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THE THIYLATION OF OLEFINS

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INTRODUCTION

A very large number of papers in the last 15–20 years have dealt with the reactions of substances containing thiyl (SH) groups (thiols, hydrogen sulphide, thio-acids) with various unsaturated compounds (we propose the name "thiylation" for these reactions). Thanks to the high reactivity of the thiyls, multiple C–C bonds can be readily thiylated in both heterolytic and homolytic conditions. This often gives crystalline adducts which are widely used in the study of the structural and steric direction of ionic and free-radical addition.

These reactions provide a convenient method of synthesising various thiols and sulphides with properties of practical interest: regulators for polymerisation processes, vulcanisation accelerators, insecticides, drugs, etc. Some of these syntheses have acquired industrial importance. The thiylation of unsaturated compounds is also of interest, since these reactions can be regarded as models for certain processes of physiological importance, taking place in living organisms, particularly the synthesis of natural mercapto-amino-acids. A knowledge of the features of these reactions is necessary for the control of

processes of technical importance, such as the processing of petroleum, the vulcanisation of rubber, the regulation of emulsion copolymerisation by means of thiols, and many others.

Interest in this problem has led to the appearance of a number of reviews. The most complete, for its time, was a review of the addition of thiyl compounds to olefins[1]. Other reviews deal with specific topics: the addition of thiols to alkenes[2], methods of synthesising sulphides from H_2S or thiols and various olefins[3], and the homolytic addition of thiyls to olefins[4,5]. An extensive bibliography covering the literature up to 1954–1955 is given in the appropriate chapters of Reid's monograph[6].

Up to the present time, however, no attempt has been made to analyse all the available data from the viewpoint of the dependence of the structural direction of these reactions on the mechanism of addition and the structure of the unsaturated compound and addend. In the present review the thiylation of ethylenic compounds has been systematised according to this principle. The literature has been reviewed up to and including 1960 and some data published in 1961–1962 have been used.

I. THE HETEROLYTIC THIYLATION OF DOUBLE BONDS IN COMPOUNDS CONTAINING ELECTRON-DONOR GROUPS

1. Electrophilic Reactions without Catalysts; "Competition" with Free-Radical Addition

The mode of addition of electrophilic reagents to unsaturated compounds containing electron-donating substituents is governed by Markovnikov's rule. It has been suggested that these reactions either are ionic processes involving carbonium ions $CH_3\overset{+}{C}HX$ [7] or — and this is now accepted as more probable — involve preliminary formation of π-complexes[8] or 5–7-membered cyclic activated complexes[9] with addend, catalyst, and solvent. In the case where the substituent contains a hetero-atom capable of undergoing complex formation, an important part is played by "onium" complexes involving this atom[10].

Since the thiols are weak acids, we should expect that they would add on to alk-1-enes in accordance with Markovnikov's rule, but the first experimental studies gave the opposite result.

Posner studied the reactions of thiophenol and toluene-ω-thiol with a number of unsaturated ketones[11,12] and unsymmetrical hydrocarbons[13]. The reaction products, without being isolated, were converted to the sulphones, whose structure was proved by synthesis by an alternative route. Posner found that irrespective of the structure of the olefin and the reaction conditions (without catalyst, in acetic and sulphuric acids), the RS residue always appears to be attached to a terminal carbon atom. This rule for the thiols was accepted for a number of years, since it appeared to be confirmed by new experimental data. Thus, for example, it was found that thioglycollic[14] and thioacetic[15] acids react with styrene to form β-carboxymethylthio- and β-acetylthio-ethylbenzene respectively; the addition of p-thiocresol to the double bonds of divinylacetylene in accordance with this rule was used to prove the structure of the latter[16]. In 1928 it was suggested for the first time that the mechanism of the "anomalous" addition of thiophenol to styrene must differ from that of the addition to styrene of other acidic reagents which takes place in accordance with Markovnikov's rule[17]. In 1938 Posner's data were subjected to thorough examination and it was shown[18] that some of his results were erroneous. Thus thiophenol reacts with lower unsymmetrical alkenes in the presence of sulphuric acid in accordance with Markovnikov's rule. In particular, trimethylethylene gives t-pentyl phenyl sulphide and not isopentyl phenyl sulphide as reported erroneously by Posner[13]. In the absence of catalyst and with heating, the course of the addition of thiophenol to the same olefins is indeed anomalous, but it was shown simultaneously that this reaction of thiols is due to the presence of peroxy-compounds[19,20], is retarded by antioxidants, and is thus a free-radical reaction, like the anomalous hydrobromination of olefins[21,22]. Unlike the case of the reactions involving HBr, however, the free-radical addition of thiols is initiated by the smallest traces of peroxides and even by oxygen, and their normal addition to olefins usually takes place at a very low rate, due to their low acidity.

In Table 1 we have arranged the most frequently used thiyls in order of increasing acidic dissociation constant K_a, measured in aqueous or aqueous-alcoholic media[23-25]. The lowest acidity is shown by t-alkanethiols. The acidity increases, while still remaining low, for primary alkanethiols, particularly those containing β-substituents, and then increases by three orders of magnitude for thiols with α-keto- or α-alkoxycarbonyl groups and by four orders of magnitude for arenethiols and H_2S. Thioacetic acid is an acid of moderate strength, and the values of K_a for dialkylphosphinodithioic and *OO*-dialkyl phosphorothiolothionic acids are comparable to that of the second dissociation constant of sulphuric acid. The values of K_a in alcoholic medium are smaller by approximately two orders of magnitude than those in aqueous medium. Substances containing thiyl groups thus include acids with dissociation constants covering a range of about ten orders of magnitude, and it might seem that for some of these we should expect successful competition between heterolytic and homolytic addition, particularly if the process is carried out in the presence of an antioxidant. The competition between these two mechanisms is complicated, however, by the fact that the most acidic thiols, as will be shown below, are also the best suppliers of free radicals, particularly those radicals most reactive towards olefins.

Nevertheless, in recent years, particularly as a result of studies carried out in our laboratory, a number of examples have been found of the autocatalytic electrophilic thiylation of ethylenic compounds having a nucleophilic double bond.

The normal addition of alkane- and arene-thiols to alkenes without catalyst requires severe conditions. Thus in the presence of 5 mole % of hydroquinone, which eliminates the homolytic reaction, no addition of thioglycollic acid to styrene or isobutene is observed at room temperature[20]. When ethanthiol and propene, or thiocresol and tridecene, free from peroxides but containing no antioxidants, are subjected to prolonged heating at 150°, a mixture of normal and anomalous products is obtained[19]. When heated in an autoclave to 150°–200°, hydrogen sulphide adds on slowly to lower alkenes in accordance with Markovnikov's rule[36]. This reaction, however, possibly involves catalysis by metal sulphides formed on the walls of the autoclave; it has been shown that such sulphides lead, for example, to the preferential formation of propane-2-thiol from propene and H_2S.[37] Dialkylphosphinodithioic and *OO*-dialkyl phosphorothiolothionic acids, which have a

TABLE 1. Acid dissociation constants of thiyl compounds RSH

R	K_a	Solution	Temperature, °C	Method of measuring pH*	References
t-C_5H_{11}—	$6.2\cdot10^{-12}$	aqueous	20±1	*a*	23
t-C_4H_9—	$8.9\cdot10^{-12}$; $7.3\cdot10^{-12}$	»	20±1	*b*; *a*	23
	$0.2\cdot10^{-12}$	80% aqueous alcohol	20±1	*c*	24
iso-C_3H_7—	$2.5\cdot10^{-11}$	aqueous	20±1	*c*	25
n-C_4H_9—	$2.21\cdot10^{-11}$; $1.65\cdot10^{-11}$	»	20±1	*b*; *a*	23
	$0.4\cdot10^{-12}$	80% aqueous alcohol	20±1	*c*	24
n-C_3H_7	$2.26\cdot10^{-11}$; $1.50\cdot10^{-11}$	aqueous	20±1	*b*; *a*	23
	$2.52\cdot10^{-11}$; $2.30\cdot10^{-11}$	»	20±1	*b*; *a*	23
	~$1.30\cdot10^{-11}$	»	20±1	*d*	26
C_2H_5—	$3.16\cdot10^{-11}$	»	20±1	*a*	27
	$1.10\cdot10^{-12}$	80% aqueous alcohol	20±1	*b*	24
	$3.98\cdot10^{-11}$	aqueous	—	*c*	25
$HOOCCH_2$**	$3.71\cdot10^{-11}$; $3.98\cdot10^{-11}$	»	20±1	*a*; *c*	27
CH_2=CH—CH_2—	$1.1\pm0.4\cdot10^{-10}$	»	25±1	*d*	26
$HOCH_2CH(OH)CH_2$—	$2.2\cdot10^{-10}$	—		*a*	28
	$3.09\pm0.05\cdot10^{-10}$	aqueous	25±1	*a*	26
	$3.02\cdot10^{-10}$	»	25±1	*a*	29
	$3.74\cdot10^{-10}$	»	25±1	*a*	26
$HOCH_2CH_2$—	$3.31\cdot10^{-10}$; $2\cdot10^{-10}$	»	20±1	*c*; *a*	27
	$2.32\cdot10^{-10}$	»	—	*c*	25
$C_6H_5OCH_2CH_2$—	$4.15\cdot10^{-10}$	»	25±1	*a*	26
$C_6H_5CH_2$—	$3.75\pm0.18\cdot10^{-10}$	»	25±1	*c*	26
	$1.58\cdot10^{-12}$	80% aqueous alcohol	20±1	*c*	24
$NH_2CH_2CH_2$—	$4.47\cdot10^{-9}$; $7.97\cdot10^{-9}$	aqueous	20±1	*c*; *a*	27
	$2.52\cdot10^{-9}$	»	25±1	*a*	29
	$5.01\cdot10^{-9}$	»	23±1	*c*	30
	$5.01\cdot10^{-9}$	»	25±1	*a*	29
$HOOCCHCH_2$—	$2.95\cdot10^{-9}$	»	23±1	*c*	30
NH_2	$4.79\cdot10^{-9}$	»	20±1	*c*; *a*	27
	$1.6\cdot10^{-8}$	»	25±1	*a*	29
$C_2H_5OCOCH_2$—	$1.17\cdot10^{-8}$; $1.11\cdot10^{-8}$	»	25±1	*c*; *a*	26
	2.10^{-8}	»	20±1	*a*	27
CH_3OCOCH_2—	$1.58\cdot10^{-8}$	»	25±1	*a*	29
CH_3COCH_2—	$1.37\cdot10^{-8}$	»	25±1	*a*	26
H***	$9.5\cdot10^{-8}$	»	25±1	*c*	31
p-$CH_3C_6H_4$	$9.3\cdot10^{-8}$	48% aqueous alcohol	25±1	*a*	32,33
	$3.0\pm0.8\cdot10^{-7}$	aqueous	25±1	*c*	26
	$1.66\cdot10^{-8}$****	»	20±1	*a*	27
C_6H_5—	$3.2\cdot10^{-7}$	»	—	*c*	25
	$1.76\cdot10^{-8}$	48% aqueous alcohol	25±1	*a*	32,33
	$5.01\cdot10^{-9}$	80% aqueous alcohol	20±1	*c*	24
p-$CH_3SO_2C_6H_4$—	$2.69\cdot10^{-6}$	48% aqueous alcohol	25±1	*a*	32
p-$NO_2C_6H_4$—	$7.66\cdot10^{-6}$	ditto	25±1	*a*	32
CH_3CO—	$4.7\cdot10^{-4}$ *****	aqueous	25±1	*a*	34
$(C_2H_5O)_2P$(=S)—	$2.40\cdot10^{-2}$	7% aqueous alcohol	20±1	*a*	35
	$3.31\cdot10^{-3}$	80% aqueous alcohol	20±1	*a*	35
$(iso\text{-}C_4H_9)_2P$(=S)—	$1.00\cdot10^{-2}$	7% aqueous alcohol	20±1	*a*	35
	$1.55\cdot10^{-3}$	80% aqueous alcohol	20±1	*a*	35

* (*a*) Titrimetrically (with glass electrode); (*b*) calculated from data on the partition between aqueous and oil phases; (*c*) determined spectrophotometrically; (*d*) calculated from the gas solubility.

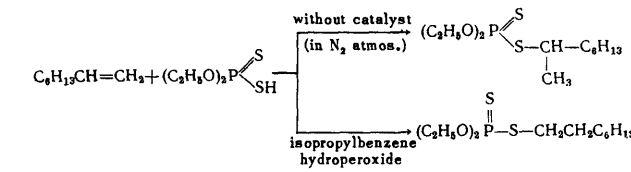
** Second acid dissociation constant, corresponding to the ionisation of the thiyl group.

*** First acid dissociation constant.

**** These data, although given in a recent paper[27], are probably erroneous since they are inconsistent with other values of K_a for this thiol.

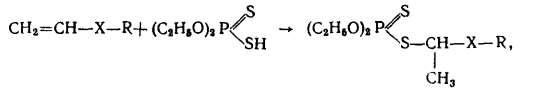
***** The only experimental data available for thioacetic acid are very old, so that the value of K_c, and not K_a, is given.

high acidity (Table 1), are still capable of undergoing exothermic electrophilic addition to olefins. Thus purified *OO*-diethyl phosphorothiolothionic acid results in an atmosphere of nitrogen with oct-1-ene, purified from peroxides, to give 87% of the normal product, whereas in the presence of isopropylbenzene hydroperoxide the anomalous product is formed exclusively, in high yield[38,39]. Olefins containing peroxides formed during storage give a mixture of the two types of product:



The addition of undistilled *OO*-dialkyl phosphorothiolothionic acids to alkenes always takes place in the normal way, due to the catalytic action of traces of sulphur–phosphorus compounds present (of the type P_4S_3)[39,40]. It is possible that analogous impurities were responsible for the normal addition of dialkyl phosphorotetrathioates $(RS)_2PSSH$ to alkenes[41].

The electrophilic thiylation of $\alpha\beta$-unsaturated sulphides and ethers is even more vigorous than that of alkenes[42-46]. Thanks to the combination of the high acidity of the addend and the marked nucleophilic character of the double bone, *OO*-dialkyl phosphorothiolothionic acids undergo quantitative exothermic addition to vinyl sulphides and ethers to give the normal adducts when the reagents are mixed in air[42-44]:



where X = O or S and R = alkyl or aryl. Adducts for which X = S and R = Ar have an acaricidic action and comparatively low toxicity towards warm-blooded animals[44,46]. Exclusively anomalous addition cannot be achieved in this case, even in the presence of free-radical initiators. Thus vinyl ethyl sulphides and *OO*-diethyl phosphorothiolothionic acid in the presence of benzoyl peroxide, azoisobutyrodinitrile, or isopropylbenzene hydroperoxide gives mixtures of 1- and *S*-(2-ethylthioethyl) *OO*-diethyl phosphorothiolothionates[43]. In this connection, the synthesis of the 2-ethylthio-derivative "M-74" and its analogues, which have a high insecticidal activity, has been found to be more conveniently carried out by alkylating salts of *OO*-dialkyl phosphorothiolothionic acids with bis-2-chloroethyl sulphide[47,48]. In the absence of atmospheric oxygen, vinyl alkyl ethers add on thioacetic acid chiefly in accordance with Markovnikov's rule[49]. The reaction is exothermic, confirming again the highly nucleophilic character of the double bond influenced by an alkoxy-group. Recently, the first example of the ready electrophilic reaction of thiophenol was discovered: its addition to vinyl lactams takes place with the exclusive formation of α-phenylthioethyl lactams, is accelerated by HCl, and, strangely, is retarded by the addition of azoisobutyrodinitrile[50].

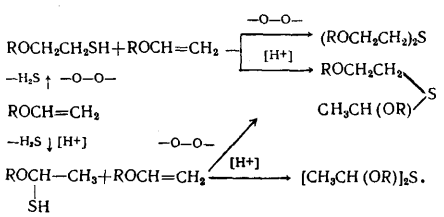
2. Thiylation in the Presence of Catalytic Quantities of Acidic Reagents

The ionic electrophilic addition of less acidic thiyls takes place in the presence of catalytic quantities of strong acids: this possibility was questioned recently in a number of papers and reviews[3,4,51].

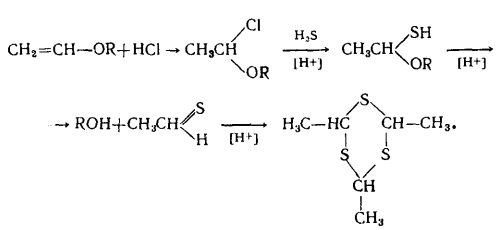
We found in our laboratory that traces of SO_2 bring about rapid and quantitative reaction between liquid H_2S and vinyl alkyl ethers with the formation of normal adducts[52-54]. In this case the true catalysts leading to the formation of the

$CH_3\overset{+}{C}HOR$ cation are apparently polythionic acids produced by the reaction between SO_2 and H_2S in the presence of traces of moisture[52,54]. The fact that SO_2 is an antioxidant and inhibits the competing free-radical reaction may also be significant. The addition of a small quantity of pyridine neutralises the action of SO_2 completely.

The competition between the ionic and free-radical addition of H_2S to a vinyl alkyl ether becomes particularly evident if this reaction is carried out in the presence of catalytic quantities of a saturated solution of HCl in anhydrous dioxan using gaseous[55,56] or liquid[54,57,58] H_2S. The dissolved HCl brings about normal addition and the traces of a peroxide of unknown structure present in the catalyst, even when the latter is prepared from thoroughly purified dioxan, bring about the anomalous reaction. As a result, all possible products were found in different proportions in the reaction mixture:

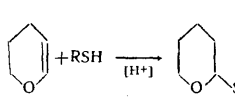


By varying the reaction conditions, particularly the quantity of catalyst, it is possible to obtain either exclusively the anomalous di-(2-alkoxyethyl) sulphides and 2-alkoxyethanethiols or mixtures of 2,2′- and 1,2′-isomeric sulphides or mixtures of all three of their isomers. The composition of the mixtures was determined titrimetrically, since it was found that sulphides and thiols containing α-alkoxy-groups, unlike ordinary sulphides and thiols, are decomposed quantitatively by mercuric chloride with the liberation of HCl.[54,59] When the reaction is carried out in a strongly acidic medium (for example by saturating the cooled vinyl ether first with HCl and then with H_2S), the chief product is 1,3,5-trimethyl-2,4,6-trithiane, whose formation is explained as follows[60,61]:



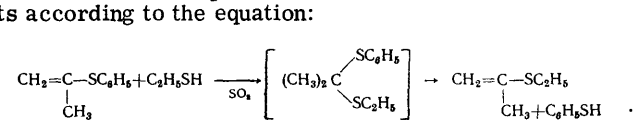
Traces of SO_2 also bring about the exothermic addition of alkanethiols[62] and thioacetic acid[49] to vinyl alkyl ethers with the formation of monothioacetals or thioacylals. The same catalyst has been used for the normal thiylation of vinyl aryl ethers, including ethers of halogenophenols[63-65].

The preparation of monothioacetals from vinyl ethers and thiols in the presence of $SOCl_2$ (0.1–0.2%)[66] or 1-chloroethyl methyl ether (1–2%)[67] has been recommended. Traces of HCl in an anhydrous medium bring about the formation of α-alkylthiotetrahydropyrans from dihydropyrans and thiols[68,69]:

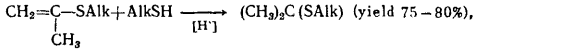


In the presence of trichloroacetic acid or 1-chloroethyl methyl ether, dithiols react with divinyl ethers to give polythioacetals[70]. Vinyl ethyl sulphide, which has a less nucleophilic double bond and slightly greater affinity for free radicals than vinyl ethyl ether[43,71], reacts with ethanethiol (traces of SO_2) to give a mixture of normal and anomalous adducts[43,72].

When 5% hydroquinone is added, the diethyl thioacetal is formed almost exclusively. When heated with ethanethiol in the presence of SO_2, 2-phenylthiopropene apparently reacts according to the equation:



The intermediate thioketal could not be isolated[73,74], whereas in the 2-alkylthiopropene series exothermic addition of thiols under the influence of traces of HCl has been observed[73,75]:



where Alk = C_2H_5, C_3H_7, or C_4H_9.

Other examples of this type of catalytic reaction include several processes, described chiefly in the patent literature, for the thiylation of branched alkenes in the presence of small quantities of HF, BF_3, etc. These are considered in the next section.

3. Thiylation in Strong Acids and in the Presence of Friedel–Crafts Catalysts

Electrophilic thiylation can be brought about by successive treatment of an alkene with a large amount of strong acid and a thiol. In this case the reaction apparently involves alkylation followed by exchange of the acid residue.

A method has been described for the synthesis of thiols and sulphides from alkanesulphonic acids[76]. In concentrated or aqueous H_2SO_4 or CH_2COOH unsymmetrical alkenes add on thiols in accordance with Markovnikov's rule, whereas H_3PO_4, because of its low acidity, does not prevent the anomalous addition[18]. Secondary and tertiary thiols and sulphides have been prepared many times from alkenes and cycloalkenes in H_2SO_4. Thus 1-methylcyclohexane-1-thiol and 2-methylpentane-2-thiol were prepared by treating the corresponding olefins with H_2SO_4 and toluene-ω-thiol, with subsequent removal of the benzyl group by the action of Na in liquid NH_3.[77]

The tertiary thiol from 2,6-dimethyloct-2-ene was prepared in analogous fashion[78]. The following additions take place in accordance with Markovnikov's rule in H_2SO_4: thioglycollic acid to a number of terpenoid hydrocarbons[79], thioglycollic acid and thiophenol to methylcyclohexene[80], and 3-oxopentane-1,5-dithiol to unsymmetrical alkenes[51].

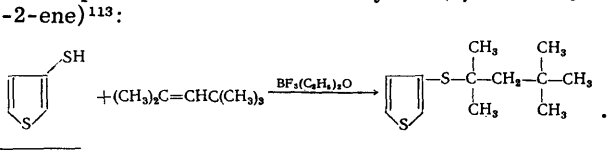
There are also a number of reports, chiefly in the patent literature, on the reaction of alkenes and terpenoid and other hydrocarbons with H_2S or thiols in the presence of H_2SO_4 and other acidic catalysts (P_2O_5, $ZnCl_2$, benzenesulphonic acid); in most cases the structure of the adducts was not proved[81-86]. Technical benzene[87] and petroleum cracking-distillates[88] are enriched with thiols during refining, as a result of reaction between the H_2S and olefins present catalysed by washing with H_2SO_4.

There are many patents† on reactions of branched alkenes with H_2S in the presence of various homogeneous and heterogeneous catalysts of the alkylating type. Tertiary thiols obtained in this way from cheap raw materials (the lower polymers of the propene–isobutene fraction from petroleum gases containing $C_{12}-C_{18}$) have been widely used as polymerisation regulators for styrene–butadiene rubber[89], corrosion inhibitors, and starting materials for the preparation of thioacetals, disulphides, etc., and used as vulcanisation accelerators, oil additives, and insecticides[90]. Reaction in a slight excess of H_2S (1.5 : 1 or 2 : 1 with respect to the alkene) gives chiefly the tertiary thiol, with almost no thioether formation. This is probably due to the marked difference in the acidities of the tertiary thiols and H_2S (Table 1).

H_2S reacts with alkenes to give secondary and tertiary thiols at comparatively low temperatures (from -70° to 0°) in the presence of HF, BF_3, and the chloride and fluorides of Al, Be, Zn, B, P, As, Sn, Ti, and Sb.[91,92] Thiols are formed when a mixture of liquid H_2S and triisobutylene in the ratio ~2 : 1, containing 1.7% BF_3, is passed through a steel coil at -30°;[93] BF_3 containing traces of HF brings about the formation of tertiary thiols from alkenes at -40° and below[94]. Tertiary thiols or their mixtures with sulphides are obtained by passing a mixture of H_2S and BF_3 through a column containing pumice, into which the alkene is introduced simultaneously[95], or by cooling their mixtures in a closed vessel. Substances recommended as catalysts include 80% aqueous HF (in this case a continuous process is described[96]) and BF_3 complexes such as $BF_3.(C_2H_5)_2O$, $BF_3.H_2O$, and $BF_3.H_3PO_4$.[97-101] H_2S adds on to propene tetramers at 0°–5° in the presence of 5–15% of $BF_3.(C_2H_5)_2O$, $BF_3.CH_3COOH$, or $BF_3.C_2H_5OH$ [102] (or in the presence of $BF_3.H_2O$ formed on introduction of moist H_2S [103]); thioglycollic acid or its esters undergo this addition in the presence of $ZnCl_2$, $AlCl_3$, or BF_3.[104] The reaction between alkenes and thiols on treatment with liquid HF has been proposed for the desulphurisation of petroleum fractions[105].

Other patents[106-115] recommend the use of various catalysts such as $AlCl_3$, $SnCl_4$, etc. The various factors influencing the reaction of H_2S with alkenes in the presence of $AlCl_3$ or a mixture of $AlCl_3$ and anhydrous HCl have been discussed in detail[106-108]. In the presence of this catalyst at 0°, H_2S and triisobutylene give t-dodecanethiol; at 50°–80°, as a result of depolymerisation, t-butanethiol and isooctanethiol are formed[109]. $AlCl_3$ in anhydrous medium completely inhibits the action of alkene peroxides, present in the reaction medium, in their reactions with H_2S and primary and secondary thiols[110].

$AlCl_3$, $BF_3.HF$, CuCl, etc. catalyse the formation of sulphides from alkenes and alkane- or arene-thiols, when equimolar quantities of the reagents are used, and the formation of alkanes if an excess of the thiol is used[111]. In the presence of $AlCl_3$ or BF_3 thiophenols or thiocresols add on to both double bonds of 2,5-dimethylhexa-2,6-diene according to Markovnikov's rule[112], whereas boron trifluoride-etherate brings about the following reaction between thiophene-3-thiol and diisobutylene (2,3-dimethylbut-2-ene)[113]:



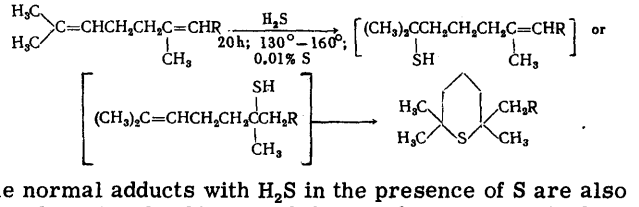
† Only the most important are cited here.

The thiylation of alkenes under the influence of strong Lewis acids takes place much more readily with branched alkenes than with normal primary alkenes, evidently due to the electron-donating effect of the alkyl groups. Thus ethylene, when passed with H_2S through a packed column (catalyst HF or BF_3), gives 17.7% C_2H_5SH and 1.3% $(C_2H_5)_2S$, whereas triisobutylene gives 75% $C_{12}H_{25}SH$.[116] These differences in reactivity make it possible to use the reaction of H_2S with mixtures of alkenes to separate tertiary alkenes, which form tertiary thiols, from primary and secondary alkenes, which do not react under the experimental conditions[117]. Thus $C_{12}-C_{18}$ sulphonic acids at 30°–60° bring about the formation of up to 98% tertiary thiols from H_2S and tertiary alkenes, whereas primary alkenes react only at 100°–120° and give the sulphides[118].

4. Thiylation in the Presence of Elementary Sulphur

Jones and Reid[19] showed that the addition of thiols and H_2S to alkenes takes place in accordance with Markovnikov's rule when the reagents are heated with elementary sulphur (150°–180°, 10–15% S). Even better results are obtained when ethyl tetrasulphide, which is readily miscible with organic substances, is used as sulphur donor. Under these conditions, the lower alkenes (ethylene and propene) reacted with H_2S to give chiefly sulphides and small amounts of thiols, isobutene and cyclohexene gave chiefly thiols, and the addition of thiophenol to all alkenes took place in accordance with Markovnikov's rule[19]. This method was subsequently used by many workers. Thus when ethanethiol was heated with allyl alcohol in a sealed tube (120°, 67 h, 2% S), the chief product was 2-hydroxyethyl isopropyl sulphide (59%); 5% of the anomalous 3-hydroxy-n-propyl ethyl sulphide was obtained simultaneously[119]. When the same alcohol was heated with monothioethylene glycol or thiophenol (3% S), however, the normal adducts were formed exclusively[120,121]. Mixtures of isomeric branched alkenes and H_2S (180°, 10–20 h, 2–3% S) gave the corresponding t-dodecanethiols, which are model regulators for polymerisation[122].

Sulphur does not, however, catalyse the addition of H_2S to the more highly branched dodecene (Butlerov's triisobutylene[99]). In the presence of S (or Al_2S_3), H_2S adds on to cyclohexene and the terpenes dihydromyrcene and geraniolene[123], the reaction in the latter case being accompanied by cyclisation of the adducts:



The normal adducts with H_2S in the presence of S are also given by natural rubber and this is of importance in determining the nature of the processes accompanying its vulcanisation[123].

The mechanism of the catalysis by sulphur in these reactions possibly resembles that of the action of iodine in processes of olefin hydrohalogenation[4]. An important part is undoubtedly played, however, by the ability of sulphur to inhibit radical processes and thus to suppress the anomalous addition.

To the reactions considered above we may add the thiylation of olefins catalysed by sulphur in the presence

of bases (ammonia, hydrazine, amines). According to the patent literature, this reaction can be used to prepare sulphur-containing polymeric products and also for the vulcanisation of rubbers[124]. It has been shown for the case of cyclohexene and 2-methylpentene that branched hydrocarbons react with sulphur and diethylamine to form tertiary sulphides and disulphides. It is suggested that the reaction proceeds *via* the polar complex $[NH_2(C_2H_5)_2]^+SH^-$, which is formed from the amine and the H_2S produced in the reaction[77]. The preferential addition of H_2S to branched olefins in accordance with Markovnikov's rule is the principal stage determining the course of the Willgerodt reaction (the preparation of amides from ketones, alcohols, aldehydes, and alkenes by the action of ammonium sulphide–polysulphide)[125].

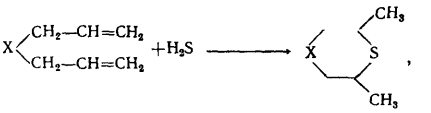
5. Thiylation in the Presence of Heterogeneous Catalysts

The mechanism of the reactions which will be considered in this section is even less clear. Interest in these compounds, which are dealt with chiefly in the patent literature, is due to the technical importance of a number of processes which have been developed. Catalysts which have been recommended at different times for the thiylation of alkenes include silica gel, fuller's earth[126-128], and metal sulphides (in conjunction with dehydrating agents[129]). Thiols react with alkenes over Ni, Fe, and Co sulphides at 35°–200° and increased pressure to form chiefly tertiary sulphides, which are converted to alkanes in excess thiol[130]. WS_2 and MoS_2 bring about the ready addition of H_2S and H_2Se to alkenes[131]. Studies have been made of the thermodynamics of the reaction of H_2S with ethylene and propene over NiS on silica gel, Ni on kieselguhr, and H_3PO_4 on kieselguhr in the range 200°–300°,[37] and the reaction of H_2S with diisobutylene in the presence of tungstosilicic acid at 230°–240°.[132] The reaction of H_2S with unsaturated cracking gases over a catalyst containing H_3PO_4 on kieselguhr at increased temperature and pressure is recommended for the removal of H_2S from these gases; valuable sulphur-containing compounds are obtained simultaneously[133]. The same catalyst brings about the reaction of considerable quantities of H_2S with mixtures of liquid unsaturated hydrocarbons, with the formation of thiols, sulphides, and other sulphur compounds; Tavtimanovskaya clay from the region of Vtoroi Baku has a slightly weaker effect. It has been suggested that these reactions are related to processes taking place in petroleum fields[134].

The reaction of H_2S with branched $C_{12}-C_{18}$ alkenes over heterogeneous catalysts forms the basis of the industrial production of polymerisation regulators of the t-dodecanethiol type[135]. It is stated in non-Soviet patents that the best catalyst is silica gel activated with a small quantity of alumina[97,136,137] or montmorillonite activated with acids[138]. The reaction can also be carried out in the presence of SiO_2 and small quantities of the oxides of metals in Groups III and IV.[136] Data have been given on the improvement of the process by decreasing the depolymerisation of the branched hydrocarbons and the improvement of methods for separating the thiols or purifying the original alkenes[136,137,139]. A continuous method for the synthesis of thiols from H_2S and homopolymers of propene with alumina–silica gel suspended in a liquid mixture of the reagents has been described[140]. Liquid H_2S adds on to the propene tetramer with the formation of up to 70% of dodecanethiol at 120°, in the presence of an aluminosilicate catalyst, which should contain not less than 9–11% Al_2O_3.[141] Under the influence of the catalyst Superfiltrol H_2S reacts with 3- and 4-vinylcyclohexenes to form monovinylcyclohexanethiols which are capable of undergoing polymerisation and copolymerisation. These compounds can also be used as regulators[142].

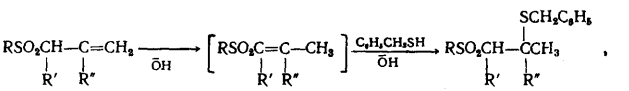
6. Thiylation in the Presence of Bases

There are comparatively few papers recommending that the thiylation of ethylenes with electron-donating substituents be carried out in the presence of bases. It has been shown that prolonged heating of allyl ether and H_2S with dibutylamine gives 2,6-dimethylthioxane in 43% yield, in addition to polymeric substances[143]. Under analogous conditions, the corresponding heterocyclic compounds are formed by the reaction of H_2S with methyl allyl ether, diallylamine[143], and diallyl sulphide[144]:



where X = O, S, NH.

In these examples the addition apparently takes place in accordance with Markovnikov's rule‡. Sulphones with allyl groups also react readily in alkaline medium, apparently in accordance with Markovnikov's rule, not only with thiols and H_2S but also with water and ammonia[145-147]. In this case, however, the action of alkali results first in allyl isomerisation to isopropenyl sulphones, which then add on nucleophilic reagents in the β-position to the electron-repelling sulphonyl group:



where R = $CH_2CH{=}CH_2$ or $C_6H_5CH_2$ and R′ and R″ = H or CH_3.

It has been stated that the thiylation of any olefinic compound appears to be catalysed by bases, irrespective of the nature of the substituent next to the double bond. Thus the addition of H_2S to various $R-CH{=}CH_2$ and $ROCH{=}CH_2$ compounds (where R = hydrogen, alkyl, aryl, alkoxycarbonyl, ether, nitrile, or heterocyclic groups) with heating and in the presence of alkalis, metal oxides, and other basic catalysts has been recommended[148,149]. Adducts of thiols with vinyl ketones, ethers, and esters ($RSCH_2CH_2OCOCH_3$, $C_6H_5SCH_2CH_2OR$, $RSCH_2CH_2COCH_3$) are obtained under analogous conditions[150]. It is stated that alkalis appear to accelerate the reaction between thiols and αβ-unsaturated sulphides with the formation of the compounds $RSCH_2CH_2SR'$.[151] The addition of H_2S [152] and thiophenols[153] to 2-vinylpyridines gives the corresponding β-(pyrid-2-yl)ethyl sulphides. The reaction proceeds spontaneously and is accelerated by the addition of piperidine or "Triton B". It is stated that Triton B is a universal catalyst for the addition of thiols to any olefin[154]. It has been shown that the reaction of allyl alcohol with toluene-ω-thiol in the presence of benzoyl peroxide or Triton B gives the same anomalous adduct, 3-benzylthiopropanol[155]. Allyl chloride also reacts in anomalous fashion with 3-oxopentane-1,5-dithiol in the presence of K_2CO_3.[156]

In all these examples, irrespective of the structure of the olefin, the thiyl adds on to the terminal carbon atom

‡ These papers, however, give no rigorous proof of the structure of the adducts.

of the double bond in the presence of alkali. In the work cited, however, no attempt was made to free the reagents from peroxides or to exclude oxygen from the reaction medium. It is therefore very probable that although true catalysis by alkalis took place in the case of unsaturated compounds containing electron-accepting groups, free-radical addition, catalysed by peroxides and unaffected by the presence of alkali, took place when electron-donating substituents were present. Direct proof of this is provided by our work on the free-radical addition of H_2S and thiols to vinyl ethers and sulphides. This will be considered in more detail below.

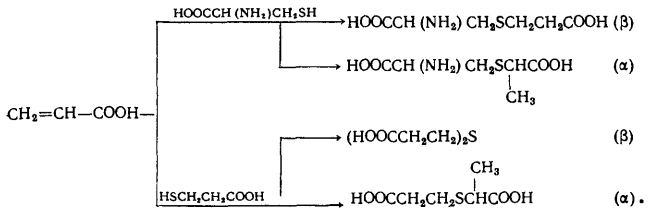
There are thus no confirmed data indicating that alkalis are universal catalysts for the thiylation of olefins.

II. THE HETEROLYTIC THIYLATION OF DOUBLE BONDS IN COMPOUNDS CONTAINING ELECTRON-ACCEPTOR GROUPS

1. General Conditions and Reaction Mechanism

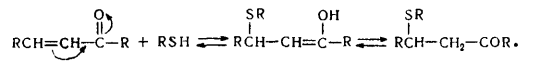
Electron-attracting groups activate a double bond towards nucleophilic attack, so that thiyls readily add on to compounds containing such groups, for the most part in the presence of basic catalysts, but sometimes in the presence of acidic catalysts if X contains carbonyl, carboxy, or alkoxycarbonyl groups. Bases which have been used include the alkalis NaOH or KOH, amines (most frequently piperidine, triethylamine, and diethylamine), trimethylbenzylammonium hydroxide (Triton B), sodium alcoholates, thiolates, and acetate, and anhydrous potassium carbonate. The acids most frequently used are HCl or a mixture of HCl and CH_3COOH. In some cases neutral substances, for example CuS, have been used. The highly nucleophilic character of the thiyl ions favours rapid thiylation, which can usually be carried out quantitatively in water or alcohol, no hydration or addition of alcohol to the double bond being observed. Thus the reaction of excess dodecanethiol in dilute alcoholic solutions with acrylonitrile, $\alpha\beta$-unsaturated esters, aldehydes, and ketones in the presence of Triton B has been proposed for the quantitative determination of these compounds; the back titration of the thiol is carried out iodometrically or amperometrically[157].

In the reactions with these olefins the thiyl residue usually enters the β-position relative to the substituent, with the formation of $RSCH_2CH_2X$, *i.e.* the order of the addition is controlled by the direction of polarisation of the double bond§. Methacrylic acid, however, reacts with cysteine, thioglycollic acid, and thiohydracrylic acids to give exclusively the β-adducts[159] only at pH > 7; in acid medium (pH ~5) a small quantity of isomers containing the thiyl in the α-position is produced[160,161].



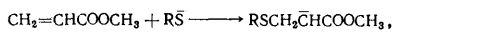
§ For substances with an "activated" C=C bond, the expression "contrary to Markovnikov's rule" is meaningless, since the rule is applicable only to olefins with electron-donating substituents[158].

It is assumed that this is due to a decrease in the selectivity of addition on going from the strongly polar acrylate ion (alkaline medium) to the much less highly dissociated carboxy-group (acid medium)[160,161]. Other analogous examples will possibly be found in the future. No deviation from the β-addition rule is to be expected in alkaline medium, however. The thiylation of $\alpha\beta$-unsaturated carbonyl compounds apparently involves reversible 1,4-addition with participation of their enolic forms[12,162]:



The corresponding adducts are capable of redissociating into their components in strongly alkaline media[162]. These theories have been extended to other groups of compounds — $\alpha\beta$-unsaturated nitro-compounds, nitriles, and sulphones — for which the reverse reaction, dissociation of the adducts, has also been observed in alkaline media.

Later it was suggested that nucleophilic addition of thiols involves an anionic chain mechanism, for example[163]:



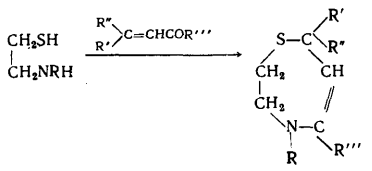
Anionic polymerisation may compete with the nucleophilic addition reaction, as observed in the reaction of excess vinyl ethyl sulphone with thiophenol in the presence of Triton B.[164]

These compounds usually give the same products $RSCH_2CH_2X$ on thiylation in both heterolytic and homolytic conditions. The ionic reactions, particularly in alkaline media, however, are exothermic and give adducts in high yield, whereas the free-radical reactions require more severe conditions and are often complicated by the formation of telomers. For the purposes of synthesis, therefore, reactions in the presence of ionic catalysts are usually employed. These will be examined below.

2. Thiylation of $\alpha\beta$-Unsaturated Ketones

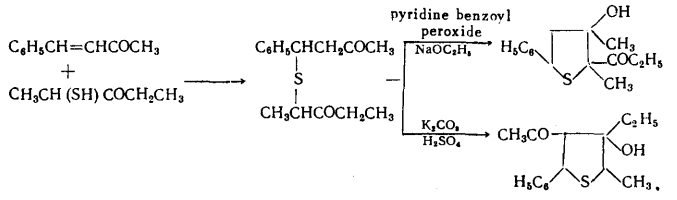
Posner showed that in a current of dry HCl in acetic acid thiols readily add on to the C=C bonds of conjugated ketones. At the same time the tendency to form thioacetals is decreased, particularly if an aryl group is present next to the keto-group[11,12]. It is much more convenient to carry out the addition of thiols to the double bond of unsaturated ketones using the basic catalysts Na ethoxide or piperidine, since under these conditions no thioacetals are formed[165]. High yields have been obtained for the adducts from thiols and substituted vinyl ketones; the substituted divinyl ketones gave di- and mono-adducts[165]. Various β-alkyl(aryl)thioketones obtained from vinyl methyl ketone, mesityl oxide, benzylidene- and dibenzylidene-acetone, benzylideneacetophenone, phorone, and various thiols with catalysis by piperidine have been proposed for use as a new type of antioxidant for fats, oils, and hydrocarbons[152,166,167]. H_2S and dithioethylene glycol add on to vinyl methyl ketone[152]. It has been shown that primary thiols, particularly those containing polar groups, react much more readily than tertiary thiols. Exothermic addition reactions take place between mesityl oxide and toluene-ω-thiol[146], vinyl methyl ketone or vinyl phenyl ketone and ethanethiol[168], and between vinyl methyl ketone and thien-2-ylmethanethiol[169] (catalyst metallic Na). Vinyl methyl ketone adds on thiols quantitatively in the presence of Triton B.[154] n-Dodecanethiol undergoes an exothermic reaction with mesityl oxide

under the influence of a current of dry HCl.[170] β-Aminoethanethiol and its derivatives add on to substances of the mesityl oxide type without catalysts, the reaction being followed by cyclisation of the adducts[171,172]:



where R = H, CH_3, C_6H_5; R′, R″, R‴ = C_2H_5 or CH_3.

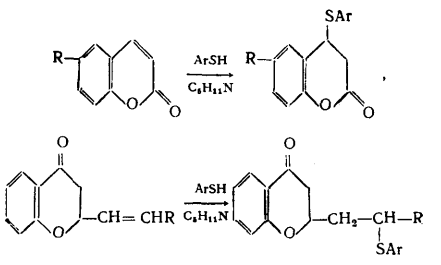
Thioglycollic acid and *p*-thiocresol react with benzylideneacetone and benzylideneacetophenone under the influence of $NaOC_2H_5$ [162] and 3-oxopentane-1,5-dithiol reacts with benzylideneacetone to give various products of the cyclisation of the primary adduct, depending on the catalyst used[173]:



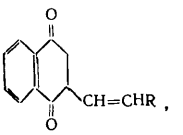
Some of the adducts obtained from substituted chalcones $R'C_6H_4CH{=}CHCOC_6H_4R'$ and alkane- or arene-thiols have an anti-tuberculosis action (catalysts $NaOC_2H_5$ [174], piperidine[175], pyridine, or diethylamine[176]; no reaction took place in the presence of HCl). The aminothiols $(C_2H_5)_2N(CH_2)_nSH$ (n = 2, 3) reacted in the form of the hydrochlorides on boiling[175]. 4-Dimethylamino-4-chlorochalcone added on *p*-thiocresol in the presence of piperidine, but no reaction took place between the chalcone and quinoline-2-thiol, since the more basic character of the addend displaced the equilibrium away from the formation of the adduct[177,178].

Protection of the thiyl group of thiophenols by addition to a 3-nitrochalcone, followed by the introduction of electrophilic groups into the nucleus and fission with $Pb(OCOCH_3)_2$ trihydrate, has been used to synthesise brominated and acylated thiophenols which could not be prepared by other methods[179]. This method of protection is not applicable to *o*-aminothiophenol, since its adduct with the chalcone readily undergoes cyclisation[180]. The method has been used to prepare various heterocyclic compounds from the thiophene analogues of the chalcones[181].

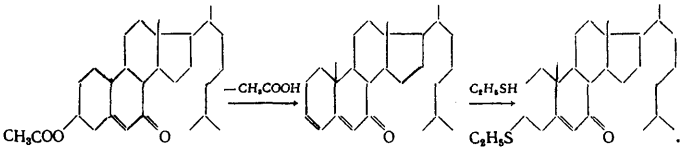
Hexamethylenedithiol and dibenzylideneacetone in benzene solution, with catalysis by piperidine or under emulsion conditions, give macromolecular products with the repeat unit $[-S(CH_2)_6SCH(C_6H_5)CH_2COCH_2CH(C_6H_5)-]$.[182,183] Arenethiols form physiologically active adducts with 6-methylcoumarin and also with 2-styrylchromone, which is a vinylogue of the chalcones:



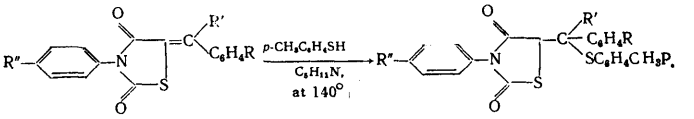
where R = H or CH_3, but do not add on to the ketone



which is a vinylogue of $ArCOCH_3$.[184] In a mixture of acetic and hydrochloric acids ethanethiol adds on to the conjugated steroid ketones 7-oxocholesteryl acetate and cholesta-3,5-dien-7-one in the 1,6-position; the expected thioacetal was not formed[185]:

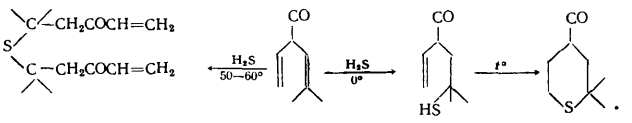


The exocyclic double bond of substituted thiazolidine-2,4-diones reacts readily with thiocresol[186]:



The addition of H_2S to carvone in the presence of ammonia in an alcoholic medium with the formation of a crystalline "hydrosulphide" was observed as early as 1849 [187] and was later used to isolate this and related unsaturated terpenoid ketones from essential oils[187-191]. The resulting crystalline ketosulphides gave the original ketone when boiled with alcoholic or aqueous alkali.

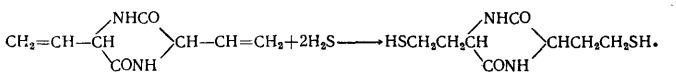
Nazarov *et al.* added H_2S to mesityl oxide and methoxyketones $CH_3OCH_2CH_2COCH{=}C(Alk){-}CH_3$ with catalysis by Na acetate in an alcoholic medium; β-ketothiols were obtained in 10–50% yield, and no ketosulphides were formed[192]. 3-Oxopentane-1,5-dithiol has been prepared by condensing H_2S into a cooled ethereal solution of mesityl oxide containing $N(C_2H_5)_3$.[193] An even simpler method involves the passage of H_2S into an alkaline aqueous-alcoholic or chloroform solution of mesityl oxide containing $N(C_2H_5)_3$,[196] at the boil[194] or with cooling to -15°.[195] In the addition of H_2S to dibenzylideneacetone[197], benzylidenemesityl oxide[198], or phorone[194] in the presence of sodium acetate or NH_3, the formation of cyclisation products of the substituted tetrahydro-γ-thiopyranone type was observed. Nazarov and Kuznetsova showed that H_2S adds on to bis-2-methylvinyl ketone only at the substituted vinyl group (with catalysis by sodium acetate in aqueous ethanol; no reaction takes place in anhydrous media); the products, depending on the reaction conditions, are the unsaturated ketothiol, its cyclisation product, or the unsaturated ketosulphide[199]:



Under analogous conditions homologues of divinyl ketone of general formula $R{-}CH{=}C(R)COCH{=}CHCH_3$ gave a range of tetrahydrothiopyranones, including the dicyclic compounds, whose stereoisomerism has been studied[200]¶.

¶ In this work[200] the original ketones were regarded as homologues of vinyl allyl ketone; later it was shown that they have the structure of substituted divinyl ketones[201].

Vinyl methyl ketone gave a mixture of the β-ketothiol and the β-ketosulphide in the presence of pyridine or 1% $NaOCH_3$ below 10°.[202] The dioxopiperazine ring causes such strong polarisation of the adjoining bonds that divinyldioxopiperazine reacts with H_2S at 0° in an alcoholic solution containing 1% CH_3COOH, according to the equation[203]:

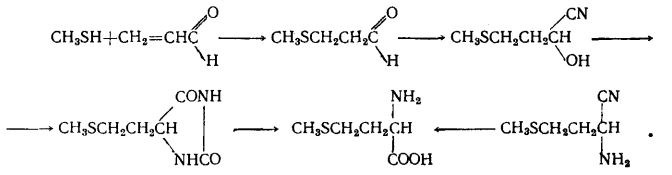


The reaction is undoubtedly heterolytic, since not only H_2S and HBr but also HCl add on in the same way.

3. Thiylation of αβ-Unsaturated Aldehydes

It was found that acrolein reacts with ethanethiol under the influence of $ZnCl_2$ in CH_3COOH to give 1,1,3-triethylthiopropane, together with a small quantity of 2-ethylthiopropanal[204].

Later, the addition of thiols to acrolein attracted the attention of many workers as one of the simplest methods of synthesising thioamino-acids, which are similar to the decomposition products of penicillin. (±)-Methionine, which is used as a beneficial additive to the food of young cattle and birds, was prepared as follows[205,206]:

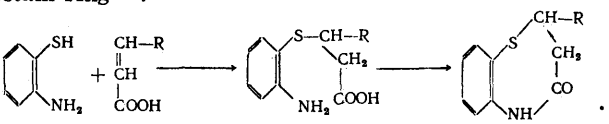


The addition of methanethiol was carried out in the presence of traces of $N(C_2H_5)_3$,[205] $Cu(OCOCH_3)_2$,[206] hydroperoxides, peroxides, polymerisation inhibitors[207], and dimethylaniline[208]. 3-Methylthiopropanal was also prepared in the vapour phase by a continuous method[209]. An analogous scheme using acrolein and the appropriate thiol [catalyst $N(C_2H_5)_3$] gave ethionine and *S*-benzylhomocysteine[210]. The reaction of acrolein with thiols is also catalysed by Amberlite IRA-400 resin in the basic form[211], piperidine[212], dimethylaniline[213], or a mixture of piperidine and organic acids[214]. Analogous syntheses were carried out using crotonaldehyde and 2-methylcrotonaldehyde, leading finally to the formation of the corresponding α-aminobenzylthio-acids[210]. Toluene-ω-thiol adds on spontaneously to crotonaldehyde at +50°, but between -50° and 0° basic catalysts are used[215]. A recommended general method involves the gradual addition of the unsaturated compound (αβ-unsaturated aldehyde, ketone, nitrile, or halogeno-derivative) to a solvent containing the thiol and catalyst [$N(C_2H_5)_3$, pyridine, piperidine] at such a rate that the temperature does not rise above 10°–20°.[216] Triton B has also been used as catalyst for the reaction of thiols with acrolein and crotonaldehyde[154,217]. The reaction of crotonaldehyde and ethanethiol under the influence of $N(C_2H_5)_3$ gives 3-ethylthiobutanal (yield 60%; exothermic reaction), whereas in CCl_4, in the presence of anhydrous HCl, the product is 1,1-diethylthiobut-2-ene, *i.e.* no addition at the double bond takes place[218]. Alkane- and arene--thiols react with crotonaldehyde and cinnamaldehyde under the influence of a small quantity of sodium dissolved in the thiol[219], and 3-oxopentane-1,5-dithiol reacts in the presence of K_2CO_3; in the latter case the adducts undergo cyclisation with the formation of 2,5-disubstituted 2-propionyltetrahydrothiophenes[173]. Crotonaldehyde slowly adds on H_2S in the presence of Triton B to give chiefly 2-thiodibutyraldehyde[220].

4. Thiylation of αβ-Unsaturated Acids and Their Esters

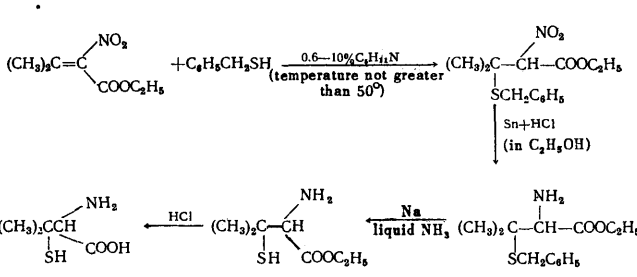
Thiophenol and ethanethiol react with acrylic, cinnamic, and α-phenyl- and *o*-, *m*-, and *p*-nitrocinnamic acids when left to stand for many days in CH_3COOH solution. Under these conditions ethanethiol does not add on to furfuracrylic or α-methylcinnamic acids or to esters of cinnamic acid[221].

The nucleophilic reactions of thiols with αβ-unsaturated acids and esters take place much more readily than the reactions with ketones and aldehydes, but are still exothermic. Piperidine catalyses the addition of thiols to methyl cinnamate[222], and Triton B gives the best yields of β-alkylthiopropionates from ethyl acrylate; a lower yield is obtained in the presence of anhydrous Na_2CO_3 or 2-hydroxyethylammonium hydroxide[154]. Triton B,[163] sodium dissolved in the thiol[168], and $NaOC_2H_5$ [170] have been used for the quantitative addition of alkanethiols to methyl acrylate. 3-Oxopentane-1,5-dithiol reacts readily with aqueous solutions of salts of acrylic and crotonic acids, and with their esters in the presence of K_2CO_3, but does not add on to esters of cinnamic acid or free acids[173]. Adducts are formed by *o*-aminothiophenol with acrylic and other unsaturated acids when the reagents are heated in an atmosphere of CO_2. These readily split off water with the formation of a lactam ring[223]:

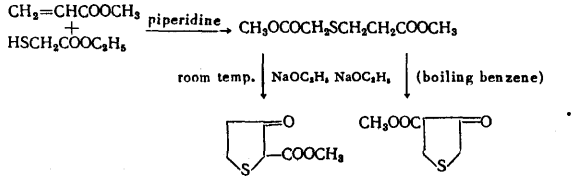


The crystalline dimethylphenylthiopropionic acids obtained in aqueous alkaline solutions from acrylic acid and isomeric thioxylenols[224], and also the 2-benzoyl-1-alkylthiopropionic acids formed under similar conditions from benzoylacrylic acid and various thiols[225], can be used for purposes of identification. β-Acetylacrylic acid reacts with thioglycollic acid in the presence of acidic or basic catalysts, or simply when the reagents are mixed, to give 2-carboxymethylthiolaevulinic acid[226].

The double bond in 2,2-dimethylacrylic acid is less reactive than that in acrylic acid. Thus H_2S reacts with the former to the extent of only 20% after 15 h at 120°, and toluene-ω-thiol to the extent of 50% after 8 h at 100°.[227] In the presence of $N(C_2H_5)_3$ neither the acid nor its esters add on H_2S or ethanethiol[193]. Esters of 1-nitro-2,2-dimethylacrylic acid are much more active in this reaction. The following methods of synthesising "penicillamine", an important intermediate in the synthesis of penicillin, and also a corrosion inhibitor, was described almost simultaneously by a number of workers[228,229]:

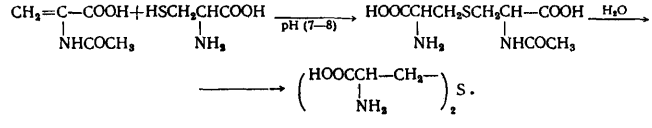


Penicillamine has also been prepared from 2,2-dimethyl--1-acetylaminoacrylic acid by the action of toluene-ω-thiol in the presence of sodium and pyridine (alcoholic medium) with subsequent removal of the benzyl and acetyl groups by sodium in liquid NH_3.[227] Keto-esters of the thiophane series are formed by the addition of esters of thioglycollic acid to esters of acrylic or substituted acrylic acids (catalyst piperidine) with subsequent cyclisation by Dieckmann's method[230,231] or directly, without isolation of the non-cyclic products, by carrying out the reaction in the presence of C_2H_5ONa.[232] The mode of the cyclisation depends on the conditions:

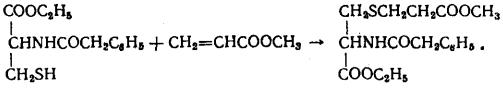


These reactions have been used for the synthesis of biotin[233]. The analogous addition of esters of thioglycollic acid to maleates and fumarates gives esters of thiophane--2,5-dicarboxylic acid[233].

Cysteine adds on to 1-*N*-acetylaminoacrylic acid in boiling aqueous solution at pH 7–8 to form lanthionine:



In this connection it has been suggested that analogous reactions are also possible during the alkaline treatment of wool, where one of the products is lanthionine. Under the same conditions, thioglycollic and thiohydracrylic acids add on quantitatively to acrylic acid[159]. The adducts formed by cysteine with methyl acrylate and benzyloxycarbonylaminoacrylic acid were obtained in an aqueous alkaline medium at pH 7–8 in an atmosphere of H_2.[234] Acylated α-amino-acids and their esters (cysteine hydrochloride and *N*-phenylacetylcysteine) add on instantaneously and quantitatively to esters of acrylic acid in a triethylamine medium which acts simultaneously as catalyst[235]:

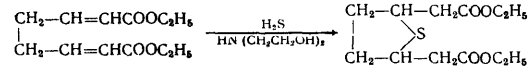


1-Nitro-2,2-dimethylacrylate gives adducts in lower yield under these conditions.

H_2S reacts readily and quantitatively with methyl acrylate in the presence of Triton B to give dimethyl 2-thiodipropionate; the reaction is strongly exothermic[220]. Methyl methacrylate does not add on H_2S, even in the presence of Triton B at 80°–90°, evidently due to steric hindrance by the methyl group[220]. H_2S reacts with butyl crotonate and other esters of αβ-unsaturated acids in the presence of anhydrous alkali metal sulphides to form chiefly the thio--diester and a small quantity of the ester thiol[236].

A number of papers have dealt with the reactions of H_2S and thiols with polybasic αβ-unsaturated acids and their esters. The kinetics of the reaction of maleic acid with thiglycollic acid, cysteine, and glutathione in aqueous alkaline solution at pH 7.4 have been studied[273]. Various esters of carboxymethylmercaptosuccinic acid have been prepared[238].

The reaction of disodium fumarate with other thiols gives crystalline alkyl(aryl)thiosuccinic acids[239]. The addition of RSH (R = alkyl or aryl) to esters of itaconic and aconitic acids is catalysed by anhydrous potassium carbonate at 30°–45°, whereas no addition is observed in the presence of benzoyl peroxide[240]. H_2S reacts smoothly with isopropylidenemalonic acid and its esters[193] with the formation, after decarboxylation, of thioloisovaleric acid. H_2S adds on readily to esters of maleic and fumaric acids at -10° in pyridine[241] or at 70°–80° with catalysis by $N(C_2H_5)_3$, piperidine, and Triton B.[242] The thiopolycarboxylic esters formed are excellent plasticisers for polymers and copolymers based on vinyl chloride. An ester of thiophane-2,5--diacetic acid has been synthesised as follows[243]:



The thiylation of vinylphosphonic acids in the presence of $NaOC_2H_5$ with the formation of the thiols $(RO)_2P(O)CH_2CH_2SH$ and sulphides $(RO)_2P(O)CH_2CH_2SR'$ [244] is a particular case of the more general reaction of "phosphonethylation"[245]. The analogous addition of RSH ($R = C_4H_9$, $C_{12}H_{25}$) under the influence of metallic sodium has been described[246].

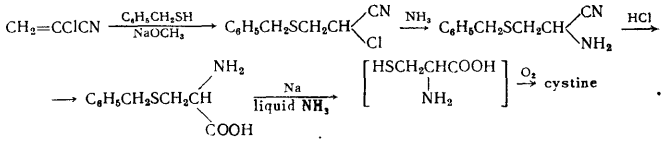
5. Thiylation of αβ-Unsaturated Nitriles†

The cyanoethylation of sulphur compounds also requires catalysis by bases. H_2S is cyanoethylated in the presence of KCN or Na_2S at 60°–80° in butanol[149], but with catalysis by $NaOCH_3$ or quaternary ammonium bases the reaction becomes exothermic[220]. The exclusive product is the dinitrile of thiodipropionic acid, from which plasticisers are readily obtained by hydrolysis followed by esterification. Alkane- and arene-thiols are quantitatively cyanoethylated in the presence of $NaOCH_3$ in dioxan[248]. Thiols, mercaptobenzothiazole, and esters of dithiocarbonic acid react in an aqueous solution of alkali, which acts simultaneously as catalyst and solvent[249], thien-2-ylmethanethiol adds on in the presence of metallic sodium[169], and 3-oxopentane-1,5-dithiol reacts in the presence of K_2CO_3.[173] With catalysis by Triton B, β-thionaphthol gives β-(2-naphthylthio)propionitrile which on saponification readily undergoes cyclisation to benzothiochromanone[250]. The reaction of diethylaminoethanethiol is exothermic and proceeds without catalyst[251]. The cyanoethylation of higher thiols in the presence of $NaOC_2H_5$ has been carried out with the aim of synthesising anti-tuberculosis compounds[252]. Under these conditions, diphenylphosphinodithioic acid gives the physiologically active $(C_6H_5)_2P(S)SCH_2CH_2CN$.[253] β-Alkylthio-acids of the type $RSCH_2CH_2COOH$ and $RSCH_2CH(CH_3)COOH$, which are active antioxidants, are prepared *via* a stage involving cyanoethylation of thiols in the presence of piperidine[254]. In the study of the comparative efficiency of different catalysts with respect to the cyanoethylation of thiophenol by the nitriles R–CH=CHCN [R = CH_3, $(CH_3)_2CH$, $(CH_3)_3C$] the best results were obtained using piperidine (or rather its salt with thiophenol) or a mixture of piperidine and Triton B. The

† Reactions of acrylonitrile described up to 1949 have already been reviewed[247].

latter by itself is a poor catalyst for the addition of thiols to substituted acrylonitriles[255]; this is confirmed by study of the reaction of 1-cyanocyclohexene with thiophenol and toluene-ω-thiol[256]. The yield of adducts obtained from acrylonitrile and various thiols in the presence of piperidine decreases in the order: RS = $C_6H_5S > C_6H_5CH_2S >$ $> HOCH_2CH_2S > t\text{-}C_4H_9S$.[257] The cyanoethylation of esters of thioglycollic acid by substituted acrylonitriles in the presence of $NaOC_2H_5$ has been used in the synthesis of biotin[232]. With catalysis by Triton B, thiols give adducts not only with ω-cyanostyrene[258] but also with *o*- and *p*-cyanostyrenes, which can be regarded as vinylogues of acrylonitrile[259]. Thiols with trialkylsilyl groups in the α-, β-, and γ-positions are readily cyanoethylated with catalysis by traces of $NaOC_2H_5$.[260]

A simple method for the synthesis of (±)-cystine from 1-chloroacrylonitrile and toluene-ω-thiol has been proposed[261]:



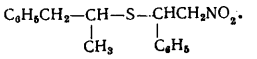
1-Chloro- and 1-bromo-acrylonitriles also react (exothermic reaction) with other alkane- and arene-thiols in the presence of sodium alcoholate in dry benzene[262].

6. Thiylation of $\alpha\beta$-Unsaturated Nitro-Derivatives

Thiols react with α-nitro-olefins in an alkaline medium more readily, and with higher yields, than their oxygen analogues, water and alcohols. Thiolates react with nitropropenes and ω-nitrostyrene in absolute alcohol with external cooling to give β-alkylthionitro-compounds in 50–80% yield, the reactivity decreasing in the order: $C_6H_5SH > C_4H_9SH > CH_3SH$.[263] The addition of thiols to these nitro-olefins proceeds to completion very rapidly in methanol or dioxan at 0°–5° in the presence of metallic sodium[264]. Dinitro-thioethers are formed by the reaction of thiols with an excess of nitro-olefins[265].

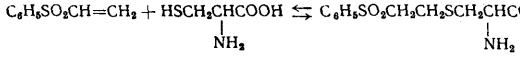
Various β-arylthiophenetylamines have been prepared with the aim of obtaining substances with antibacterial action[266] or substances for the treatment of rheumatoid arthritis and other inflammations[267]. For this purpose, use was made of the exothermic reaction between substituted thiophenols and ω-nitrostyrenes with various substituents in the ring, in the presence of piperidine: the nitro-group was then reduced to the amino-group. The adducts are stable in acid and neutral media but decompose in alkaline media to regenerate the original thiol and nitro-olefin. The passage of dry H_2S into a solution of a nitro-olefin in dioxan, cooled with ice [catalyst $N(C_2H_5)_3$], gives 2-nitroalkyl sulphides which are used as corrosion inhibitors, vulcanisation accelerators, and starting materials for the preparation of polymers of the nylon type[268]. Nitrostyrenes and nitro-olefins also add on H_2S without catalysts at moderate temperatures[264]. A convenient method for the synthesis of β-nitrosulphides related to biotin is based on the exothermic reaction between aldehydes, thiols, and nitroparaffins in the presence of piperidine; in the case of nitromethane and alkanethiols, the intermediate acyclic products are obtained in quantitative yield[269].

The reaction of the optically active 1-phenylpropanethiol or its racemate with ω-nitrostyrene in the presence of piperidine or ascaridole gives a mixture of various diastereoisomeric forms of the sulphide[270]:



7. Thiylation of $\alpha\beta$-Unsaturated Sulphoxides and Sulphones

The high reactivity of $\alpha\beta$-unsaturated sulphones towards thiyl ions was first observed in the case of divinyl sulphone. Kretov[271] ‡ first prepared this compound from bis-2-chloroethyl sulphone and showed that on boiling in the presence of traces of alkali it reacts with thiols to give various bis-2-alkyl(aryl)thioethyl sulphones. Their structure was confirmed by the fact that they were identical with the sulphones of substances previously prepared from bis-2-chloroethyl sulphide and thiolates[273]. Alexander and McCombie[272] showed that H_2S and thiophenol add on to divinyl sulphone in the presence of $NaOCH_3$. The reactivity of divinyl sulphone towards amino and thiyl groups was later studied in detail because of its genetic relationship to bis-2-chloroethyl sulphone, which for some time was considered to be the active metabolite responsible for the toxicity of bis-2-chloroethyl. Later, however, the formation of this sulphone *in vivo* was considered unlikely[274]. In the reactions of cysteins or its hydrochloride with divinyl and phenyl vinyl sulphone in aqueous $NaHCO_3$ solution, the addition involves the thiyl group[275]; at pH ~3, *i.e.* under conditions close to physiological conditions, the reaction is reversible[275,276] [this does not agree with the statements in the original papers (Ed. of Translation)]:



The crystalline adduct $SO_2[CH_2CH_2SCH_2CH(NH_2)COOH]_2$ is recommended for the quantitative determination of divinyl sulphone[274]. The reaction of divinyl sulphone with thiols depends greatly on the pH of the medium. Thus the rate of addition of cysteine is doubled when the pH is changed from 4.4 to 6.2 and the same increase in the rate of addition of 2-mercaptoethanol is observed when the pH is increased from 5.4 to 6.5.[274] In an aqueous solution of cellosolve without catalyst thiophenol adds on to divinyl sulphone at 22° to the extent of 73% in 90 min; when 0.018 mole of $N(C_2H_5)_3$ is added, the reaction becomes exothermic and is complete in 7 min. No reaction takes place without solvent and catalyst. In the presence of a drop of $N(C_2H_5)_3$, 2-mercaptoethanol adds on quantitatively and exothermally, the adduct $SO_2(CH_2CH_2SCH_2CH_2OH)_2$ being stable in alkaline solution[274].

The passage of H_2S into boiling *p*-tolyl vinyl sulphone in the presence of $NaOC_2H_5$ gives $(p\text{-}CH_3C_6H_4SO_2CH_2CH_2)_2S$, and various arenethiols in toluene give compounds of the $p\text{-}CH_3C_6H_4SO_2CH_2CH_2SAr$ series. The reaction of *o*-aminothiophenol involves the mercapto-group, the adduct being

‡ In non-Soviet literature Alexander and McCombie's paper[272], published more than a year later, is usually erroneously cited as the first example.

readily diazotised[151,277]. β-Phenylvinyl *p*-tolyl sulphone adds on thiocresolate at room temperature in ether–benzene solution to form $C_6H_5CH(SC_6H_4CH_3)CH_2SO_2C_6H_4CH_3$.[278] In the presence of traces of $N(C_2H_5)_3$ *p*-tolyl vinyl sulphone adds on thiophenol and *o*-mercaptobenzoic acid[279], and phenyl vinyl sulphone adds on thiocresol, *o*-mercaptobenzoic, and thioglycollic acids[276]. The unsaturated cyclic sulphones benzothiophen dioxide[280] and 2- or 3-sulpholenes (the latter with isomerisation to the 2-sulpholenes) are also thiylated in alkaline media with the formation of β-thiosulphones. The sulpholenes have been used to prepare insecticides, vulcanisation accelerators, etc.[281-283]

In the presence of traces of $N(C_2H_5)_3$ vinyl ethyl sulphone undergoes exothermic reaction with thiophenol, and on heating vinyl methyl sulphone and vinyl ethyl sulphone add on *OO*-dialkyl phosphorothiolothionates with the formation of $RSO_2CH_2CH_2SP(S)(OR)_2$,[284] which has insecticidal action. Thiols add on to methyl propenyl and benzyl propenyl sulphones when boiled with $N(C_2H_5)_3$ in tetrahydrofuran to form $RSO_2CH_2CH(SR'')CH_3$.[144-147] Substances with antibacterial action have been synthesised by the addition of butanethiol to vinyl methyl and vinyl phenyl sulphones by boiling with an alcoholic NaOH solution[285]. It has been shown in our laboratory that Triton B is a particularly convenient catalyst for the quantitative exothermic addition of nucleophilic reagents, especially thiols, to various αβ-unsaturated sulphones (vinyl ethyl sulphone, vinyl dicycloheptenyl sulphone, and 1,4-dialkylsulphonylbutadi-1,3-enes)[164,286,287]. Vinyl ethyl sulphone and liquid H_2S (in the presence of Triton B) in different proportions react to give mixtures of bis-2-ethylsulphonylethyl sulphide and β-ethylsulphonylethanethiol[287]. Also in the presence of Triton B vinyl ethyl and vinyl butyl sulphones give $(C_2H_5O)_2P(S)SCH_2CH_2SO_2R$, which are powerful acaricides[164,289]. Triton B has also been used for the addition of ethanethiol to vinyl ethyl sulphone with the aim of synthesising a new type of antioxidant[288].

There are many fewer data on nucleophilic reactions of thiols with αβ-unsaturated sulphoxides. These reactions are much less vigorous than those of the analogous sulphones. Thus divinyl sulphoxide does not react with thiophenol without catalyst; in the presence of $NaHCO_3$ in aqueous medium the reaction is slower than that of divinyl sulphone, and at high pH values the compound combines with 2-mercaptoethanol[272,274] or cysteine[274,290]. Vinyl ethyl, vinyl *p*-tolyl, and vinyl 8-chloronaphthyl sulphoxides add on *p*-thiocresol on prolonged boiling in the presence of $NaOCH_3$.[151,277] The yields were not given. Vinyl ethyl sulphoxide reacts with *o*-mercaptobenzoic acid in excess aqueous $NaHCO_3$, with cysteine in aqueous medium containing $N(C_2H_5)_3$, and with thioglycollic acid in the presence of $Ba(OH)_2$.[290] The comparative reactivity of unsaturated sulphones and sulphoxides towards thiols in the presence of Triton B was studied in our laboratory. Vinyl ethyl and vinyl butyl sulphoxides undergo exothermic reaction with alkanethiols and thiophenol, but the yield of adducts is lower than in the case of vinyl ethyl sulphone and the quantity of catalyst required and the duration of the reaction are greater, indicating that the nucleophilic character of the C=C bond decreases on going from the sulphone to the sulphoxide[287]. It has been shown that the reaction of ethanethiol with vinyl ethyl sulphoxide gives the β-adduct exclusively[287]. *OO*-Diethyl phosphorothiolothionic acid undergoes exothermic reaction with vinyl ethyl sulphoxide without catalyst, but the yield of acaricidal *OO*-diethyl *S*-(2-ethylsulphinylethyl)phosphorothiolothionate is low and is not increased by the addition of Triton B.[289]

8. Thiylation of Perhalogeno-olefins

Perfluoroethylene reacts readily with various alkane- and arene-thiols in the presence of sodium dioxane, dimethylformamide, or dimethylcellosolve[291]. Trifluorochloroethylene adds on alkanethiols quantitatively at room temperature with catalysis by 0.02% Triton B, 2% $N(C_2H_5)_3$, or 0.05% of the thiolate[292]. The structure of the adducts, with general formula RSC_2F_3ClH, was not proved. Knunyants and Fokin[293] have shown that the same olefin reacts with alkane- and arene-thiols when heated in an autoclave in the presence of powdered KOH for 6 h at 115°–120° to give 60–90% of $RSCF_2-CFClH$, whose structure was proved by the fact that the action of alkali gives $ClFC=CFSR$. Under the same conditions thiols readily add on to tetrafluoro- and *sym*-dichlorofluoro-ethylene[294], and perfluoropropene gives $CF_3CHF-CF_3SR$ in low yield[294]. Less extensively halogenated olefins also add on thiols in position β to the more extensively halogenated group. Thus 1,1,1-trichloropropene reacts with thiophenol, in the presence of elemental sulphur to eliminate the free-radical reaction, giving 1,1,1-trichloromethyl-3-phenylthiopropane[295]. No addition to the double bond takes place when perfluoro- and chlorofluoro--olefins are treated with thiols and excess K_2CO_3. Instead, halogen is partly replaced by SR groups with the formation of a range of monomers containing sulphur and halogen[296].

9. Thiylation of Vinylsilanes

A trialkylsilyl group next to a double bond has been assumed to acquire electron-accepting properties as a result of the interaction of the π electrons of the C=C bond and the *d*-level of the Si.[297] The nucleophilic character of the double bond of vinylsilanes is apparently low, however, since alkanethiols give 2-alkylthioethylsilanes only in low yield on prolonged boiling in the presence of the thiolate[298]. Electrophilic attack also gives β-alkylthio-compounds, for example in the reaction of vinylsilanes with *OO*-dialkyl phosphorothiolothionic acids[299]. On the other hand, allylsilanes add on *OO*-dialkyl phosphorothiolothionic acids in accordance with Markovnikov's rule[260].

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Despite the fact that the above data were obtained under the most varied conditions, so that comparison is difficult, analysis indicates that the ease of nucleophilic thiylation increases in the same sense as the electron-accepting power of the substituent. Thus it decreases on going from vinyl ketones to acids and their esters, and from αβ-unsaturated sulphones to the sulphoxides. The introduction of methyl groups in the position α to the electron--withdrawing group hinders the addition (compare the reactions of H_2S with methyl acrylate and methyl methacrylate), while the introduction of methyl groups in the β-position facilitates the reaction (for example, divinyl ketones add on H_2S chiefly at the alkylated double bond)§. Electron--withdrawing substituents in the α-position facilitate the reaction considerably (compare the reactivities of 2,2-dimethylacrylic acid and its 1-nitro-derivatives). The reactivity of the thiyl ions in these reactions apparently increases with increase in their nucleophilic character (compare the reactions with αβ-unsaturated ketones,

§ In view of this, it is difficult to understand the low reactivity of ββ-dimethylacrylic acid and its esters.

nitriles, and nitro-derivatives), but in this case it is difficult to establish definite correlations, since there are no confirmed data on the change in the nucleophilic character of these ions with change in structure[27]. The reactivity of thiols in these reactions is much higher than that of water or alcohols, in agreement with the nucleophilic character of the corresponding ions.

III. HOMOLYTIC THIYLATION

1. Mechanism and Properties of the Individual Stages of the Chain Process

From the time when Kharasch proposed a free-radical chain mechanism for the anomalous addition of first HBr [22] and then thiols[20], so many data have accumulated on these and other homolytic reactions of olefins in solution that their chain mechanism may be taken as proved, while many of their properties have been fairly well studied[5]. The homolytic addition of a thiyl to an olefin M can be broken down to the following stages:

1. Initiation $RSH \rightarrow RS^{\cdot}$, ($k_1$)
2. Attack $RS^{\cdot} + M \rightarrow A^{\cdot}$, ($k_2$)
3. Chain transfer $A^{\cdot} + RSH \rightarrow AH + RS^{\cdot}$, etc. ($k_3$)

Chain rupture is brought about by recombination

$$RS^{\cdot} + RS^{\cdot} \rightarrow RSSR; \quad A^{\cdot} + A^{\cdot} \rightarrow A_2; \quad A^{\cdot} + RS^{\cdot} \rightarrow ASR.$$

Calculation shows that reactions 2 and 3 are appreciably exothermic, and this leads to rapid propagation of the chain[5]. Its kinetic length is usually high, reaching 10^3 links and above, so that the process is characterised by steady-state kinetics. Successful kinetic studies have been carried out by the sector method[300-304], which makes it possible to find the absolute rate constants of the stages. The overall rate of the process is usually determined by the rate of chain transfer. Thus the values found for the reaction of butanethiol with pent-1-ene are $k_2 = 7 \times 10^6$ litre mole^{-1} $\times$ $\times$ sec^{-1} and $k_3 = 1.4 \times 10^6$ litre mole^{-1} sec^{-1}; [301] for the reaction of thiophenol with styrene, the values of k_2 and k_3 are 2×10^7 and 3×10^3 litre mole^{-1} sec^{-1} respectively[303].

Reactions 1 and 3 are similar in that they involve homolytic rupture of an S–H bond[5,300,305-307]. One method which has been used to compare the ease of this fission involves the reaction of different thiyl compounds with dinitropicrylhydrazyl. This method has shown that the rate of removal of H$^{\cdot}$ decreases by a factor of about 20 in the series n-$C_6H_{11}SH$ > n-C_4H_9SH > iso-C_4H_9SH > t-C_4H_9SH, whereas the activation energy remains almost unchanged[308]. The ease of removal of H$^{\cdot}$ from thiophenol is greater by a factor of several hundred than the ease of removal from butanethiol[303]. Another criterion which can be used to estimate the ease of homolytic rupture of an S–H bond is the rate of oxidation of different thiols under standard conditions. Different authors have obtained the following almost identical series of thiols arranged in decreasing order of rate of oxidation: ArSH > $HOCOCH_2SH$ > RCH_2SH > > RR'CHSH > RR'R"CSH¶; [306] C_6H_5SH > $HOCOCH_2SH$ > > CH_3SH, $C_{18}H_{37}SH$ > t-C_4H_9SH, t-$C_{12}H_{25}SH$; [307] ArSH (Ar = C_6H_5, $C_6H_5CH_2$) > RCH_2SH (R = CH_3, C_3H_7) > t-thiols (C_4H_9) > mercaptobenzothiazole[309].

¶ The rate of addition of thiols to styrene changes in the same order[306].

The acidity of the thiols changes in approximately the same order (Table 1), so that the most strongly acidic thiols are also the best donors of radicals. Similar relationships were also obtained by a method based on the determination of the constants for chain transfer by thiols in the polymerisation of styrene[5,310]: $C_6H_5SH \gg C_2H_5OCOCH_2SH >$ > primary n-AlkSH (Alk = C_4H_9, $C_2H_5OCH_2CH_2CH_2$, C_5H_{11}, $C_{12}H_{25}$, C_8H_{17}) > t-AlkSH (Alk = C_4H_9, C_8H_{17}) > mercaptobenzothiazole.

Although the overall rate of the addition reaction, as shown above, is determined by the rate of transfer, comparison of data on the reactions of different thiols with the same olefin, or of different olefins with the same thiol, can be used to estimate the comparative ease of attack, on which the possibility of combining with a radical depends. Interesting semiquantitative results were obtained by the method of competing reactions. The available data show good agreement with the theory of the electron-accepting character of the thiyl radical. Electron-donating groups in the radical itself decrease its reactivity towards a double bond (the reactivity decreases, for example, from primary to tertiary radicals[5]). On the other hand, the presence of electron-withdrawing groups in the thiol increases the reactivity of the radical†; the reactivity increases, for example, in the order iso-$C_5H_{11}SH$ < $HOCOCH_2SH$ < < C_6H_5SH < CH_3COSH < $CH_2ClCOSH$ < $CHCl_2COSH$ < < CCl_3COSH.[80,311] Thioglycollic acid, its esters, and thiols with β-substituents, such as 2-mercaptoethanol, ethanedithiol, and bis-2-mercaptoethyl sulphide[312] are very reactive. On the other hand, olefins with electron-withdrawing substituents have a low reactivity towards thiyl radicals; for example, vinyl ethyl sulphone and sulphoxide[164,237] add on thiophenol very slowly at 20°–60° in the presence of azoisobutyrodinitrile. The method of competing reactions has shown that the $\dot{S}CH_2COOH$ radical combines much more readily with α-methylstyrenes with electron-donating groups (p-CH_3O, CH_3) in the nucleus, than with unsubstituted α-methylstyrene or with p-fluoromethylstyrene[313]. The same method has been used to determine the relative reactivity of the dodecanethiyl radical towards various compounds containing a double bond, using oct-1-ene as standard[314]. The observed relationships (Table 2) in general confirmed the increase in the rate of reaction of radicals with olefins having electron-donating substituents and the decrease in the rate of reaction with olefins having electron-accepting substituents. The method of competing reactions has also shown that the C = C bond in the conjugated bicycloheptene is approximately 45 times more reactive towards the p-thiocresyl radical than the double bond in cyclohexene[315].

The thiyl radical, like other free radicals[316], always attacks the terminal carbon atom of a vinyl double bond. It is assumed that this mode of addition is due to the lower activation energy necessary for the formation of a secondary radical during attack[317]. Similar explanations have been put forward for the fact that the rate of attack by thiyl radicals on terminal C = C bonds is approximately 50 times that on internal double bonds, while the corresponding rate

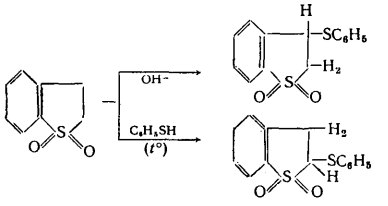
† Thiyls with electron-withdrawing groups are generally also stronger acids (Table 1), although there are exceptions to this rule: for example, the values of K_a for thioglycollic acid and alkanethiols are of the same order of magnitude. It is quite clear, however, that the high activity of these thiols in homolytic addition reactions cannot depend on the ease of removal of a proton, as was previously assumed[1,80,311].

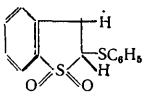
TABLE 2. The relative reactivity (a) of olefins towards dodecanethiol (60°, 0.2% azoisobutyrodinitrile)[314].

Olefin	a	Olefin	a
Styrene	17±3	Allylbenzene	0.99±0.08
β-Methylstyrene	5.5 ±0.4	Vinyl acetate	0.82±0.04
Vinyl butyl ether	3.9 ±0.4	Allyl chloride	0.72±0.04
Methyl methacrylate	2.4 ±0.2	Cyclopentene	0.64±0.04
Methyl acrylate	2.04±0.2	Allyl acetate	0.59±0.06
Allyl alcohol	1.5 ±0.15	Allyl cyanide	0.37±0.05
2-Methylbut-1-ene	1.2 ±0.08	Cyclohexene	0.25±0.15
Oct-1-ene	1.00 (stand.)	*cis*-Dichloroethylene	>0.2

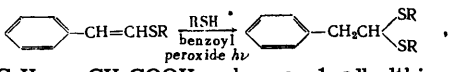
for conjugated double bonds (in styrene for example) is 100 times that for isolated and terminal double bonds[300]. According to other data[314], however, the factor is much smaller in the latter case, being about 20.

The question of the orientation of a radical in its reactions with compounds containing an internal double bond is much more complex. Thus thioacetic acid reacts with alkenes RCH=CHR′ to give an approximately equimolar mixture of adducts, whose composition is not influenced significantly by the structure of the alkyl groups[318]. In other examples, however, the orientation is determined by the possibility of formation of a more favourable radical. It has been found, for example, that the mode of addition of thiophenol to benzothiophen dioxide on heating is different from that for basic catalysis[319]:



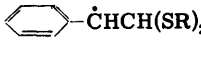
due to the greater stability of the radical  .

In this connection, however, it is difficult to understand why the addition of alkanethiols to benzothiophen dioxide and the addition of thiophenol to the sulphone $C_6H_5CH=CHSO_2C_6H_4CH_3$-$p$ take place only in the position β to the sulphonyl group both with catalysis by alkali and on heating[319]. The homolytic addition of thioglycollic acid[320] and ethanethiol[321] to the corresponding 1-alkylthio-2-phenylethylenes obtained from phenylacetylene and a thiol takes place according to the equation



where R = C_2H_5 or CH_2COOH, whereas 1-alkylthio- and 3,3-dimethylbut-1-enes give adducts with 1,2-disposition of the thiyls[322]:

$$(CH_3)_3C{-}CH{=}CHSR \xrightarrow[\text{azoisobutyrodinitrile}]{RSH} (CH_3)_3CCH(SR){-}CH_2SR.$$

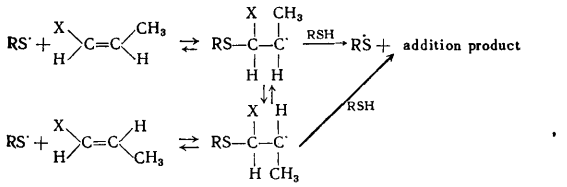
It is evident that as far as electron delocalisation is concerned, the radical  is more favourable in the first case and the radical $(CH_3)_3CCH(SR)\dot{C}HSR$ is more favourable in the second case.

Kinetic studies have revealed that attack on the C=C bond by thiyl radicals is reversible in both the gaseous and liquid phases[302-304].

This reversibility is possibly due to the formation of an unstable cyclic complex of the radical RS· with the C=C bond of the olefin[302]. Since, however, the stereochemical data (see below) indicate that "classical" radicals, and not π-complexes or cyclic complexes, take part in the homolytic reaction, it appears more correct to assume that equilibrium is established between the formation and dissociation of a complex radical[5]:

$$R\dot{S} + CH_2{=}CHR' \rightleftarrows RSCH_2\dot{C}HR'.$$

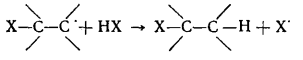
The reversibility of this reaction may be proved experimentally for systems for which the rate of transfer is comparatively low. Thus tihyl radicals produce rapid *cis–trans* isomerisation of but-2-enes[303,314] and 2-chlorobut-2-ene:[323]



where X = CH_3, Cl; R = CH_3, C_6H_5, CH_3CO. It has been found that in the reaction of methanethiol with but-2-ene (initiator azoisobutyrodinitrile) the rate constant for the formation of *trans*-butene from the complex radical is 80 times greater, and that for *cis*-butene 20 times greater, than the rate constant for the conversion of this radical to the addition product[314]. A method has been proposed for the modification of rubbers, based on the *cis–trans* isomerisation of polyisoprene chains by treatment with thiols or thio-acids on the rollers[324].

2. Stereochemical Data

The formation of the C–H bond in the act of chain transfer usually takes place in the *trans*-position relative to the C–X bond produced previously in attack by the radical X:

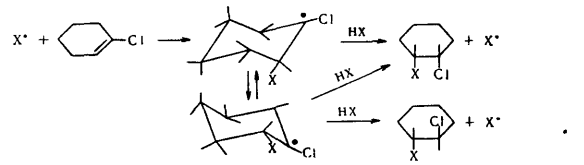


(the "*trans*-addition" rule).

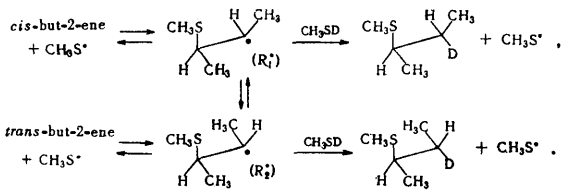
Exclusive *trans*-addition (> 99.5%) was observed in the homolytic addition of HBr to 1-bromo- and 1-chloro-cyclohexenes[325,326], and the reaction remained stereoselective for other cyclohalogenoalk-1-enes and methylcycloalk-1-enes with five- and seven-membered rings[327,328]. The thiylation of 1-chlorocyclohexene, initiated photochemically or in the presence of peroxide, also yields predominantly the product of *trans*-addition (*i.e.* *cis*-2-chlorocyclohexyl sulphide or the thiol), but the stereoselectivity decreases in the order $C_6H_5SH > H_2S > CH_3COSH$.[329] With photochemical initiation, thioacetic acid adds on to 1-methylcyclohexene to give 85% of the *cis*-adduct and 15% of the *trans*-adduct, and in the case of addition to 1-methylcyclopentene the corresponding proportions are 70% and 30% respectively. The addition of thiophenol also takes place predominantly according to the *trans*-scheme[330]; on irradiation by ultraviolet light, thiophenol, *p*-chlorothiophenol, and *p*-thiocresol react with 1-chlorocyclohexene

to give *cis*-2-chlorocyclohexyl sulphides[331], and thioacetic acid and 1-acetoxycyclohexene react in sunlight to give *cis*-1-acetoxyacetylthiocyclohexene[332].

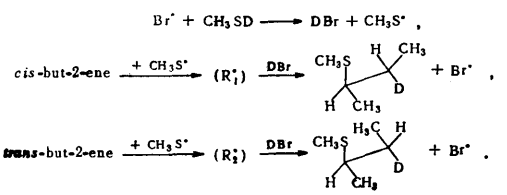
All these facts are readily explained if it is assumed that attack produces radicals in which the substituent lies in the axial position, creating conditions which are sterically more favourable for the formation of products with the *cis*-structure on collision with HX. For complete stereospecificity, however, the act of transfer should take place before conformational equilibrium is attained, since a radical with a second substituent in the equatorial position can form both isomeric products with equal probability[329].



A high stereoselectivity may be expected if the life-time of the intermediate radical is very low. For this the addend should either be a very effective carrier (this in the case with HBr) or be present in considerable excess, in order to accelerate the stabilisation of the radical as the final product. The free radicals formed in the reactions of olefins with an open chain are capable of even more rapid spatial isomerisation as a result of free rotation. Thus, although stereospecific *trans*-addition could be achieved in the photochemical hydrobromination of *cis*- and *trans*-1-halogenobut-2-enes at -80° [326,333], the addition of thiols, which are poorer carriers, to these compounds was found to be non-stereoselective. Thioacetic acid reacts with both *cis*- and *trans*-chlorobut-2-enes (on irradiation by a mercury lamp at -78° in the presence of t-butyl peroxide) to give a mixture of the *erythro*- and *threo*-forms of 2-acetylthio-3-chlorobutanes, with the latter predominating[334]. The photo-addition of CH_3SD to *cis*- and *trans*-but-2-enes at -70° also gives a mixture of *erythro*- and *threo*-3-deutero-2-methylthiobutanes. These facts, which are not understandable from the viewpoint of the theory of intermediate cyclic complex formation, can be explained if we assume the existence of an "open" radical capable of undergoing isomerisation before transfer can take place[334]:



Stereospecific addition in the latter system has been carried out in the presence of DBr, which is such an efficient carrier that it is able to react with radicals before they isomerise[334].

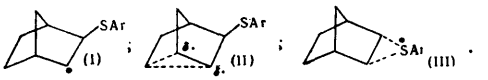


If transfer does not take place sufficiently rapidly, the radical A$^{\bullet}$ may undergo more extensive structural isomerisation. A characteristic example of this change is the transfer of halogen atoms along the chain of a polyhalogenoalkene during its photo-initiated reaction with a thiol, observed by Nesmeyanov *et al.*[295]:

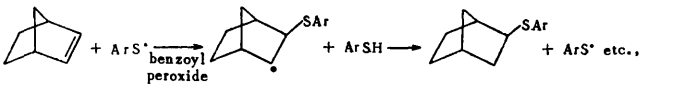
$$CCl_3CH{=}CH_2 + RS^{\bullet} \rightarrow CCl_3\dot{C}HCH_2SR \rightarrow \dot{C}Cl_2CHClCH_2SH \xrightarrow{RSH} \rightarrow CHCl_2CHClCH_2SR + RS^{\bullet}.$$

Isomerisation (with the transfer of phenyl) of the radical produced from 3,3-diphenylbutene does not take place during the addition of butanethiol or thioacetic acid to the compound, but is observed in the reaction with n-butyraldehyde; the removal of H$^{\bullet}$ from the latter is 4×10^4 times more difficult than its removal from a thiol[335].

The stereochemical data obtained for reactions involving bridged polycyclic hydrocarbons show that in this case also the reaction takes place *via* the formation of classical radicals (of type I) rather than "mesomeric" radicals (of type II) or cyclic complexes (of type III).[336]



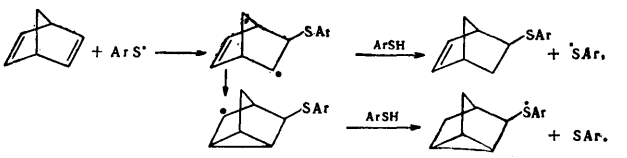
Homolytic addition to these systems therefore differs significantly from the heterolytic reactions, which are usually accompanied by nor-tricyclenic rearrangement of the cation[337]. Bicyclo[2,2,1]heptene undergoes exothermic reaction with *p*-thiocresol to give pure *exo*-*p*-tolyl nor-bornyl sulphide in 85% yield[315].



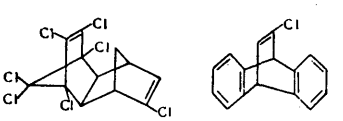
where Ar = *p*-$CH_3C_6H_4$.

Substituted bicycloheptenes react with thiophenol in analogous fashion[338].

The reaction of thiophenol or thiocresol with bicycloheptadiene gives mixtures of *exo*-5-nor-bornen-2-yl aryl sulphide and 3-nor-tricyclyl aryl sulphide, the relative yield of the products of the first type being greater, the higher the concentration of thiol in the reaction mixture[339]. From this it follows that the radical formed may (a) add on the hydrogen atom of the thiol in the act of transfer, or (b) isomerise to the nor-tricyclenyl radical, which is subsequently stabilised as the "homo-conjugate" addition product. Excess thiol favours process (a).



The thiocresyl radical has also been added on to more complex bridged systems: 6-chloroaldrin and 11-chloro-9,10-dihydro-9,10-ethenoanthracene[340].



It was found that the resulting adducts show chiefly *trans*-disposition of the halogen and thiyl, *i.e.* they are produced according to the *cis*-mechanism. This is due to the general tendency of bridged compounds to favour the *exo*-introduction of groups: chain transfer may take place predominantly when the thiol approaches the already-formed radical from the *exo*-direction.

3. Telomerisation in the Presence of Thiols

Thiylation accompanied by telomerisation, in the case of alkenes, is observed only under specially selected conditions. Thus a pressure of the order of 700–900 atm facilitates the formation of telomers from H_2S and ethylene[341]. Telomerisation is also favoured by the presence of excess alkene. At a very low thiol concentration the process observed is not addition but polymerisation, initiated or regulated by the thiol. Consideration of these very important processes is outside the scope of the present review.

Olefins with an activated double bond, which usually have a comparatively high reactivity towards their "own" free radical, may, however, give telomers even at equimolar reagent ratios, particularly in the presence of a slight excess of olefin. Esters of acrylic and 1-alkaneacrylic acids in mixtures with arenethiols react on irradiation by a mercury lamp to give, in addition to the 1 : 1 adducts, dimeric acrylates containing one molecule of thiol. These compounds have been recommended for use as plasticisers[342]. Kharasch and Fuchs[163] studied the reaction of methyl acrylate with thiols in the presence of ascaridol and isolated a number of telomeric adducts containing two, three, and more molecules of acrylate:

$$CH_2{=}CHCOOCH_3 + RS^{\cdot} \rightarrow RSCH_2\dot{C}HCOOCH_3,$$
$$RSCH_2\dot{C}HCOOCH_3 + RSH \rightarrow RSCH_2CH_2COOCH_3 + RS^{\cdot},$$
$$RSCH_2\dot{C}HCOOCH_3 + CH_2{=}CHCOOCH_3 \rightarrow RSCH_2CHCH_2\dot{C}HCOOCH_3,$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad COOCH_3, \text{ etc.}$$

The reaction of butyl acrylate with alkanethiols containing 10–18 C atoms (at a ratio of 10 : 1) gives viscous polymeric adducts which can be used as oil additives[343]. Telomers are also obtained from ethyl acrylate and dodecanethiol under the influence of benzoyl peroxide at 100°–240° [344] and from vinyl methyl ketone and thiols on illumination (λ = 3600 Å), with or without azoisobutyronitrile[345]. In the reaction of various thiols with styrene the ratios of the quantities of the 1 : 1 adducts and telomers formed depend on the transfer constant for the given thiol. Thioglycollic acid and styrene in equimolar mixtures give chiefly the mono-adduct; propanethiol gives, in addition to the mono-adduct, considerable quantities of the 1 : 2, 1 : 3, and higher adducts; and t-butanethiol gives a small quantity of the mono-adduct, higher telomers predominating[305].

4. Coupled Addition of Thiols and Oxygen

A process which often competes with the transfer reaction is the reaction of $A^{\cdot}$ with peroxides or oxygen present in the reaction medium: $A^{\cdot} + O_2 \rightarrow A{-}O{-}O^{\cdot}$.

The formation of stable peroxide radicals explains the retardation of the addition of thiyls to oxygen and peroxides, observed in some systems, and also the inhibition of polymerisation processes initiated by a thiol[306]. Kharasch[306] has shown that if the reaction between olefin and thiol is carried out in the presence of excess oxygen, coupled addition takes place, leading finally to the formation of a mixture of the two racemic forms of the β-hydroxy sulphoxides:

$$RS^{\cdot} + R'CH{=}CH_2 \rightarrow RSCH_2\dot{C}HR',$$
$$RSCH_2\dot{C}HR' + O_2 \rightarrow RSCH_2CH(O{-}O^{\cdot})R',$$
$$RSCH_2CHR' + RSH \rightarrow RSCH_2CHR'(O{-}O^{\cdot}) + RS^{\cdot},$$
$$RSCH_2CHR'(O{-}O^{\cdot}) \rightarrow RSCH_2CHR'(OOH),$$

and (or):

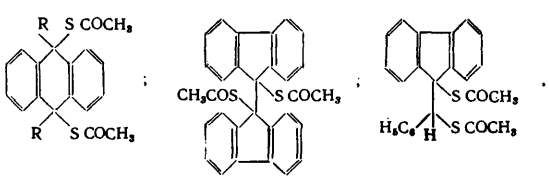
$$RSCH_2CHR' \rightarrow RSCH_2CHR'(O{-}O^{\cdot}),$$
$$RSCH_2CHR'(O{-}O^{\cdot}) + RSH \rightarrow RSCH_2CHR'(OH) + RS^{\cdot}.$$

The coupled oxidation of styrene and primary thiols does not require additional catalysts: with t-butanethiol the reaction takes place only in the presence of a redox system (isopropylbenzene hydroperoxide–$FeCl_2$).[306]

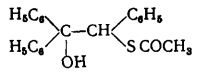
A number of examples of the oxidative addition of thiols to olefins have been given in patents[346,347]. Styrene and toluene-ω-thiol in the presence of benzoyl peroxide in an atmosphere of CO_2 give 85% of the mono-adduct and 15% of the di-adduct $C_6H_5(CH_2)_2(C_6H_5)CHCH_2SCH_2C_6H_5$, but in an atmosphere of oxygen $C_6H_5CH(OH)CH_2SOCH_2C_6H_5$ is formed[348].

Recently, Kharasch's mechanism has been confirmed by direct synthetic experiments in which the intermediate peroxides, previously hypothetical, were isolated. In the coupled oxidation of indene and thiophenol at room temperature, it has been possible to determine titrimetrically up to 70% of the hydroperoxide; however, this was not isolated[349]. In the action of air on mixtures of various arenethiols with such reactive olefins as styrene, methylstyrene, and indene dissolved in hydrocarbons at 0°, it has been possible to isolate the intermediate compounds ArSCH(R)CR'R"OOH and to study their rearrangement to the corresponding ArSOCH(R)CR'R"OH. The hydroperoxide obtained from indene and 2-thionaphthol was found to be so stable that it could be purified by recrystallisation (m.p. 70°). These reactions are responsible for the rapid peroxidation of cracking-distillates of the kerosene type containing thiols and olefins, and also for the loss of stability by motor fuels[350]. Reactions involving the oxidative addition of various alkane- and arene-thiols to styrene, *p*-substituted styrenes, methyl acrylate and crotonate, acrylo- and methacrylo-nitriles, methyl vinyl ketone, and cyclohexene have been described. These reactions are catalysed by Cl^- ions, usually provided by $(C_4H_9)_2NH.HCl$. A mechanism explaining this catalysis has been proposed[351,352].

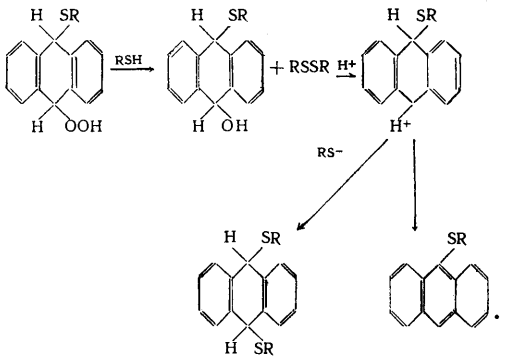
Coupled olefin oxidation reactions include the addition, discovered by Mikhailov and Blokhina, of thioacetic acid to anthracenes and certain polyarylated ethylenes. This reaction takes place only in an atmosphere of oxygen. Of the 9,10-disubstituted anthracenes[353], dibiphenylethylene [1,2-difluoren-9'-yl ethylene (Ed. of Translation)] and benzylidenefluorene[354] gave chiefly the dithioloacetates:



Triphenylethylene gave the hydroxy-thioloacetate:



Thiobenzoic acid reacts with anthracenes in analogous fashion[355]. It is suggested that these reactions take place, as in Kharasch's mechanism, *via* the formation of a hydroperoxide which reacts further as follows‡ [355]:



The biological importance of these reactions has been emphasised[355].

Examples of the coupled addition of thiyls and carbon monoxide to olefins are also known. Thiols R'SH and alkenes $CH_2=CHR$ under a CO pressure of up to 3000 atm in the presence of peroxides at 100°–110° gave chiefly the aldehydes $R'SCH_2CHRCHO$ by the reaction of the radical A• with CO. Under the same conditions H_2S and ethylene gave $C_2H_5SCH_2CH(SC_2H_5)_2$ and $(C_2H_5)_2S$. [356]

5. Application of Homolytic Thiylation Reactions in Organic Synthesis

Syntheses based on the use of homolytic thiylation cover almost all classes of olefinic compounds and thiyls. The number of papers devoted to these reactions is so great that it is difficult to guarantee an exhaustive review. In this section the material is grouped somewhat arbitrarily according to the reactions of the most widely used thiyls or definite groups of olefins and according to the methods of initiation. The addition of H_2S is considered in a separate paragraph.

a. Initiation conditions. Various methods are used for the initiation of free-radical thiylation. Sufficiently active thiols add on "spontaneously" with catalysis by the small quantities of peroxides present in the original materials or by atmospheric oxygen. Such reactions are often exothermic but sometimes require heat. The efficiency of thermal initiation is increased by adding catalytic quantities of peroxides, azo-compounds, and other initiators. In the presence of these additives the mechanism of initiation involves essentially oxidation:

$$R'OOR' \xrightarrow{t^\circ} 2R'O^\bullet;\quad R'O^\bullet + RSH \rightarrow RS^\bullet + R'OH,$$
$$(R'O^\bullet + CH_2=CHR'' \rightarrow R'OCH_2\dot{C}HR'' \xrightarrow{RSH} R'OCH_2CH_2R'' + RS^\bullet),$$
$$R'_3CN{=}NCR'_3 \xrightarrow[t^\circ]{} 2R'_3C^\bullet + N_2;\quad R'_3C^\bullet + RSH \rightarrow RS^\bullet + R'_3CH$$

(reaction between $R'_3\dot{C}$ and $CH_2=CHR''$ is also possible).

‡ A slightly different mechanism was proposed by Mikhailov and Blokhina[353,354].

Initially, the importance attached to the part played by peroxides was so great that the chief characteristic of a free-radical reaction was assumed to be its initiation by peroxides and inhibition by anti-oxidants. At the present time, however, there are many examples of free-radical addition reactions to which these criteria do not apply: organic peroxides have a low efficiency, or even bring about inhibition, and the same is true of oxygen. Detailed study of the process makes it possible to establish the reasons for these anomalies. Sometimes the peroxide combined rapidly with the olefin and is used up by a non-chain mechanism, and in other cases A• is apparently oxidised readily to a stable peroxy-radical A–O–O•, interrupting the normal course of the addition. In these cases, good results are obtained by using redox systems, removing oxygen or the undesirable peroxides from the reaction medium, and initiating with azo-compounds. Thus benzoyl peroxide, dihydroxypentane peroxide, and ascaridol do not bring about the addition of ethanethiol to cetene (hexadecene) (30°, 5 h), and the effect of diethyl peroxide, tetralin, or cetene itself is slight (yield of adduct 6–15%). Under the same conditions, however, a 94% yield is achieved by the combined action of ascaridol and $FeCl_2$. [357]

Oct-1-ene[358] and limonene[79] containing peroxides react with thioglycollic acid with difficulty, but after removal of the peroxides, exothermic addition takes place in the presence of atmospheric oxygen. The anomalous addition of H_2S to vinyl ethers is inhibited completely by atmospheric oxygen or benzoyl peroxide but can be carried out with good yield by catalysis with traces of oxygen or by the action of azoisobutyrodinitrile[54,57,58].

An unusual example of initiation is that described by Mikhailov and Tutorskaya[359] for the addition of thiols to allyl compounds of boron. This gives anomalous products, although the reaction appears to have been carried out in an oxygen-free medium:

$$CH_2=CH-CH_2B(SC_2H_5)_2 \xrightarrow{C_2H_5SH} C_2H_5SCH_2CH_2CH_2B(SC_2H_5)_2,$$
$$CH_2=CH-CH_2B(OC_4H_9)_2 \xrightarrow{C_2H_5SH} C_2H_5SCH_2CH_2CH_2B(OC_4H_9)_2.$$

In this case the initiators are apparently boron-containing free radicals, formed from trialkylboron and traces of O_2 present in the original materials. It is known that these radicals bring about the active polymerisation of many monomers in catalysis by boron compounds[360].

A particularly widespread method is that based on the photolysis of a thiyl compound[361]: $RSH \xrightarrow{h\nu} RS^\bullet + H^\bullet$, which can be carried out under very mild conditions, often at low temperatures of the order of -80°. In photo-addition oxygen can also play a double role as promoter and inhibitor. For example, the best yield of the adduct formed by methanethiol and allyl alcohol is obtained on illumination by sunlight in the presence of $Hg(SCH_3)_2$ and O_2, [362] whereas traces of O_2 inhibit the addition of thiols to olefins, brought about by illumination with ultraviolet light in the presence of azoisobutyrodinitrile[300,301] or initiated by X- or γ-rays[363].

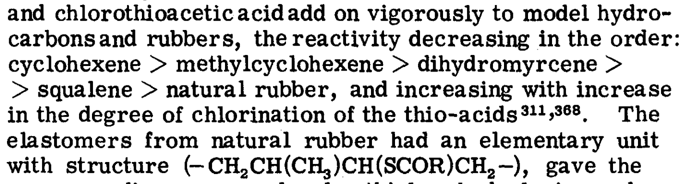
b. Addition of thioacetic acid. In the reactions studied one of the most widely-used thiyls is thioacetic acid (TAA). This is due not only to its high reactivity, but also to the extensive synthetic possibilities opened up by its use. The β-acetylthio-compounds formed in the reaction of TAA with olefins readily undergo alcoholysis in alkaline or acid medium, and this is a convenient method for preparing substituted thiols[364]:

$$XCH{=}CH_2 + CH_3COSH \rightarrow XCH_2CH_2SCOCH_3 \rightarrow XCH_2CH_2SH.$$

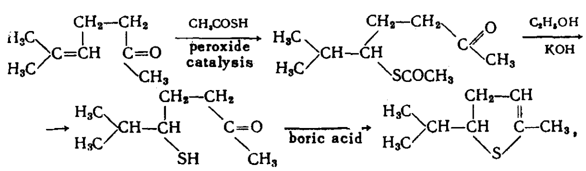
TAA undergoes exothermic reaction with styrene[15] and adds on quantitatively to $\alpha\beta$-unsaturated monobasic and polybasic acids. Hydrolysis of the products gives various mercapto-acids or thio-lactones[365]. The reaction with styrene in the presence of atmospheric oxygen was so vigorous that it was not inhibited by diphenylamine and was even accelerated when hydroquinone was added[332]. The reaction with allyl chloride required heat[366]. A method has been developed for synthesising cyclohexanethiol, based on the exothermic addition of TAA or thiobenzoic acid to cyclohexene; from the preparative viewpoint, the synthesis *via* the acetylthio-derivatives is more convenient[367]. TAA and chlorothioacetic acid add on vigorously to model hydrocarbons and rubbers, the reactivity decreasing in the order: cyclohexene > methylcyclohexene > dihydromyrcene > > squalene > natural rubber, and increasing with increase in the degree of chlorination of the thio-acids[311,368]. The elastomers from natural rubber had an elementary unit with structure ($-CH_2CH(CH_3)CH(SCOR)CH_2-$), gave the corresponding macromolecular thiol on hydrolysis, and, particularly in the case where R = CCl_3, had a high stability towards solvents, while retaining their elasticity[311,368].

The addition of TAA to $\alpha\beta$-unsaturated acids and aldehydes has been used as a stage in the synthesis of mercapto-amino-acids. Thus *NS*-diacetylcysteine is obtained from TAA and *N*-acetylaminoacrylic acid[369–372] and penicillamine is obtained from 2,2-dimethyl-1-acetylaminoacrylic acid[373].

TAA undergoes exothermic reaction with acrolein and its homologues[210], but this reaction has been found to be less convenient for the synthesis of *S*-substituted 1-amino-2-mercaptopropionic acid than the method described above (see Section II. 3)[210,215]. TAA reacts with a mixture of an unsaturated aldehyde and urea or acetamide[374]. TAA has also been used in the synthesis of water-soluble thiols[375] and dithiols of the BAL (2,3-dimercaptopropanol) type[376]:



partly hydrogenated sulphides of the thiophen series[377]:

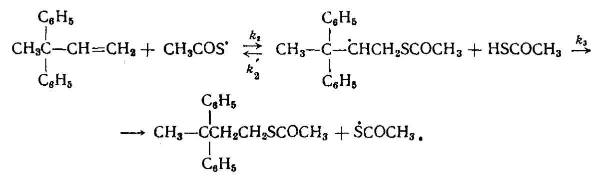


and all the isomeric mercaptovaleric acids. It was observed that the reactivity of the double bond in the pentenic acids used for the last synthesis increases with the increase in its distance from the carboxy-group[378]:

$$CH_3CH_2CH{=}CHCOOH < CH_3CH{=}CHCH_2COOH < CH_2{=}CH{-}CH_2CH_2COOH.$$

TAA adds on readily to vinyl acetate[379] and other enol acetates[332]; in the presence of ascaridol or benzoyl peroxide it adds on to various alkenes, $\alpha\beta$-unsaturated aldehydes, ketones, and esters, and allyl and crotyl alcohols, to give quantitative yields of the corresponding acetylthio-derivatives[380]. Its reaction with oct-2-ene gave a mixture or equal quantities of 2- and 3-acetylthio-derivatives. TAA could not be added on to cinnamic alcohol and stilbene[380].

TAA reacts with vinyl pyridines without catalyst at temperatures between -20° and +20°.[381] When TAA is mixed with vinyl alkyl and vinyl aryl ethers in air, a strongly exothermic reaction takes place with the predominant formation of the β-adducts $CH_3COSCH_2CH_2OR$.[62,49] Hydrolysis of the latter is a convenient method for synthesising 2-alkoxy(aryloxy)ethanethiols[49]. TAA adds on to the adducts obtained by diene synthesis from cyclopentadiene and various dienophiles, and when the molecule contains a halogen the latter is also replaced by an acetylthio-group[240]. In photochemically initiated addition to alkenes 95–99% of the addition took place contrary to Markovnikov's rule[318,382]. A general method has been proposed for the synthesis of cyclic sulphides from halogenoalkenes and TAA.[318] TAA adds on to 3,3-diphenylbutene under unusually severe conditions (with prolonged heating in a tenfold excess of the acid in the presence of t-butyl peroxide). This is due to the steric hindrance associated with the process of chain transfer, leading to an increase in the probability of the reverse reaction — removal of the acetylthio-radical with formation of the original olefin[335]:



The long-chain 9(10)-mercaptostearic, 2-mercaptostearic, and 11-mercaptoundecanoic acids have been synthesised from the corresponding unsaturated acids and TAA with irradiation by a mercury lamp[383]. An analogous reaction has been used to synthesise model substances in the study of the vulcanisation process[78,384]. A stage involving the addition of TAA to limonene and cyclohexene[385], diallyldimethylsilane, diallyltetramethylsiloxane[386], and divinyltetramethylsiloxane[367] has been used in the preparation of the corresponding dithiols, which were then used to prepare rubber-like polyalkylene sulphides by emulsion copolymerisation with the original[385] or other[386] diolefins, or converted to silicon-containing polyalkylene polysulphides by emulsion oxidation with atmospheric oxygen[387]. TAA undergoes exothermic reaction with trimethylalkenylsilanes to give the corresponding acetylthio-derivatives and thiols, which have an anomalous structure[260]. Thio-acids containing two thioacyl groups, for example $CH_2(CH_2COSH)_2$ or $HSOC(CH_2)_6COSH$, undergo exothermic reaction with methylcyclohexene and vulcanise rubber in the presence of light and peroxides[388].

Under the same conditions, with illumination by ordinary light and heating, dithiols $HS(CH_2)_nSH$ (n = 3, 6) react slowly with cyclohexene and do not react with rubber; the reaction is accelerated slightly by irradiation with ultraviolet light[389].

c. Addition of thioglycollic (mercapto-acetic) acid. Thioglycollic acid (TGA) and its esters add on to olefins slightly less vigorously than TAA. The resulting carboxymethylthio-derivatives are of interest as physiologically active substances and as precursors in the synthesis of various penicillins. Holmberg first observed the spontaneous reaction of TGA with styrene and cinnamaldehyde and proved that the course of the reaction was anomalous[14]. Kharasch used the reaction of TGA with styrene, and also with isobutene, to prove the existence of the peroxide effect in the reaction of thiols with olefins[20].

The reaction of TGA with unsaturated acids and natural unsaturated oils[390,391] and mixtures of alkenes of the type present in petroleum fractions[358] or peat tar[392] have been studied with the aim of developing methods for the analysis of these substances. The *S*-alkylthioglycollic acids obtained from C_7-C_{11} alkenes, and the corresponding alkanesulphinyl(sulphonyl)acetic acids have been proposed for identification purposes[392]. The crystalline products of the addition of TGA to terpenoid hydrocarbons may be used for the same purpose[79].

Data on the reaction of TGA with natural rubber are contradictory. Holmberg[393] has stated that rubber slowly swells and dissolves in TGA, which is added on to the rubber; Japanese authors have prepared an adduct of composition $(C_5H_8)_{10}(HSCH_2COOH)_5$ by the action of TGA on a 5% solution of rubber in benzene[394]. Cunneen found, however, that TGA does not add on to rubber, either in the presence of peroxides or on prolonged irradiation with ultraviolet light[80,368,395]. The same author found that cyclohexene, dihydromyrcene, and 1-methylcyclohexene containing peroxides undergo exothermic reaction with TGA and that the adducts have exclusively the anomalous structure; this was proved rigorously for the case of methylcyclohexene[368]. The copper salt of the acid formed when TGA is mixed with dicyclopentadiene has fungicidal activity[85]. TGA adds on to unsaturated long-chain aliphatic acids and esters[396] in the presence of lauryl peroxide on irradiation by a mercury lamp. The reaction must be carried out with an excess of freshly-distilled TGA.[397] The reaction with thioglycollic acid proceeds smoothly in the presence of peroxide and is inhibited by hydroquinone[398].

$$CH_2{=}CHCH_2SCH_2COOH + HSCH_2COOH \rightarrow CH_2(CH_2CH_2SCH_2COOH)_2.$$

The anomalous addition of ethyl thioglycollate to vinyl and allyl lactams in the presence of azoisobutyrodinitrile was more vigorous than the same reaction with alkanethiols. The adducts showed considerable activity as precursors in the synthesis of penicillins when added to the culture medium of the fungus *Penicillium chrysogenum*[399].

d. Addition of arenethiols. Arenethiols and toluene-ω-thiol are among the most reactive thiyls. The spontaneous anomalous addition of thiophenol to styrene was noted by Posner[13]. The reaction is accelerated by the action of light[17]; for addition to lower alkenes, prolonged heating is required. Toluene-ω-thiol and toluene-*p*-thiol add on to αβ-unsaturated ketones at 100°.[222] The peroxide effect has been observed in the addition of thiophenol, thiocresol, thionaphthol, and higher thiols and dithiols to alkenes (propene, butene, and linear alkenes of the pentadecene type)[19]. An attempt to use the anomalous adducts formed by 4-mercaptobiphenyl with alkenes for identification purposes was unsuccessful, since the melting points of the alkyl biphenylyl sulphides and sulphones corresponding to homologous hydrocarbons were found to be too close[400]. In the study of the reactions of different thiols with cyclohexene it was established that the most reactive, after TAA and TGA, were thiophenol and toluene-ω-thiol, which after 25 h in sunlight gave 65% and 75% of adduct respectively, whereas to achieve the same yield with (±)-mercaptosuccinic acid, irradiation for 117 h by light with a wavelength of 3600 Å was required[367]. Analogous relationships were observed in the study of the reaction of thiols with cyclohexene, methylcyclohexene, dihydromyrcene, and rubber[80,311], and also with 2-vinylpyridine[401]. Thiocresol adds on to 2-methyl-5-vinylpyridine on heating[402], and the reaction of toluene-ω-thiol with crotonic acid, crotonaldehyde, and allyl alcohol with formation of the anomalous adducts takes place readily in the presence of ascaridol[155]. Arenethiols have been added on to the exocyclic double bond of 2-arylmethyleneindanediones[403] or 2-arylmethylene-3-(2*H*)-thianaphthenone 1,1-dioxides[404] on heating for a short time without catalyst; thiophenol reacts with benzylidenephenylmethylpyrazolone in the cold[405]. *p*-Thiocresol has been added on to 1-*p*-tolyl-1-phenylethylene in the presence of benzoyl peroxide[406], and thiophenol and toluene-ω-thiol have been added on to vinylsilanes with heating, to give the adducts $RS(CH_2)_2Si(OC_2H_5)_n(CH_3)_{3-n}$ (n = 1, 2, 3).[407] Indene reacts with various arenethiols in heptane solution to give adducts in up to 99% yield[408].

e. Addition of various thiols. This paragraph deals with work aimed for the most part at the synthesis of products with various useful properties.

Equimolar mixtures of thiols react with vinyl methyl ketone on boiling to give $RSCH_2CH_2COCH_3$ (R = C_3H_7, C_6H_5), which can be used as solvents, plasticisers, and intermediates in the synthesis of insecticides and flotation reagents[409], while benzylideneacetophenone and n-dodecanethiol under the same conditions give an adduct which has been tested as a regulator in emulsion polymerisation[410]. Thiols and H_2S add on when heated without catalyst to derivatives of abietic alcohol[411] and rosin[412], ore flotation reagents being obtained in the latter case. On standing in contact with styrene, thiophene-3-thiol forms 3-thienyl-2′-phenylethyl sulphide, which is a stabiliser for motor oils[113]. The addition of a wide variety of thiols to safrol and isosafrol in the presence of ascaridol has given more than one hundred new sulphides, some of which are active acaricides with a low toxicity towards warm-blooded animals[413,414]. *OO*-Dialkyl phosphorothiolothionic acids have been added on to various olefins with the aim of synthesising insecticides[415]. The adducts which are readily formed when dithiocarboxylic acids are heated with αβ-unsaturated aldehydes, ketones, acids, ethers, nitriles, sulphones, and sulphoxides can be used as antioxidants and intermediate products in the synthesis of drugs and poisons[416]. The passage of methanethiol through acrolein containing catalytic quantities of acetyl peroxide has been recommended for the synthesis of methionine[417].

In a number of cases thiylation gives polymeric substances. But-2-enethiol, 3-phenylbut-2-enethiol, and other thiols with double bonds in the βγ- or γδ-positions polymerise slowly on standing and rapidly on heating if the degree of screening of the C=C bond by neighbouring methyl groups is not too great[418,419]. Marvel and coworkers[385,386,420,421] prepared a very large number of polyalkylene sulphides with molecular weights up to 60 000, exhibiting rubber-like properties in a number of cases, by the reaction of various thiols (chiefly hexamethylenedithiol, but also various others, including silicon-containing thiols) with a variety of diolefins containing non-conjugated C=C bonds (diallyl, dibenzylideneacetone, diallylphenol, diallylmethanol, etc.). The reaction was studied in detail both in block and in emulsions. The preparation of a new class of elastomers by the addition of lower alkanethiols to the double bonds of butadiene rubbers in the latex stage has been described. A high degree of saturation is reached without rupture of the main chain of the polymer; the adducts have high thermal stability and resistance to the action of ozone and γ-rays[422,423]. For example, an adduct with up to 95% of the C=C bonds saturated with methanethiol resisted attack by ozone for 300 h under conditions

in which neoprene broke down in 1 h and butyl rubber in 20 h. [423]

f. Addition of thiols to $\alpha\beta$-unsaturated ethers and sulphides. These reactions are considered in a separate paragraph since they are fairly characteristic from the viewpoint of the conditions of their initiation and, more particularly, their inhibition. This has been shown by work in our laboratory.

Vinyl alkyl ethers undergo exothermic reaction when mixed in the presence of air with sufficiently active thiols [thiophenol, TAA, dithiols such as $O(CH_2CH_2SH_2)$, and even with butanethiol] to give high yields of adducts containing 95–98% of the anomalous addition product [62,424,425]:

$$ROCH{=}CH_2 + R'SH \longrightarrow ROCH_2CH_2SR'.$$

The reaction of ethanethiol, which has been studied in detail for vinyl butyl and vinyl ethyl ethers [62], is much less predictable. When mixed in air, these substances react slowly and always give a mixture of the anomalous and normal products. The peroxides formed when vinyl ethers are allowed to stand in air decrease the overall rate of the process and facilitate the normal addition. Purely anomalous reaction was observed between freshly-distilled reagents in the presence of the traces of oxygen remaining in the reagents after degassing by evacuation to 2–5 mm Hg (with preliminary freezing); quantitative reaction under these conditions required heating [62]. The reaction is accelerated slightly by the presence of 0.1–0.2% of azoisobutyrodinitrile and by traces of moisture present in the thiol [424]. In the presence of azoisobutyrodinitrile thiols add on contrary to Markovnikov's rule to the vinyl ester of phthalylglycine [426] and to vinyl aryl ethers, including halogenophenyl ethers [65]. The adducts formed by the latter have insecticidal properties. The adducts formed by thiols with vinyl butyl ether have been used for the laboratory synthesis of insecticidal *OO*-dialkyl *S*-(2-alkylthioethyl)phosphorothiolothionates [47].

$$RSCH_2CH_2OC_4H_9 \xrightarrow{HCl} RSCH_2CH_2Cl \xrightarrow{NaSP(S)(OR')_2} RSCH_2CH_2SP(S)(OR')_2.$$

Ethers of 1,2-dithioglycol with different structures are formed by an exothermic reaction when various alkyl-(aryl)thioethylenes are mixed in air with excess alkane- or arene-thiol [427,428]:

$$RSCH{=}CH_2 + R'SH \longrightarrow RSCH_2CH_2SR'$$

(where R = R' = C_2H_5, C_3H_7, C_4H_9, iso-C_3H_7, C_6H_5, $AlkOCH_2CH_2$) and also when 1-alkylthiopropenes are mixed with alkanethiols [75]:

$$CH_2{=}C(CH_3)S\,Alk + Alk\,SH \rightarrow Alk\,SCH_2CH(CH_3)S\,Alk$$

(where Alk = C_2H_5, C_3H_7, C_4H_9).

These reactions, which always accompany the synthesis of $\alpha\beta$-unsaturated sulphides from thiols and acetylene in alkaline media, are homolytic in character, since they are inhibited by hydroquinone [72], are retarded when the quantity of oxygen in the reaction mixture is decreased [427], and are not catalysed by bases, as pointed out earlier [151]. Ethanethiol adds on to vinylmercaptobenzothiazole on heating; mercaptobenzothiazole does not react under these conditions [429].

The addition of thiols to 1- and 2-arylthiopropenes [74] and to 2-(2'-oxopyrrolidin-*N*-yl)ethyl vinyl sulphide [430] required heating in the presence of azoisobutyrodinitrile. 2-Hydroxyethyl vinyl sulphide reacts with ethanethiol on heating to give a mixture of normal and anomalous adducts, and with 2-mercaptoethanol to give only the anomalous 1-(hydroxyethylthio)-2-ethylthioethane [431].

g. Addition of H_2S in the presence of radical initiators. When lower alkenes and H_2S are heated in a steel autoclave without special precautions to eliminate oxygen, the addition takes place in accordance with Markovnikov's rule, but the resulting thiol reacts anomalously with a second molecule of alkene, so that, for example, H_2S and isobutene give finally $(CH_3)_3CSCH_2CH(CH_3)_2$. [36] Very severe conditions (high temperature and pressure) are recommended in patents for the addition of H_2S to olefins [432–434]. At first, therefore, a somewhat incorrect impression arose regarding the reaction of H_2S with olefins. It was considered that H_2S has a low reactivity and adds on to double bonds chiefly in accordance with Markovnikov's rule, peroxides and oxygen producing no change in the mode of addition [1,4]. It was pointed out, however, that in the presence of redox systems consisting of peroxides and salts of Fe, Mg, Mn, etc. with strong inorganic acids (chiefly HCl) not only thiols but also H_2S may add on in anomalous fashion to various hydrocarbons with C=C and C≡C bonds [435]. The addition of H_2S to alkenes in the synthesis of primary thiols can be carried out under pressure in the liquid phase using anhydrous $FeCl_2$ and 0.5–8% of the hydroperoxide or peroxide of an aldehyde, ketone, ester, or aromatic hydrocarbon [436]. H_2S and unsaturated compounds with powerful electron-donating substituents react by a homolytic mechanism under even milder conditions with catalysis by a trace of oxygen [57,58,72]. This gives almost exclusively the β-alkoxy(alkylthio)-ethanethiols and bis-2-alkoxy(alkylthio)ethyl sulphides in proportions depending on the ratio of reagents in the original mixture:

$$RX{-}CH{=}CH_2 + H_2S \longrightarrow RXCH_2CH_2SH \xrightarrow{RXCH=CH_2} (RXCH_2CH_2)_2S$$

(where X = O, S).

The initiation conditions were studied in detail for the case of the reaction of H_2S with vinyl butyl ether [57,58,437]. The anomalous reaction is catalysed by ascaridol and azoisobutyrodinitrile; benzoyl peroxide is ineffective, probably because it combines rapidly with the vinyl ether to form the acylal of benzoylacetaldehyde [438]. Inhibition of the anomalous addition leads to the appearance, in the reaction medium, of a large quantity of the unstable normal adducts. This inhibition is observed not only in the presence of hydroquinone but also under the influence of the peroxides formed by the vinyl ethers during storage and also under the influence of excess oxygen. Only the normal adducts are obtained when the reaction is carried out under a pressure of atmospheric oxygen. Inhibition by oxygen is not observed in the homolytic hydrobromination of olefins in the liquid phase [439] but is shown in the reaction with thiols (particularly in the case of vinyl ethers), and is especially marked in the case of reactions with H_2S. It may be concluded that the ease of the reaction $A^{\bullet} + O{-}A \rightarrow A{-}O{-}O^{\bullet}$, which competes with the chain transfer, increases in the order:

$$RCHCH_2Br < RCHCH_2SR < ROCHCH_2SR < ROCHCH_2SH.$$

The structure of $R^{\bullet}$ in the OR group of the vinyl ether also influences the oxidisability of the radical $A^{\bullet}$, since the inhibition effects are particularly marked for ethers with branched chains and are much less marked for ethers with long straight chains [58]. Vinyl aryl ethers add on H_2S much more slowly than vinyl alkyl ethers; the reaction requires prolonged heating in the presence of azoisobutyrodinitrile, and always gives the anomalous adducts [54,64,437].

Under the influence of azoisobutyrodinitrile, H_2S also adds on to divinyl ether with the formation of dithiols containing oxygen atoms and sulphide groups[426], and also to vinyl lactams. Vinylcaprolactam gives good yields of thiol and sulphide, and *N*-vinylpyrrolid-2-one, even in the presence of excess H_2S, gives exclusively bis-2-(2′-oxopyrrolidin--*N*-yl)ethyl sulphide[440]. The addition of H_2S to allylamine in the presence of azoisobutyrodinitrile takes place chiefly in accordance with Markovnikov's rule, due to the inhibiting action of the amino-group[441].

It is clear from the foregoing that the anomalous thiylation of *O*-, *S*-, and *N*-vinyl compounds described in patents must be regarded as homolytic, although the authors emphasise the catalysis by bases[151,442].

Recently it has been shown that azo-compounds (azoisobutyrodinitrile and others) or peroxides (benzoyl peroxide) can be used for the anomalous thiylation of various alkenes by hydrogen sulphide in the absence of air and with the addition of water[443].

All these results indicate that, when conditions ensuring the absence of inhibitors are observed, the ease of addition of H_2S to the ethylenic bond in the presence of free-radical initiators is no less than that for thiols.

The reaction of HS· radicals plays an important part in the sulphur vulcanisation of rubbers[444]. In this connection the thermal decomposition of hydrogen disulphide, which is a much better HS· radical donor than H_2S, has been studied in solution in various alkenes. It was found that styrene and α-alkenes are more active acceptors of HS· radicals than β-alkenes and cyclohexene[445].

h. Photochemical thiylation. When reactions of thiyl radicals are initiated photochemically, the addition is rapid and almost no differences between thiols and H_2S are observed.

The accelerating action of light on the anomalous addition of a thiol was first observed in 1928.[17] Japanese workers made a detailed study of the addition of CH_3SH to a number of olefins under the influence of sunlight and various promoters[362,446]. For the reaction with allyl alcohol in the presence of $Hg(SCH_3)_2$, light, and O_2, the yield was 93%, for that with light and O_2 it was 61%, for that with the salt and light 33%, and for that with the salt and O_2 22%; no reaction took place on illumination without promoters[362]. Analogous relationships were observed in the reaction of CH_3SH with acrylic acid, acrolein, maleic acid, and styrene[446]. On illumination by sunlight in a quartz apparatus, thiols add on to acetals of vinylacetaldehyde with the formation of adducts $R'SCH_2CH_2CH_2CH(OR)_2$, which have been used for the synthesis of drugs[447].

Initiation with ultraviolet light[361,448,450] was found to be most effective. On irradiation by light with a wavelength below 3000 Å in a quartz apparatus, photolysis of the S–H bond takes place readily and H_2S and thiols add on rapidly and quantitatively to alkenes in both gaseous and liquid phases with the exclusive formation of the anomalous adducts.

Quantitative addition of H_2S in the liquid phase to prop--1-ene, but-1-ene, vinyl chloride, and methyl acrylate is observed at 0°–20° on illumination in a quartz tube after only 4–10 min. With a twofold excess of H_2S, 15–30% of sulphides and 65–90% thiols are formed[361,448]. Diallyl (hexa-1,5-diene) and allyl ether form polymeric adducts with H_2S.[361] With promoters (sensitisers) undergoing photolysis on irradiation by light of longer wavelength (metal alkyls[361,451], aldehydes, ketones, or other carbonyl compounds[361,450]), the reaction can be carried out in a Pyrex vessel, which transmits light above 3200 Å; this method has been used, for example, for the addition of H_2S to halogenoalkenes to form halogenated thiols and sulphides[361,449]. Irradiation by a mercury lamp has been used for the addition of H_2S and thiols to higher alkenes such as cetene (hexadecene)[452], of β-mercaptoethanol to vinyl acetate[453] and vinyl chloride in the presence of benzoyl peroxide[454,455], of methanethiol to cyclohexene[456,457], and also to vinyl acetate, vinyl chloride, and allyl alcohol [in the presence of $Hg(SCH_3)_2$ and O_2].[458] Different thiols react with vinyl acetate on illumination in the presence of O_2, but azoisobutyrodinitrile or benzoyl peroxide must be added[459]. Disulphides (diphenyl, dianisyl) (0.5–1%) considerably accelerate the rate of the photochemical addition of propane- and dodecane-thiols to styrene[460]. With promotion by $(C_6H_5)_2S_2$, the reaction between vinyl chloride and dithioethylene glycol is rapid and quantitative under illumination in a Pyrex vessel by a tungsten lamp[461]. 2-Mercaptoethyl ethers of diols are prepared from H_2S and divinyl ethers $(CH_2=CHO)_2(CH_2)_n$ (n = 2, 3, 4) with irradiation by light having a wavelength of 3000–4000 Å in the presence of anthracene, fluorene, divinylbenzene, divinyltoluene, divinylxylene, and polychlorostyrenes[462]. In an atmosphere of O_2, with irradiation by ultraviolet light, thiophenol and toluene-ω-thiol add on quantitatively to vinyl butyl ether after 3 h; the less active butanethiol adds on to the extent of less than 30%. In an atmosphere of N_2 the reaction is most effectively promoted by azoisobutyrodinitrile slightly less effectively by benzoyl peroxide and $Hg(SCH_3)_2$.[463] The addition of alkanethiols to undecanoic acid required illumination in a quartz vessel for 3 h.[464] H_2S reacts with trifluorochloroethylene on irradiation by a 500 W filament lamp in the presence of benzoyl peroxide; HF splits off from the adduct and polymers containing S, F, and Cl are formed[465]. The photochemical addition of H_2S to allylamine hydrochloride, vinyl lactams, etc. is promoted by trialkyl phosphites[441].

In the present review an attempt has been made to reveal the extensive possibilities for theoretical and practical studies latent in the, at first sight simple, reaction of thiylation of the double bonds in olefinic compounds.

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THE CHEMICAL ACTION OF IONISING RADIATIONS ON INORGANIC CRYSTALS

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1. INTRODUCTION

Considerably greater interest has recently been taken in the study of the chemical changes occurring in solids under the influence of ionising radiations. The results of these investigations have especially great prospects of practical application in the search for radiation-resistant materials for the construction of atomic reactors and plant and for intensifying many solid-state reactions of practical importance. These problems are also encountered in developing the technology of the production of artificial radioactive isotopes by irradiating solids in a reactor. It will therefore be useful to reach, from accumulated data, some general conclusions concerning the chemical changes produced by radiations in solids and their influence on the physicochemical properties of the solids.

The experimental data which have accumulated are so extensive and diverse that it is impossible to cover them in a short review. Since fairly complete surveys have appeared[1-13] of the action of radiation on metals and on polymeric materials, we shall confine ourselves to an examination of work on the chemical changes produced by radiation in ionic crystals. The variation in physical properties under these conditions has been considered[14], and therefore we shall disregard this question, too, in the present paper.

2. ACTION OF HEAT, LIGHT, AND IONISING RADIATIONS ON MATTER

In contrast to heat and light quanta, the energy of which is less than, or at best comparable with, that of chemical bonds, the energy of γ-quanta, electrons, or heavy particles formed in radioactive disintegration or in artificial (instrument) sources of radiation — accelerators — is much larger, usually by several orders of magnitude, than the chemical bonding energy, and this governs many specific aspects of radiochemical processes in the solid phase, which distinguish them from photolysis and thermal decomposition.

The action of heat on a solid results in atomic vibrations in the lattice, caused by the greater number of heat quanta; only a few of them correspond to the high-energy limit of the Boltzmann distribution and can lead to rupture of the chemical bond. Under isothermal conditions heat quanta are distributed uniformly throughout the volume of the crystal, and if this alone governed the start of thermal decomposition, the latter could begin at any point in the crystal, and its kinetics would be represented by a first-order equation. But different positions in the crystal are not equivalent in reactivity. Therefore bond rupture takes place at those points in the lattice where at a given instant the bond is for some reason weaker than at other points, and it is this which causes the localisation of the initial centres of thermal decomposition at defects in the crystal.

In the decomposition of solids under the influence of visible light or ultraviolet radiation the energy of the quantum is comparable in magnitude with that of a chemical