# Chemical Conversions using Sheet Silicates: Novel Intermolecular Eliminations of Hydrogen Sulphide from Thiols

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*Summary* Aliphatic primary and secondary thiols react in the interlamellar layers of ion-exchanged montmorillonite catalysts to produce dialkyl sulphides *via* intermolecular elimination of hydrogen sulphide; similar processes result in the production of diphenyl sulphide from benzenethiol and poly(phenylenemethylene) from α-toluenethiol.

IN our previous communications[1–4] we have shown that the interlamellar region of certain ion-exchanged montmorillonites provides a microenvironment which facilitates a variety of intermolecular reactions. Alk-1-enes have been shown to react with the resident intercalated water to produce di-(alk-2-yl) ethers,[1] and with intercalated carboxylic acids to yield esters.[2] Primary amines react by elimination of ammonia to furnish secondary amines,[3] and primary alcohols eliminate water to give di-(alk-1-yl) ethers.[4] In all of these examples, the montmorillonite catalyst has been envisaged to act as a proton generator with subsequent reaction proceeding either by addition of a nucleophile,[1,2] or displacement by a nucleophile.[3,4]

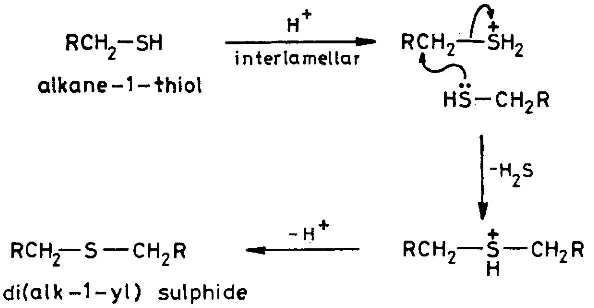
In an extension of this investigation we have examined the reactions of thiols with ion-exchanged montmorillonites. Primary and secondary alkyl thiols were found to eliminate hydrogen sulphide in clean reactions to give dialkyl sulphides as the predominant products. The competitive intramolecular elimination to the alkenes was not favoured. Typical product yields are shown in the Table. The reactions were carried out in small stainless steel vessels (*ca.* 20 $cm^3$ capacity) and a typical charge would be 0·5 g of solid catalyst and 5·0 g of reactant. The reaction vessels were immersed in a thermostat capable of operating up to 220 °C.

TABLE. Product distribution (weight %) for reactions of thiols with $Al^{3+}$-exchanged montmorillonite at 200 °C; reaction time 4 h.

| Reactant | Recovered reactant | R–S–R | R–S–S–R | Alkene | Others |
|---|---|---|---|---|---|
| Primary thiols | | | | | |
| Ethanethiol | 70 | 27 (44)[a] | 3 | — | — |
| Propane-1-thiol | 87 | 11 (34)[a] | 2 | — | — |
| Butane-1-thiol | 89 | 7 (21)[a] | 2 | 1 | 1 |
| 2-Methylpropane-1-thiol | 83 | 4 (9)[a] | 11 | 2 | — |
| Secondary thiols | | | | | |
| Propane-2-thiol | 50 | 41 | 5 | 3 | 1 |
| Butane-2-thiol | 60 | 32 | 3 | 2 | 3 |
| Cyclohexanethiol | 20 | 76 | 1 | 1 | 2 |
| Tertiary thiol | | | | | |
| 2-Methylpropane-2-thiol | 57 | 7 | 2 | 4 | 30[b] |
| Aromatic thiols | | | | | |
| Benzenethiol | 48 | 15 | 16 | — | 21[c] |
| α-Toluenethiol | Gives poly(phenylenemethylene) | | | | |

[a] % Yield after 48 h reaction at 200 °C. [b] Alkene dimers, trimers, tetramers *etc*. [c] 12% Benzene and 9% thianthrene.

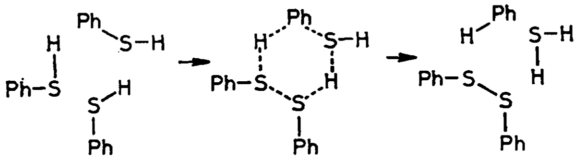
Since the primary thiols yielded di-(alk-1-yl) sulphides, this precludes the intermediacy of either carbocations or alkenes as they would be expected to give the branched Markownikoff products.[1,2] The products are predictable in terms of analogues of mechanisms already proposed for the production of ethers[4] and secondary amines.[3] Thus, protonation of the thiol in the interlamellar region is followed by nucleophilic displacement of hydrogen sulphide by a neighbouring unprotonated thiol molecule to give the dialkyl sulphide as outlined in Scheme 1. As far as we are aware the only analogy for such production of dialkyl sulphides is to be found in the very early work of Sabatier and Mailhe[5] who pyrolysed thiols over cadmium sulphide at 350—400 °C.



Scheme 1

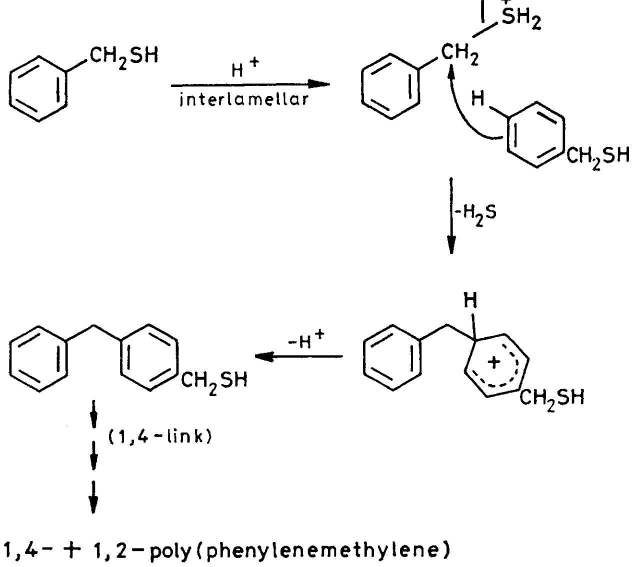
The production of dialkyl sulphides is much faster from secondary than from primary thiols, but the yields from the latter can be markedly increased by longer reaction periods (Table). In all the reactions small amounts of the dialkyl disulphides were produced. These, in the main, derive from air oxidation since, after careful degassing, their yields were much diminished.

The tertiary thiol which was examined failed to give significant amounts of the dialkyl sulphide; instead, the alkene and its oligomers were produced by competitive intramolecular elimination. The reaction of benzenethiol was of special interest as, in addition to the normal production of diphenyl sulphide, significant quantities of benzene, diphenyl disulphide, and thianthrene were produced. Clearly some sort of novel oxidation–reduction process is operating here, in which the benzenethiol is oxidised to diphenyl disulphide, and/or thianthrene, by abstraction of hydrogen, with simultaneous reduction to benzene. Air oxidation of the thiol to the disulphide is well known and the production of thianthrene is a known acid-catalysed oxidation process,[6] but the observation that benzene can be obtained by reductive elimination of sulphur is novel. A mechanism such as that outlined in Scheme 2 may be envisaged as taking place in the interlamellar layer, and similar hydrogen-transfer processes have been observed previously in sheet silicates: *e.g.* the conversion of 9,10-dihydroanthracene into 1,1-diphenylethene.[7]



Scheme 2. Interlamellar hydrogen exchange.

The reaction of α-toluenethiol with the catalyst gave poly(phenylenemethylene) in a similar manner to that proposed for benzyl alcohol.[4] Protonation followed by nucleophilic displacement of hydrogen sulphide by the aromatic ring system as in Scheme 3 would provide the basis for repeated reaction leading to the polymer.



Scheme 3

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