following reaction equation[2,3]

$$2\,\mathrm{RSH} + \mathrm{H_2O_2} \longrightarrow \mathrm{RSSR} + \mathrm{H_2O}$$

It has been suggested in a U. S. Patent by Johnstone[4] that hydrocarbon hydroperoxides react with mercaptans in hydrocarbons in a similar manner:

$$2\,\mathrm{RSH} + \mathrm{R'O_2H} \longrightarrow \mathrm{RSSR} + \mathrm{R'OH} + \mathrm{H_2O}$$

This was confirmed by further examination of the latter reaction in this laboratory. The reaction proceeded at a slow rate in the absence of catalysts at room temperature. Aliphatic amines were found to be very effective catalysts of the reaction. The 1,1,3,3-tetramethylbutylamine catalysis of the oxidation of benzenethiol by *t*-butyl hydroperoxide is shown in Fig. 1. The mercaptan level curves in the presence of the amine indicate very fast mercaptan oxidation. In the absence of an amine, no oxidation was evident after four hours. The rate of mercaptan oxidation was generally greater in the presence of primary amines than in the presence of tertiary amines. When the molar concentration of the 1,1,3,3-tetramethylbutylamine was decreased from twice to one-tenth of the mercaptan concentration, the rate of oxidation changed only slightly. The catalysis of the oxidation of *n*-dodecanethiol by *t*-butyl hydroperoxide in the presence of 1,1,3,3-tetramethylbutylamine is also shown in Fig. 1. The rate of oxidation of dodecanethiol in the presence of the amine was much smaller than that of a similar system with benzenethiol.

The oxidation of benzenethiol by bis-*t*-butyl peroxide in the presence of 1,1,3,3-tetramethylbutylamine was also attempted under similar experimental conditions. No benzenethiol oxidation was observed after twenty-four hours standing of the reaction mixture.

The amount of *p*-toluenethiol oxidized by styrene peroxide in the presence of bases has been used by Mayo and Miller[5] for analyses of styrene peroxide preparations.

$$2\,\mathrm{C_7H_7SH} + 1/n\,[\text{—}\mathrm{OCH_2CH(C_6H_5)O}\text{—}]n \xrightarrow{\text{Base}} \mathrm{C_7H_7SSC_7H_7} + \mathrm{HOCH_2CH(OH)C_6H_5}$$

Between 79–82% of the theoretical mercaptan for the above was uniformly oxidized.

In this laboratory, the peroxide content of various hydrocarbon hydroperoxides was determined on the basis of the quantity of 2-naphthalenethiol oxidized to disulfide in the presence of 1,1,3,3-tetramethylbutylamine.

$$2\,\mathrm{C_{10}H_7SH} + \mathrm{RO_2H} \xrightarrow{t\text{-}\mathrm{C_8H_{17}NH_2}} \mathrm{C_{10}H_7SSC_{10}H_7} + \mathrm{ROH} + \mathrm{H_2O}$$

The peroxide values obtained on the basis of this reaction were almost identical with those of the iodide method.[6]

It was thought that salt formation of amines with mercaptans and hydroperoxides may be important in this catalysis. Therefore, in the following part of our work, these salts were studied.

Gordy and Stanford[7] observed in 1940 that piperidine, cyclohexylamine, and tripentylamine form white crystalline solids when mixed with thiophenol. In 1950, Grillot and Brooks[8] reported the synthesis of a number of secondary alkylammonium salts of aromatic thiols. Conductivity measurements in 95% alcohol have shown that these salts were somewhat ionized. In water, the salts were rapidly and nearly completely hydrolyzed.

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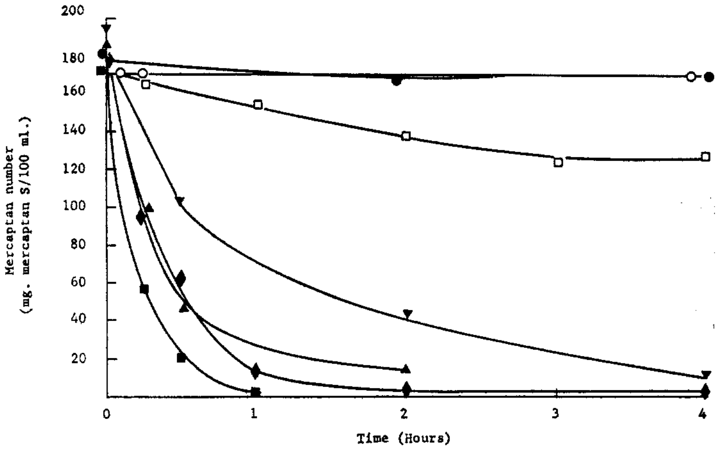

Fig. 1. Oxidation of thiols by *t*-butyl hydroperoxide in the presence of various amines

Added Compounds in Benzene Containing
0.028 mole/l. *t*-Butyl Hydroperoxide

Symbols	-Thiol, 0.056 Mole/L.	-Amine	
			Mole/L.
●	Benzene	—	Nil
▲	Benzene	1,1,3,3-Tetramethylbutyl	0.112
●	Benzene	1,1,3,3-Tetramethylbutyl	0.056
■	Benzene	1,1,3,3-Tetramethylbutyl	0.0056
▼	Benzene	Tri-*n*-propyl	0.056
○	*n*-Dodecane	—	Nil
□	*n*-Dodecane	1,1,3-Tetramethylbutyl	0.056

TABLE I

Alkylammonium Thiolates

No.	Salt of		Formula	M.P.[a]	Yield,[b] %	Calcd.			Found		
	-Amine	-Thiol				C	H	S	C	H	S
I	*n*-Dodecyl	4-Toluene	$C_{19}H_{35}NS$	89–90.5	84	73.72	11.39	10.36	73.96	11.40	10.46
II	*n*-Dodecyl	2-Naphthalene	$C_{22}H_{35}NS$	94–95.5	83	76.45	10.21	9.28	76.81	10.32	9.34
III	*n*-Dodecyl	4-Chlorobenzene	$C_{18}H_{32}NS$	87–88.5	97	65.51	10.40	9.72	66.05	9.89	9.62
IV	*n*-Decyl	Benzene	$C_{16}H_{29}NS$	87.5–89	85	71.85	10.93	12.37	71.98	10.96	12.45
V	*n*-Decyl	2-Naphthalene	$C_{20}H_{33}NS$	87–88.5	87	75.65	9.84	10.10	75.60	9.77	10.28
VI	2-Hydroxyethyl	2-Naphthalene	$C_{12}H_{15}NS$	84–86	75[c]	70.19	7.36	15.62	69.75	7.23	15.45
VII	*t*-Octyl	Benzene	$C_{14}H_{25}NS$	83–84	96	70.23	10.54	13.4	70.64	10.45	13.2
VIII	*t*-Octyl	2-Naphthalene	$C_{18}H_{27}NS$	112–114	86	74.68	9.40	11.1	74.90	9.51	11.3
IX	Cyclohexyl	Benzene	$C_{12}H_{25}NS$	122–125	84	68.84	9.15	15.3	69.01	9.31	15.5
X	Cyclohexyl	Phenylmethane	$C_{13}H_{27}NS$	56–58	85	69.90	9.48	14.4	69.56	9.47	14.9
XI	Tri-2-hydroxyethyl	2-Naphthalene	$C_{16}H_{23}NO_3S$	72–75	98[d]	—	—	10.4	—	—	9.8
XII	Triethylenedi	Benzene	$C_{12}H_{18}N_2S$	96.5–98.5	88	64.82	8.16	14.4	65.02	8.48	13.9

[a] Uncorrected. [b] From ethereal reaction mixture. [c] From chloroform. [d] From acetone.

In this laboratory, it was found that both primary and tertiary aliphatic amines form colorless crystalline salts with aromatic thiols in aliphatic hydrocarbons, ether, or acetone. Some physical and analytical data of the synthesized salts are shown in Table I. The salts were mostly prepared in ether. The salts of 2-hydroxyethylamine (ethanolamine) and tri-2-hydroxyethylamine (triethanolamine) were prepared in chloroform or acetone because these highly polar amines are insoluble in ether. The monothiophenolate of triethylenediamine (1,4-diazabicyclo[2.2.2]octane) was also prepared. When one mole of triethylenediamine was added to two moles of benzenethiol only the equimolar salt was formed. Phenylmethanethiol (benzyl mercaptan) also formed a crystalline salt with cyclohexylamine, but not with *n*-propylamine or tri-*n*-propylamine. *n*-Octanethiol did not form crystalline salts with the primary or tertiary propylamines either. This is in agreement with the decreased acidity of aliphatic thiols as compared with aromatic thiols. Aliphatic thiols according to Gordy and Stanford[7] form weak hydrogen bonds with alkylamines.

In the synthesis of the 2-hydroxyethylammonium

2-naphthalenethiolates, it was found necessary to minimize the contact with air. These salts, even after isolation and drying, turned yellow on standing in the presence of air. The other alkylammonium thiolates were more stable. In hydrocarbon solution, these salts could be also oxidized by molecular oxygen to yield the corresponding disulfides, amines, and water:

$$4\ R_3N \cdot HSR + O_2 \longrightarrow 2\ RSSR + 4\ R_3N + 2H_2O$$

Solutions of mercaptans in the absence of amines are more difficult to oxidize under similar conditions. Alkylammonium thiolates are also thermally unstable; on heating they dissociate into the thiol and amine components. In this respect, they are similar to the alkylammonium sulfides.[9]

On the basis of the formation and properties of alkylammonium thiolates, the removal of aromatic thiols from cracked petroleum distillates by treating them with anhydrous, oil-insoluble aliphatic amines seemed possible. Experiments using 5 vol. % mono-, di- and triethanolamine showed substantial removal of the thiols from a light catalytically cracked heating oil of boiling range 190–330°.

It was thought at first that the catalyzed oxidation of mercaptans by hydroperoxides in the presence of alkylamines is due to the formation of alkylammonium thiolates as reactive intermediates. However, amines also catalyze the oxidation of aliphatic thiols by hydroperoxides. The formation of salts between alkylamines and hydrocarbon hydroperoxides was therefore examined as an alternative explanation for the catalysis.

Alkylammonium peroxides were unknown. Alkylamines and hydroperoxides were reported to react on heating yielding alcohol and water.[10] The hydrogen atoms of the water were apparently abstracted from the amine.

It was found in the course of this work that alkylamines and hydroperoxides react at room temperature to form alkylammonium peroxide salts.

Table II shows a number of crystalline alkylammonium peroxides synthesized in this laboratory. For the synthesis of crystalline peroxide salts of long straight chain alkylamines (*e.g.*, cetylamine) the high melting crystalline 2,5-dimethylhexane 2,5-dihydroperoxide could be used. Among the alkylamines, the high melting crystalline triethylenediamine, 1,4-diazabicyclo[2.2.2]octane was particularly suitable to form crystalline salts with liquid hydroperoxides such as butyl and phenylisopropyl hydroperoxide.

A basic peroxide salt could be prepared by the addition of up to one mole of *t*-butyl hydroperoxide to one mole of triethylenediamine. Hexamethylenetetramine and *t*-butyl hydroperoxide formed a salt in 1:2 molar ratio when mixed in a proportion of 1:4. On the other hand 1 mole of piperazine formed a salt with two moles of 2,5-dimethylhexane 2,5-dihydroperoxide, leaving half of the hydroperoxy groups free. It is believed that the formation of these salts, which do not contain the amine and the hydroperoxide component in equivalent proportion, is due to steric factors.

Crystalline salts of some heterocyclic bases (acridine, phenazine) with 2,5-dimethylhexane 2,5-dihydroperoxide were also prepared.

The salts were isolated as crystalline solids. The salts derived from tertiary hydroperoxides were stable. They usually melted without decomposition and did not lose their peroxide content on standing at room temperature. A secondary hydroperoxide derivative, triethylenediammonium tetrahydronaphthyl peroxide, especially when impure, was unstable on standing at room temperature. The peroxide contents of some of the salts was determined by the iodide method[6] and were found to be close to the theoretical. The salts are formed as precipitates when pentane solutions of the corresponding hydroperoxide and triethylenediamine are mixed. They are usually quite soluble in toluene or ether at room temperature but crystallize out of their solutions when cooled to −15 to −70°. All these salts can be conveniently isolated as crystals from cold toluene or ether.

Characteristic infrared absorption spectra of alkylammonium peroxides in chloroform showed only weak absorption peaks for hydroperoxides at 2.8 μ (Table III). This indicated the transfer of a proton of the hydroperoxy group to the amino nitrogen. It was observed that the other absorption maxima of the hydroperoxides showed up in the corresponding salts. The absorption maxima of the amine components were usually also retained in their salts. For example in the triethylenediammonium peroxides all of the absorption maxima of triethylenediamine were retained except a peak at 3.95 μ.

Other hydroperoxide-amine reactions yielded liquid salts. For example, 1,1,3,3-tetramethylbutylamine and phenylisopropyl hydroperoxide also reacted exothermically and instantaneously on mixing. Their equimolar mixture showed the original peroxide content of phenylisopropyl hydroperoxide as determined by the iodide method. It was not possible to crystallize the salt; even by cooling in a Dry Ice–acetone mixture. Determination of the infrared spectrum of the product showed the disappearance of the characteristic hydroperoxy peak (Fig. 2). This supports the salt structure.

Equimolar mixtures of other alkylamines and hydroperoxides behaved similarly. Therefore, it is believed that salt formation between hydroperoxides and aliphatic amines is a general reaction.

Alkylammonium peroxides may be the active intermediates in the reaction of hydroperoxides with

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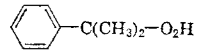
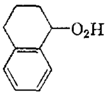
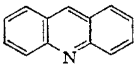
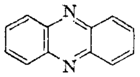
(10) C. W. Capp and E. G. E. Hawkins, *J. Chem. Soc.*, 4106 (1953).

TABLE II

N-SUBSTITUTED AMMONIUM ALKYL PEROXIDES

	Compounds				
	Components				
	Nitrogen Compound		Hydroperoxide		Summary Formula
No.		Mole		Mole	
I	$C_{16}H_{33}—NH_2$	2	$HO_2—C(CH_3)_2—(CH_2)_2—C(CH_3)_2—O_2H$	1	$C_{40}H_{88}N_2O_4$
II	$N(CH_2—CH_2)_3N$	1	$(CH_3)_3C—O_2H$	2	$C_{14}H_{32}N_2O_4$
III	$N(CH_2—CH_2)_3N$	1		1	$C_{24}H_{36}N_2O_4$
IV	$N(CH_2—CH_2)_3N$	1		2	$C_{26}H_{36}N_2O_4$
V	$N(CH_2—CH_2)_3N$	1	$HO_2—C(CH_3)_2—(CH_2)_2—C(CH_3)_2—O_2H$	1	$C_{14}H_{30}N_2O_4$
VI	$CH_3—N(CH_2—CH_2)_2N—CH_3$	1	$HO_2—C(CH_3)_2—(CH_2)_2—C(CH_3)_2—O_2H$	1	$C_{14}H_{42}N_2O_4$
VII	$HN(CH_2—CH_2)_2NH$	1	$HO_2—C(CH_3)_2—(CH_2)_2—C(CH_3)_2—O_2H$	2	$C_{20}H_{46}N_2O_8$
VIII	$N(CH_2—CH_2)_3N$	1	$(CH_3)_3C—O_2H$	1	$C_{10}H_{22}N_2O_2$
IX	Hexamethylenetetramine	1	$(CH_3)_3C—O_2H$	2	$C_{14}H_{32}N_4O_4$
X	Hexamethylenetetramine	2	$HO_2—C(CH_3)_2—(CH_2)_2—C(CH_3)_2—O_2H$	5	$C_{22}H_{48}N_4O_8$
XI		2	$HO_2—C(CH_3)_2—(CH_2)_2—C(CH_3)_2—O_2H$	1	$C_{34}H_{36}N_2O_4$
XII		1	$HO_2—C(CH_3)_2—(CH_2)_2—C(CH_3)_2—O_2H$	1	$C_{20}H_{26}O_4N_2$

[a] Uncorrected.

mercaptans in the presence of alkylamines. This is supported by the high reactivity of hydrocarbon solutions of the crystalline triethylenediammonium peroxides toward mercaptans.

$$4\ RSH + R'O_2H \cdot N(CH_2—CH_2)_3N \cdot HO_2R' \longrightarrow 2\ RSSR + 2\ R'OH + N(CH_2—CH_2)_3N + 2\ H_2O$$

The reaction was followed by determination of the mercaptan concentrations. When aromatic thiols were used as reagents, the above salts showed peroxide equivalents close to the theoretical (Table II). As expected, the addition of 1,1,3,3-tetramethylbutylamine to such reaction mixtures did not change the reaction rates.

Further support for the peroxide salt intermediates is given by the formation of bisperoxide salts from triethylenediamine with hydroperoxides and the monothiolate with benzenethiol.

It is believed that the catalysis of mercaptan oxidation by alkylammonium peroxides may explain the action of aliphatic amine oil-stabilizer additives such as Primene 81-R (mixture of tertiary alkyl primary amines). Further studies in this respect will be reported in this series.

EXPERIMENTAL

The liquid mercaptans, olefins, and monoamines used in the experiments were vacuum distilled under nitrogen before use. The solid mercaptans were recrystallized from *n*-heptane. This was necessary to avoid catalysis or inhibition of the reactions studied by minor impurities. The triethylenediamine was a 99% minimum substance from the Houdry Process Corp., Philadelphia, Pa. Phenylisopropyl and *t*-butyl hydroperoxides, from the Lucidol Division of the Wallace and Tiernan Corp., were used on the basis of their hydroperoxide content.

Oxidation of 1,1,3,3-tetramethylbutylammonium 2-naphthalenethiolate by t-butyl hydroperoxide. To a stirred suspension of 15.0 g. (0.05 mole) of 1,1,3,3-tetramethylbutylammonium 2-naphthalenethiolate in 290 ml. of toluene, a solution of 2.2 g. (0.025 mole) of *t*-butyl hydroperoxide in 250 ml. of toluene was added. The resulting clear reaction mixture was saturated with hydrogen chloride and concentrated to 200 ml. *in vacuo*. From the heterogeneous concentrate, 1,1,3,3-tetramethylbutylammonium hydrochloride was extracted by two 100-ml. portions of 5% aqueous hydrochloric acid. Filtration and recrystallization yielded 4.4 g. (86%) of bis-2-naphthyl disulfide, m.p. 139–140°, identified with another sample prepared by the peracetic acid oxidation of the thiol. The combined aqueous hydrochloric acid extracts yielded 5.9 g. (91.4%) 1,1,3,3-tetramethylbutylamine hydrochloride of m.p. 230–236°, which was treated with 2,4-dinitrobenzenesulfenyl chloride and identified as 2,4-dinitrobenzenesulfenyl-*N*(1,1,3,3-tetramethyl)butylamide, m.p. 103–104°.

Anal. Calcd. for $C_{14}H_{21}NS$: C, 51.19; H, 6.44. Found: C, 51.53; H, 6.78.

Analysis by partition chromatography of another sample of the original reaction mixture showed that about 85% of the calculated *t*-butyl alcohol concentration was present. Karl Fischer water determination in a distillate of a sample gave 105% of the theoretical amount of water.

Determination of peroxide content of hydroperoxides and alkylammonium peroxides by the mercaptan method. About 0.2 g. of the peroxide compound was dissolved in about 20 ml. of benzene containing 0.25 mole/l. of 2-naphthalenethiol. About 0.1 ml. of 1,1,3,3-tetramethylbutylamine was added to the solution and the reaction mixture was left to stand for 0.5 hr. to complete the reaction. Then an aliquot sample was titrated for thiol content with silver nitrate using a potentiometer having a silver-glass electrode pair.

The reaction between the thiol and peroxide compound was usually completed in a few minutes in the presence of the 1,1,3,3-tetramethylbutylamine and was indicated by

TABLE II (*Continued*)

M.P.^{a}	Solvent	Yield, %	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N	Peroxide Content Mercaptan method	Peroxide Content Iodide method
50–56	Toluene	73	72.67	13.41	4.24	72.58	13.31	4.11	94	—
74–76	Ether	93	57.51	11.03	9.58	57.90	11.22	9.70	100	100
87.5–88.5	Ether	96	69.20	8.71	6.73	69.54	8.89	6.63	99	99
47–48	Ether	91	70.88	8.24	6.36	70.96	8.34	6.25	97	98
128–131	Ether	82	57.90	10.41	9.65	57.92	10.39	9.68	98	—
Semisolid	Toluene	86	57.50	11.03	9.58	57.48	11.10	9.12	—	—
74–75	Toluene	88	54.27	10.48	6.33	54.21	10.50	6.76	—	—
52–55	Ether	90	59.37	10.96	13.85	58.50	11.23	13.40	101	—
74 dec.	—	52	52.48	10.06	17.49	52.61	10.54	17.04	99	—
88–90	Toluene	8	53.31	9.81	9.57	53.59	9.87	9.36	102	—
104–105	Ether	92	76.09	6.76	5.22	76.24	6.93	5.20	96	—
90 dec.	Toluene	61	67.01	7.31	7.82	67.10	7.37	7.87	94	—

TABLE III

CHARACTERISTIC INFRARED ABSORPTION PEAKS^{a} OF ALKYLAMMONIUM HYDROPEROXIDES

t-Butyl Hydroperoxide^{b}	*t*-Butyl Hydroperoxide + Triethylenediamine^{b}	Triethylenediamine^{b}	Phenylisopropyl Hydroperoxide + Triethylenediamine^{b}	Phenylisopropyl Hydroperoxide^{b}	Phenylisopropyl Hydroperoxide + 1,1,3,3-Tetramethylbutylamine^{c}	1,1,3,3-Tetramethylbutylamine^{c}	Tetrahydronaphthyl Hydroperoxide + Triethylenediamine^{b}	Tetrahydronaphthyl Hydroperoxide^{b}
2.79 vs	2.78 vw	—	2.79 vw	2.79 m	—	—	2.79 vw	2.79 s
2.91 vs	—	—	—	—	3.0 vw	3.0 m	—	2.88 s
—	—	3.95 m	—	—	—	—	—	—
6.11 s	—	—	6.20 vw	6.20 w	6.28 m	6.28 m	6.20 vw	6.20 w
—	—	—	6.65 s	6.65 s	6.68 s	—	6.68 w	6.68 s
6.80 vs	6.80 vs	6.84 s	6.84 s	6.80 w	6.80 s	6.80 s	6.85 w	6.85 s
—	—	—	6.88 s	6.88 s	6.90 s	—	6.92 w	6.90 s
7.30 vs	7.30 vs	7.34 m	7.33 s	7.30 s	7.34 s	7.34 s	7.34 w	7.32 w
7.55 vs	7.55 s	7.56 s	7.56 s	7.51 s	—	—	7.56 m	7.62 s
—	—	—	7.88 s	7.88 s	7.91 s	—	7.87 vw	7.87 w
8.05 vs	8.05 vs	—	—	—	8.13 w	8.13 m	—	—
8.42 vs	8.42 vs	—	—	—	—	—	—	—
—	—	—	8.67 s	8.67 s	8.68 s	8.74 m	8.65 w	8.65 m
—	—	—	9.05 w	9.05 w	9.06 w	—	8.95 w	8.95 w
—	9.44 vs	9.45 vs	9.45 s	9.29 m	9.32 m	9.32 vw	9.43 s	9.35 s
9.75 w	—	—	9.71 s	9.71 s	9.73 m	9.73 vw	9.67 w	9.67 m
—	10.02 s	10.10 s	10.10 s	—	—	—	10.08 w	—
—	—	—	—	—	13.18 s	—	—	—
—	—	—	14.33 vs	14.33 vs	14.36 s	—	—	—

[a] m, medium; s, strong; v, very; w, weak. [b] In chloroform. [c] As such.

the yellow coloration of the solution due to the disulfide formed.

Analyses of some hydroperoxide samples gave the values as shown.

Method	Hydroperoxide, % *t*-Butyl	Hydroperoxide, % Phenylisopropyl	Hydroperoxide, % Tetrahydronaphthyl
Mercaptan	73	65	99
Iodide	74	63	101

Some analytical values of triethylenediammonium peroxides are shown in Table II.

Preparation of alkylammonium thiolates. To 50 ml. of an

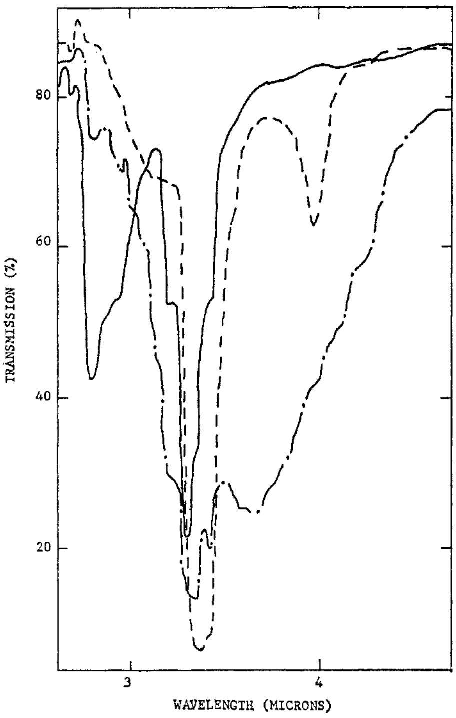


Fig. 2. Infrared spectrum of triethylenediammonium phenylisopropyl peroxide (–·–· in chloroform as compared to that of triethylenediamine (------) and phenylisopropyl hydroperoxide (——)

ethereal solution of 0.05 mole of an aliphatic amine, 0.05 mole of a thiol was added dropwise with shaking. The crystalline precipitate formed was filtered by suction, washed with ether, and dried for 0.5 hr. at 10 mm. in the presence of calcium chloride and paraffin flakes.

Oxygenation of 1,1,3,3-tetramethylbutylammonium 2-naphthalene thiolate. 1,1,3,3-Tetramethylbutylammonium 2-naphthalenethiolate (13 g., 0.044 mole) was dissolved in 4000 ml. of 3:1 benzene:*n*-heptane. The solution was oxygenated in a 5000- ml. measuring cylinder using a sintered glass inductor and stirring. In 6 hr. the mercaptan concentration of the solution decreased to 10% of the original. By concentration *in vacuo* and crystallization, 6 g. (85%) of 2-naphthyl disulfide was obtained. Hydrogen chloride introduction into the mother liquor resulted in the precipitation of 6.6 g. (90%) of 1,1,3,3-tetramethylbutylamine hydrochloride, m.p. 250–254°, identified as 1,1,3,3-tetramethylbutylammonium picrate, m.p. 177–180°.

The amine content of the aerated reaction mixture was also determined by extraction using aqueous hydrochloric acid and was found to be 5.3 g. (93%). The water content of the mixture by the Karl Fischer method was 20 mg./ml. (120%) of the theoretical.

When a solution of 0.84 g. (0.0044 mole) of 2-naphthalenethiol in 100 ml. 3:1 benzene:*n*-heptane mixture was aerated in the absence of amine, the thiol concentration decreased to 87% of the original.

Synthesis of triethylenediammonium alkyl peroxides. A hydrocarbon hydroperoxide (0.05 mole) was added to a solution of 2.8 g. (0.025 mole) of diazabicyclo[2.2.2]octane in 50 ml. of ether. A slightly exothermic reaction took place. The solution was cooled in a carbon dioxide–acetone mixture to crystallize the colorless triethylenediammonium alkyl peroxide which was removed by filtration with suction, washed with cold ether, and dried in a calcium chloride desiccator *in vacuo*. Yields and some physical and analytical data of the products obtained are shown in Tables I and II.

Triethylenediammonium alkyl peroxides can be also synthesized in hydrocarbon solvents or in the absence of any solvent. Toluene and petroleum ether are particularly suitable solvents for the laboratory synthesis of triethylenediammonium phenylisopropyl and tetrahydronaphthyl peroxides, respectively.

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Organic Sulfur Compounds. VI. The Effect of Alkylamines on the Course of the Co-Oxidation of Mercaptans and Indene

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In the presence of alkylamines, mercaptans and indene are co-oxidized by molecular oxygen with a chain mechanism to form substituted 2-mercapto-1-indanols, disulfides and water, instead of substituted 2-mercapto-1-indanyl hydroperoxides. The initiation reaction forming the mercapto radicals may take place between alkylammonium thiolates and oxygen. The change of the reaction products is due to the catalysis by the amines of the oxidation of mercaptans by substituted 2-mercapto-1-indanyl hydroperoxides. It is proposed that this catalytic action is important in the stabilization of some hydrocarbon fuels by alkylamines.

It has been reported in this series that mercaptans and olefins are readily co-oxidized by molecular oxygen to form substituted 2-mercaptoethyl hydroperoxides.[2]

$$\mathrm{RSH} + \mathrm{CHR'{=}CR_2''} + \mathrm{O_2} \longrightarrow \mathrm{R{-}S{-}CHR'{-}CR_2''{-}O_2H}$$

These hydroperoxides readily rearrange to yield substituted 2-sulfinyl-ethanols.

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