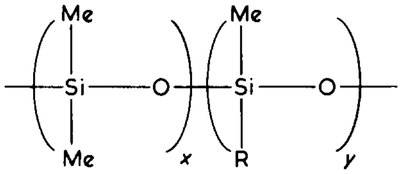
Metal catalysed oxidative coupling of mercaptan-containing poly(dimethyl siloxanes)

Donald A. Seanor and Joseph A. Swift
Special Materials Technology Center, Joseph C. Wilson Center for Technology, Xerox Corporation, Rochester, New York, 14603, USA

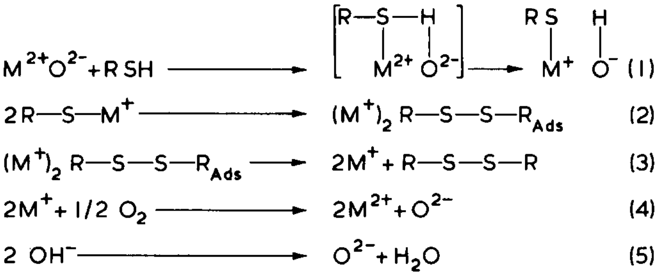
(Received 23 August 1977; revised 31 January 1978)

The oxidative coupling of mercaptan-containing poly(dimethyl siloxane) polymers:



$$\left(-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{O}-\right)_x\left(-\underset{\mathrm{R}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{O}-\right)_y$$

catalysed by different metals has been studied. In the presence of excess oxygen, the kinetics obey the law, $d(\mathrm{SH})/dt = -k(\mathrm{SH})^n$, where $n = 0$ or 2 dependent upon temperature and the specific metal. The rate constant, k, is independent of x and y in the range studied but is a function of the metal. An activation energy of 18.4 ± 0.6 kcal/mol was found. It is postulated that the following sequence of reactions occurs:



$$M^{2+}O^{2-} + RSH \longrightarrow \left[\begin{array}{cc} R-S & -H \\ M^{2+} & O^{2-} \end{array}\right] \longrightarrow \begin{array}{cc} RS & H \\ M^{+} & O^{-} \end{array} \quad (1)$$

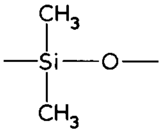
$$2R-S-M^{+} \longrightarrow (M^{+})_2\, R-S-S-R_{\mathrm{Ads}} \quad (2)$$

$$(M^{+})_2\, R-S-S-R_{\mathrm{Ads}} \longrightarrow 2M^{+} + R-S-S-R \quad (3)$$

$$2M^{+} + 1/2\ O_2 \longrightarrow 2M^{2+} + O^{2-} \quad (4)$$

$$2\ OH^{-} \longrightarrow O^{2-} + H_2O \quad (5)$$

Depending upon the metal and temperature, desorption (step 3) or reaction (step 2) may be the rate-limiting step. Steps (3) and (4) may occur simultaneously. Metals for which no oxidation/reduction couple exists show little catalytic effect even though a strongly bonded interfacial layer is formed. The interfacial layer which formed rapidly was studied via reflection spectroscopy and protective ability. It is strongly bonded, of low critical surface energy and consists primarily of:



$$-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-$$

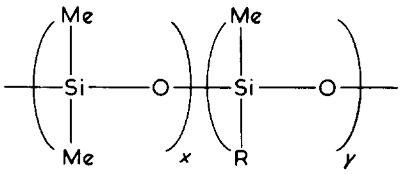
However, it is enriched in sulphur over the bulk polymer.

INTRODUCTION

The oxidation of mercaptan groups to form disulphide groups is of technical[1] and biological importance[2]. There have been numerous studies of both biologically important molecules[2] and simple alkyl thiols, mainly using metal ion catalysts[3,4]. Thiols also play an important role in metal protection where the ability to form a strong metal–sulphur bond is critical to corrosion resistance[5]. However, the oxidative coupling of mercaptans by metals does not appear to have been extensively investigated, particularly in liquids of low dielectric constant.

In our recent work investigating the behaviour of mercaptan groups attached to poly(dimethyl siloxanes)[6] it was observed that the kinetics of loss of mercaptan groups under oxidative conditions were markedly affected by the specific metal substrate. Not only was the rate of oxidation dependent upon the specific metal but the reaction order could also be different or, with certain metals, change with the particular temperature regime.

This paper deals with metal catalysed oxidative coupling of mercaptan groups attached by propyl spacers to poly(dimethyl siloxane) molecules of the form:



$$\left(-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{O}-\right)_x\left(-\underset{\mathrm{R}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{O}-\right)_y$$

in which $x \gg y$. In addition to studies of reaction rates, the nature of the interfacial film formed with these metals is also considered.

0032–3861/78/1908–0934\$02.00

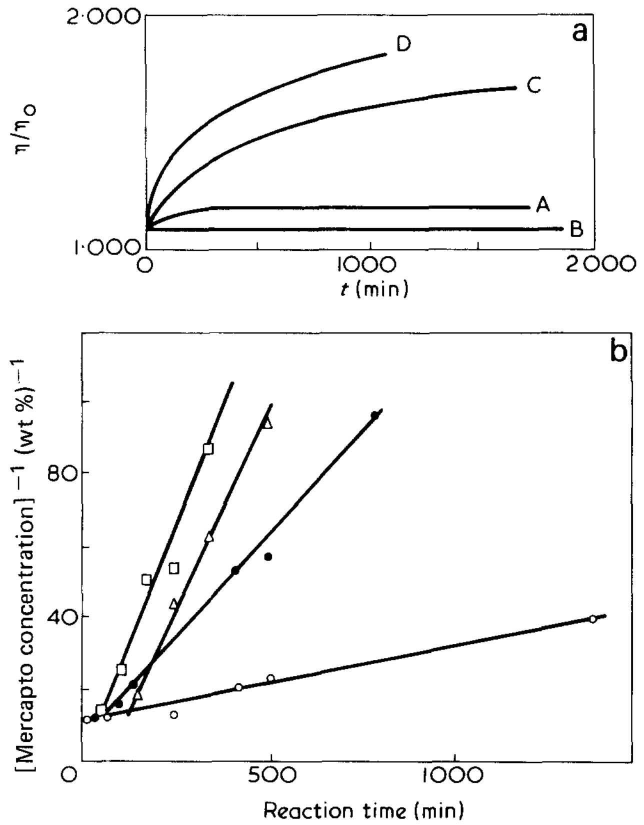


Figure 1 Kinetics of oxidation. (a) A, Mercapto fluid under nitrogen, 177°C; B, poly(dimethyl siloxane) under oxygen, 177°C; C, mercapto fluid under oxygen, 150°C; D, mercapto fluid under oxygen, 205°C. (b) Mercapto fluids under oxygen at 177°C. 0—0, no catalyst; ●, copper; △, brass; □, bronze

EXPERIMENTAL

The materials used were mercapto functional polysiloxanes having viscosities ranging from 100 cs to ~500 cs and were obtained as samples from major US silicone manufacturers. Characterization was performed by infra-red spectroscopy, gel permeation chromatography, atomic absorption spectroscopy, nuclear magnetic resonance, differential thermal analysis viscometry, and wet titrimetry. Due to the low concentrations of mercaptan typically encountered (e.g. 100–1000 ppm) adaptations of wet titrimetry proved most appropriate for its measurement.

Poly(dimethyl siloxanes) are non-polar and water insoluble and attempts at mercaptan determination by conventional aqueous methods were found to yield a gummy precipitate or milky solution which inhibited accurate end-point detection by any means. Special procedures were developed to yield reliable, accurate and convenient analyses.

The first procedure involved titrating 1 g of sample dissolved in 50 ml of a 3:2 toluene/isopropanol solution containing 10 ml of dimethyl sulphoxide and 5 ml distilled water with a 0.005 N ethanolic iodine solution to a permanent faint yellow end-point.

The second procedure was found ideally suited for oxidized samples which turned yellow as a result of reaction. The method involved a silver, silver chloride, sodium acetate bridge, calomel electrode potentiometric detection of titration using ~4 g of sample dissolved in 100 ml 1:1 methanol/toluene to which had been added 0.2 g ammonium nitrate. The titrant was 0.01 N silver nitrate in ethanol.

Kinetics of oxidation were studied by heating 250 ml samples in the presence of excess oxygen to temperatures up to 180°C. In the catalytic experiments 200 cm^2 of metal catalyst were used.

The metals used were commercial alloys, cleaned with dilute nitric acid and acetic acid and washed in distilled water. After air drying, the samples were presumed to have reached an equilibrium between surface oxide and ambient air.

RESULTS

Kinetics

Preliminary experiments established the following points.

(1) The reaction observed with the mercaptan fluids was not caused by poly(dimethyl siloxane) degradation Thermal oxidative degradation of poly(dimethyl siloxane) did occur at the temperatures of interest but viscosity changes were at least an order of magnitude smaller than those observed with mercapto silicones.

(2) The glassware had to be well cleaned in order to obtain reproducible results.

(3) Little dissolved metal was discovered in the bulk fluids after reaction. This observation appears to rule out soluble metal ion complexes as being responsible for the catalysis.

Figure 1 shows typical reaction rate curves obtained by measuring the mercaptan concentration and viscosity as functions of time and in the absence of oxygen, in the presence of excess oxygen, and in the presence of excess oxygen and copper metal. At these temperatures, the copper was well oxidized although the rate of copper oxidation was found to be inhibited by the presence of an adsorbed layer of mercapto silicone. In the absence of oxygen, viscosity changes were minimal. The total sulphur content remained constant within experimental error. Both $\bar{M}_w$ and *MWD* increased with the extent of reaction as shown in *Figure 2*. In addition to the overall increase in $\bar{M}_w$, a small (~1–2%) quantity of low molecular weight material developed with time.

In the absence of catalyst, the reaction was always second order with respect to –SH concentration (in the presence of excess oxygen), i.e.:

$$\frac{d[-SH]}{dt} = -k_2[-SH]^2[O_2]$$

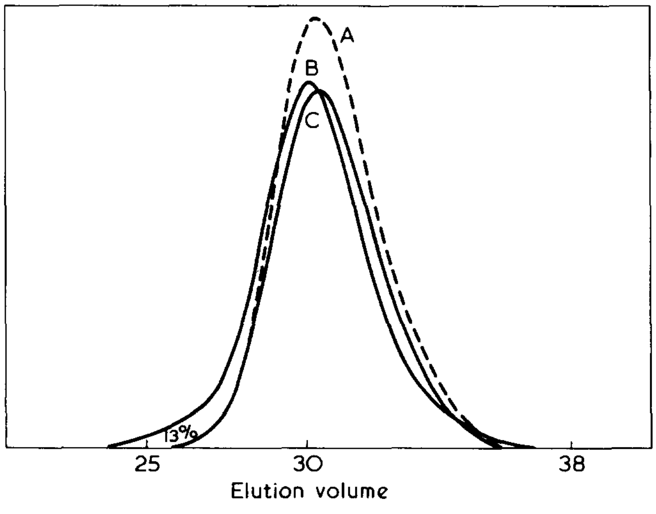


Figure 2 Molecular weight changes. A, Virgin fluid, B, 30 h +N$_2$ at 150°C; C, 30 h + O$_2$ at 150°C

Table 1 Catalysis by metals

	Order of reaction	Rate constant*	Pre-exponential term*	E_{act} (kcal/mol)
Control (no metal)	2	4.0×10^3 (T = 160°C)	4.1×10^6	18.4 ± 0.6
Copper	2 (T > 160°C)	9×10^{-2} (T = 170°C)	9.3×10^7	18.4 ± 0.6
	0 (T < 160°C)	5.1×10^{-4} (T = 160°C)	5.4×10^6	20.0 ± 1.0
Brass	2	2.3×10^{-1}		
Bronze	2	2.5×10^{-1}		
Cu/1.3% Be	0	1.6×10^{-4}		
Silver	Inert	—	—	—

* Units k_2, l/mol sec; k_0, mol/l sec

The rate constant, k_2, obeyed the Arrhenius equation:

$$k_2 = k\exp(-E/kT)$$

with an activation energy of 18.4 kcal/mol. $k_2 = 4.0 \times 10^{-3}$ l/mol and $k = 4.1 \times 10^6$ at 160°C.

The second order rate constant was independent of the mercaptan content in the range considered (y/x = 1/300 to 1/10). Little gel formation was observed at low y/x ratios but rapid gelation, particularly on metal surfaces, was observed at higher y/x ratios. This is to be expected since most molecules become polyfunctional when y/x = 1/70. Given a fully equilibrated synthesis, the distribution of SH groups should be random. Thus any polymer, in addition to having a distribution of molecular weights, will also have a distribution of SH groups per molecule. Beyond noting that gelation occurred rapidly as the SH content exceeded 1 per molecule, no attempts were made to study gelation. A consequence of gelation on the metal surface was to force a low mercaptan concentration in order to study metal catalysis. Thus, most of the work on metal surfaces was carried out at approximately 0.03 molar SH concentration.

Experiments carried out on copper and oxidized copper surfaces showed no detectable differences. The rate of copper oxidation at 160°C is rapid even after reaction with mercaptan containing fluids. The reaction of the mercapto silicone fluid over copper was rapid and, above 160°C, second order, as in the non-catalysed case. However, at lower temperatures (<160°C) the reaction rate was independent of mercaptan concentration. The activation energies were: E_2 = 18.4 ± 0.6 kcal/mol and E_0 = 20.0 ± 1.0 kcal/mol.

The catalytic effect of copper and the change in order of reaction prompted a more detailed investigation of the surface chemistry and other metal substrates.

Working at equivalent surface to volume ratios, a number of copper-based alloys were studied as well as metals such as nickel and silver and metals in which surface oxidation/reduction couples were thought not to exist. The catalytic effect of the metals studied is shown in *Table 1*. In order to rule out the homogeneous metal ion catalysed reaction of the type discussed by Cullis *et al* [3], the level of metal in the fluid was determined. While this determination was complicated by the excess of SiO_2 formed upon pyrolysis, levels of metal ions in solution were estimated to be no more than 2 ppm at the completion of any given experiment. *Table 1* indicates that the copper-based alloys were catalytically active. Metals which could have surface oxidation/reduction couples were usually active but oxidatively inert metals were catalytically inert.

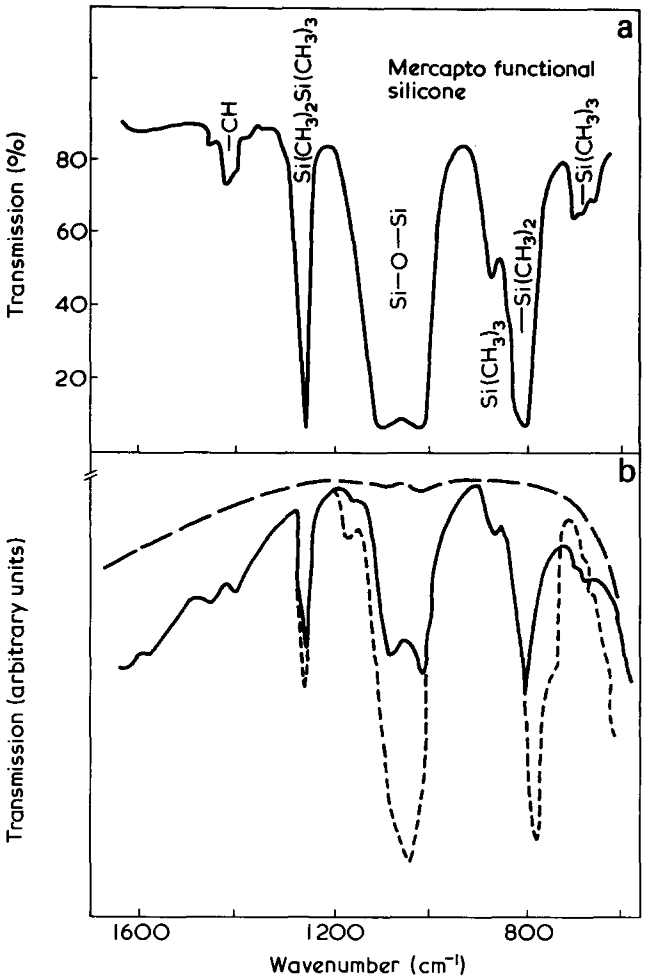


Figure 3 Spectra of treated copper surfaces. (a) Transmission spectrum of mercapto containing poly(dimethyl siloxane) (0.03 molar in [SH]); (b) a.t.r. spectra. ——, Thick film (unwashed) of mercapto fluid; — · — · ; surface treated with poly(dimethyl siloxane) after washing in boiling toluene; — — —, mercapto treated surface after washing in boiling toluene (higher gain than unwashed film)

Surface chemistry

In view of the catalysis and different orders of reaction, the nature of the surface film formed by the mercapto silicone was investigated. Copper strips treated with non-functional and mercapto fluid were washed three times in fresh boiling toluene and examined by a.t.r. spectroscopy. The spectra are shown in *Figure 3*. The non-functional silicone was almost completely removed from the surface by washing. The a.t.r. spectra of the treated metal closely resembled the spectrum of the parent fluid. Even for the parent fluid, it was extremely difficult to assign bands to either the —S—H or the $(CH_2)_3$ group. These bands are either weak (those involving the S atom) or masked by the parent molecule. The reflection spectra in general showed the de-

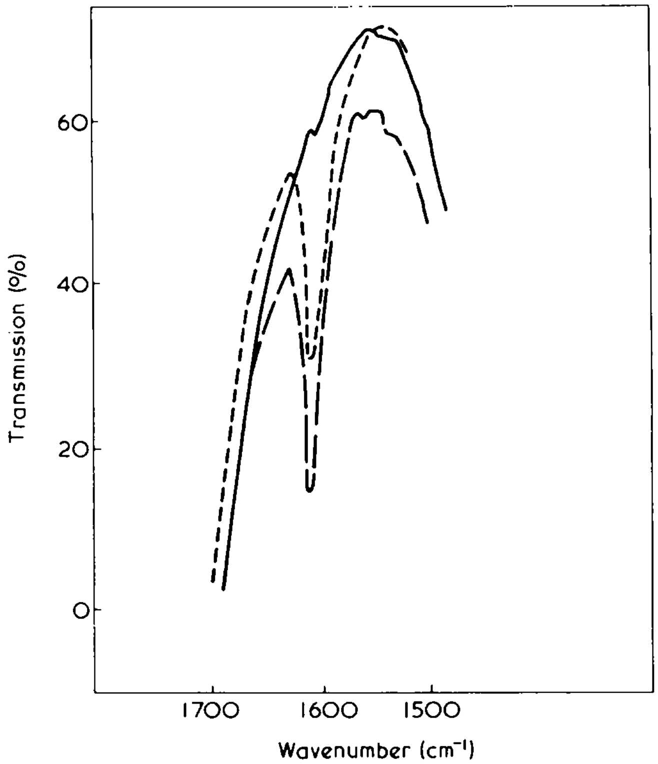


Figure 4 Reaction of ethylene to acrylic acid copolymer with treated copper surfaces, 30 min at 150°C. — — —, Untreated; ——, mercapto fluid treated and washed; — · — ·, poly(dimethyl siloxane) treated and washed

velopment of one new band at long wavelengths. In the case of copper, the band at 580 cm^{-1} is characteristic of the oxide as is the band observed at 545 cm^{-1} with nickel. In common with earlier studies[7–9], no bands characteristic of M–S, C–S, or C–M groups were detected. E.s.c.a. indicated some surface enrichment with sulphur over that in the bulk fluid but gross surface sulphidation did not occur. Within experimental accuracy, there was no loss of sulphur from the fluid system. (Note that the surface to volume ratio is small.) The e.s.c.a. studies indicated Cu^{I}, Cu^{0}, Cu^{II} and S^{II}. On silver substrates, the sulphur appeared in the S^{IV} state and was slightly enriched over the fluid (based on S:Si ratios). Since a strongly coherent interfacial film was formed on silver while dimerization was not accelerated, it was suspected that the residence time of a mercaptan-containing molecule was longer on silver and that the sulphur atom may have been oxidized to an oxygen-containing group.

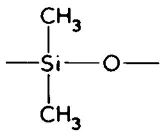
Close study of the a.t.r. spectra and bulk fluid revealed no sign of oxidation to carboxylic acid or of copper carboxylate formation. Experiments using carboxylic acid functional polydimethyl fluids showed rapid attack on copper and formation of a soluble, readily detectable, copper carboxylate. The formation of a surface crosslinked, oxidized film of the type discussed by Willis[10,11] seems unlikely within the times of these experiments at these temperatures (<180°C).

Wetting measurements of the treated surface indicated a critical surface energy[12] of 21.5 dyne/cm. This is typical of a poly(dimethyl siloxane) surface. It was noted, however, that the film on copper was either weaker than that on silver or the coverage was less. This conclusion is based on the observation that an aqueous solution of ethylene diamine which causes the base catalysed hydrolysis of Si–O–Si bonds readily attacked the interfacial layer on copper and within 10 min had spread over the surface. No spreading occurred on a mercapto silicone-treated silver surface in 60 min.

In addition to their low surface energy, the interfacial films also acted as excellent corrosion inhibitors. The reaction of an ethylene coacrylic acid polymer at 150°C with copper was found to be a simple means of studying corrosion inhibition. The decrease in –COOH and build-up of $-COO^-$ was easily monitored from the i.r. spectra of thin films. It was again shown that treatment with poly(dimethyl siloxane) provided little corrosion protection whereas reaction was slow after mercapto silicone treatment as shown by the spectra in *Figure 4*.

DISCUSSION

The experimental evidence indicates that a strongly bonded interfacial layer is formed by the mercapto silicone polymers upon a number of metal surfaces. The low surface energy and reflection spectra indicate that the film is predominantly



$$-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-$$

However, it has not been possible to identify the precise means by which the polymer is attached to the surface. This is in agreement with previous observations by other workers who studied the interaction of alkyl mercaptans with metal surfaces[7–9]. Blyholder[7,8] discussed the infra-red spectra of alkyl mercaptans, RSH, on metals such as nickel in terms of a Ni–S–R structure. The weak absorption of the –S–R and the –SH groups precludes their detection except at high concentrations. In the copper–poly(dimethyl siloxane) such bands might also be masked by the absorption by the –Si–O or the $Si-CH_3$ groups

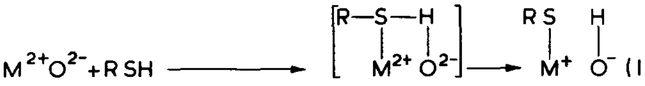
In the case of silver a very stable interfacial layer was formed. No catalysis was observed. The surface oxide of silver, reported to be $Ag^+O_2^-$ [14] is not stable. Since the sulphide of silver is stable in the presence of oxygen[15], oxidation of a sulphided surface is unlikely to take place. Thus, with silver surfaces, no oxidation/reduction couple is possible and the adsorbed film is more stable than that on more readily oxidized surfaces such as copper. E.s.c.a. studies of silver surfaces showed the predominant species (other than dimethyl siloxane) to be Ag^{I} and S^{IV}. Thus it appears that the residence time of the mercaptan-containing molecule on silver is long compared with that on copper and that the sulphur atom may be oxidized to an $-SO_x$ group. Given that most silver salts are insoluble, such an oxidized group would remain on the silver surface and not be desorbed into the bulk of the fluid.

The reaction kinetics observed over copper show a definite change in the order of reaction. At temperatures < 160°C zero order kinetics were observed which changed to second order as the temperature of reaction was increased. The second order rate constant had an activation energy of 18.4 kcal/mol similar to that of the uncatalysed reaction, whereas the activation energy of the zero order reaction was 20.0 kcal/mol. The small difference suggests that the mechanism of the catalytic reaction could be sensitive to small changes in the nature of the surface.

A zero rate constant for the overall reaction can be explained by a very rapid reaction with the surface or a reaction limited by a slow desorption step. It is difficult to reconcile a rapid initial reaction with the surface with the activation energy considerations and change in reaction order. For this reason the desorption rate-limiting step is preferred. Such a rate-limiting step implies that both the initial adsorption step and subsequent reactions on the surface occur more rapidly than desorption.

However, with increasing temperature desorption takes place more rapidly until it is no longer the rate-limiting step; the rate of reaction is then limited by reaction of two molecules on the surface.

In order to account for these observations the following sequence of reactions on an oxidized metal surface is postulated:



$$M^{2+}O^{2-} + RSH \longrightarrow \left[\begin{array}{cc} R-S & -H \\ | & | \\ M^{2+} & O^{2-} \end{array}\right] \longrightarrow \begin{array}{cc} RS & H \\ | & | \\ M^{+} & O^{-} \end{array} \qquad (1)$$

$$2R-S-M^{+} \longrightarrow (M^{+})_2\,R-S-S-R_{Ads} \qquad (2)$$

$$(M^{+})_2\,R-S-S-R_{Ads} \longrightarrow 2M^{+} + R-S-S-R \qquad (3)$$

$$2M^{+} + 1/2\,O_2 \longrightarrow 2M^{2+} + O^{2-} \qquad (4)$$

$$2\,OH^{-} \longrightarrow O^{2-} + H_2O \qquad (5)$$

Overall:

$$2M^{2+}O^{2-} + 2R-S-H + 1/2\,O_2 \longrightarrow 2M^{2+}O^{2-} + H_2O + R-S-S-R$$

Such a sequence of reactions is very similar to that postulated to occur between alkyl mercaptans and metal ion substituted zeolites[13].

The zero order reaction would be limited by step (3), desorption of the dimer, R–S–S–R, whereas the rate-limiting step for the second order reaction would be step (2). It has not been possible to determine whether or not reoxidation of the metal surface occurs subsequent to desorption or if a reaction such as the following is necessary for the coupling reaction to occur:

$$2\,R-S-M^{+} + 1/2\,O_2 \longrightarrow 2M^{2+}O^{2-} + R-S-S-M$$

The need for simultaneous oxidation and coupling of sulphur atoms could be based on the following. Metals for which oxidation/reduction couple is not normally seen do not catalyse the reaction even though a strongly bonded interfacial layer is rapidly formed. In addition, beryllium copper exhibits a zero order reaction, i.e. desorption is rate-limiting. The oxidation rate of beryllium copper is much less than that of copper[16] and the surface layer becomes enriched in Be (as BeO). However, little is known about catalysis over Be/Cu or over copper alloys other than copper/nickel which is often used as a model for alloy catalysts.

The non-catalysed reaction mechanism has not been studied beyond the experiments noted in which the rate constant was established to be characteristic of structure but not to depend on molecular weight or mercaptan level per molecule. The reaction was second order in [–SH] as compared to the first order reaction of alkyl thiols in alkaline media reported[3]. The differences may lie in the use of non-ionizing solutions and the excess O_2 used in our experiments.

ACKNOWLEDGEMENTS

The e.s.c.a. measurements were carried out by A. DeLuca and G. Ceasar and the g.p.c. work by J Pacco.

REFERENCES

1 See, e.g. Berenbaum, M. in 'High polymers' (Ed. E. M. Fettes) Interscience, Vol XIX, Chapter XI, p.893

2 See, e.g. Whitfield, R. E. and Wasley, W. L. in 'High Polymers' (Ed. E. M. Fettes) Interscience, Vol XIX, Chapter VI, p.452

3 Cullis, C. F. and Trimm, D. L. *Faraday Soc. Discuss.* 1968, **46**, 144; Cullis, C. F., Hopton, J. D. and Trimm, D. L. *J. Appl. Chem.* 1968, **18**, 330; Cullis, C. F., Hopton, J. D., Swan, C. J. and Trimm, D. L. *J. Appl. Chem.* 1968, **18**, 335; Swan, C. J. and Trimm, D. L *J. Appl. Chem.* 1968, **18**, 340

4 Wallace, T. J., Schriesheim, A., Hurwitz, H. and Glaser, M. B. *Ind. End. Chem. Process Des. Dev.* 1964, **3**, 237

5 Fujii, S. and Kobayashi, K. *Ann. Univ. Ferrara Sez.* IV, 1966, p 829; *Chem. Abstr.* **66**, 110916

6 US Pat 4 029 827

7 Blyholder, G. D. and Bowen, D. O. *J. Phys. Chem.* 1962, **66**, 1288

8 Blyholder, G. D. and Cagle, G. W. *Environ. Sci. Technol.* 1971, **5**, 158

9 Neff, C. D. and Kitching, S. C. *J. Phys. Chem.* 1974, **78**, 1648

10 Willis, R. F. and Shaw, R. F. *J. Colloid Interface Sci.* 1964, **13**, 347

11 Tabor, D. and Willis, R. F. *Wear* 1969, **13**, 413

12 Zisman, W. A. 'Adhesion and Cohesion' (Ed. P. Weiss) Elsevier, Amsterdam, 1962, p.176

13 Bergk, K. H. and Wolf, F. *Z. Chem.* 1974, **14**, 344

14 Clarkson, R. B. and Cirillo Jr, A. *J. Catal.* 1974, **33**, 392; Czanderna, A. W. *J. Phys. Chem.* 1964, **68**, 2765

15 'Lange Handbook of Chemistry', 7th Edn, Handbook Publishers, p.1582

16 Sanderson, M. D. and Scully, J. C. 'Oxidation of Metals' 1971, **3**, 50