Methyl Δ^{1}-cholenate (IIc) (*tentative*). Treatment of IIb (100 mg.) with W-2 Raney nickel (*ca.* 8 g.) in acetone (25 ml.)-methanol (25 ml.), as previously described for the preparation of Ic, gave a solid which, upon recrystallization from aqueous methanol, melted at 42–44°. The melting point remained unchanged upon further crystallizations; $[\alpha]_D$ + 56° (*c* 1.2); positive tetranitromethane test.

Anal. Calcd. for $C_{25}H_{40}O_2$ (372.57): C, 80.59; H, 10.82. Found: C, 80.34; H, 11.18.

Acknowledgment. We are grateful to the Research Corporation and to the Arts and Sciences Research Committee of the American University of Beirut for financial support, and to Professors Kenneth Sauer and Leiper Freeman for many stimulating discussions.

BEIRUT, LEBANON

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, IMPERIAL OIL LTD.]

Organic Sulfur Compounds. III. Co-Oxidation of Mercaptans with Styrenes and Indene

ALEXIS A. OSWALD[1a]

Received March 4, 1960

Co-oxidation of mercaptans and styrenes or indene by air in hydrocarbon solution at 0° results in the formation of substituted 2-mercaptoethyl hydroperoxides. These hydroperoxides are unstable and are readily converted to the corresponding isomeric 2-sulfinylethanols. The reactions reported may be important in causing hydrocarbon fuel instability.

Kharasch and co-workers[1b] were the first to show that mercaptans and olefins co-oxidize in an atmosphere of oxygen at room temperature to yield substituted 2-sulfinylethanols. For the formation of these compounds, Kharasch tentatively suggested a chain mechanism with two reaction routes having a hydroperoxide and an alkoxy radical intermediate.

Ford, Pitkethly, and Young[2] examined the co-oxidation of benzenethiol and indene in greater detail. On the basis of peroxide determination, they have obtained 2-phenylmercapto-1-indanyl hydroperoxide in 77% yield although they did not isolate the product.

In this laboratory, preliminary studies[3] showed that, on aeration of hydrocarbon solutions of aromatic mercaptans and reactive olefins at 0°, the hydroperoxide intermediates of such co-oxidation reactions can be isolated. More detailed studies of the co-oxidation of mercaptans with styrenes and indene, reported here, were made primarily to relate such reactions to the rapid peroxidation of cracked petroleum distillates containing mercaptans and olefins.[4]

Formation of 2-mercaptoethyl hydroperoxides. Aeration of hydrocarbon solutions containing an aromatic mercaptan and styrene or α-methylstyrene or indene, each at 0.3 mole/l. concentration at 0°, resulted in a rapid peroxidation. After a few hours' air introduction, almost colorless oils separated. These oils contained a high percentage of hydroperoxide according to both the iodide[5] and the ferrous sulfate[6] methods. A typical member of these new hydroperoxides is 1-(2-naphthylmercapto)-2-phenyl-2-propyl hydroperoxide. This was obtained by the co-oxidation of 2-naphthalenethiol and α-methylstyrene and had a m.p of −10° and a peroxide content of 85%. The co-oxidation product of 2-naphthalenethiol and indene, 2-(2-naphthylmercapto)-1-indanyl hydroperoxide showed exceptional stability; and could be isolated as a colorless solid in a substantially pure state.

n-Dodecanethiol did not form any hydroperoxide under similar conditions. For example, with styrene, no reaction was evident even after six hours' aeration at room temperature. However, when the reaction mixture was irradiated by an ultraviolet lamp, 9% yield of solid co-oxidation product with a peroxide content of 13% was obtained after thirty minutes reaction time.

The above results indicate that the co-oxidation of styrenes and indenes with both aromatic and aliphatic thiols results in hydroperoxides. The chain mechanism of the reaction is supported by earlier work on thiol-olefin addition[7-9] and co-oxidation.[1,2]

Rearrangement to 2-sulfinylethanols. The aforementioned substituted 2-mercaptoethyl hydroperoxides are usually unstable at room temperature, and rearrange to the more stable corresponding 2-sulfinylethanols. The latter are colorless, crystalline compounds, mostly melting with decomposition (Table I and II). On the basis of this

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(1b) M. S. Kharasch, W. Nudenberg, and G. J. Mantell, *J. Org. Chem.*, **16**, 524 (1951).

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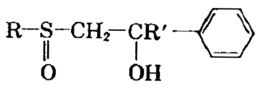
TABLE I

2-SULFINYLETHANOLS FROM THE CO-OXIDATION OF STYRENES AND MERCAPTANS

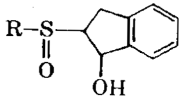


No.	R	R′	Formula	M.P.[a]	Calcd. C	Calcd. H	Calcd. S	Found C	Found H	Found S	Infrared Absorption Peaks (μ) Hydroxy	Sulfoxy			Aromatic	Methylene
I	C_6H_5	H	$C_{14}H_{14}O_2S$	128–129.5	68.26	5.75	13.0	68.46	5.52	12.6	2.95	9.23	9.55	10.02	6.3	6.9
II	2-$C_{10}H_7$	H	$C_{18}H_{16}O_2S$	145–147	72.97	5.40	10.8	72.66	5.40	10.5	3	9.5		9.9	6.28	6.91
				124–126				72.94	5.48	10.7	3.05	9.45		9.9	6.28	6.91
III	n-$C_{12}H_{25}$	H	$C_{20}H_{34}O_2S$	105–106	70.95	10.12	9.5	70.50	10.47	8.9	3	9.3		9.85	6.25	6.9
				69–70				70.57	10.17	9.3	3	9.3		9.95	6.25	6.9
IV	4-Cl—C_6H_4	H	$C_{14}H_{13}ClO_2S$	153.5–158.5[b]	59.89	4.67	11.4	59.85	4.75	10.9	2.96	9.19		9.94	6.35	6.8 6.95
				86–88[c]				60.15	4.77	11.2	2.96	9.19		9.96	6.35	6.8 6.95
V	2-$C_{10}H_7$	CH_3	$C_{19}H_{18}O_2S$	115–118	73.52	5.84	10.3	73.17	5.85	10.3	3.05	9.4		9.95	6.28	6.85
				94–95.5				73.53	6.03	10.5	3	9.4		9.78	6.28	6.93
IV	n-$C_{12}H_{25}$	CH_3	$C_{21}H_{36}O_2S$	47.5–48.5	71.32	10.30	9.1	71.97	10.55	8.8	2.95	9.4		10.05	6.25	6.85

[a] Uncorrected. [b] Calcd.: Cl, 12.63. Found: Cl, 12.3. [c] Calcd.: Cl, 12.63. Found: Cl, 12.0.

TABLE II

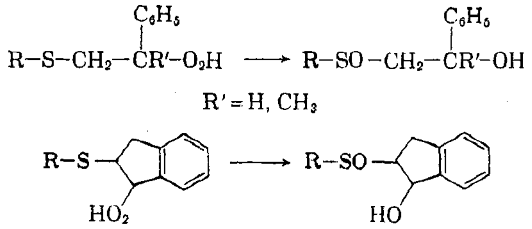
2-SULFINYL-1-INDANOLS FROM THE CO-OXIDATION OF INDENE AND MERCAPTANS



No.	R	Formula	M.P.[a]	Calcd. C	Calcd. H	Calcd. S	Found C	Found H	Found S	Infrared Absorption Peaks (μ) Hydroxy	Sulfoxy			Aromatic		Methylene		
I	C_6H_5	$C_{15}H_{14}O_2S$	158–159[c]	69.77	5.46	12.4	69.69	5.68	12.0	3.03	9.25	9.68	9.85	6.22	6.30	6.79	6.86	6.95
			148–150				69.81	5.66	10.8	3.0	9.25		9.85	6.22	6.30	6.79	6.86	6.95
			132–135				69.82	5.63		3.02	9.25		9.85	6.22	6.30	6.79	6.86	6.96
II	4-H_3C—C_6H_4	$C_{16}H_{16}O_2S$	166–167.5	70.59	5.88	11.8	69.76	5.85	11.5	2.09	9.23		9.88	6.25		6.70	6.77	6.85
			144–144.5				70.36	6.16	11.3	3.0	9.25		9.93	6.27		6.71	6.78	6.86
			128–130				70.55	6.01	11.2	3	9.2		9.9	6.25				
III	4-Cl—C_6H_4	$C_{16}H_{15}ClO_2S$	144–146[b]	61.53	4.47	10.9	60.98	4.51	10.5	3.01	9.19	9.32	9.94	6.33		6.79		6.85
IV	2-$C_{10}H_7$	$C_{18}H_{16}O_2S$	157–158[c]	73.99	5.23	10.4	74.12	5.36	10.3	2.96	9.37	9.66	9.85	6.27		6.67	6.77	6.84
			149–150				73.66	5.32	10.4	3.0	9.39	9.7	9.85	6.28		6.67	6.77	6.85
			138.5–139.5[c]				74.26	5.48	10.3	3.0	9.39		9.84	6.28		6.66	6.76	6.84
			125–127.5[c]				73.25	5.29	9.9	2.95	9.38	9.67	9.83	6.27		6.66	6.76	6.83
V	n-$C_{12}H_{25}$	$C_{21}H_{34}O_2S$	107–109	71.94	9.78	9.2	71.69	9.74	9.9	3.05	9.55		9.85	6.24			6.88	
			67–68.5				71.64	9.53	9.0	3.0	9.55		9.90	6.24			6.86	

[a] Uncorrected. [b] Calcd.: Cl, 12.1. Found: Cl, 12.3. [c] With decomposition.

and some previous work on the structure of 2-sulfinylethanols,[1,2] these rearrangements are formulated as follows:



$$R{-}S{-}CH_2{-}\overset{C_6H_5}{\overset{|}{C}}R'{-}O_2H \longrightarrow R{-}SO{-}CH_2{-}\overset{C_6H_5}{\overset{|}{C}}R'{-}OH$$

$R' = H, CH_3$

Solutions of 2-mercaptoethyl hydroperoxides lost their peroxide content within a few days on standing at room temperature. At 40°, the loss of peroxide was complete within a few hours. Concurrent with the decrease in peroxide content, the 2-sulfinylethanol rearrangement product precipitated from the saturated solutions of the corresponding hydroperoxides. The isolated liquid hydroperoxides solidified on standing at room temperature because of the rearrangement. The solid 2-(2-naphthylmercapto)-1-indanyl hydroperoxide is normally stable at room temperature.

The transformation of the mercaptoethyl hydroperoxides to the sulfinylethanols was followed by observing the change of the infrared spectra of the peroxide intermediates in the presence or absence of solvent. For example, in the case of the co-oxidation product of indene and 2-naphthalenethiol, a comparison of the spectra obtained at different time intervals showed an increase in the absorption at about 3 μ which corresponds to the hydroxy group. An increase in absorption was also obtained in the 9–10 μ region, where the sulfoxy group absorbs.

When the rearrangement of the hydroperoxide intermediate of indene-naphthalenethiol co-oxidation was carried out in the presence of 2-(4-chlorophenylmercapto)-1-indanol, none of the latter was oxidized and 2-(2-naphthylsulfinyl)-1-indanol was obtained. This may indicate an intramolecular rearrangement. However, the reactions of the hydroperoxide co-oxidation intermediate may involve radical intermediates. This was suggested by the polymerization of styrene by the same hydroperoxide.

Formation of 2-sulfinylethanols. When solutions containing aromatic mercaptans and styrenes or indene were aerated at room temperature, the isomeric 2-sulfinylethanols (Table I and II) precipitated as colorless crystals. The problem of different steric isomers was discussed in detail in the case of indene-thiophenol co-oxidation products by Ford, Pitkethly, and Young.[2]

The co-oxidation of *n*-dodecanethiol with indene at room temperature was also examined. In this case, ultraviolet light irradiation was necessary to form the 2-sulfinylethanol co-oxidation product.

Co-oxidation and fuel instability. From the viewpoint of the chemistry of fuel instability it was of interest to examine the co-oxidation of dilute hydrocarbon solutions of aromatic thiols and styrenes or indene on standing in the presence of air. Such solutions (cetane, *n*-heptane, benzene) were found to peroxidize rapidly at room temperature or at 43°; then their peroxide content slowly decreased and crystalline precipitates of substituted 2-sulfinylethanols were formed. *n*-Dodecanethiol and a styrene also co-oxidized to yield 2-dodecylsulfinyl-1-phenylethanol. In solutions containing indene and aromatic thiols, 2-indanyl aryl sulfides were also formed as byproducts. It is believed that the formation of the addition products[9] was due to the inadequacy of oxygen supply by diffusion. The color of these hydrocarbon solutions containing an aromatic thiol and a reactive olefin remained light (above 25 units on the Tag-Robinson colorimeter). The solutions also remained close to neutral, gave no acid number values. This showed that sulfonic acid formation, which was claimed as one of the main reactions causing instability of cracked petroleum distillates[10,11] did not occur at all in our "storage experiments" in synthetic hydrocarbons.

EXPERIMENTAL

The reagents used in the experiments were vacuum distilled under nitrogen or recrystallized before use. All aerations were carried out by bubbling in air by means of a sintered glass bubbler with 7.5 sq. cm. sintered area into the reaction mixture contained in a measuring cylinder. The mercaptan concentrations of the reaction mixtures were determined by potentiometric titration with silver nitrate. Peroxide contents were determined by the iodide method.[6]

Isolation of hydroperoxide intermediates. Benzenethiol (0.1 mole) and styrene or α-methylstyrene or indene (0.1 mole) were dissolved in 310 ml. of cold *n*-heptane. The solution was placed into a 500-ml. measuring cylinder with 50 mm. diameter which was cooled by ice water and air was introduced to the bottom of the reaction mixture for 6 hr. By this time, a heavy, viscous, almost colorless oily product separated at the bottom of the solution which could be isolated by decantation of the supernatant phase.

The yields and hydroperoxide contents of the products are shown in the following:

Thiol	Olefin	Yield, %	Peroxide, %
Benzene	Styrene	30	84
Benzene	α-Methylstyrene	52	44
Benzene	Indene	33	67
Chlorobenzene	α-Methylstyrene	64	58

Low temperature co-oxidation of 2-naphthalenethiol and indene. A solution of 16 g. (0.1 mole) of 2-naphthalenethiol and 11.6 g. (0.1 mole) of indene was prepared in a mixture of 100 ml. of benzene and 300 ml. of *n*-heptane. Air was introduced into the solution in a manner described above for

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[10] R. D. Offenhauer, J. A. Bennan, and R. C. Miller, *Ind. Eng. Chem.*, 49, 1265 (1957).

[11] A. L. Williams and R. D. Offenhauer, *Ind. Eng. Chem.*, 49, 1259 (1957).

4 hr., while the reaction mixture was cooled by ice water. By the end of the 4 hr., 4 g. (13%) of a colorless, crystalline precipitate was formed. A peroxide analysis showed this product to be 98% 2-(2-naphthylmercapto)-1-indanyl hydroperoxide. This substance melted at 70° with decomposition. Attempts to recrystallize it from benzene and chlorobenzene resulted in loss of peroxide content.

Anal. Calcd. for $C_{19}H_{16}O_2S$: C, 73.99; H, 5.23; S, 10.40. Found: C, 74.12; H, 5.43; S, 10.3.

Further introduction of air at 0° into the filtrate resulted in the separation of a semisolid with a peroxide content of 85%. After 6 hr., the cooling was discontinued, but the introduction of air was continued for 42 hr. more. At the end of this period, the separated phase, which became solid in character, was removed by filtration. In this manner, 26 g. (84%) of co-oxidation product was obtained in addition to the 4 g. obtained previously. However, this product contained only 2% of peroxide. On fractional recrystallization of the 26 g. of crude product from benzene-*n*-heptane, the 2-(2-naphthylsulfinyl)-1-indanol isomers which are listed in Table II at Formula IV were obtained.

Some characteristics of 2-(2-naphthylmercapto)-1-indanyl hydroperoxide. (a) *Conversion of 2-(2-naphthylsulfinyl)-1-indanol.* A 100-ml. benzene solution of 9.2 g. (0.03 mole) of 2-(2-naphthylmercapto)-1-indanyl hydroperoxide showed negative peroxide test after standing 16 hr. at 43° and deposited 3.4 g. (36.8%) of colorless crystals. Recrystallization of this substance from benzene yielded a compound melting between 138.5–139.5°. A mixed melting point determination of this compound with one of the 2-(2-naphthylsulfinyl)-1-indanol isomers obtained in the previous experiment gave no depression.

The hydroperoxide is sensitive to acids. A sample suffered violent exothermic decomposition after being stored in a desiccator in the presence of sulfuric acid for 10 min. at 2 mm. From the reddish decomposition product, 2-(2-naphthylsulfinyl)-1-indanol isomers of m.p. 157–158° and 138.5–139.5° were isolated by fractional crystallization from benzene.

(b) *Catalysis of low temperature styrene polymerization.* A solution of 0.3 g. (0.001 mole) of 2-(2-naphthylmercapto)-1-indanyl hydroperoxide in 34.6 g. (0.3 mole) of styrene was kept in a cold box at +5° for 3 months. From the resulting very viscous liquid only 75% of the styrene could be recovered by distillation at 20 mm. from a steam bath. The remaining 25% is a solid rubbery substance. Styrene without added hydroperoxide in a control experiment could be distilled under the same conditions with 99% recovery.

Synthesis of 2-(4-chlorophenylmercapto)-1-indanol.) 4-Chlorobenzenethiol (12.8 g., 0.09 mole) and 10.7 g. (0.09 mole) of indene were dissolved in a mixture of 250 ml. benzene and 20 ml. chlorobenzene. The solution was cooled to 0° and aerated for 4 hr. at this temperature. The resulting reaction mixture was 0.17*M* with respect to peroxide concentration (51% yield).

Using a procedure analogous to that of Ford and coworkers,[3] the fresh peroxide solution was reduced by lithium aluminum hydride in refluxing ether medium in an hour. Recrystallization of the raw product from 1:1 benzene-*n*-heptane yielded 8.6 g. (68%) of colorless 2-(4-chlorophenylmercapto)-1-indanol, m.p. 110–112°.

Anal. Calcd. for $C_{15}H_{13}ClOS$: C, 65.08; H, 4.73. Found: C, 65.20; H, 4.98.

Attempted oxidation of 2-(4-chlorophenylmercapto)-1-indanol with 2-(2-naphthylmercapto)-1-indanyl hydroperoxide 2-(2-Naphthylmercapto)-1-indanyl hydroperoxide (6.0 g., 0.02 mole) was dissolved in a mixture of 600 ml. of benzene, 150 ml. of chlorobenzene, and 20 ml. of methanol to yield a 0.02*M* peroxide solution. To this solution, 4.3 g. (0.015 mole of 2-(4-chlorophenylmercapto)-1-indanol was added. After standing 3 days at room temperature unchanged 2-(4-chlorophenylmercapto)-1-indanol, m.p. 110–112° and 2-(2-naphthylsulfinyl)-1-indanol, m.p. 157–158° were isolated from the reaction mixtures.

Rearrangement of substituted 2-mercaptoethyl hydroperoxides to 2-sulfinylethanols. A 4-g. sample of the liquid 2-mercaptoethyl hydroperoxide was allowed to stay for 3 days at room temperature, during which time solidification occurred. The resulting solid was fractionally recrystallized from toluene-*n*-heptane to yield the corresponding isomeric 2-sulfinylethanol rearrangement product. For example, 1-(4-chlorophenylmercapto)-2-phenyl-2-propyl hydroperoxide yielded 1 g. of each of the isomeric 1-(4-chlorophenylsulfinyl)-2-phenyl-2-propanols shown in Table I.

Similar rearrangement reactions were carried out in about 0.3*M* benzene (chloroform, tetrahydronaphthalene) solution of the mercaptoethyl hydroperoxide in 16 hr. at 43°. Using this method from 33 ml. of benzene solution of 3.1 g. (0.01 mole) of 1-(2-naphthylmercapto)-2-phenyl-2-propyl hydroperoxide, m.p. −10° by the freezing curve method, 0.74 g. (27%) of 1-(2-naphthylsulfinyl)-2-phenyl-2-propanol, m.p. 115–118°, was isolated.

Co-oxidation of aromatic mercaptans and reactive olefins at room temperature. About 300 ml. of an aliphatic hydrocarbon (*n*-heptane, cetane, straight run petroleum distillate boiling between 70° and 200°) solution containing 0.1 mole of an aromatic (benzene-, toluene, chlorobenzene-) thiol and a reactive olefine (styrene, α-methylstyrene, indene) was aerated (or oxygenated) for 3 days at room temperature. After a few hours the liquid hydroperoxide started to separate. This later became a crystal slurry. More crystals were precipitated with the progress of co-oxidation. By the end of the 3 days' reaction period the peroxide number[6] of the liquid phase of the reaction mixture was less than 5 and the mercaptan number (mg. mercaptan S in 100 ml.) less than 10. The solid co-oxidation products were separated by filtration with suction, recrystallized from toluene-*n*-heptane to yield 40–80% yield of mixtures of isomeric substituted 2-sulfinylethanols. On fractional recrystallization these isomers were separated with about 30% yield loss.

Some analytical and physical data of the compounds prepared are shown in Tables I and II. The infrared spectra of the 2-sulfinylethanols showed a strong hydroxy absorption at about 3 μ. Absorption peaks in the region between 9–10 μ, where the sulfoxy group absorbs, were at different wave lengths depending on the starting mercaptan and olefin. The isomers of the same composition showed absorption peaks at about the same wave length in this region, although the relative strengths of these peaks were different. The spectra of the isomers also showed minor differences outside this region. Minor differences in the wave length of the aromatic absorption peaks in the region between 6.2–6.3μ were observed at compounds of different composition, but not at isomers. Methylene absorption of varying intensity at about 6.85μ was observed at all products. The compounds derived from indense and aromatic mercaptans in addition to this peak showed associated peaks in the same region.

Co-oxidation of n-dodecanethiol and reactive olefins with ultraviolet catalysis. A solution of 20.2 g. (0.1 mole) of *n*-dodecanethiol and 0.1 mole of a reactive olefin (styrene, α-methylstyrene, indene) in 300 ml. of *n*-heptane was placed in a 500-ml. Vycor (95% quartz) round bottom flask. Air was introduced to the bottom of the reaction mixture through a sintered glass inductor, while it was irradiated by an ultraviolet lamp (250 V, 1000 W, 60 cycle; G.E.-9T64Y20) placed 4.5 cm. from the flask. When the thiol content had decreased to less than 10% of the original, the reaction mixture was cooled by a solid carbon dioxide-ethanol mixture, filtered, and recrystallized to yield the substituted 2-dodecylsulfinylethanols.

Using the above procedure, the two crystalline 2-(n-dodecylsulfinyl)-1-phenylethanol isomers (Table I, Formula III) were obtained in a total yield of 75% from the co-oxidation with styrene. The co-oxidation of *n*-dodecanethiol with α-methylstyrene and indene yielded only single dodecyl sulfoxide isomers in 10% and 31% yield, respectively (Table I, Formula VI; Table II, Formula V).

Peroxidation of cetane solutions containing mercaptan and *styrene or indene.* A cetane solution (300 ml.) containing 2-naphthalenethiol and indene or styrene both in 0.01 mole/l. concentration was stored in a 500 ml. open Pyrex (borosilicate glass) Erlenmeyer flask at room temperature. A rapid peroxidation followed by a decrease in peroxide content as measured by the ferrous sulfate method[8] occurred. Under the same conditions, cetane solutions of any of the components alone did not show any peroxidation. From the indene-thiol solution after 70 hr., some 2-(2-naphthylsulfinyl)-1-indanol, m.p. 138.5–139.5° with decomposition, from the styrene-thiol solution after 23 hr., some 2-(2-naphthylsulfinyl)-1-phenylethanol, m.p. 145–147° precipitated.

Similar peroxidation was observed with indene-thiol solutions at 43°.

Formation of 2-sulfinylethanol sediments during storage at 43°. For the study of the role of mercaptan-olefin co-oxidation in sediment formation accelerated storage tests at 43° were carried out with cetane solutions(300 ml.) containing mercaptans and styrene or indene, each in 0.3 mole/l. concentration. In 2 weeks precipitation (0.2–4.0g.) occurred. The precipitates, which were only in part crystalline in the case of the thiophenol-indene and *p*-toluenethiol-indene combinations, were all recrystallized from benzene-*n*-heptane and gave the corresponding 2-arylsulfinyl-1-indanols shown in Table II. The mother liquors were distilled *in vacuo* and yielded about 200 mg. of 2-indanyl phenyl sulfide and 180 mg. of 2-indanyl 4-tolyl sulfide, respectively.

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SARNIA, ONTARIO, CANADA

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY]

The Thermal Decomposition of Tributyl Phosphate[1]

CECIL E. HIGGINS AND WILLIS H. BALDWIN

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The thermal stability of tributyl phosphate (TBP) was measured by determining the rate of formation of dibutyl phosphoric acid (DBP) as a function of temperature. Tributyl phosphate decomposed to form 1.2% acid in seventy hours at 178° and 8.4% acid in two hours at 240°. Stability increased if the alkoxy bonds were replaced with carbon-to-phosphorus bonds; the rate of scission of the remaining C—O bonds was retarded to a much greater degree than might have been expected simply from the statistical reduction in number of C—O bonds per molecule. The reaction TBP $\xrightarrow{\Delta}$ DBP + C_4H_8 was first order only in the dilute acid range (up to 3% dibutyl phosphoric acid). The specific reaction rates in this range were: 0.389, 3.33, 20.1, 27.1, and 132 × 10^{-7} sec.$^{-1}$ at 178°, 198°, 221°, 223°, and 240°, respectively. From these was calculated an "apparent" activation energy of 40 kcal. per mole for the formation of dibutyl phosphoric acid by thermal decomposition of tributyl phosphate. Butene-1 comprised at least 99% of the gases formed in eight hours at 221°. Minor yields of butanol, dibutyl ether, and tetrabutyl pyrophosphate were obtained, indicating a dealkoxylation mechanism to be occurring in addition to the main dealkylation reaction to simultaneously form dialkyl phosphoric acid plus alkene.

Trialkyl-, alkyl aryl-, and triaryl phosphates are remarkably thermally stable compounds at temperatures up to 100°.[2] Only at elevated temperatures do they decompose to form unsaturated hydrocarbons and phosphorus acids. With prolonged heat at 150° Gamrath, Hatton, and Weesner[2] converted 2-ethylhexyl diphenyl phosphate into 2-ethyl-1-hexene and diphenyl phosphoric acid. Baumgarten and Setterquist[3] pyrolyzed tributyl phosphate and many other alkyl phosphates at optimum temperatures of 300–350° to obtain essentially quantitative yields of olefins. Cherbuliez, Cordahi, and Rabinowitz[4] also observed nearly quantitative formation of octene from the pyrolysis of trioctyl phosphate. However, no study of the effect of temperature on the rate of decomposition has been made.

It was the purpose of this investigation to determine, if possible, the rate constants for dibutyl phosphoric acid formation as a result of heat on tributyl phosphate at several temperatures. The experiments were performed under conditions whereby the acid formed normally constituted less than 10 mole percent because the decomposition of trialkyl phosphates was found to be acid catalyzed.[2,4,5] Mixtures of the alkyl phosphoric acids are known to react vigorously[5,6]; Hochwalt, Lum, Malowan, and Dyer[6] reported the vacuum distillation of a mixture of mono- and diethyl phosphates at 200° to yield alcohol, ethylene, triethyl phosphate, and a condensed phosphate residue. Only by performing the study in the low acidity range where the acid formed was the dialkyl phosphoric acid would the desired constants be obtainable.

It was also of interest to demonstrate the effect

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(3) H. E. Baumgarten and R. A. Setterquist, *J. Am. Chem. Soc.*, 79, 2605 (1957).

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(6) C. A. Hochwalt, J. H. Lum, J. E. Malowan, and C. P. Dyer, *Ind. Eng. Chem.* 34, 20 (1942).