

PYROLYSIS AND HYDROPYROLYSIS OF DIPHENYLMETHANE AND SULPHUR-CONTAINING COMPOUNDS IMMOBILISED ON SILICA

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ABSTRACT

The use of high pressures and dispersed catalysts, such as sulphided molybdenum (Mo) in fixed-bed hydropyrolysis of coals give rise to increased tar yields. In order to improve our understanding of these phenomena, particularly in relation to cleavage of C-C and C-S bonds, experiments have been conducted on samples of silica-immobilised benzene, diphenylmethane, thioanisole and dibenzothiophene (DBT). These model substrates have the inherent advantage that they do not soften and thus stay in the reactor. Moreover, for the surface-immobilised benzene, the Si-O-C bond linking the substrate to the surface is reasonably stable and does not show significant cleavage until 550°C (peak maximum) with a high yield of benzene being achieved at 150 bar hydrogen pressure. For the diphenylmethane substrate, the use of 150 bar hydrogen pressure and the Mo catalyst both reduced the peak evolution temperatures for benzene and toluene clearly demonstrating their separate contributions to promoting C-C bond cleavage. Desulphurisation of the DBT substrate occurred only in hydrogen and the thermal decomposition of the thioanisole substrate was altered markedly by the Mo catalyst.

INTRODUCTION

Diphenylalkanes have been extensively used as model substrates to probe the free radical mechanisms involved in C-C bond cleavage reactions in coal liquefaction (1). However, the fact that the macromolecular structure in coals is undoubtedly subject to highly restricted motion suggests intuitively that free radical pathways are likely to be somewhat different from those encountered in the vapour phase. Indeed, this has been confirmed by the use of silica-immobilised substrates where bimolecular reaction steps are significantly perturbed in the cases of diphenylethane, propane and butane compared to the corresponding vapour phase reactions (2-4). Thus far, immobilised diphenylalkanes have only been studied at temperatures close to 400°C, but the fact that silicas do not melt below ca 1000°C means that the immobilised substrates also have considerable potential for probing coal and oil shale pyrolysis mechanisms at temperatures in the range 500-600°C which are generally used to maximise tar yields in both fluidised-beds and well-

swept fixed-beds (5-7). The maximum temperature at which the substrates can be used will clearly be dictated by the cleavage of the C-O bond between the immobilised species and the silica. However, there are a number of phenomena related to coal pyrolysis, particularly under hydrogen pressure (hydropyrolysis), which cannot be adequately modelled using model compounds in the vapour phase (8). For example, the use of hydrogen pressure increases tar yields but without a concomitant increase in hydrocarbon gas yields at relatively low temperatures (< 600°C) where char hydrogasification would not appear to occur to a significant extent (5). Secondary reactions of volatiles in coal pyrolysis are often implicated to explain reduced tar yields but, again, these are difficult to model, for example, with respect to non-thiophenic sulphur forms where C-S bonds are inherently weak but readily inter-convert to thiophenes (9).

In this study, pyrolysis and hydropyrolysis experiments have been conducted on silica-immobilised samples of benzene, diphenylmethane, thioanisole and dibenzothiophene (DBT) to begin to quantify the effects of hydrogen pressure and dispersed catalysts on C-C and C-S bond cleavage. The sulphur-containing substrates are also particularly useful in relation to temperature programmed reduction (TPR) where the authors from University of Strathclyde have devised a well-swept high pressure reactor (10) to enable virtually all the organic sulphur in coals to be released as hydrogen sulphide and, to a much lesser extent, as thiophenic compounds in tars. The only model substrates which can be possibly used to determine standard reduction temperatures in this regime for different organic sulphur forms are those which do not soften below the decomposition temperatures of the C-S bonds.

EXPERIMENTAL

The silica-immobilised benzene, diphenylmethane, thioanisole and DBT substrates were prepared as described previously (2-4) from the appropriate phenol. In the case of the sulphur-containing substrates, commercially available thioanisole and 3-hydroxyDBT synthesised from the corresponding bromo derivative were used (11). The purity and loadings for the substrates as determined by base hydrolysis and subsequent gas chromatographic analysis of the silylated products were as follows. For DBT, GC/MS indicated that the remainder of the substrate appears to be derived from dihydroxyDBTs in the starting material.

	Loading, mmol g ⁻¹	purity, %
Benzene	0.36	98.4
Diphenylmethane	0.45	99.5
Thioanisole	0.60	99.9
Dibenzothiophene	0.60	94.7

The sulphided Mo catalyst was prepared from ammonium dioxodithiomolybdate as previously described (12,13) which was loaded onto the substrates in methanol to give nominal Mo loadings of 2 or 5% w/w substrate. This helped to agglomerate the fine silica particles but there is the possibility that hydrolysis may have occurred to a limited extent. However, little difference was observed in the volatile evolution profiles without catalyst for the thioanisole substrate when the sample was contacted with methanol as a control experiment.

The high pressure apparatus used here is the same as that used recently for TPR (10). The reactor tube was smaller but otherwise identical to that used previously in fixed-bed hydropyrolysis

studies (18" c.f. 42" both with 9/16" o.d., Incoloy) (12,13). Between 0.2 and 0.5 g of sample (<75 μ) mixed with sand (up to 1:5 mass ratio, 75-250 μ sand to limit pressure drop across the reactor) was loaded into the reactor and held in place with steel wool plugs. The reactor tube was heated resistively up to 600°C at either 2 or 5°C min⁻¹. Hydrogen and nitrogen pressures of 30 and 150 bar were used with superficial gas velocities in the range 0.2-0.5 m s⁻¹. After pressure let-down through either a metering valve or a mass flow controller, the gas stream was sampled through a 1.8 m length of heated capillary tubing at a rate of 25 cm³ min⁻¹ into a quadrupole mass spectrometer (VG Monitor, 0-100 a.m.u.). The signal from the control thermocouple situated in the coal bed was also fed to the mass spectrometer facilitating the construction of direct plots of evolved gas concentrations against temperature. The evolution profiles for the various species monitored can be fitted using the Redhead equation (14) to derive activation energies assuming first-order kinetics are operative.

RESULTS AND DISCUSSION

Benzene

The evolution profiles for benzene in 150 bar nitrogen and 150 bar hydrogen with and without catalyst and those for benzene, methane and toluene in 150 bar hydrogen are shown in Figures 1 and 2, respectively. In both nitrogen and hydrogen, the peak maxima for benzene are close to 550°C although, in nitrogen, there is also a peak at 500°C. However, much less benzene evolves in nitrogen and it is estimated that the amount is below 20% of that obtained with hydrogen at 150 bar. This is to be expected because the only source of hydrogen is the coupling of two molecules of surface-attached benzene. Indeed, the samples recovered from the nitrogen pyrolysis experiments were black qualitatively confirming that much less benzene had been released than in hydrogen where a small amount of methane and a trace of toluene were also observed at ca 570-600°C suggesting that hydrogasification is beginning to occur. No methane and toluene were observed with nitrogen confirming that hydrogasification does not occur under these conditions. Further, no phenol was detected indicating that the Si-O bond is unaffected. Benzene pyrolysis in fluid phases is a complicated process that follows an incompletely understood pathway (1) but it is interesting to note that the pyrolysis of benzene to give diphenyl and hydrogen begins to occur at reasonable rates at ca 550°C, the same temperature found here for benzene formation.

Catalyst addition at 150 bar hydrogen pressure vastly reduced the amount of benzene released. Further, the peak evolution temperature for the relatively small amount evolved was close to ca 500°C which is significantly lower than without catalyst (Figure 1). However, ions corresponding to methane and a number of alkene species including C₄H₆ and C₅H₈ were also observed suggesting that the benzene released above ca 500°C had been hydrocracked to a significant degree.

Diphenylmethane

The peak evolution temperatures for benzene and toluene formation are both 550°C with nitrogen (Figure 3) and the recovered sample was coloured indicating that some char must be formed on the substrate. Taking into account the response factors (benzene/toluene = ca 1.3 for the ions monitored), it is evident that more toluene is released than benzene (Figure 3, mass ratio being ca 2.5). Activation energies for fluid diphenylmethane have been found to be highly dependent on reaction conditions (1). At low pressures, they are governed by dissociation of the weakest bonds (C-C and C-H are comparable at ca 82 kcal mol⁻¹) and hence temperatures in excess of 700°C are

required. However, at higher pressures (18-62 bar in diphenyl diluent), the activation energy is 66 kcal mol⁻¹ in the temperature range 550-600°C (1) and this is close to the value of 63 kcal mol⁻¹ derived from the evolution profile of benzene with nitrogen. The reaction mechanism in nitrogen is not well-understood but the hydrogen must come from the diphenylmethane itself probably through cyclisation to fluorene. Hence, it is possible that surface-immobilisation and the *para*-silyloxy substituent are lowering the activation energy for toluene release in some unknown fashion.

In hydrogen (without catalyst), roughly equal amounts of benzene and toluene evolve (Figure 4) with the white colour of the residue suggesting qualitatively that the char yield is small. Indeed, comparing the peak areas for benzene and toluene with those in the traces for the nitrogen runs, it is evident that, as anticipated, the amounts evolved are greater (ca 60 % more toluene and 4 times as much benzene). However, both evolution profiles would appear to be comprised of two components. The higher temperature one (550-580°C) is consistent with that anticipated for cleavage of the Si-O-C bond in surface-immobilised benzene and toluene is similarly formed following the prior hydrogenolysis of the C-C linkages in diphenylmethane according to the reaction scheme below.



Interestingly, the peak evolution temperature from C-C bond cleavage for toluene (495°C) is lower than that for benzene (530°C). The peak areas in the evolution profiles for the run with catalyst are lower than with hydrogen pressure alone (Figure 5) even allowing for the fact that less sample was used. The peak evolution temperatures for benzene and toluene are in the range 430-450°C and are significantly lower than those without catalyst. Further, with catalyst, no high temperature components in the evolution profiles of benzene and toluene are evident presumably because hydrocracking has occurred in a similar manner to the immobilised benzene (see above). The results clearly demonstrate that the use of hydrogen pressure and then the catalyst vastly reduce the activation energies for the dissociation of the C-C linkages in the immobilised diphenylmethane.

Thioanisole

Without catalyst at 150 bar hydrogen pressure, a H₂S peak with a maximum at ca 360°C is observed between 320-480°C (Figure 6) but there is no detectable CH₃SH. The methane profile comprises two components and the lower temperature one would appear to match the H₂S peak. Benzene, and to a lesser extent toluene, evolve from 380°C with the bulk evolving between 480 and 600°C probably from cleavage of the Si-O-C bond as found for the benzene substrate (Figure 2). Further, the high temperature component of the CH₄ peak between 520 and 600°C broadly corresponds to the tail off in toluene concentration.

With catalyst, a low temperature CH₃SH peak is observed (Figure 7) with only a small amount of H₂S and a hint of methane being evolved at this stage. Some of the H₂S is undoubtedly from the thermal decomposition of the ammonium dioxodithiomolybdate but the overall H₂S concentration is considerably lower with catalyst which might be partly attributable to chemisorption of H₂S on the sulphided Mo (see below for DBT). The component of the methane peak at 350°C observed without catalyst has almost disappeared. Again, high temperature benzene and toluene peaks are observed from Si-O-C bond cleavage but the ratio of benzene to toluene is much higher than without catalyst due to more sulphur being eliminated as CH₃SH. These experiments clearly

demonstrate the catalyst markedly affects the desulphurisation pathways of the immobilised thioanisole favouring cleavage of the phenyl-SCH₃ bond.

Dibenzothiophene

No detectable H₂S is evolved in nitrogen from the DBT substrate but, as anticipated from previous TPR and pyrolytic experiments on coals⁽¹⁰⁾, significant quantities are released with hydrogen pressures of 30 and 150 bar (Figure 8). The peak evolution temperature of ca 500°C (slightly lower at the higher pressure) is close to those in the range 450-500°C found in high pressure TPR for a number of coals⁽¹⁰⁾ confirming that the dominant peaks arise from thiophenes; lower temperature peaks between 300 and 400°C, attributed to non-thiophenic forms are also observed for low-rank coals.

Catalyst addition to the DBT substrate vastly reduces the amount of H₂S evolved at 150 bar (Figure 8). This is thought to arise from chemisorption of H₂S on the sulphided Mo catalyst as the mole ratio of Mo to evolved sulphur is relatively high (ca 0.4). The peak maximum of ca 430°C is again similar to those observed thus far for coals in TPR⁽¹⁰⁾. However, because the mole ratio of Mo to evolved H₂S was much lower for the coals, no loss of intensity was observed upon catalyst addition.

CONCLUSIONS

The benzene results have demonstrated that immobilised model compounds are stable enough to be used in the type of pyrolysis and hydroxyrolysis regimes used here. It has been shown using the diphenylmethane substrate that dispersed sulphided Mo catalyses the hydrocracking of C-C bonds in the solid-state. The thioanisole and DBT samples have demonstrated the promise of using immobilised sulphur compounds as standards in TPR.

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REFERENCES

1. M.L. Poutsma, *Energy & Fuels*, **4**(2), 113 (1990) and references therein.
2. A.C. Buchanan III and C.A. Biggs, *J. Org. Chem.*, **54**, 517 (1989).
3. A.C. Buchanan III, P.F. Britt and M.L. Poutsma, *Prepr. Am. Chem. Soc. Div. Fuel Chem.*, **35**(1), 217 (1990).
4. P.F. Britt and A.C. Buchanan III, *J. Org. Chem.*, **56**, 6132 (1991).
5. C.E. Snape, *Fuel*, **70**, 285 (1991) and references therein.
6. Z.S. Gonenc, J.R. Gibbins, I.E. Katheklakis and R. Kandiyoti, *Fuel*, **69**, 383 (1990).
7. A.M. Ruben and T.T. Coburn, *Proc. 1981 Eastern US Oil Shale Symp.*, 21.
8. R. Cypres, C. Braekman-Danheux and A. Progneaux, *Fuel*, **65**, 1299 (1986).

9. M.L. Gorbaty, S.R. Kelemen, G.N. George, P.J. Kwiatek and M. Sansome, *Fuel*, **70**, 396 (1991) and references therein.
10. C.J. Lafferty, S.C. Mitchell, R. Garcia and C.E. Snape, *Fuel*, accepted for publication and C.J. Lafferty, C.E. Snape, R. Garcia and S.R. Moineho, *Prepr. Am. Chem. Soc. Div. Fuel Chem.*, **36(3)**, 877 (1991).
11. M. Gates and W.G. Webb, *J. Am. Chem. Soc.*, **80**, 1186 (1957).
12. C.E. Snape and C.J. Lafferty, *Prepr. Am. Chem. Soc. Div. Fuel Chem.*, **35(1)**, 1 (1990).
13. C.E. Snape, C.J. Lafferty, S. Mitchell, F. Donald, C. A. McArthur, G. Eglinton, N. Robinson and R. Collier, *Final Report, EC Project EN3V-0048-UK(H)* (1991).
14. P.A. Redhead, *Vacuum*, **12**, 203 (1962).

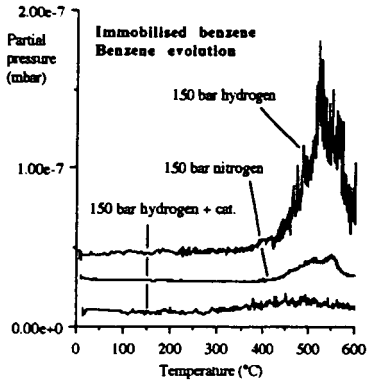


Figure 1. Evolution profiles of benzene from immobilised benzene.

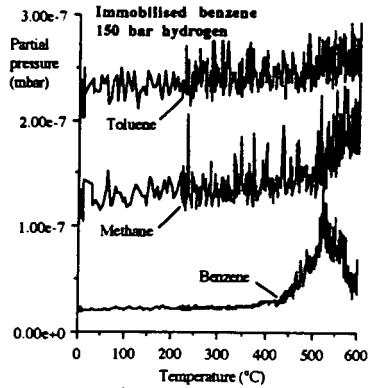


Figure 2. Evolution profiles of benzene, methane and toluene from immobilised benzene in 150 bar hydrogen.

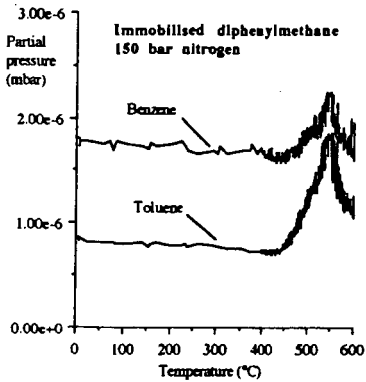


Figure 3. Evolution profiles of benzene and toluene from immobilised diphenylmethane in 150 bar nitrogen.

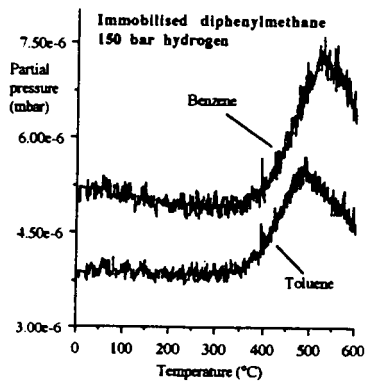


Figure 4. Evolution profiles of benzene and toluene from immobilised diphenylmethane in 150 bar hydrogen.

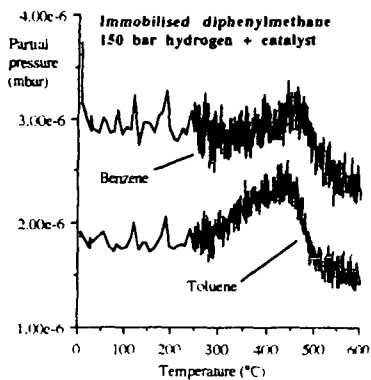


Figure 5. Evolution profiles of benzene and toluene from immobilised diphenylmethane in 150 bar hydrogen with the Mo catalyst.

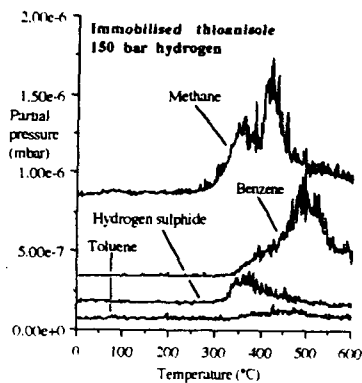


Figure 6. Evolution profiles of hydrogen sulphide, methane, benzene and toluene from immobilised thioanisole in 150 bar hydrogen.

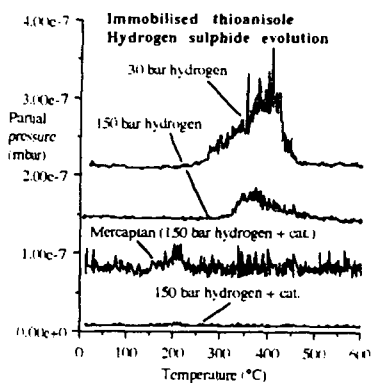


Figure 7. Evolution profiles of hydrogen sulphide and mercaptan from immobilised thioanisole.

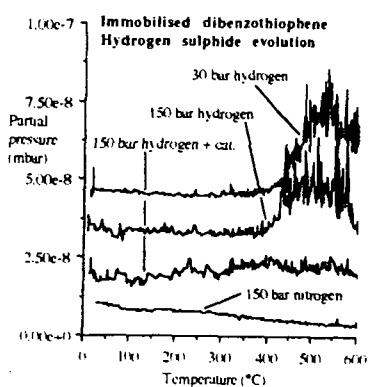


Figure 8. Evolution profiles of hydrogen sulphide from immobilised dibenzothiophene.

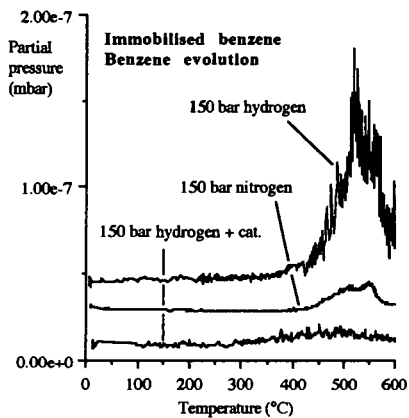


Figure 1. Evolution profiles of benzene from immobilised benzene.

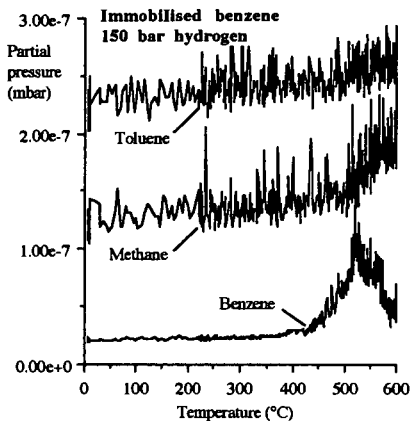


Figure 2. Evolution profiles of benzene, methane and toluene from immobilised benzene in 150 bar hydrogen.

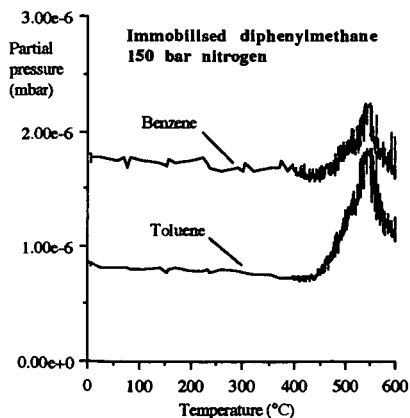


Figure 3. Evolution profiles of benzene and toluene from immobilised diphenylmethane in 150 bar nitrogen.

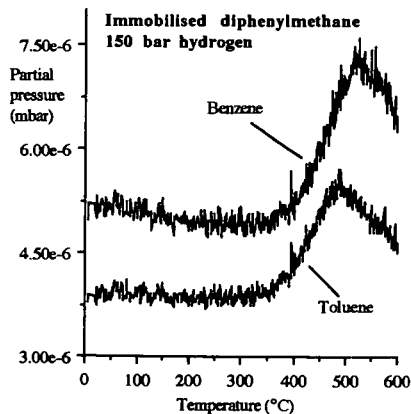


Figure 4. Evolution profiles of benzene and toluene from immobilised diphenylmethane in 150 bar hydrogen.

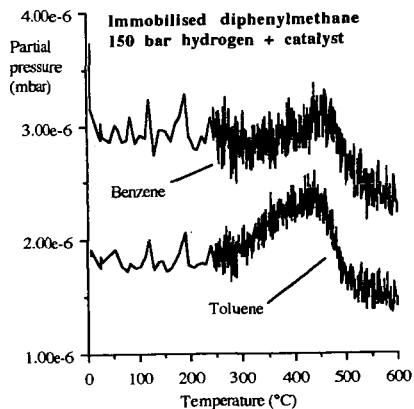


Figure 5. Evolution profiles of benzene and toluene from immobilised diphenylmethane in 150 bar hydrogen with the Mo catalyst.

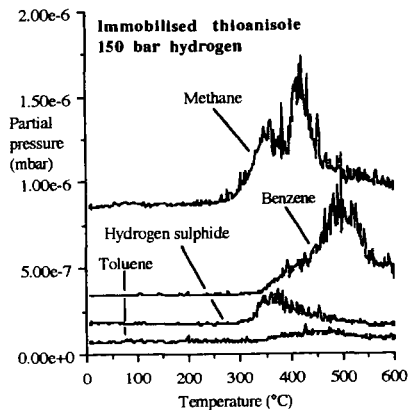


Figure 6. Evolution profiles of hydrogen sulphide, methane, benzene and toluene from immobilised thioanisole in 150 bar hydrogen.

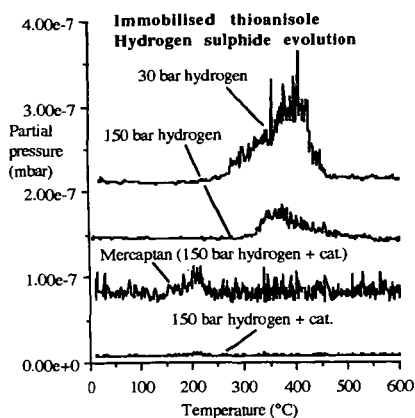


Figure 7. Evolution profiles of hydrogen sulphide and mercaptan from immobilised thioanisole.

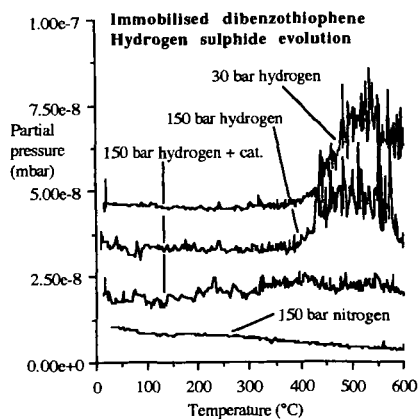


Figure 8. Evolution profiles of hydrogen sulphide from immobilised dibenzothiophene.