

USE OF HYDROLYSIS-MS TO PROBE THE HYDROCRACKING OF DIPHENYLALKANE LINKAGES IN THE SOLID STATE

S.D. Brown ⁽¹⁾, O. Sirkecioglu ⁽¹⁾, K. Ismail ⁽¹⁾, J. Andresen ⁽¹⁾, C.E. Snape ⁽¹⁾, A.C. Buchanan III ⁽²⁾ and P.F. Britt ⁽²⁾

- (1) University of Strathclyde, Department of Pure & Applied Chemistry, Glasgow G1 1XL, UK
(2) Chemistry and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

Keywords: hydrolysis, resites, silica-immobilised substrates

INTRODUCTION

Diphenylalkanes have been extensively used as model substrates to probe the free radical mechanisms involved in C-C bond cleavage reactions during 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 for diphenylalkanes compared to the corresponding vapour phase reactions ⁽²⁻⁵⁾. For pyrolysis studies, these model substrates have the inherent advantage that they do not soften and so remain in the reactor. Thus, immobilised substrates have considerable potential for modeling coal pyrolysis phenomena, particularly the effects of high hydrogen pressures (hydrolysis). Indeed, for immobilised benzene, the Si-O-C bond linking the substrate to the surface is reasonably stable and does not cleave until above 500°C (peak maximum at 550°C) with 150 bar hydrogen pressure ⁽⁶⁾. For immobilised diphenylmethane (DPM), it was demonstrated previously that the use of 150 bar hydrogen pressure and a sulphided Mo catalyst both reduced the peak evolution temperatures for benzene and toluene clearly demonstrating their separate contributions to promoting C-C bond cleavage ⁽⁶⁾.

An alternative class of materials to immobilised substrates that should prove equally as suitable for modeling pyrolysis phenomena are cured phenol-formaldehyde resins. These offer the option of incorporating a wide variety of hydrocarbon and heteroatomic moieties into the basic phenolic macromolecular structure. A series of co-resites were recently prepared from phenol and, as the second component, a series of sulphur-containing precursors, namely 2-hydroxydibenzothioephene, *p*-hydroxydiphenylsulphide, 4-hydroxyphenylbenzylsulphide and 4-hydroxythioanisole ⁽⁷⁾. These precursors have also been used previously for the preparation of silica-immobilised substrates ⁽⁸⁾ which, together with the resites have been used as calibrants in temperature programmed reduction ⁽⁷⁻⁹⁾. To investigate the hydrocracking of diphenylalkane linkages in the solid state with the additional aim of elucidating how the nature of a particular substrate might influence the reaction pathways, hydrolysis experiments with on-line mass spectrometric analysis have been conducted on silica-immobilised substrates, phenolic resites and a polystyrene-divinylbenzene network using hydrogen pressures of 5 and 150 bar.

EXPERIMENTAL

Substrates and their synthesis The diphenylmethane co-resites were prepared using the procedure described by Bar and Aizenshtat ⁽¹⁰⁾ which was used previously for the sulphur-containing resites ⁽⁷⁾. A total phenol to formaldehyde mole ratio of 1:2.5 was used with sodium hydroxide as catalyst for the condensation reaction, a mole ratio of 0.1 with respect to phenol being employed. The mole ratio of phenol to the monohydroxydiphenylalkanes (diphenylethane and propane) was 3:1 to ensure that a reasonably high degree of crosslinking was achieved in the initial resoles. DSC indicated that co-resoles prepared with a mole ratio of only 1:1 melted to a considerable extent in the temperature range,

250-280°C. The co-resites were cured in an oven purged with nitrogen gas at a temperature of 200°C. Solid state ^{13}C NMR was used to monitor the conversion of the ether/alcohol functional groups to methylene bridges during curing. Cross polarisation/magic-angle spinning (CP/MAS) spectra were obtained using a Bruker MSL100 instrument operating at 25 MHz for carbon.

The silica-immobilised samples were prepared from the appropriate phenol as previously described (2-5). The loadings of the diphenylmethane (DPM) and diphenylethane (DPE) substrates investigated here are summarised below. These were determined by hydrolysing the substrates with base and conducting GC analysis of the resultant phenols which were silylated.

	Loading, mmol g ⁻¹
Diphenylmethane, normal	0.45
Dideuterated diphenylmethane (PhCD ₂ Ph)	0.31
Co-attached diphenylmethane/tetralin	0.28/0.18
Diphenylethane	0.60

The polystyrene-divinylbenzene (PS-DVB) sample used, XAD-4 is commercially available.

Hydroxyprolysis-MS Details on the high pressure system have been reported previously (7,8,11). Hydrogen pressures of 5 and 150 bar were used with a heating rate of 5°C/min over the range 100-600°C. Typically, between 0.2 and 0.3 g of the resite (particle size range of ca 0.1-1.0 mm) was mixed with 2-3 g sand. The volatile species evolved were detected on-line using a quadrupole mass spectrometer (VG Sensorlab, 0-300 a.m.u).

RESULTS AND DISCUSSION

C₁-linkages Figure 1 shows the evolution of benzene, toluene and cresol at 150 bar pressure from a normal phenol resite not containing a second constituent. The benzene evolving at high temperature (T_{MAX} of 550°C) is considered to arise mainly from the hydrodeoxygenation of phenol, cresols and xylenols. The cresol profile and, to a lesser extent, that for m/z 91 (this probably comprises fragment ions of 108) contain peaks at ca 550°C which are attributed to the primary cleavage of the methylene bridges. Figure 2 compares the benzene evolution profiles at 150 bar pressure from the immobilised DPM substrates. As found previously (6), the profiles can be resolved into two broad components. The higher temperature one (530-600°C) is consistent with that anticipated for cleavage of the SiO-C bond in surface-immobilised benzene. Toluene is similarly formed following the prior hydrogenolysis of the C-C linkages in diphenylmethane according to the reaction scheme:



The T_{MAX} of 480-500°C of the lower component at is very similar to that for the resite suggesting that the additional free radical chemistry that occurs in the resite does not significantly promote the cleavage of the methylene bridges at high hydrogen pressure.

The similar intensities of the m/z 78 and 79 intensities indicates that, as anticipated, extensive scrambling of the methylene deuteriums has occurred. The co-attachment of tetralin had little effect on the benzene and toluene evolution profiles both at low and high pressure (Figure 2). The greater m/z 78 intensity observed for the co-attached DPM is probably attributable to the likely contributions from tetralin breakdown products. No naphthalene was detected indicating that hydrogen transfer had not occurred to a significant extent.

C₂-linkages Figures 3 and 4 show the benzene and toluene profiles from the immobilised DPE at low and high pressure and Figure 4 compares the toluene evolution profiles for the immobilised DPE and DPE-containing resite at 150 bar. Given that the relative response factor of benzene to toluene is ca 3.1, the toluene concentration is much the higher at low pressure. This is consistent with

all the low pressure isothermal work on DPE (both free and immobilised) (1,2) where there is little evidence of cleaving the aryl-C bonds. At high pressure, this is clearly no longer the case with benzene concentration being considerably higher (ca 30% of that for toluene, Figures 3 and 4). Increasing the hydrogen pressure has also given rise to a slightly lower T_{MAX} for benzene and toluene (430 cf 450°C) and, as for DPM, resulted in much more benzene evolving above 500°C indicating the role of hydrogen pressure in circumventing char-forming reaction pathways.

By comparison with Figure 2, the contribution below 480°C in the profile for the resite can be ascribed to cleavage of the DPE linkage. Although the high temperature contributions from the remainder of the resite dominate the trace, the low temperature region matches fairly closely that for the immobilised DPE with an initial T_{MAX} occurring at ca 430°C.

C₃-linkages Figure 5 shows the virtually identical toluene and ethyl benzene evolution profiles from the PS-DVB at 5 and 150 bar pressure. The concentration of styrene evolving at low pressure was comparable to that of ethylbenzene. At low pressure, a sharp T_{MAX} occurs at 450°C with smaller amounts of toluene and ethylbenzene evolving at higher temperatures from secondary reactions. At high pressure, the evolution profiles are considerably broader. The volatiles begin to evolve at 320°C but the broad peak in the temperature range is the superposition of more than one distinct reaction pathway. Further, much greater quantities evolve above 470°C which again is indicative of the role of hydrogen pressure in circumventing char-forming reaction pathways.

Figure 6 compares the evolution profile of toluene from the PS-DVB and DPP-containing resite. The traces are very similar indicating again that, with high hydrogen pressures, the primary scission of the C-C bonds in diphenylalkanes is fairly independent of the nature of the substrate.

CONCLUSIONS

The results have indicated increasing the hydrogen pressure reduces the extent of retrogressive chemistry for all the model substrates investigated. The primary pyrolytic event at high hydrogen pressure, as characterised by the evolution of benzene, toluene and ethylbenzene/styrene, occurs at virtually the same temperature for a given alkane linkage in the different substrates used. The C₂ and C₃ linkages investigated are cleaved at ca 50-100°C lower than their C₁ counterparts. The pyrolysis of immobilised diphenylmethane appears to be largely unaffected by the co-attachment of tetralin.

ACKNOWLEDGEMENTS

The research was supported at (i) the University of Strathclyde by the Science & Engineering Research Council (Grant No. GR/J/08997) and the Department of Trade & Industry and at (ii) Oak Ridge National Laboratory by the Division of Chemical Sciences, Office of Basic Energy Systems, US DoE (Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.).

REFERENCES

1. M.L. Poustma, Energy & Fuels, 1990, 4(2), 113 and references therein.
2. A.C. Buchanan III, T.D.J. Dunstan, E.C. Douglas and M.L. Poustma, J. Am. Chem. Soc., 1986, 108, 7703.
3. A.C. Buchanan III and C.A. Biggs, J. Org. Chem., 1989, 54, 517.
4. A.C. Buchanan III, P.F. Britt and M.L. Poustma, Prepr. Am. Chem. Soc. Div. Fuel Chem., 1990, 35(1), 217.
5. P.F. Britt and A.C. Buchanan III, J. Org. Chem., 1991, 56, 6132.
6. S.C. Mitchell, C.J. Lafferty, R. Garcia, K. Ismail, C.E. Snape, A.C. Buchanan III, P.F. Britt and E. Klavetter, Energy & Fuels, 1993, 7, 331.
7. K. Ismail, G.D. Love, S.C. Mitchell, S.D. Brown and C.E. Snape, Prepr. Amer. Chem. Soc. Div. Fuel Chem., 1994, 39(2), 1691.
8. S.C. Mitchell, C.J. Lafferty, R. Garcia, K. Ismail, C.E. Snape, A.C. Buchanan III, P.F. Britt and E. Klavetter, Prepr. Amer. Chem. Soc. Div. Fuel Chem., 1992, 37(4), 551.

9. K. Ismail, R. Garcia, S.C. Mitchell, C.E. Snape, A.C. Buchanan III, P.F. Britt, D. Franco and J. Yperman, Proc.1993 Int.Conf. on Coal Science, Banff, September 1993.
10. H. Bar and Z. Aizenshtat, J. Anal. Appl. Pyrolysis, **19**, 1991, 265.
11. C.J. Lafferty, S.C. Mitchell, R. Garcia and C.E. Snape, Fuel, 1993, **72**, 367.

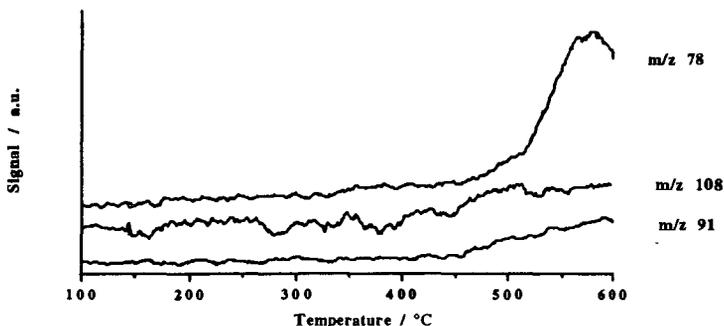


Figure 1. Hydropyrolysis evolution profiles of benzene, toluene and cresol from the normal phenolic resite under 150 bar H₂

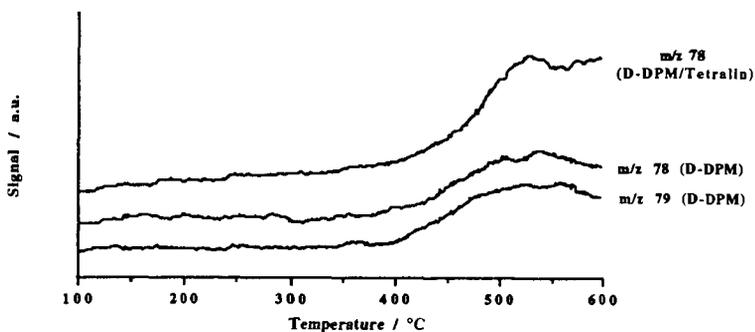


Figure 2. Evolution profiles of benzene from silica-immobilised di-deuterated diphenylmethane and silica-immobilised di-deuterated diphenylmethane with co-attached tetralin under 150 bar H₂

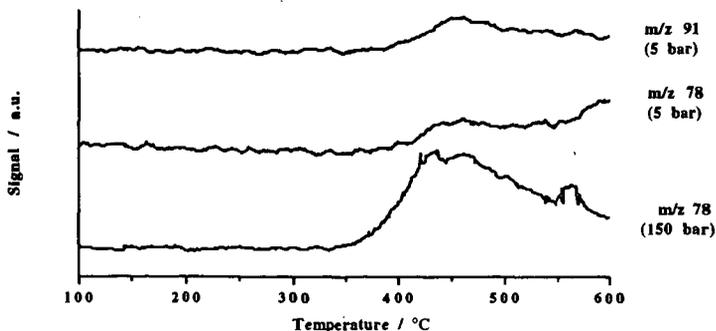


Figure 3. Hydropyrolysis-m.s. profiles of silica-immobilised diphenylethane under 5 and 150 bar H₂

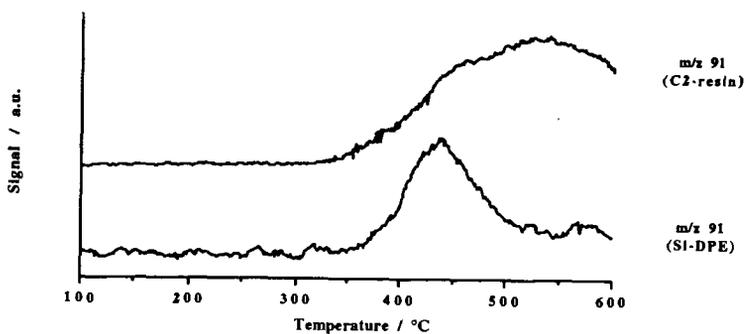


Figure 4. Toluene evolution profiles from the diphenylethane phenolic resite and the silica-immobilised diphenylethane under 150 bar H₂

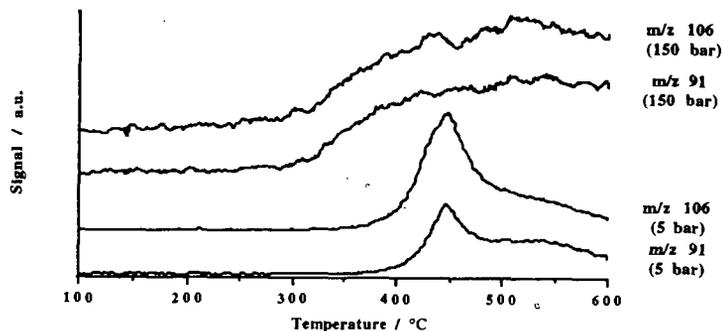


Figure 5. Evolution profiles of toluene and ethylbenzene from the PS-DVB under 5 and 150 bar H₂

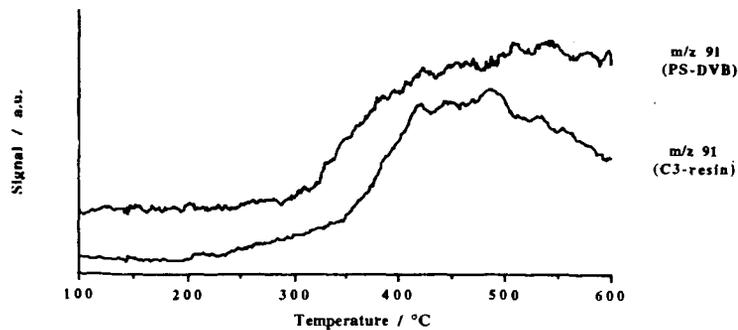


Figure 6. A comparison of the toluene evolution profiles from the PS-DVB and the diphenylpropane phenolic resite under 150 bar H₂