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THE THIOL-OLEFIN CO-OXIDATION (TOCO) REACTION—IV

TEMPERATURE EFFECTS ON PRODUCT DISTRIBUTION IN THE TOCO REACTION OF INDENE AND AROMATIC THIOLS

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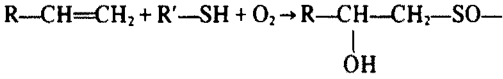
Abstract—The stereochemistry of the TOCO reaction is found to be temperature dependent: increasing amounts of *cis* addition products (approaching 50%) are formed as the temperature is lowered to −23° and also when the temperature is raised to *ca* 60°. The sensitivity of this temperature effect depends on the electronic character of the substituent present in the benzenethiol. The product distribution under a variety of experimental conditions and the kinetics of the TOCO reaction were examined in order to arrive at a self-consistent mechanism.

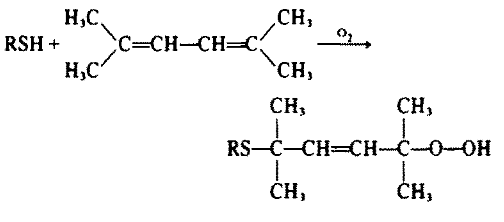
INTRODUCTION

The co-oxidation (or TOCO) reaction between a thiol, an olefin, and molecular oxygen to give a β-hydroxy sulfoxide,



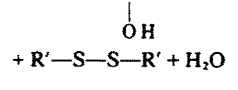
$$\mathrm{R{-}CH{=}CH_2 + R'{-}SH + O_2 \rightarrow R{-}\underset{\displaystyle OH}{\underset{|}{C}H}{-}CH_2{-}SO{-}R'} \qquad (1)$$

was first described in 1951 by Kharasch *et al.*[2] This reaction was next utilized in 1956 by Szmant and Lapinski[3] to prepare the co-oxidation product of styrene and phenethyl mercaptan, while Miyoshi and Oda[4] reported the formation of the TOCO byproduct when a benzene solution of styrene, benzyl mercaptan and benzoyl peroxide was heated in a stream of air. Ford *et al.*[5] studied the co-oxidation of indene and phenyl mercaptan in some detail and reported the formation of only trace amounts of the *cis* product (less than 0.25%). The same and related reactions were then described by Oswald[5,6] who, with several collaborators, extended the reaction to non-conjugated diolefins,[7] conjugated diolefins,[8-10] and to a modified reaction in the presence of an amine and excess of thiol.[11,12] However the last mentioned two reactions are not reported to give β-hydroxy sulfoxides. The conjugated diolefins give a hydroperoxy sulfide,



$$\mathrm{RSH + (H_3C)_2C{=}CH{-}CH{=}C(CH_3)_2 \xrightarrow{O_2} RS{-}C(CH_3)_2{-}CH{=}CH{-}C(CH_3)_2{-}O{-}OH} \qquad (2)$$

which tends to decompose to a complex mixture of products, while the TOCO reaction in the presence of amines follows the stoichiometry

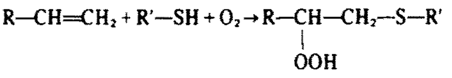


$$\mathrm{R{-}CH{=}CH_2 + 3R'{-}SH + O_2 \xrightarrow{(amine)} R{-}\underset{\displaystyle OH}{\underset{|}{C}H}{-}CH_2{-}SR' + R'{-}S{-}S{-}R' + H_2O} \qquad (3)$$

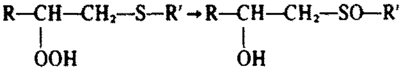
It was suggested that the amine-catalyzed co-oxidation differs from the reaction in the absence of catalyst simply by promoting the reduction of an intermediate hydroperoxide by two equivalents of thiol,

$$\mathrm{R{-}OOH + 2R'{-}SH \xrightarrow{(amine)} R{-}OH + R'{-}SS{-}R' + H_2O} \qquad (4)$$

in preference to the reduction of the hydroperoxide by the sulfide function in the initial addition product,



$$\mathrm{R{-}CH{=}CH_2 + R'{-}SH + O_2 \rightarrow R{-}\underset{\displaystyle OOH}{\underset{|}{C}H}{-}CH_2{-}S{-}R'} \qquad (5)$$



$$\mathrm{R{-}\underset{\displaystyle OOH}{\underset{|}{C}H}{-}CH_2{-}S{-}R' \rightarrow R{-}\underset{\displaystyle OH}{\underset{|}{C}H}{-}CH_2{-}SO{-}R'} \qquad (6)$$

The existence of the β-hydroperoxy sulfide intermediate was considered by Kharasch *et al.*,[2] deduced on the basis of peroxide analysis by Ford *et al.*,[4] and proved through isolation by Oswald.[6,7,10] In 1960 Bredereck *et al.*[14] reported the accelerating effect of chloride and bromide ions (but inhibition by iodide) on the oxygen uptake in the TOCO reaction of a variety of thiols and olefins, and suggested that the function of the halide ions is to catalyze the conversion of the hydroperoxy sulfides to the hydroxy sulfoxides.

Apart of the intermediacy of the hydroperoxy sulfides the mechanism of the TOCO reaction was not clarified any further since the original suggestion by Kharasch[2] that one deals here with a chain reaction involving the following steps:

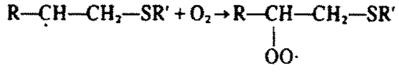
(a) the formation of thiyl radicals from the thiol,

$$\mathrm{R'{-}SH \rightarrow R'{-}S\cdot} \qquad (7a)$$

(b) the anti-Markovnikoff addition of the thiyl radical to the olefin,

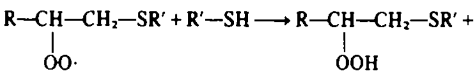
$$\mathrm{R'{-}S\cdot + R{-}CH{=}CH_2 \rightarrow R{-}\dot{C}H{-}CH_2{-}SR'} \qquad (7b)$$

(c) the combination of the preceding radical with molecular oxygen,



$$\mathrm{R{-}\dot{C}H{-}CH_2{-}SR' + O_2 \rightarrow R{-}\underset{\displaystyle OO\cdot}{\underset{|}{C}H}{-}CH_2{-}SR'} \qquad (7c)$$

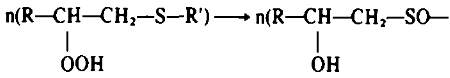
(d – 1) the chain-transfer reaction of the peroxy radical with another thiol molecule,



$$\underset{\text{OO}\cdot}{\text{R—CH}}\text{—CH}_2\text{—SR}' + \text{R}'\text{—SH} \longrightarrow \underset{\text{OOH}}{\text{R—CH}}\text{—CH}_2\text{—SR}' + \text{R}'\text{S}\cdot \quad (7\text{d-1})$$

From here on, Kharasch considered the possibility of two reaction paths:

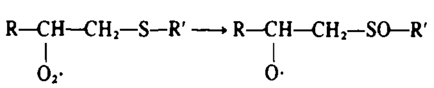
(e-1) the "hydroperoxide route" in which the hydroperoxide oxidizes a sulfide function,



$$\text{n}(\underset{\text{OOH}}{\text{R—CH}}\text{—CH}_2\text{—S—R}') \longrightarrow \text{n}(\underset{\text{OH}}{\text{R—CH}}\text{—CH}_2\text{—SO—R}') \quad (7\text{e-1})$$

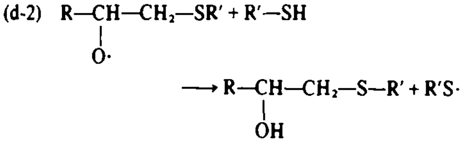
(here n can be 1 or 2 depending on whether the redox process is *intra*- or *inter*molecular),

(e-2) the "alkoxyl radical route" in which the peroxide radical of step (c) oxidizes a sulfide function,



$$\underset{\text{O}_2\cdot}{\text{R—CH}}\text{—CH}_2\text{—S—R}' \longrightarrow \underset{\text{O}\cdot}{\text{R—CH}}\text{—CH}_2\text{—SO—R}' \quad (7\text{e-2})$$

and the resulting alkoxyl radical contributes to chain transfer in a manner analogous to step d-1 shown above,



$$(\text{d-2})\ \underset{\text{O}\cdot}{\text{R—CH}}\text{—CH}_2\text{—SR}' + \text{R}'\text{—SH} \longrightarrow \underset{\text{OH}}{\text{R—CH}}\text{—CH}_2\text{—S—R}' + \text{R}'\text{S}\cdot \quad (7\text{d-2})$$

Kharasch *et al.* visualized the initiation of the radical chain process through the reaction of thiols with hydroperoxide impurities present in the reaction mixture in a manner analogous to the manner by which cumene hydroperoxide catalyzed addition of thiols to olefins,[16] or by the reaction of a thiol with molecular oxygen,

$$(\text{f})\quad \text{R}'\text{—SH} + \text{O}_2 \longrightarrow \text{R}'\text{—S}\cdot + \text{HO}_2\cdot \qquad (7\text{f})$$

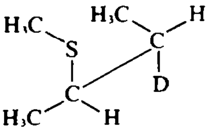
Once the chain process was initiated, thiyl radicals were believed to be generated in the above mentioned steps (d-1) and (d-2). Thiyl radicals can also be initiated photochemically,

$$(\text{g})\quad \text{R}'\text{—SH} \xrightarrow{h\nu} \text{R}'\text{—S}\cdot + \text{H}\cdot \qquad (7\text{g})$$

and this method has been used in the synthetic work described by Oswald *et al.*[6–14] and, more recently, by Tsuchihashi *et al.*[17,18] However, in the absence of photochemical and chemical initiators, the validity of the initiation process (f) involving molecular oxygen had never been elucidated. Also without clarification remained the question of the intra- or intermolecular redox process shown in (e). In order to answer this question Oswald[7] generated the hydroperoxide by the co-oxidation of indene and 2-naphthalenethiol in the presence of 2-*p*-chlorophenylmercapto-1-indanol, and on the basis of the absence of cross-over oxidation concluded that (e) occurs by way of an "intramolecular rearrangement."

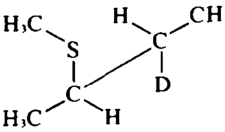
Finally, the stereochemistry of the TOCO reaction was not elucidated even when the olefin is not free to rotate in the course of the addition to the double bond. In the case of indene, for example, both Ford[5] and Oswald[6,7] described only the *trans* hydroxysulfoxides (while acknowledging yields smaller than 1% of uncharacterized co-oxidation products). These reports together with the observation of Skell *et al.*[19–22] concerning the stereospecificity of the addition of deuteriothiols to *cis*- and *trans*-2-butenes in the presence of a fast chain-transfer agent DBr,

cis-2-butene- + -$\text{CH}_3\text{SD} \xrightarrow[\text{(DBr)}]{}$



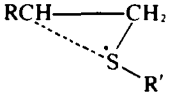
(*threo*) (8)

trans-2-butene + $\text{CH}_3\text{SD} \xrightarrow[\text{(DBr)}]{}$



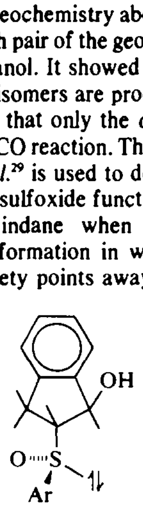
(*erythro*) (9)

gave rise to the belief[23] that the stereospecificity of thiol addition reaction in the presence or absence of oxygen is due to the bridged radical nature of the thiyl radical-olefin adduct,



1

Specifically, the view of the exclusive *trans*-addition in the course of the TOCO reaction was propagated further by the 1966 review of this subject by Oswald and Wallace.[24] Apparently these authors were unaware of the 1964 report by Szmant and Rigau[25] dealing with the isolation in substantial yield (12–14%) of *cis*-2-phenylsulfinyl-1-indanol from the co-oxidation of indene and thiophenol. In 1967 Szmant *et al.*[26,27] reported that the relative yields of the *cis* and *trans* co-oxidation products of indene and substituted thiophenols are related to the electronic nature of the substituents. The work by Szmant and Rigau[28] also lead to the assignment of the stereochemistry about the sulfur atom of the sulfoxides in each pair of the geometrical isomers of 2-phenylsulfinyl-1-indanol. It showed that the *trans-syn* (**2**) and *trans-anti* (**3**) isomers are produced in a ratio of approximately 1:2, and that only the *cis-anti* isomer (**4**) is produced in the TOCO reaction. The nomenclature employed by Ghersetti *et al.*[29] is used to denote the orientation of the oxygen in the sulfoxide function with reference to the benzene ring of indane when the molecule is examined in the conformation in which the aryl group of the sulfoxide moiety points away from the indane ring.



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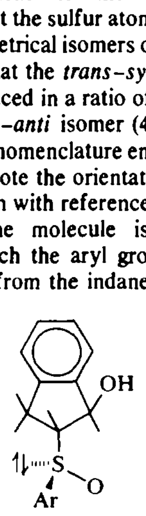

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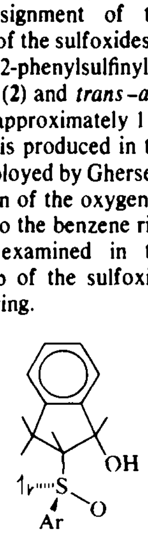
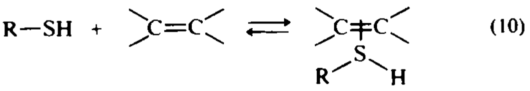
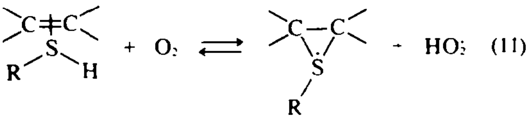


4

An observation relevant to the understanding of the co-oxidation reaction was made in 1967 by Fava *et al.*[30] who noted the fact that the reaction of molecular oxygen with thiols is relatively slow and that the presence of an olefin causes significant acceleration. It was suggested that the difference in the thiol oxidation behavior may be due to the existence of a charge-transfer complex between the olefin and thiol and to the greater reactivity of such complex with oxygen because of the formation of a thiyl radical-olefin complex.



$$R{-}SH + {>}C{=}C{<} \rightleftarrows {>}\underset{\underset{R\quad H}{S}}{C{\nparallel}C}{<} \qquad (10)$$



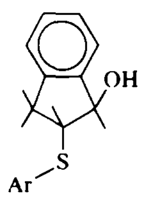
$$\underset{\underset{R\quad H}{S}}{{>}C{\nparallel}C{<}} + O_2 \rightleftarrows \underset{\underset{R}{S}}{{>}C{-}C{<}} + HO_2^{\cdot} \qquad (11)$$

Since the formation of such charge-transfer complexes cannot be studied conveniently by spectrophotometric means because of the ease with which an olefin and thiol mixture undergo hetero- and homolytic addition reactions,[31] an attempt to ascertain the formation of analogous charge-transfer complexes was made[32] by a spectrophotometric examination of mixtures of indene and a series of methyl aryl sulfides. The provisional results of this study suggest that the complex formation is favored in the case of methyl aryl sulfides carrying electron-withdrawing substituents. If this conclusion is carried over to the situation of indene and aromatic thiols, it follows that the latter are acceptors in the charge-transfer complex.

The work described here serves to elucidate further details of the TOCO reaction, the product distribution under a variety of experimental conditions and some kinetic aspects of this complex process.

I. PRODUCT DISTRIBUTION

In the course of the exploration of the TOCO reaction under a variety of experimental conditions it was discovered that in addition to the expected three β-hydroxy sulfoxides **2**, **3** and **4** there could also be isolated the corresponding *trans* and *cis*-1-hydroxy-2-indanyl aryl sulfides **5** and **6**, respectively, the diaryl disulfides **7**, and the anti-Markovnikoff thiol-indene addition products **8**. The complex reaction mixtures were analyzed by nearly quantitative column chromatography as described under Experimental and summarized in the appropriate Tables 1-7.



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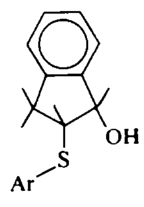
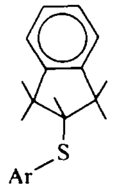


6

Ar–S–S–Ar

7



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1. *Effect of temperature*

The conversion of indene and three substituted benzene thiols to TOCO products as a function of temperature is shown in Fig. 1. It can be seen that under non-photochemical reaction conditions the optimum TOCO conversions over a 48 hr period were achieved near room temperatures and the decrease of TOCO products was especially notable in the higher temperature range. Attempted reactions at 99° failed to give TOCO products. Photochemically-induced TOCO reactions were affected even more strongly at the higher reaction temperatures. The yields of the TOCO products were calculated on the basis of the % TOCO products among all the reaction products that were isolated. They remained relatively constant (75–95%) in the temperature range −10° to +35° and tended to decrease below or above these temperature limits.

Table 1. Effect of temperature on the distribution of products in the thermal cooxidation of indene and m-methylthiophenol in hexane.[a]

Expt. No.	Temp.	ArSH[b] moles × 10̄²	Indene[b] moles × 10̄²	(ArS)₂ (%)	ArSAr′ (%)	THS (%)	CHS (%)	TSO (%)		CSO (a) (%)	Total[d] *cis* Products	Coox Conv (%)	Coox yield (%)
								(s)	(a)				
10	−25	23.03	23.03	12.7	13.1	25.2	25.8	10.3	21.3	17.2	42.9	57.4	75.6
14	−25	23.03	23.03	15.6	5.90	22.9	21.7	11.9	20.5	22.8	44.6	68.7	79.6
12	−15	23.03	23.03	16.5	4.70	27.4	21.5	11.3	18.5	21.4	42.8	54.1	69.4
17	0	23.03	23.03	1.4	5.90	15.2	11.4	14.7	33.2	25.5	36.9	68.8	79.5
19	15	23.03	23.03	8.3	0.90	10.9	8.3	15.4	44.2	21.3	29.5	75.5	79.4
90	36	23.03	23.03	10.8	—	10.5	3.1	39.9	34.1	12.5	15.6	74.4	78.7
91	56	23.03	23.03	13.8	—	13.8	5.1	53.0	16.7	16.6	21.7	62.8	71.1
86	66	46.06	46.06	18.3	—	14.6	6.5	47.2	15.1	16.5	23.1	59.9	73.2

[a] Abbreviations: ArSAr′ = anti-Markovnikoff addition product; THS = *trans*-hydroxy sulfide; CHS = *cis*-hydroxy sulfide; TSO (s) = *trans-syn*-hydroxy sulfoxide; TSO (a) = *trans-anti*-hydroxy sulfoxide; CSO (a) = *cis-anti*-hydroxy sulfoxide; Conv. = conversion. After a reaction period of 48 hr the mixture was quenched by pouring into aqueous thiosulfate solution to destroy the hydroperoxides.

[b] Solution was *ca* 0.25–0.30 M in both indene and in thiol.

[c] Temperature control within ±2°C below 0°.

[d] % Yield of *cis*-products of the total cooxidation products and includes both sulfide and sulfoxide.

Table 2. Effect of temperature on the distribution of products in the thermal cooxidation of indene and *p*-methoxythiophenol in hexane[a]

Expt. No.	Temp. (0°C)	ArSH moles $\times 1\bar{0}^2$	Indene moles $\times 1\bar{0}^2$	$(ArS)_2$ (%)	THS (%)	CHS (%)	TSO (%)		CSO (a) (%)	Total *cis* Products (%)	Coox Conv (%)	Coox yield (%)
							(s)	(a)				
88	−25	23.03	23.03	30.3	28.2	6.4	15.7	26.7	22.8	29.2	44.4	69.3
93	−15	12.50	12.50	10.6	18.1	5.4	20.7	34.3	21.5	26.9	75.8	88.9
25	0	50.00	50.00	3.3	9.8	3.8	21.3	38.4	27.1	30.8	80.4	83.2
28	20	25.00	25.00	1.2	7.4	2.3	33.0	44.8	12.4	14.7	92.6	93.7
29	33	25.00	25.00	1.9	9.2	2.2	30.3	49.7	8.50	10.6	90.7	92.5
98	56	12.50	12.50	16.7	12.9	4.1	46.7	17.0	19.3	23.4	67.7	85.6
85	66	25.00	25.00	19.2	15.8	10.8	35.8	18.2	19.2	30.1	58.3	78.1

[a] Abbreviations and experimental conditions as in Table 1.

Table 3.[a] Effect of temperature on the distribution of products in the thermal cooxidation of indene and *p*-chlorothiophenol (Solvent is hexane unless specified otherwise)

Expt. No.	Temp. (0°C)	ArSH moles $\times 1\bar{0}^2$	Indene moles $\times 1\bar{0}^2$	$(ArS)_2$ (%)	ArSAr′ (%)	THS (%)	CHS (%)	TSO (%)		CSO (a) (%)	Total *cis* Products (%)	Coox conv (%)	Coox yield (%)
								(s)	(a)				
6[c]	0	46.06	46.06	—	21.9	22.2	19.8	6.4	36.3	15.2	35.0	59.8	76.6
7	0	46.06	46.06	—	23.8	19.6	13.7	14.7	33.0	18.9	32.6	56.4	74.2
95	0	46.06	23.03	13.3	18.3	33.3	12.5	7.8	24.1	22.2	34.7	47.8	62.8
22	15	23.03	23.03	—	18.1	14.4	12.0	14.9	39.5	19.2	31.2	67.0	81.8
100	21	23.03	23.03	—	5.0	9.7	7.8	19.7	44.6	18.1	25.9	75.5	80.5
5[c]	32	46.06	46.06	—	4.0	9.3	3.7	12.7	62.7	11.5	15.4	77.0	80.2
87	55	23.03	23.03	9.6	—	5.7	4.8	42.8	29.6	16.9	21.8	75.4	84.5
82	66	46.06	46.06	16.3	—	10.4	13.8	54.4	6.40	15.1	25.4	57.3	73.8
94[b]	99	46.06	46.06	50.2	—	—	—	—	—	—	—	0.0	—

[a] Abbreviations and experimental conditions as in Table 1.

[b] Isooctane is used as the solvent instead of hexane.

Table 4.[a] Effect of solvent on the distribution of products at various temperatures in thermal cooxidation of indene and *p*-chlorothiophenol

Expt. No.	Temp. (0°C)	ArSH mol $\times 1\bar{0}^2$	Indene mol $\times 1\bar{0}^2$	$(ArS)_2$ (%)	ArSAr′ (%)	THS (%)	CHS (%)	TSO (%)		CSO(a) (%)	Total *cis* Products (%)	Coox Conv (%)	Coox yield (%)
								(s)	(a)				
11[b]	−25	23.03	23.03	—	14.4	20.7	12.9	16.6	22.8	26.9	39.8	56.6	63.6
81[b]	−25	23.03	23.03	—	12.0	24.5	23.3	11.4	16.0	24.8	48.1	69.4	76.7
13[b]	−15	23.03	23.03	—	12.3	17.0	10.4	20.0	29.5	23.0	33.4	70.9	80.9
16[b]	0	23.03	23.03	—	0.0	9.5	6.5	31.6	42.7	9.3	15.9	84.3	84.3
77[c]	0	46.06	46.06	8.5	—	4.9	3.4	74.8	—	16.8	20.3	76.6	78.8
37[d]	0	46.06	46.06	—	26.6	19.2	14.9	9.8	30.5	25.5	40.4	61.4	83.6
36[d]	33	46.06	46.06	—	29.8	31.6	—	16.0	38.8	16.5	16.5	57.6	80.8
80[e]	33	46.06	46.06	6.6	—	13.6	5.3	75.8	—	5.9	11.0	89.3	90.6

[a] Abbreviations and experimental conditions as in Table 1 except where noted.

[b] Solvent is hexane: benzene (3:1 v/v) mixture.

[c] Solvent is hexane: benzene (1:3 v/v) mixture.

[d] Solvent is a mixture of 100 ml hexane and 100 ml water.

[e] Solvent is benzene.

The effect of temperature on the *cis*/*trans* ratio of the TOCO products of *p*-chloro, *m*-methyl and *p*-methoxythiophenols and indene using hexane as the solvent is shown in Fig. 2. For the purpose of representing the stereochemistry of the TOCO process, the hydroxy sulfides and sulfoxides are grouped together according to their *cis* or *trans* nature since it is assumed that the stereochemical fate of the reaction is decided once the hydroxylated products are formed. The yields of the *cis* products can be seen to decrease as the temperature is increased, to reach a minimum, and again to increase. No cooxidation products were identified from, the reaction carried out at 99°.

The effect of temperature on the extent of hydroxy sulfide formation is shown in Fig. 3. It is noted that the yields of **5** and **6** pass through a minimum at room temperature and increase more so as the temperatures are lowered than when they are raised.

The ratio of *trans*-*syn*- and *trans*-*anti*-sulfoxides was also found to be temperature dependent and as noted in Fig. 4 the *syn*/*anti* ratio increases significantly as the temperature is raised. It is of interest to point out that only the *trans*-*syn* isomer was isolated in the TOCO reactions induced photochemically or carried out in the presence of cumyl hydroperoxide.

Figure 5 shows the amounts of disulfides **7** derived from

Table 5.[a] The effect of thiosulfate, tetrathionate and phenyl N-butyl nitrone on the distribution of TOCO reaction products

Expt. No.	Temp. (°C)	Additive	$(ArS)_2$ (%)	ArSAr (%)	Total (%) *cis* products	CSO(a) (%)	COOX CONV (%)	COOX YIELD (%)
p-Methoxythiophenol								
39	0	$S_2O_3^{2}$	6.0	0.0	15.9	11.4	81.9	91.1
25	0	none	3.3	0.0	30.8	27.1	80.4	83.2
38	33	$S_2O_3^{2}$	9.8	0.0	0.0	0.0	78.8	92.2
29	33	none	1.9	0.0	10.6	8.5	90.7	92.5
p-Chlorothiophenol								
34	0	$S_2O_3^{2-}$	0.0	27.6	22.8	8.9	59.3	81.9
97	0	$S_4O_6^{2-}$	0.0	22.4	39	25.6	46.9	83.2
6, 7	0	none	0.0	*ca* 22	*ca* 34	*ca* 17	*ca* 58	*ca* 7.5
35	16	$S_2O_3^{2-}$	0.0	37.8	21.0	5.6	49.2	79.2
22	15	none	0.0	18.1	31.2	19.2	67.0	81.8
33	32	$S_2O_3^{2}$	0.0	38.2	0.0	0.0	42.7	69.2
107	33	PTBN[b]	65.3	0.0	9.5	—	21.5	82.6
5	32	none	0.0	4.0	15.4	11.5	77.0	80.2

[a] Abbreviations and experimental conditions as in Table 1 except where noted.
[b] Phenyl t-butyl nitrone.

Table 6. Effect of temperature on the distribution of products in the photochemical cooxidation[a] of indene and *p*-chlorothiophenol (Solvent is cyclohexane[b] unless specified otherwise)

Expt. No.	Temp[c] (0°C)	ArSH moles $\times 10^{-2}$	Indene moles $\times 10^{-2}$	$(ArS)_2$ (%)	THS (%)	CHS (%)	TSO (%) (s)	CSO (%)	Total *cis* Products	Coox Conv. (%)	Coox yield (%)
60	−8	11.50	11.50	2.6	19.6	17.0	53.3	10.1	27.1	81.5	86.4
59	−5	11.50	11.50	3.2	16.8	13.2	60.5	9.5	22.7	81.1	86.9
58	0	11.50	11.50	4.1	23.9	18.3	49.4	8.3	26.6	71.6	82.2
74	0	11.50	11.50	4.6	21.7	13.0	56.6	8.6	21.6	71.8	80.3
99	0	11.50	11.50	8.7	22.3	12.1	56.6	9.0	21.1	76.2	85.3
56	4	11.50	11.50	7.8	13.6	5.4	78.3	10.8	16.3	86.1	93.6
54	11	11.50	11.50	6.9	16.7	2.6	72.9	9.7	11.3	89.0	98.2
53	18	11.50	11.50	14.1	12.6	—	80.8	6.5	6.5	64.7	78.5
112	26	11.50	11.50	19.9	17.2	4.2	73.8	4.8	9.0	58.7	69.9
113	36	11.50	11.50	26.1	18.1	—	77.8	4.2	4.2	51.9	64.1
52	40	11.50	11.50	35.7	21.6	—	67.5	10.7	10.7	34.0	65.0
51[d]	45	11.50	11.50	24.1	14.7	—	73.5	11.6	11.6	33.9	51.4
92	65	11.50	11.50	4.5	—	—	74.6	25.4	25.4	14.6	20.5
83[e]	0	11.50	11.50	12.6	24.4	15.3	51.5	8.8	24.1	62.5	75.2
89[f]	0	23.03	11.50	48.7	49.4	17.2	25.9	7.4	24.6	44.7	57.3

[a] Irradiation using PCQ–XI Photochemical lamp. Abbreviations as noted in Table 1.
[b] Volume of cyclohexane used 75 ml.
[c] Temperature control within ±3°C.
[d] Irradiation for 7 hr.
[e] Solvent is hexane: benzene (3:1 v/v).
[f] Solvent is cyclohexane.

Table 7. Effect of excess cumyl hydroperoxide[a] on the product distribution in the thermal cooxidation of indene and *p*-chlorothiophenol

Expt. No.	Temp. (0°C)	ArSH moles $\times 10^{-2}$	Indene moles $\times 10^{-2}$	$(ArS)_2$ (%)	ArSAr' (%)	TSO (%) (s)	TSO (%) (a)	CSO (a) (%)	Total *cis* Products (%)	Coox Conv (%)	Coox yield (%)
111	−25	23.03	23.03	13.1	—	69.6	15.3	15.1	15.1	62.6	70.6
109	0	23.03	23.03	17.7	—	83.8	3.5	12.7	12.7	58.2	64.1
115	20	23.03	23.03	10.5	—	77.6	11.8	10.6	10.6	53.8	56.8
96	33	23.03	23.03	11.3	—	82.9	—	17.1	17.1	79.9	89.9
101	56	23.03	23.03	23.4	—	72.7	—	27.3	27.3	23.2	50.4
105	66	23.03	23.03	37.8	14.4	55.4	—	44.6	44.6	5.90	13.5

[a] Cumyl hydroperoxide 0.04606 moles. Abbreviations and experimental conditions as noted in Table 1.

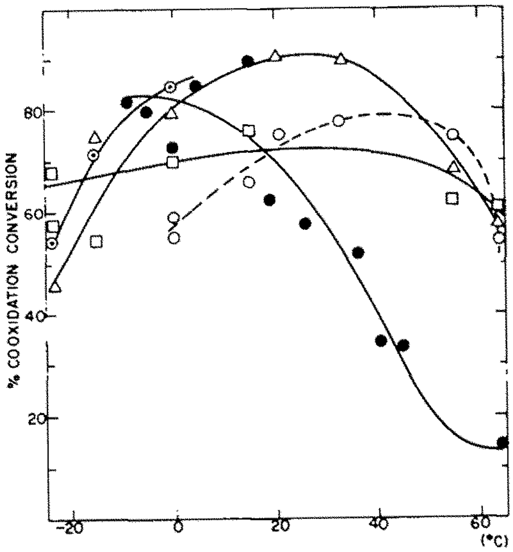


Fig. 1. Effect of temperature on conversion in the co-oxidation of indene and aromatic thiols. Symbols: m-thiocresol (squares), *p*-methoxythiophenol (triangles), and *p*-chlorothiophenol (circles). In the case of the last mentioned thiol: ○, indicate the use of hexane, ⊙ the use of hexane-benzene (3:1 v/v) ● represent photochemical experiments in cyclohexane.

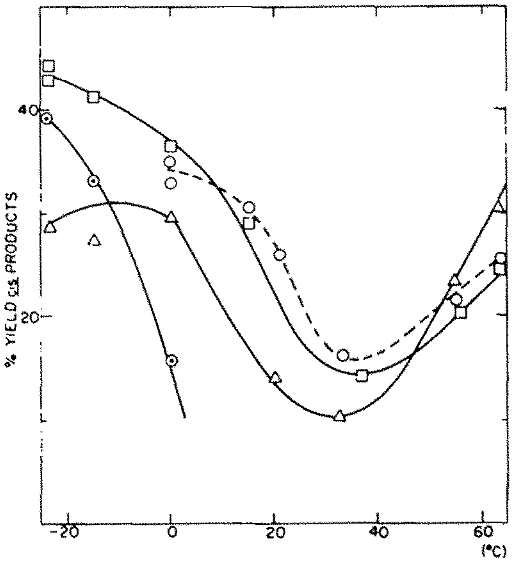


Fig. 2. Effect of temperature on the formation of *cis* cooxidation products in the thermal cooxidation reaction. For explanation of symbols see Fig. 1.

the original thiol that were isolated at various temperatures. Above 30° there seems to be little difference in the behavior of the three substituted thiophenols and the yields increase rapidly as the temperature rises. Below 30°, however, *p*-chlorothiophenol failed to give any disulfide unless a two-fold excess of thiol was employed. On the other hand, the *m*-methyl and *p*-methoxythiophenols gave considerable amounts of the disulfides at the lower temperatures even though equimolar quantities of thiols and indene were employed.

The formation of the *anti*-Markovnikoff addition product **8** was observed in the case of the TOCO reaction of *p*-chloro- and *m*-methylthiophenols but not when *p*-methoxythiophenol was employed. As shown in Fig. 6

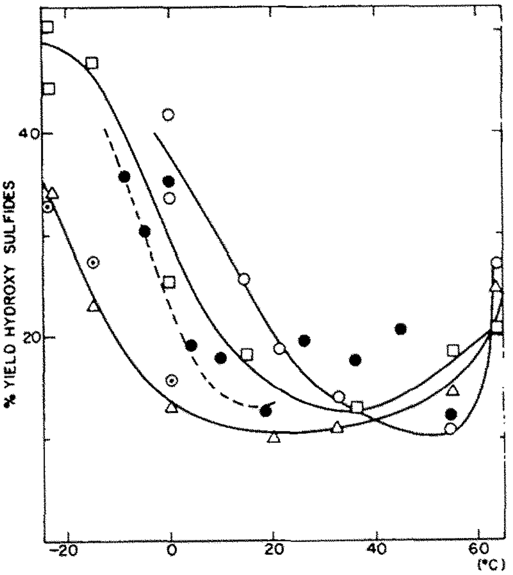


Fig. 3. Effect of temperature on the formation of hydroxy sulfides. For explanation of symbols see Fig. 1.

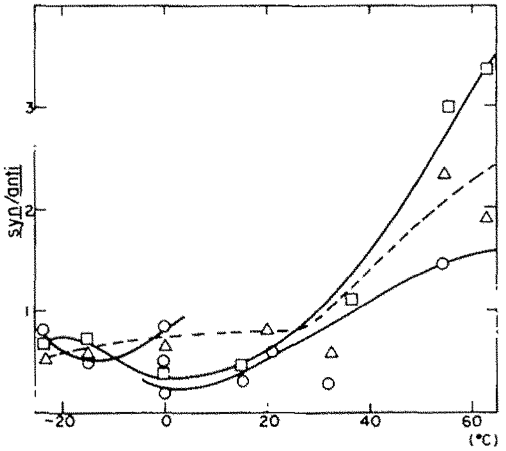


Fig. 4. Effect of temperature on the *syn*/*anti* ratio of the *trans* sulfoxides. For explanation of symbols see Fig. 1.

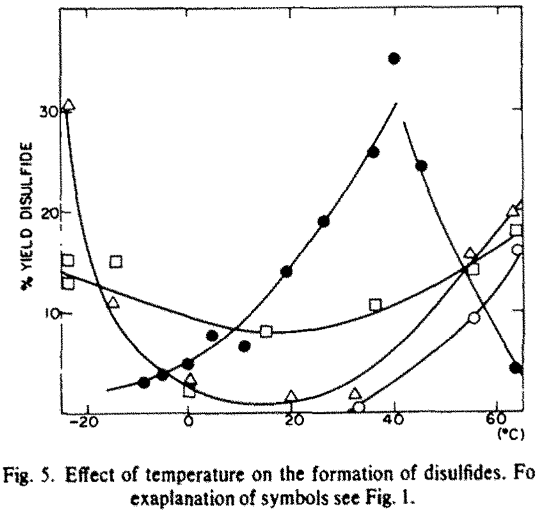


Fig. 5. Effect of temperature on the formation of disulfides. For exaplanation of symbols see Fig. 1.

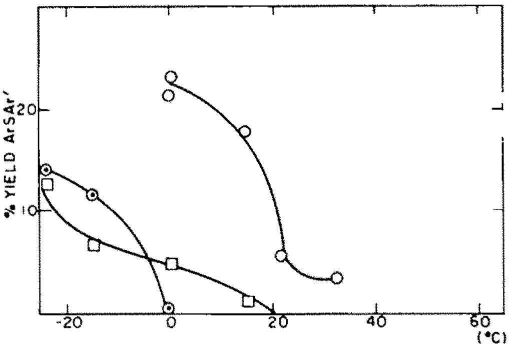


Fig. 6. Effect of temperature on the formation of anti-Markovnikoff thiol addition products. For explanation of symbols see Fig. 1.

the yields of **8** become more significant as the reaction temperature is lowered.

2. *Effect of solvent*

For reasons of solubility it was necessary to add benzene to the hexane solution when the TOCO reaction of p-chlorothiophenol and indene was studied at temperatures below 0°. As shown in Fig. 7 the change of solvent from pure hexane to a 3:1 mixture (by volume) of hexane and benzene was found to have a pronounced influence on the *cis/trans* ratio of the TOCO products and the yields of the *cis*-products were markedly decreased. The use of benzene alone as solvent did not cause any further significant changes in the results. For reasons mentioned below it was of interest to carry out the TOCO reaction of p-chlorothiophenol in the presence of water, and it can be seen in Fig. 7 that the presence of water did not affect the *cis/trans* ratio to any great extent.

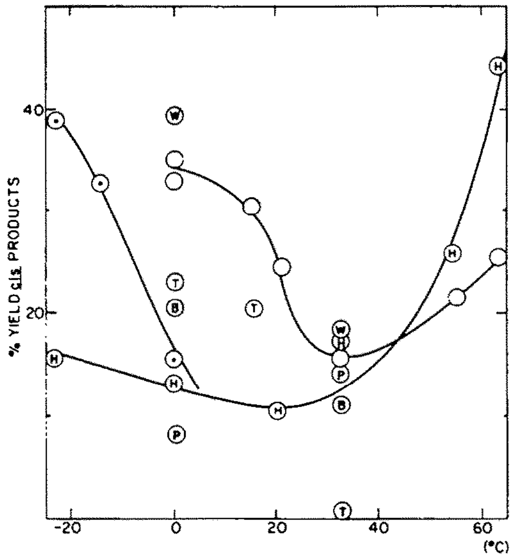


Fig. 7. Effect of solvent, cumene hydroperoxide, sodium thiosulfate and potassium persulfate on the *cis* cooxidation products in the cooxidation of indene and p-chlorothiophenol. For explanation of symbols see Fig. 1. Circles with H, T, P, W and B represent experiments carried out in the presence of cumene hydroperoxide, sodium thiosulfate, potassium persulfate, water and benzene, respectively.

3. *Effect of thiol structure*

An examination of Fig. 2 reveals that the *cis/trans* ratio of the TOCO products is influenced by a change in thiol structure. Under equivalent experimental conditions p-chlorothiophenol gave more *cis* products than m-methylthiophenol, and p-methoxythiophenol gave the least amounts of *cis* products. These results are consistent with the substituent effects observed in the room temperature reaction of indene and molecular oxygen with a series of five aromatic thiols (Table 8). Although the Hammett plot of the *cis* product formation gives a poor correlation (most likely because of the absence of good temperature control in these comparative experiments), nevertheless the *rho* value can be estimated to be *ca* +0.6 (using either σ or σ^{+} constants).

4. *Experiments expected to favor homolytic chain reactions*

In order to test the effect of a homolytic chain reaction mechanism on the distribution of the TOCO products, a number of experiments were designed to favor the formation of thiyl radicals.

(a) *Use of cumene hydroperoxide.* The cooxidation of indene and p-chlorothiophenol was carried out at various temperatures rangeing from −25 to +65° in the presence

Table 8. Substituent effect on the distribution of 2-arylsulfinyl-1-indanols[a]

		trans-anti			*trans-syn*			*cis-anti*			
Substituent	Sample chrom.[a] (g)	recov'd (g)	% of total	m.p.[b] (°C)	recov'd (g)	% of total	m.p.[b] (°C)	recov'd (g)	% of total	m.p.[b] (°C)	*trans* *cis* ratio
p-OCH$_3$	1.5000 (1.4582)	0.3637	26.5	125–126	0.8980	65.4	117–119	0.1105	8.0	139–140	11.4
p-CH$_3$	0.4370 (0.3960)	0.999	24.5	148–150	0.2589	65.3	155–156	0.0371	9.3	173–174	9.5
p-t-C$_4$H$_9$	1.0920 (1.0347)	0.2761	28.8	158–159	0.6200	59.4	141–142	0.1225	11.8	174–175	7.5
None[c]	1.0000 (0.908)	0.267	29.4	158	0.511	56.3	101	0.130	14.7	158	5.8
p-Cl	1.1235 (0.9488)	0.2232	23.4	168–169	0.5436	57.3	159–160	0.1820	19.1	163–164	4.1

[a] Reaction carried out at room temperature using an equimolar solution of indene and thiol in ligroin. A sample of the products obtained by filtration of the reaction mixture was subjected to column chromatography. The total weight of recovered fractions is given in parentheses.

[b] All m.ps with decomposition.

[c] From Ref. (28).

of a two-fold excess of cumene hydroperoxide. These results are included in Fig. 7 and it can be seen that compared to the thermally induced reaction in the absence of cumene hydroperoxide the yield of the *cis* cooxidation products was considerably decreased below room temperatures while the opposite was true at the higher temperatures.

(b) *Use of Fenton's reagent or potassium persulfate.* No TOCO products could be isolated when the reaction of *p*-chlorothiophenol and indene was carried out in the presence of Fenton's reagent and only 2-indianyl-*p*-chlorophenyl sulfide was obtained in 73.4% yield. As shown in the Fig. 7 presence of potassium persulfate reduced the yield of *cis* cooxidation products significantly at 0° (from 38 to 8%), but not so at 32°.

(c) *Photochemical cooxidation experiments.* Figure 8 shows the effect of temperature on the relative yields of *cis* products in the photochemically induced TOCO reaction of indene and *p*-chlorothiophenol at temperatures ranging from −8° to +65° using a PCQ-X1 photochemical lamp. The analogous thermal cooxidation results are included for comparison, and it can be noted that the photochemical condition caused a drop in the yield of the *cis* products when the temperature is 45° or lower, but at 65°, this difference disappeared.

5. *Experiments designed to suppress homolytic chain reactions*

(a) *Use of galvinoxyl.* No TOCO products could be identified and no other products could be isolated when *p*-chlorothiophenol and indene were allowed to react in the presence of galvinoxyl. TLC on silica gel suggested the presence of more than fifteen components.

(b) *Use of sodium thiosulfate.* Since according to the accepted TOCO reaction mechanism the peroxy and hydroperoxide intermediates react with thiol to generate thiyl radicals, an attempt was made to suppress this process by carrying out the reaction in the presence of sodium thiosulfate solution. Control experiments with cumene hydroperoxide showed that thiosulfate reacts rapidly and quantitatively with the hydroperoxide. As shown in Fig. 7, the yields of *cis* products obtained in the TOCO reaction of indene and *p*-chlorothiophenol when the reaction was carried out in the presence of sodium thiosulfate were found to decrease at lower temperatures and reached zero at 35°. As expected, the yield of the sulfoxides was also decreased in favor of the sulfides. The presence of sodium thiosulfate was also shown to decrease the yield of *cis* TOCO products in the case of *p*-methoxythiophenol (from *ca.* 30 to 16% at 0°).

(c) *Use of phenyl* N-*t*-*butyl nitrone.* The TOCO reaction of indene and *p*-chlorothiophenol carried out at 32° in the presence of phenyl N-t-butyl nitrone gave a large amount of the disulfide **7** (65.3%) and a relatively small conversion of indene to TOCO products (21.5%), and the relative yield of *cis* TOCO product **6** was decreased from *ca.* 15 to 9.5%.

II. KINETICS OF THE TOCO REACTION

The kinetic experiments were carried out using chlorobenzene as the solvent in order to maintain a homogeneous reaction mixture even at 0°. The distribution of the TOCO products was not significantly affected by this choice of solvent or the use of the relatively volatile *m*-thiocresol. The consumption of indene and thiol was followed by GLC and that of oxygen by means of a gas burette.

The TOCO process exhibits complex kinetic behavior. Its most noteworthy feature is the accelerated consumption of the reagents after the first 20–45% of the reaction had occurred. This behavior is illustrated in Fig. 9 in which the disappearance of each of the three reagents is represented by a pseudo-first order rate plot. The accelerated consumption of the reagents after the initial, relatively slow phase of the reaction is more pronounced at 32° than at 0° (Fig. 10). The other noteworthy observation is that under comparable conditions, the TOCO process tends to occur more rapidly at 0° than at 32°. Thus, for example, for equimolar concentrations of indene and thiol (0.025 M) at 0° and 32° the pseudo-first order rate constants for their consumption were found to be $0.585 \times 10^{-5}\,\text{sec}^{-1}$, $1.1 \times 10^{-5}\,\text{sec}^{-1}$ and $0.54 \times 10^{-5}\,\text{sec}^{-1}$, $0.23 \times 10^{-5}\,\text{sec}^{-1}$, respectively. Similarly, the pseudo-first order rate constant for the disappearance of indene (initial concentration 0.025 M) in the presence of a three-fold excess of thiol was found to be $2.8 \times 10^{-5}\,\text{sec}^{-1}$ and $1.9 \times 10^{-5}\,\text{sec}^{-1}$ at 0° and 32°, respectively. This "negative activation energy" effect could arise because of the greater effective concentration of dissolved oxygen in the reaction mixture at the lower temperature,[33] but it may

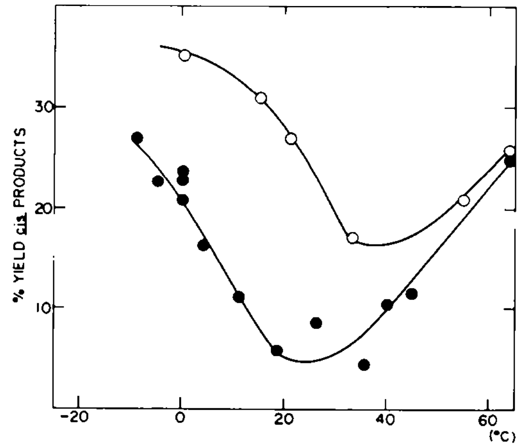


Fig. 8. Effect of temperature on the formation of *cis* products in the photochemical cooxidation of indene and *p*-chlorothiophenol. For explanation of symbols see Fig. 1.

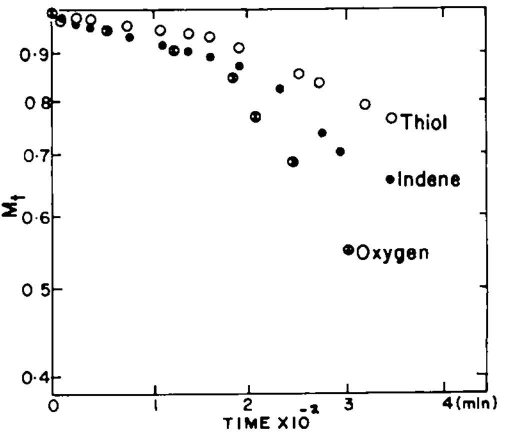


Fig. 9. Representative pseudo-first order plot of consumption of reactants (*m*-thiocresol and indene both 0.025 M, O_2 pressure 1 atm, chlorobenzene solution at 0°).

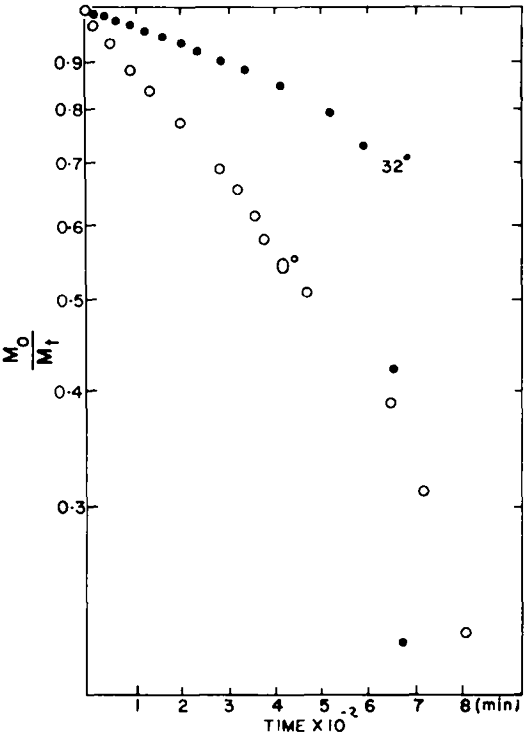


Fig. 10. Temperature dependence of *m*-thiocresol consumption in co-oxidation reaction with indene (0.025 M solution in chlorobenzene).

also be the result of a more interesting phenomenon suggested in the Discussion.

Since the volume of available oxygen at atmospheric pressure was greatly in excess of the stoichiometric amount required for the TOCO process, and in view of its relatively large solubility (*ca* 10^{-3} M)[33] and diffusion rates[34-36] (*ca* 10^{10} cm^2/sec.), it is safe to assume that the reaction has a pseudo-zero order dependence in oxygen. Variation of the partial pressure of oxygen under otherwise equivalent experimental conditions revealed a first-order dependence in oxygen.

The rates of consumption of indene and thiol were approximately equal when equimolar concentrations of these two reactants were present, but the thiol was consumed at a slightly greater rate and the experimentally determined stoichiometry at 0° was 1.1 moles of thiol to 1.0 moles of indene.

The analysis of the kinetic data is limited to the experiments carried out at 0° because at this lower temperature the autocatalytic phase of the reaction was conveniently delayed.

The log-log plot of the pseudo-first order rate of the initial disappearance of thiol (maintained at a constant initial concentration) in the presence of increasing initial excess concentrations of indene showed a nearly first-order dependence of the TOCO reaction on indene. The analogous log–log plot of the pseudo-first order rate of the initial disappearance of indene (maintained at a constant initial concentration) in the presence of increasing initial excess concentrations of thiol showed a complex dependence of the TOCO reaction on the thiol concentration. A relatively small excess of thiol (up to 3 : 1 molar ratio) gave a first-order dependence while a 6–9 fold excess of thiol increased the order in thiol to a value of *ca* 1.5.

Control experiments of the rate of reaction of *m*-thiocresol with excess oxygen at 0° gave a specific rate constant of 5×10^{-7} sec^{-1}. This result is consistent with the rate of 1.6×10^{-6} sec^{-1} reported[30] for the reaction of *p*-chlorothiophenol with oxygen at 110° in cyclohexane solution when one takes into consideration the difference in oxygen concentrations under the experimental conditions. In any case, it is noteworthy that the absence of indene decreases the reaction of thiol and oxygen *ca* 22 fold. Similarly the disappearance of indene in the presence of excess oxygen, presumably to give a polymeric peroxide,[37] gave a specific rate constant of 1.2×10^{-7} sec^{-1} at 25°. Finally, control experiments were carried out by following the consumption of oxygen when the TOCO reaction mixture was shielded from light and no significant differences in the rates were observed.

DISCUSSION

The temperature dependent stereochemistry (Fig. 2) and irregular kinetic behavior (Figs. 9 and 10) suggest the existence of at least two different and competitive reaction paths for the TOCO reaction.

The first of these seems to be favored at lower temperatures and it appears to consist of a relatively slow reaction conducive to relatively high yields of *cis* TOCO products. This point was tested by carrying out an experiment at 0° in which the TOCO reaction of indene and *m*-thiocresol was interrupted at 33–35% completion. Under these conditions the *cis*/*trans* ratio of the TOCO products was indeed double when compared to the ratio of products obtained if the reaction was allowed to run to completion. The apparent "negative activation energy" suggests the dependence of the low-temperature reaction path on the formation of a molecular complex between the thiol and the olefin. The observed substituent effect on the relative yields of *cis* TOCO products suggests further that we may be dealing here with a charge transfer complex in which the olefin is the donor and the thiol the acceptor. If we accept this hypothesis it is till necessary to account for the tendency of the low-temperature reaction path to give *cis* TOCO products. A plausible mechanism may be a reaction of molecular oxygen with the thiol-olefin complex in a solvent-cage pictured in Scheme 1.

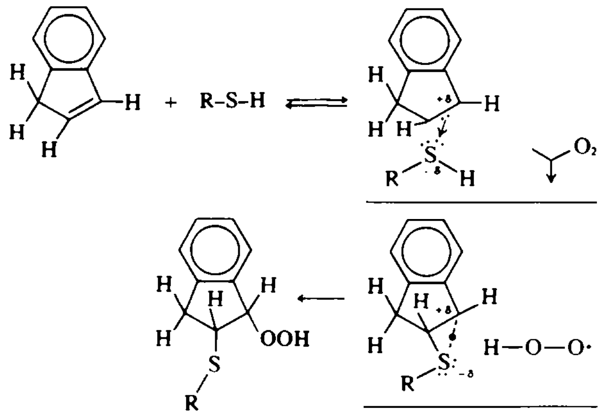
The low-temperature reaction mechanism suggested in Scheme 1 is consistent with the observed solvent effects (Fig. 7) on the relative yield of *cis* TOCO products at low temperatures since it is reasonable to assume that the presence of a "soft" basic solvent benzene will compete with the formation of the olefin-thiol molecular complex. On the other hand, the presence of the relatively "hard" basic solvent water (or ethyl acetate employed in more recent work) does not seem to exert a significant effect on the *cis*/*trans* ratio of TOCO products at low temperatures.

The escape of the hydroperoxy radical from the solvent caged aggregate pictured in Scheme 1 creates a situation that can give rise to an appreciable concentration of thiyl radicals by either a direct interaction of the hydroperoxy radical with thiol as shown in (12)

$$HO_2\cdot + Ar{-}S{-}H \longrightarrow HO_2H + ArS\cdot \qquad (12)$$

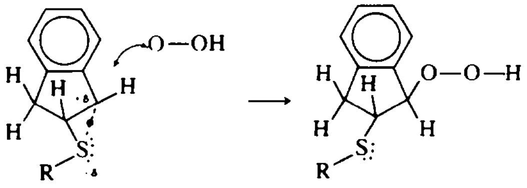
or by the relatively slower and thus somewhat more delayed process involving the hydrogen peroxide formed in (12),

$$2ArSH + H_2O_2 \longrightarrow 2ArS\cdot + 2H_2O \qquad (13)$$



Scheme 1. Proposed mechanism for the low-temperature formation of *cis*-TOCO products.

However, one may also visualize that the hydroperoxy radical returns to the olefin-thiyl radical complex left behind in the original solvent cage. In this connection it is convenient to assume that the TOCO reaction involves a bridge sulfur radical species[23] and that the latter reacts stereospecifically to give the *trans* product as pictured in Scheme 2.



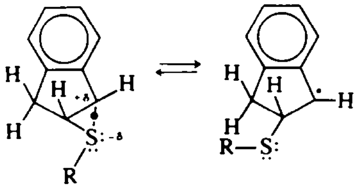
Scheme 2. Stereospecific reaction of bridged olefin-thiyl radical.

The same bridged radical pictured in Scheme 2 may, of course, also originate from the addition reaction of indene and thiyl radicals generated as shown above in eqns 7d, 7f and 7g. Furthermore, the bridged radical may also react stereospecifically with molecular oxygen to give the *trans*-2-arylmercapto-1-indanyl peroxyl radical.

In summary, the proposed low-temperature TOCO mechanism assumes the formation of *cis* products *via* the solvent caged process pictured in Scheme 1 and *trans* products *via* a bridged thiyl-olefin complex as pictured in Scheme 2. This mechanism incorporates the generally recognized electrophilic nature of thiyl radicals,[38] the acceleration of the thiol-oxygen reaction in the presence of an olefin observed by Fava[30] and confirmed here, and the bridged nature of the thiyl radical-olefin complex. The latter concept seems necessary to account for the apparent *trans* stereospecificity of the thiyl-olefin radicals vs the complete loss of stereoselectivity in the reaction of molecular oxygen with 2-substituted, non-bridged 1-indanyl radicals during the formation of polymeric indene peroxides.[37]

In accord with the preceding low-temperature mechanism, a gradual increase of the reaction temperature would be expected to lower the relative yields of *cis* TOCO products by virtue of the more ready dissociation of the solvent-caged aggregate pictured in Scheme 1 and an increasing possibility of the stereospecific reactions of the bridged thiyl radical-olefin complex with either the hydroperoxy radical or molecular oxygen. At the same time, however, the increasingly present thiyl radicals (from processes (12) or (13)) would be expected to induce relatively rapid free radical chain reactions postulated originally by Kharasch.[2]

However, we must also account for the upturn of the relative yields of *cis* products when the TOCO reaction temperatures are raised above 30° (Figs. 2, 7 and 8) and for that purpose it is convenient to involve the temperature dependent equilibrium between the bridged thiyl radical-olefin complexes and their "open" or "classical" counterparts (Scheme 3).



Scheme 3. Equilibrium between "bridged" and "open" 2-arylmercapto-1-indanyl radicals.

The complete loss of stereoselectivity of "open" 2-substituted 1-indanyl radicals in their reaction with molecular oxygen[32] was mentioned above and the same behavior may be expected of the "open" radicals present in the TOCO reaction. Experiments designed to test the formation of limiting 50% yields of *cis* TOCO products were unsuccessful because the conversions of thiols and indene to TOCO products dropped off sharply above 60°. Thus, at 66° (and in the presence of cumene hydroperoxide), the yield of *cis* TOCO products reached 44.6% but at this temperature the conversion dropped already to 5.9%. Such a low conversion can be explained, in part, by the well recognized reversibility of radical-olefin adducts.[39] In other words, at relatively high temperatures not only is the "bridged"-"open" radical equilibrium displaced toward the "open" species but also the dissociation of the adduct to thiyl radical and olefin becomes increasingly more prominent. It is of interest to note (Fig. 1) that the combination of thermal and photochemical conditions causes a dramatic decrease of TOCO conversions at temperatures above 25–30°.

The thiol substituent effect on the *cis* stereoselectivity in the course of the low temperature TOCO process (p-Cl > m-CH$_3$ > p-CH$_3$O) is accounted for by an acceptor role of the thiol in the formation of the charge transfer complex with indene. *A priori*, there is no reason to assume a reversal of this role when we are considering the complex between indene and the corresponding thiyl radicals.

The results of the control experiments carried out with *p*-methoxy- and *p*-chlorothiophenol in the presence of aqueous thiosulfate are compiled in Table 4 together with the corresponding data for the TOCO experiments in the absence of thiosulfate in order to facilitate the comparisons. Also included in Table 4 are the results that were obtained in the presence of tetrathionate and phenyl t-butyl nitrone.

The common feature of all the TOCO experiments that contained aqueous thiosulfate is the significant reduction in the formation of the *cis* products. This effect becomes more dramatic as the reaction temperature is raised to 32° when the TOCO reaction becomes stereospecifically *trans*. The presence of thiosulfate above 0° also caused a significant decrease in the conversion of indene and thiol to TOCO products, i.e. the formation of the by-products was favored. A very surprising feature of the TOCO experiments carried out in the presence of thiosulfate was the observation that the concentration of the latter was unchanged at the end of the experiment even though *a priori*, one would have expected that the hydroperoxides formed in the course of the TOCO process would have oxidized the thiosulfate to tetrathionate.

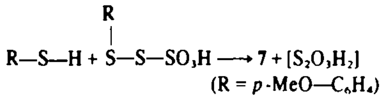
An explanation of the above mentioned results (based on the assumption that the low-temperature reaction mechanism (Scheme 1) predominates in the temperature range 0–32° employed in these control experiments) focuses on the decrease of the effective thiol concentration caused by the presence of thiosulfate. Under normal TOCO reaction conditions the initial thiol concentration is reduced as oxygen radicals are generated (eqns 7e, 7f) and react with thiol to give thiyl radicals (eqns 7d, 7f, 12, 13). In the presence of an excess of thiosulfate it is likely that the oxygen radicals, or their precursors, will react preferentially with thiosulfate as illustrated in the case of a hydroperoxyl radical,

$$2RO_2\cdot + 6S_2O_3^{2-} + 6H^+ \longrightarrow 2ROH + 3S_4O_6^{2-} + 2H_2O. \quad (14)$$

The tetrathionate ion generated in this or similar manner can now react with the thiols by a process well documented in the literature,[40]

$$R{-}S{-}H + S_4O_6^{2-} \longrightarrow \underset{(9)}{R{-}S{-}S{-}SO_3H} + S_2O_3^{2-} \quad (15)$$

The fate of 9 apparently depends on the nature of the substituent present in the benzenethiol moiety. In the case of the electron-donating *p*-methoxy group the presence of thiosulfate in the TOCO reaction causes a 2–4 fold increase in the formation of disulfide 7. This suggests that 9 is subject to a facile nucleophilic attack by unreacted thiol,



$$R{-}S{-}H + \overset{R}{\overset{|}{S}}{-}S{-}SO_3H \longrightarrow 7 + [S_2O_3H_2] \quad (16)$$
$$(R = p\text{-MeO}{-}C_6H_4)$$

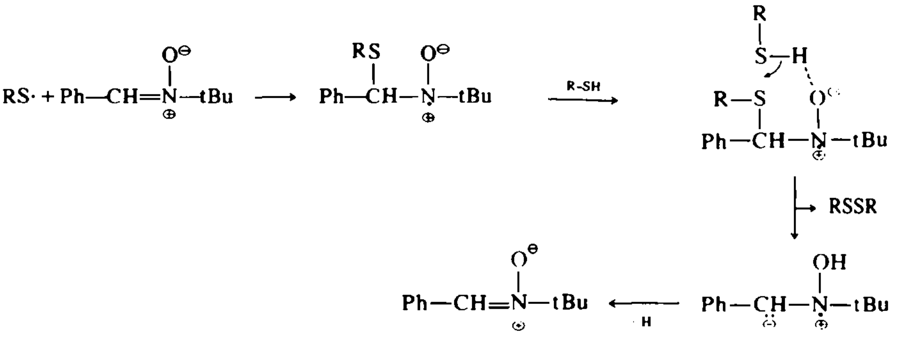
It is noteworthy that process (14) implies a proton requirement that could be readily satisfied by either thiol or thiosulfuric acid in which case the formation of 7 by the above mentioned reaction becomes even more reasonable.

In the case of the *p*-chloro-substituted benzenethiol the presence of thiosulfate does not lead to disulfide formation (hence an unlikely role of the thiosulfate as a promotor of thiyl radicals) but one observes a nearly ten-fold increase in the formation of the anti-Markovnikoff addition product 8. This result may come about by the enhancement of the acceptor role of the sulfur atom after *p*-chlorothiophenol has been converted to 9. In any case, while these suggestions are being subjected to experimental verification, it is clear that the above suggestions explain the regeneration of the thiosulfate in the TOCO reaction.

The product distribution in the TOCO experiment carried out in the presence of excess tetrathionate ion differs significantly from the result obtained in the absence of tetrathionate in that the yield of *cis* TOCO products is increased from *ca* 34% to 39.3% (at 0°) without a decrease in the yield of 8. In the context of the preceding mechanistic suggestions this result implies that species 9 is involved in both the formation of 8 and the *cis* TOCO products. With respect to the formation of the *cis* TOCO products it would seem that molecular oxygen can function as well as shown in Scheme 1 when the thiol moiety is replaced by species 9.

The presence of phenyl t-butyl nitrone caused, first of all, a large drop in the conversion of the starting materials to TOCO products in favor of an even larger increase in disulfide formation. The nitrone is well known to trap carbon radicals,[41,42] but since we failed to isolate any addition products of the thiyl radical, it would seem that the nitrone is catalyzing the formation of disulfide by first stabilizing the thiyl radical through the formation of a relatively unstable adduct that reacts subsequently with thiol to give disulfide. This process may be represented in Scheme 4.

The other notable effect observed by the presence of phenyl t-butyl nitrone was the complete disappearance of the sulfoxides from among both the *cis* and *trans* TOCO

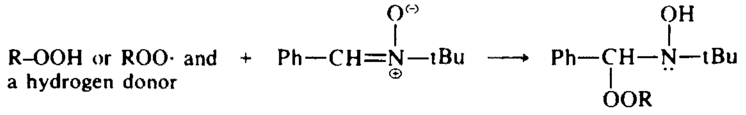


Scheme 4. Proposed catalytic role of nitrene in conversion of thiol to disulfide.

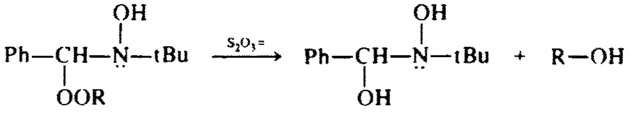
products. The result can be explained if we assume that the nitrone efficiently traps the peroxy radicals or hydroperoxides formed as suggested above and gives an adduct that is reduced to the hydroxy sulfide TOCO products when the reaction mixture is quenched in thiosulfate at the end of the standard reaction period employed in the series of experiments. The series of proposed transformations that explain the formation of hydroxy sulfide TOCO products and the recovery of the nitrone are shown in eqns (17–19).

the experimental results indicate that a strictly bimolecular collision between the oxidant and the *trans*-sulfide is more favorable from the *syn* direction.

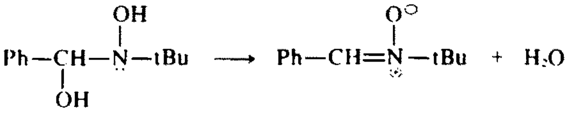
The results of the TOCO experiments carried out in the presence of two equivalents of cumene hydroperoxide are consistent with the mechanistic conclusions discussed so far. The formation of thiyl radicals by a process similar to that shown in eqn (13) would be expected to compete with the low temperature mechanism proposed in Scheme 1. Consequently, we expect a a lowered yield of *cis* TOCO



$$\text{R–OOH or ROO· and a hydrogen donor} + \text{Ph—CH}=\overset{O^{(-)}}{\underset{\oplus}{\text{N}}}\text{—tBu} \longrightarrow \text{Ph—}\underset{\text{OOR}}{\text{CH}}\text{—}\overset{\text{OH}}{\underset{\cdot\cdot}{\text{N}}}\text{—tBu} \qquad (17)$$



$$\text{Ph—}\underset{\text{OOR}}{\overset{}{\text{CH}}}\text{—}\overset{\text{OH}}{\underset{\cdot\cdot}{\text{N}}}\text{—tBu} \xrightarrow{S_2O_3^{=}} \text{Ph—}\underset{\text{OH}}{\text{CH}}\text{—}\overset{\text{OH}}{\underset{\cdot\cdot}{\text{N}}}\text{—tBu} + \text{R—OH} \qquad (18)$$



$$\text{Ph—}\underset{\text{OH}}{\text{CH}}\text{—}\overset{\text{OH}}{\underset{\cdot\cdot}{\text{N}}}\text{—tBu} \longrightarrow \text{Ph—CH}=\overset{O^{\ominus}}{\underset{\oplus}{\text{N}}}\text{—tBu} + H_2O \qquad (19)$$

(ROH = hydroxy sulfide TOCO products)

The decrease of the *cis* TOCO yields in the lower temperature range under photochemical reaction conditions suggests that the photolysis of the S–H bond can occur also in the molecular complex of indene and thiol and that the resulting indene-thiyl radical complex remains mostly in the bridged form at the lower temperatures. Hence the relative yields of the *trans* TOCO products are higher then under thermally induced reaction conditions. However, unlike under the latter conditions, the photochemical TOCO reaction of *p*-chlorothiophenol produces some disulfide even at −8° and the yield of this byproduct increases systematically up to 40°. This is indicative of the fact that the photolysis of free thiol produces relatively energy-rich thiyl radicals that dimerize in preference to the formation of an adduct with indene. The reversibility of this adduct formation also explains why the conversions to TOCO products decline above 11°. An unexpected feature of the photochemically induced TOCO reaction was the absence of the *trans-anti* sulfoxide. In the thermally induced TOCO process we note that in the case of *p*-chlorothiophenol the *trans-anti* sulfoxide predominates at the lower temperatures but that the preference shifts in favor of the *trans-syn* sulfoxide somewhere between 32 and 55°. Since no *trans-anti* sulfoxide could be detected in the photochemically-induced TOCO process even at −8° this result confirms that the latter reaction conditions involve relatively energy-rich species. It is difficult to imagine any *intra*-molecular redox reactions involving the hydroperoxyl and sulfide functions in the *trans* TOCO intermediate and thus one is forced to consider only an *inter*molecular process. However, the preference for the *trans-anti* sulfoxide formation under low-energy conditions suggests that the *trans-anti* sulfoxide is produced internally in dimers or higher aggregates of the hydroperoxides in which the association of the oxygen-containing group induces a preferential oxidation of the sulfide from the *anti* direction. On the other hand, all of products while, at the same time the yield of disulfide **7** is raised significantly. However, at the higher temperatures, the effect of cumene hydroperoxide is to reinforce the free radical chain reaction process and the exothermicity of the redox reaction apparently displaces the bridged-open radical equilibrium (Scheme 3) in favor of the latter and thus promotes an increase in *cis* TOCO products. Also, in line with the ideas presented above with regard to the *syn-anti* radio of *trans* sulfoxides, we note that the presence of cumene hydroperoxide reverses the trend in favor of the *syn* isomer at the lower temperatures and completely supresses the formation of the *anti* isomer at the higher temperatures.

The formation of the anti-Markovnikoff addition product **8** at low temperatures in the case of *p*-chloro- and *m*-methylthiophenol, is subject to additional study and will be discussed in a future publication. The kinetic results during the initial, slow phase of the TOCO reaction support the conclusion that the rate determining step involves all three species, namely thiol, indene and molecular oxygen as pictured in Scheme 1. The fact that the first order dependence in thiol tends to increase when the thiol/indene ratio becomes greater than 3 suggests that thiol dimers may be complexing better with indene than the thiol monomer.

EXPERIMENTAL

Materials. Indene, *p*-chlorothiophenol, *m*-methylthiophenol, *p*-methoxythiophenol, cumylhydroperoxide, potassium persulfate, galvinoxyl, phenyl N-t-butylnitrone.

Indene and *m*-methylthiophenol were distilled under vacuum. *p*-Chlorothiophenol was recrystallized from aqueous EtOH; *p*-methoxythiophenol was prepared by the reduction of *p*-methoxybenzenesulfonyl chloride with Zn dust[43] and distilled under reduced pressure, b.p. 90° (5 torr), lit.[44] 89–90° (5 torr). Cumyl hydroperoxide was titrated with $Na_2S_2O_3$ in isopropyl alcohol using the method of Siggia.[45] Galvinoxyl was prepared by the oxidation of methylenebis-(2,6-di-t-butyl) phenol with lead dioxide in diethyl ether.[46] Reagent-Grade potassium persulfate was purchased from Fisher Scientific Company. Phenyl N-t-butylnitrone,[47] m.p. 73–75°, was purchased from Eastman Kodak Company and used as such.

Cooxidation experiments. The results of representative experiments are summarized in Tables 1-7. The procedures used in the study of the different experimental variables are described below. The following method of calculating yields and conversions was used:

If a = The initial limiting concentration of thiol or indene
b = Total moles of isolated cooxidation products and
c, d, etc. = Moles of products other than the cooxidation products

Then the cooxidation yield $= b/(a - c + d + \cdots) \times 100\%$ and the cooxidation conversions $= b/a \times 100\%$. The yields of products other than the cooxidation products are calculated on the basis of the initial limiting concentration of thiol or indene.

Thus the "cooxidation yield" reflects the formation of the cooxidation products based on the limiting concentration of the reactants that are not accounted for by the isolated substances other than the cooxidation products. Theoretically, the cooxidation yield could be 100% if the fate of the initial amounts of the reagents are accounted for, and values lower than 100% signify either an incomplete reaction or the failure to isolate some of the reaction products.

On the other hand, "cooxidation conversion" simply represents the degree to which the limiting initial amounts of the reagents are converted to the cooxidation products regardless of what may have become of the remaining amount of the reagents. The yields and conversions of a number of duplicate experiments gave good agreement with the representative experiments cited in Tables 1-7.

a. *Thermal cooxidation experiments.* Equimolar amounts of freshly distilled indene and thiol were dissolved in hexane (*ca* 0.25–0.30 molar both in indene and in thiol) and the solution was maintained at constant temperature by means of an ice water bath for 0° or by using a Haake circulator. The reactions at 66° and 99° were done in refluxing hexane and isooctane, respectively. An ethylene glycol bath was used for temps below 0°. Oxygen was bubbled through the mixture continuously. All thermal cooxidation reactions were allowed to go for 48 hr. At that time the mixture was stirred with a 10% soln of sodium thiosulfate and filtered to remove any solid product. The hexane solution was separated from the thiosulfate solution and and washed first with a NaOHaq to remove any unreacted thiol and then with water. The hexane layer was separated, dried over Drierite and the solvent was evaporated. The products of the reaction mixture were separated as described below.

The comparative TOCO experiments to test the distribution of *cis* and *trans* products as a function of the thiol substituent (Table 8) were carried out at room temp. by stirring an equimolar soln of thiol and indene in ligroin under an atmosphere of O_2 until its absorption ceased. The mixture was allowed to stand for 2-3 days in order to insure the decomposition of the hydroperoxides, the resulting ppt was filtered off, washed with ligroin, and then a representative sample was subjected to column chromatography using an approximately 300:1 ratio of silica gel and sample. The column chromatography was monitored by means of TLC.

(b) *Thermal cooxidation in the presence of sodium thiosulfate.* Equimolar amounts of freshly distilled indene and *p*-chlorothiophenol were dissolved in hexane (*ca* 0.3 molar in indene and in thiol) and introduced into a Morton flask fitted with a mechanical stirrer. 10% $Na_2S_2O_3$ (110 ml) was added to the hexane soln of indene and thiol. Oxygen was bubbled through the mixture continuously. After a period of 48 hr, the hexane layer was separated from the thiosulfate soln and washed with water. Any unreacted thiol was removed by washing the hexane soln with a dil NaOHaq. The hexane soln was again washed with water, dried over Drierite, the solvent evaporated and the products separated as described below.

(c) *Experiments in the presence of cumyl hydroperoxide.* Indene (0.0230 mol), thiol (0.0230 mol) and cumyl hydroperoxide (0.0460 mol) were dissolved in 150 ml hexane and stirred at the desired temp. for 48 hr. O_2 was bubbled through the mixture continuously. The mixture was worked up as described above. The products of the mixture were separated as described below.

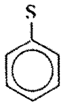
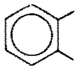
(d) *Cooxidation experiment in the presence of sodium tetrathionate.* Indene (0.0460 mol), and *p*-chlorothiophenol (0.0460 mol) were dissolved in 150 ml hexane. A soln of sodium tetrathionate (*ca* 10%) was added to the hexane soln. (Sodium tetrathionate was made in soln by titrating a soln of $Na_2S_2O_3$ in

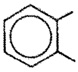
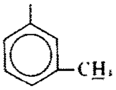
Table 9. Representative separation (Exp. No. 22)

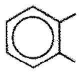
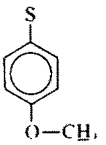
Fractions[a]	% Benzene in eluent	TLC spots[b]	R_f value[c]	Weight (g)[d]	Remarks	Product(s)[i]
Hexane wash[e]		none				
Benzene wash[f]	100	none				
1–6	75	none				
7–21	75	1	0.96	0.1943	white crystals mp 88–90°C	anti-Markovnikoff addition product
22–28	75	none				
29–50	50	1	0.86	0.1100	white crystals mp 110–111°C	*trans*-hydroxy sulfide
51–55	50	none				
56–75	50 25	1	0.70	0.0915	white crystals mp 97–98°C	*cis*-hydroxy sulfide
76–88	25	none				
89–98	0[g]	1	0.61	0.0991	white crystals mp 158–60°C	*trans-syn*-hydroxy sulfoxide
99–101	0[g]	2	0.61 0.52	0.0427	white crystals	mixture of isomers
102–131	0[g]	1	0.52	0.2966	white crystals mp 148–50°C	*trans-anti*-hydroxy sulfoxide
132–137	0[g]	none				
138–150	0[g]	1	0.40	0.1545	white crystals mp 172–73°C	*cis-anti*-hydroxy sulfoxide
Ethyl acetate wash[h]						

[a] Fractions of 25–30 ml each. [b] TLC on silica plate. [c] R_f values using 100% ethyl acetate. [d] Weight of reaction mixture used was 1.000 g. Total weight of products isolated from chromatography was 0.9887 g. [e] 500 ml hexane. [f] 500 ml benzene. [g] 100% ethyl acetate. [h] 500 ml ethyl acetate. [i] The products described refer to the 1-hydroxy-2-*p*-chlorophenylmercaptoindane system.

Table 10. NMR chemical shift values (in DMSO-d_6) of the cooxidation products obtained from idene and *p*-chloro, *m*-methyl, and *p*-methoxy-substituted thiophenols (Solvent is DMSO-d_6 unless specified otherwise; TMS is used as internal standard)

Subst.	Comp.*				$\mathrm{C}\genfrac{}{}{0pt}{}{\mathrm{OH}}{\underline{\mathrm{H}}}$	$\mathrm{C}\genfrac{}{}{0pt}{}{\mathrm{H}}{\underline{\mathrm{OH}}}$	$\mathrm{C}\genfrac{}{}{0pt}{}{\mathrm{S}}{\underline{\mathrm{H}}}$	$\mathrm{C}\genfrac{}{}{0pt}{}{\underline{\mathrm{H}}}{\underline{\mathrm{H}}}$
p-Cl	THS^{b}		δ7.5	7.2	4.95 (t) J = 6.5 cps	5.8 (d) J = 6.5 cps	3.85 (g)	3.05 (m)
		$\delta_{\mathrm{CDCl_3}}$	7.3	7.2	5.0 (d) J = 6.5 cps	3.55 (s)	3.75 (q)	2.95 (m)
p-Cl	CTS^{c}		δ7.6	7.1	3.3 (t) J = 6 cps	3.42 (d) J = 6 cps	3.8 (q)	2.9 (m)
		$\delta_{\mathrm{CDCl_3}}$	7.5	7.1	3.2 (d) J = 6 cps	3.15 (s)	3.6 (q)	2.8 (m)
p-Cl	TSs^{d}		δ7.7	7.2	5.35 (t) J = 6 cps	6.05 (d) J = 6 cps	3.6 (q)	3.0 (m)
		$\delta_{\mathrm{CDCl_3}}$			$\delta_{\mathrm{CDCl_3}}$ 5.6 (d) J = 6 cps	3.8 (s)		
p-Cl	TSa^{e}		δ7.7	7.2	5.4 (t) J = 6 cps $\delta_{\mathrm{CDCl_3}}$ 5.7 (d) J = 6 cps	6.1 (d) J = 6 cps 3.7 (s)	3.6 (q)	3.0 (m)
p-Cl	CSa^{f}		δ7.7	7.2	5.3 (t) J = 5.5 cps $\delta_{\mathrm{CDCl_3}}$ 5.5 (d) J = 5.5 cps	6.05 (d) J = 6 cps 4.5 (s)	3.7 (q)	3.0 (m)

Subst.	Comp.*					$\mathrm{C}\genfrac{}{}{0pt}{}{\mathrm{OH}}{\underline{\mathrm{H}}}$	$\mathrm{C}\genfrac{}{}{0pt}{}{\mathrm{H}}{\mathrm{O}\underline{\mathrm{H}}}$	$\mathrm{C}\genfrac{}{}{0pt}{}{\mathrm{S}}{\underline{\mathrm{H}}}$	$\mathrm{C}\genfrac{}{}{0pt}{}{\underline{\mathrm{H}}}{\underline{\mathrm{H}}}$
m-CH_3	THS^{g}		δ7.3	7.15	2.3	4.9 (t) J = 6 cps	5.7 (d) J = 6 cps	3.8 (q)	3.1 (m)
		$\delta_{\mathrm{CDCl_3}}$	7.26	7.04	2.3	5.0 (d) J = 6 cps	3.55 (s)	3.8 (q)	2.8 (m)
m-CH_3	CHS^{h}		δ7.4	7.1	2.35	3.5 (t) J = 6 cps	3.9 (d) J = 6 cps	3.6 (q)	3.05 (m)
		$\delta_{\mathrm{CDCl_3}}$	7.4	7.1	2.35	3.25 (d) J = 6 cps	3.4 (s)	3.6 (q)	2.9 (m)
m-CH_3	TSs^{i}		δ7.45	7.2	2.4	5.4 (t) J = 6.5 cps	6.05 (d) J = 6.5 cps	3.6 (q)	3.1 (m)
m-CH_3	TSa^{j}		δ7.5	7.2	2.4	5.3 (t) J = 6 cps	5.5 (d) J = 6 cps	3.6 (q)	3.1 (m)
m-CH_3	CSa^{k}		δ7.4	7.1	2.4	5.27 (t) J = 6 cps	5.9 (d) J = 6 cps	3.6 (q)	3.1 (m)

Subst.	Comp.*					$\mathrm{C}\genfrac{}{}{0pt}{}{\mathrm{OH}}{\underline{\mathrm{H}}}$	$\mathrm{C}\genfrac{}{}{0pt}{}{\mathrm{H}}{\mathrm{O}\underline{\mathrm{H}}}$	$\mathrm{C}\genfrac{}{}{0pt}{}{\mathrm{S}}{\underline{\mathrm{H}}}$	$\mathrm{C}\genfrac{}{}{0pt}{}{\underline{\mathrm{H}}}{\underline{\mathrm{H}}}$
p-CH_3O	THS^{l}		δ7.2		3.75	4.95 (t) J = 6 cps	5.75 (d) J = 6 cps	3.7 (q)	2.95 (m)
		$\delta_{\mathrm{CDCl_3}}$	7.05		3.75	5.0 (d) J = 6 cps	2.65 (s)	3.55 (q)	2.95 (m)
p-CH_3O	CHS^{m}		δ7.3		3.75	4.85 (d) J = 6 cps	3.65 (s)	3.55 (q)	2.95 (m)
		$\delta_{\mathrm{CDCl_3}}$	7.15		3.75	5.0 (d) J = 6 cps	2.55 (s)	3.55 (q)	2.85 (m)
p-CH_3O	TSs^{n}		δ7.4		3.8	3.15 (t) J = 6 cps	3.33 (d) J = 6 cps	3.7 (q)	2.85 (m)
p-CH_3O	TSa^{o}		δ7.4		3.8	5.4 (t) J = 6 cps	6.1 (d) J = 6 cps	3.5 (q)	2.75 (m)
p-CH_3O	CSa^{p}		δ7.4		3.8	5.3 (t) J = 6 cps	5.5 (d) J = 6 cps	3.6 (q)	2.95 (m)

*Abbreviations as noted in Table 1. All compounds gave satisfactory C, H, S analyses.

water with H_2O_2 using a dilute I_2 soln and a starch soln as an external indicator. The resulting soln was neutralized with dil HCl using phenolphthalein as indcator.) The resulting mixture was stirred at 0° for 48 hr. O_2 was bubbled through the mixture continuously. When the reaction was completed, the hexane layer was removed from the aqueous layer and worked up as described above. The products were separated as described below. The aqueous layer was collected and titrated with standard I_2 soln using starch as an indicator. Only one drop of 0.1N I_2 was required to reach the end point showing that no thiosulfate was formed from sodium tetrathionate.

(e) *Thermal cooxidation experiment in the presence of phenyl N-t-butylnitrone.* Freshly distilled indene (0.0115 mol), *p*-chlorothiophenol (0.115 mol) and phenyl N-t-butylnitrone (0.0115 mol) were dissolved in 50 ml hexane and stirred at 32° for 48 hr, while a stream of O_2 was maintained. The mixture was worked up as described above. Evaporation of the hexane soln gave 4.23 g of a solid which on separation on a silica gel column gave a 65.3% yield of disulfide and an 84.5% yield of the recovered nitrone. The conversion to cooxidation products was 21.5% of which 90.4% was the *trans*-hydroxy sufilde and 9.6% was the *cis*-hydroxy sulfide.

(f) *Photochemical cooxidation experiments.* Freshly distilled indene (0.0115 mol) and *p*-chlorothiophenol (0.0115 mol) were dissolved 75 ml cyclohexane and introduced into a 1.5 in. × 8 in. quartz tube. The quartz tube was equipped with a cold finger reaching almost the bottom, a thermometer, and a glass tube used to bubble O_2 through the mixture. The quartz tube was irradiated for 2.5 hr using a PCQ-X1 photochemical lamp that consists of four individually controlled circular lamps. The unit is equipped with a cylindrical ALZAC reflector that produces an intensity of 30,000 $\mu W/cm^2$ of 2537 Å radiation in the axis of the cylindrical cavity. The temperature of the reaction mixture was controlled to within ±3° by passsing ethylene glycol or water at the desired temp. through the cold finger. It was found that 99.9% of the thiol was consumed in 2.5 hr. After the irradiation the mixture was transferred into a separatory funnel and shaken thoroughly with a 10% $Na_2S_2O_4$aq. Any solid remaining in the quartz tube was dissolved in benzene or EtOAc and combined with the cyclohexane soln. The organic layer was separated from the thiosulfate soln and washed with water. The cyclohexane soln was then washed with a dil NaOHaq to remove any unreacted thiol and again washed with water. The soln was dried over Drierite, the solvent was evaporated and products separated as described below.

Separation of cooxidation products

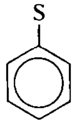
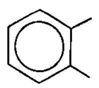
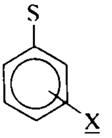
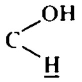
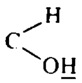
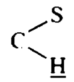
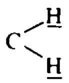
The cooxidation products were separated by column chromatography. J. T. Baker's silica was activated overnight at 120°, and 300 g was packed in a 1.5 in. × 6.5 ft column. A homogeneous mixture of 1.000 g of the reaction products was introduced into the column. The column was first washed with 500 ml hexane followed by 500 ml benzene. Then the column was eluted with various v/v mixtures of benzene and EtOAc. Finally, the column was washed with 600–700 ml EtOAc. The 150–200 fractions of approximately 25–30 ml were collected without interruptions. The fractions and washings were evaporated, individually analyzed by TLC, and the residues of the appropriate beakers were combined and weighed. The recovery of the sample usually was about 90%. A typical separation and TLC analysis is given in Table 9. TLC was done on 8 × 8 in. plates using silica gel (Grade G supplied by Woehlm) activated overnight at 110–120°. The plates were eluted with 100% EtOHc (40–45 min) and developed in an iodine chamber.

Identification and characterization of cooxidation products. The cooxidation products were characterized by elemental analysis, their IR and NMR spectra and also by chemical methods as described in previous work.[28]

The IR spectra taken in methylene chloride showed differences in the –OH stretching frequencies among the different isomers. The *trans*-hydroxy sulfides and *cis*-hydroxy sufildes showed –OH stretching frequencies at 3580 cm^{-1} indicating the absence of H-bonding. The *trans*-hydroxy sulfoxides showed stretching frequencies for free OH at 3590 cm^{-1}. The *cis* sulfoxides showed a sharp band at 3570 cm^{-1} for the free hydroxyl and broad band at 3300 cm^{-1} characteristic of intramolecularly H-bonded OH group.

The NMR spectra of all cooxidation products were taken in DMSO-d_6 soln. The chemical shift values of all isomers are given in Table 10. Chemical shift values are also reported in $CDCl_3$ solns wherever solubility permitted. The assignments of the bands are consistent with spectra reported[28] for the corresponding cooxidation products of indene and thiophenol although the compounds here are derived from substituted thiophenols. In this work, attempts were made to identify and assign the bands by deuterium

Table 11. NMR chemical shift values (in DMSO-d_6) of the hydroxy sulfones obtained by the oxidation of the cooxidation products[a]

Compound							
trans-2-*p*-Chlorophenylsulfonyl-1-indanol, m. 156–158°, R_f 0.73.	7.7	7.2		5.4 (t) J = 7 cps	5.7 (d) J = 7 cps	3.95 (q)	3.2 (d) J = 8 cps
cis-2-*p*-Chlorophenylsulfonyl-1-indanol, m. 166–167°, R_f 0.62.	7.8	7.2		5.1 (t) J = 7 cps	5.55 (d) J = 7 cps	4.2 (q)	3.25 (m)
trans-2-*m*-Methylphenylsulfonyl-1-indanol, m. 128–130°, R_f 0.71.	7.6	7.2	2.4	5.4 (t) J = 7 cps	5.75 (d) J = 7 cps	3.95 (q)	3.2 (d) J = 7 cps
cis-2-*m*-Methylphenylsulfonyl-1-indanol, m. 110–111°, R_f 0.62.	7.6	7.1	2.4	5.5 (t) J = 7 cps	5.8 (d) J = 7 cps	4.2 (q)	3.15 (m)
trans-2-*p*-Methoxyphenylsulfonyl-1-indanol, m. 129–130°, R_f 0.70.	7.45	7.45	3.85	5.35 (t) J = 7 cps	5.75 (d) J = 7 cps	3.9 (q)	3.15 (d) J = 8 cps
cis-2-*p*-Methoxyphenylsulfonyl-1-indanol, m. 133–135°, R_f 0.58	7.45	7.45	3.85	5.3 (t) J = 7 cps	5.5 (d) J = 7 cps	4.0 (q)	3.1 (m)

[a] TMS was used as internal standard. R_f values for silica gel plates and ethyl acetate as eluent. All compounds gave satisfactory C, H, S analyses.

exchange and also by analogy with the spectra obtained from 2-*p*-chlorophenylmercaptoindane and the corresponding sulfone. The bands in the above spectra were identified by deterium exchange. For example, in the case of 2-indanyl *p*-chlorophenylsulfone obtained by the oxidation of the anti-Markovnikoff adduct, its NMR spectrum in $DCCl_3$, 7.55 (q, 4), 7.05 (S, 4), 3.95 (m, 1), 3.2 (m, 4) upon treatment with NaOD in D_2O gave the deuterated sulfone in which the proton α to the *p*-chlorophenylsulfonyl group was replaced by deuterium: NMR ($DCCl_3$) 7.55 (q, 4), 7.05 (S, 4), 3.2 (q, 4). The individual isomers in the three series studied here were oxidized and in all cases, two common sulfones, the *cis* and *trans*-hydroxysulfones, were obtained. The m.p. and NMR chemical shifts of the sulfones are given in Table 11.

Kinetic experiments. Solns of known concentrations were prepared using freshly redistilled reactants under nitrogen atmosphere and chlorobenzene as solvent. The solns were stored in the dark and in a cool and O_2-free atmosphere during periods shorter than 2 weeks.

The kinetic experiments were carried out in a constant temp bath controlled by means of a Haake circulator set at 31.0 ± 0.01°. For the experiments at 0° an ice water bath was used.

The mixture was stirred by a immersed magnetic stirrer. The reaction flask was a regular 25 ml Erlenmeyer flask with an attached arm that had a 14/20 ground joint connection to a gas burette. The other end of the Erlenmeyer flask was sealed with a rubber septum through which aliquots of 9 μl were removed at desired intervals and injected into a gas chromatograph (Hewlett Packard 700) in order to measure the disappearance of indene and *m*-thiocresol. The absorption of O_2 was measured volumetrically. The amounts of indene and thiol were calculated using a previously prepared calibration curve.

A satisfactory separation of the indene and m-thiocresol peaks was obtained by using a SS Colum, 6 ft, o.d. 1/8, packed with 5% Silicone Rubber SE-30 on Chromosorb G, at 105°, with the detector and the injection port temperatures of 195°, and He flow of 30 ml per min. A typical set of results (Run nos. 95 and 64) is shown in Fig. 5. The initial rates of disappearance of indene, thiol, and O_2 were determined by means of the integrated first order rate law as shown in Fig. 5.

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