

The Pyrolysis Behaviour of Sulphur Model Compounds: A Mass Spectroscopic Study

S. Mullens^a, J. Yperman, G. Reggers, R. Carleer, A.C. Buchanan, III¹, and P. F. Britt¹

Laboratory of Applied Chemistry, IMO, Limburgs Universitaire Centrum,
B-3590 Diepenbeek, Belgium

¹Chemical & Analytical Sciences Division, Oak Ridge National Laboratory,
P.O. Box 2008, M.S. 6197 Oak Ridge, Tennessee 37831-6197, USA

^a*Present address: Material Technology, VITO, Boeretang 200, B-2400 Mol, Belgium*

Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-00OR22725. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

The pyrolysis behaviour of sulphur model compounds: a mass spectroscopic study.

S. Mullens^a, J. Yperman, G. Reggers, R. Carleer, A.C. Buchanan III¹, and P. F. Britt¹

Laboratory of Applied Chemistry, IMO, Limburgs Universitair Centrum, B-3590 Diepenbeek, Belgium.

¹Chemical & Analytical Sciences Division, Oak Ridge National Laboratory, P.O.Box 2008, M.S. 6197 Oak Ridge, Tennessee 37831-6197, USA.

^a Present address: Material Technology, VITO, Boeretang 200, B-2400 Mol, Belgium

Abstract

For the determination of sulphur functionalities in coal or other matrices, model compounds are often used as a reference material. In this study, the pyrolysis behaviour of such compounds is investigated. Although results on the model compounds can not be completely transferred to real samples, since the matrix itself can influence the different reactions, some trends regarding the evolution of hydrocarbons and the efficiency of the hydrogenation reaction can be applied to real samples as well. The on-line connection of a mass spectrometer with the pyrolysis reactor offers a tool for a complete description of the simultaneous and successive reactions that are occurring during the degradation. This provides some explanations regarding the efficiency of reduction reactions of sulphur compounds.

Introduction

The quantitative determination of sulphur functionalities in different matrices still remains a difficult task. Atmospheric Pressure – Temperature Programmed Reduction (AP-TPR) is a pyrolysis technique, which applies a constant heating rate to the sample in a hydrogenating or reducing atmosphere¹. The sulphur distribution is based on the hypothesis that each type of sulphur functionality has a characteristic temperature region in which it is hydrogenated into H₂S. By monitoring the H₂S evolution as a function of temperature, the sulphur distribution originally present in the sample can be deduced. The assignment of the temperature region in which a certain sulphur compound is hydrogenated is based on the pyrolysis of model compounds. The use of silica-immobilized model compounds prevents volatilization of the organic compound during the analysis. However, the efficiency of the reduction or hydrogenation reaction, both of model compounds and of real samples, is in some cases rather low. Consequently, the evolution of only H₂S does not permit a reliable determination of the sulphur distribution in these cases. This study concentrates on the pyrolysis behaviour of sulphur model compounds in a hydrogenating atmosphere. Monitoring the pyrolysis gasses, which evolve from the reactor, enables a complete description of the degradation process of these compounds. In this way, the simultaneous and successive side reactions with respect to the reduction reaction into H₂S can be identified, providing an explanation for the low reduction efficiency of thiophenes and oxidised sulphur functionalities.

Results and discussion

1. Organic sulphur model compounds

The first model compound studied is benzylthiophene immobilised on silica ($\approx C_6H_4-CH_2-C_4H_3S$). AP-TPR experiments showed that only 45 % of the sulphur is reduced into H_2S . Figure 1 presents the evolution of mass fragments during the pyrolysis of

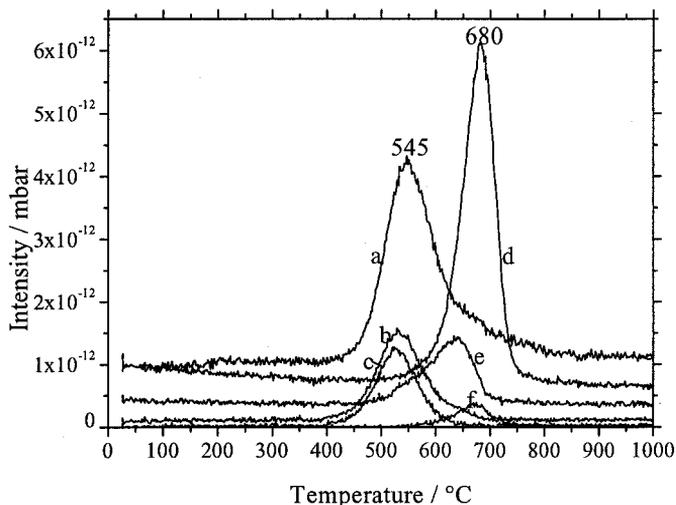


Figure 1. Evolution of (a) H_2S ($m/z = 33 + m/z = 34$) (b) $C_4H_4S^+$ ($m/z = 84$) (c) $C_3H_5S^+$ ($m/z = 97$) (d) $C_6H_6^+$ ($m/z = 78$) (e) $C_7H_7^+$ ($m/z = 91$) and (f) $C_{10}H_8^+$ ($m/z = 128$) during reductive pyrolysis of benzylthiophene immobilised on silica.

the model compound as a function of the temperature. As clearly can be noticed, the degradation in a hydrogenating/reducing atmosphere takes place as a two-step process. The first step is characterised by a maximum around 545 °C corresponding to the release of H_2S (fig. 1a) together with thiophene (fig. 1b) and methylthiophene (fig. 1c). This indicates the simultaneous reduction of the thiophene ring (producing H_2S) and the competitive thermal breakdown of the

compound. In the second stage, the residue undergoes charring accompanied by the release of benzene (fig. 1d), alkylbenzene (fig. 1e), and even a small amount of naphthalene (fig. 1f) at 680 °C. The release of thiophene and methylthiophene provides a partial explanation for the low reduction efficiency. The incomplete reduction of (methyl)thiophene in that temperature region gives rise to the low

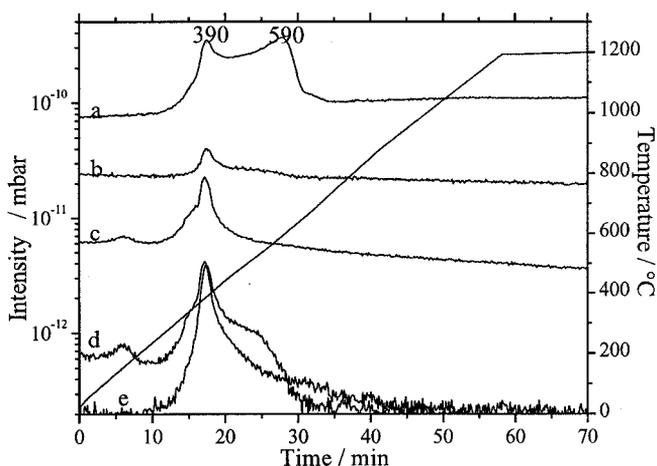


Figure 2. Evolution of (a) CO_2^+ ($m/z = 44$) (b) SO_2 ($m/z = 48 + m/z = 64$) (c) $C_3H_7^+$, CH_3CO^+ ($m/z = 43$) (d) $C_4H_{10}^+$, $C_3H_6O^+$ and (e) CH_3COOH^+ ($m/z = 60$) during the combustion of tar and char residue after reductive pyrolysis of benzylthiophene immobilised on silica

organic sulphur, which has been incorporated in the matrix. Therefore, these

the degradation in a hydrogenating/reducing atmosphere takes place as a two-step process. The first step is characterised by a maximum around 545 °C corresponding to the release of H_2S (fig. 1a) together with thiophene (fig. 1b) and methylthiophene (fig. 1c). This indicates the simultaneous reduction of the thiophene ring (producing H_2S) and the competitive thermal breakdown of the

reduction efficiency. However, a second side reaction must be considered, namely the incorporation of sulphur into the matrix during charring. Figure 2 presents the AP-TPO-MS results, i.e. the progress of the oxidation of the residue after the reductive pyrolysis of the sample. During the oxidation, CO_2 (fig 2a) and some other (oxidised) hydrocarbons (fig 2c,d,e) are released resulting in a maximum at 390 °C. The maximum for the evolution of SO_2 at 390 °C (fig 2b) points to the oxidation of

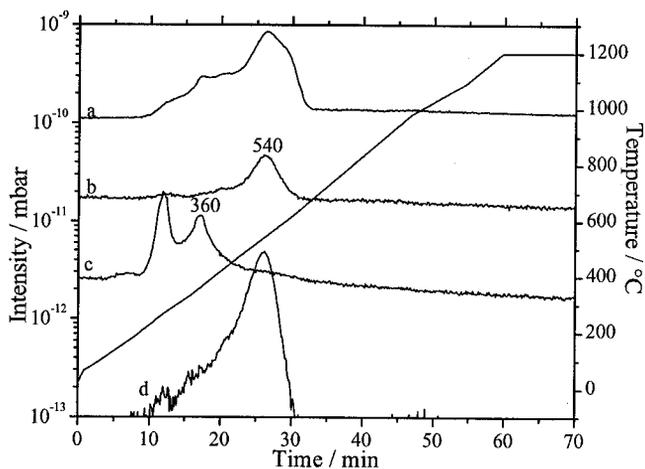


Figure 3. Evolution of (a) CO_2^+ ($m/z = 44$) (b) SO_2 ($m/z = 48 + m/z = 64$) (c) C_3H_7^+ , CH_3CO^+ ($m/z = 43$) and (d) CH_3COOH^+ ($m/z = 60$) during the combustion of tar and char residue after reductive pyrolysis of dibenzothiophene immobilised on silica

an organic sulphur model compound, dibenzothiophene immobilised on silica was chosen to represent a more complex thiophene. The reduction efficiency is even lower than for the simple thiophene model. Only 25 % of the sulphur is released as H_2S during the reductive pyrolysis. The evolution of the mass spectra shows a maximum only for H_2S and benzene at $T_{\text{max}} = 690^\circ\text{C}$ (figure not shown). The T_{max} for H_2S evolution is much higher than that for the simple thiophene model as expected. Contrary to the experiments with benzyl-thiophene (fig. 1), no other sulphur species could be detected. Probably, less volatile sulphur compounds are condensed in the reactor and, therefore, can not be detected by the mass spectrometer. During the combustion (AP-TPO-MS experiment) of the tar and char residue after the experiment in a reducing atmosphere, a substantial amount of SO_2 is released (fig. 3b), with a maximum at 540°C . Again, these results point to the

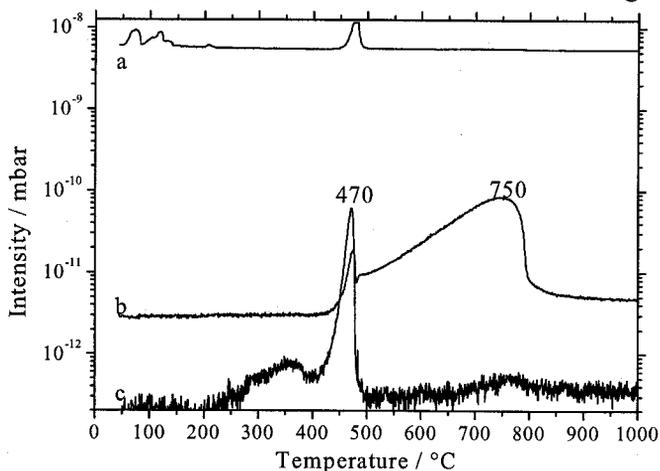


Figure 4. Evolution of (a) H_2O^+ ($m/z = 18$) (b) H_2S ($m/z = 33 + m/z = 34$) (c) SO_2 ($m/z = 48 + m/z = 64$) during reductive pyrolysis of FeSO_4 .

incomplete reduction of the model compounds into H_2S occurs.

experiments indicate that, apart from the reduction into H_2S , two side reactions are occurring during the reductive pyrolysis, both lowering the emission of H_2S . Firstly, the emission of volatile sulphur molecules that are not completely reduced into H_2S originating from the thermal degradation and, secondly, the incorporation of sulphur into the matrix which is resistant to reduction up to 1000°C .

As a second example of the incorporation of sulphur into more complex and thus reduction-resistant structures during the charring of the sample. Previous experiments on the reductive pyrolysis of sulphoxides (46-70 % reduction efficiency) and sulphones (12-30 % reduction efficiency) also showed the simultaneous release of both oxidised sulphur species (SO and SO_2) and H_2S in an AP-TPR-MS experiment². This again confirms that

2. Inorganic sulphur model compounds

Sulphates along with pyrite are part of the inorganic sulphur fraction in coal. The pyrolysis behaviour of these sulphates can differ according to the metal counterion. Both the temperature of the degradation and the reduction efficiency are probably determined by catalytic reactions. The reduction efficiency of FeSO_4 is 84 %, while for CaSO_4 this is only 6 %. The on line connection with a mass spectrometer reveals the different pyrolysis mechanisms for both compounds. Figure 4 shows the evolution of some mass fragments during reductive pyrolysis of FeSO_4 . The degradation is clearly a two-step process, in which the release of a substantial amount of SO_2 (fig. 4c) together with a small H_2S maximum at 470 °C (fig. 4b) precedes a second broad and more intense H_2S maximum at 750 °C. The SO_2 maximum is assigned to the thermal decomposition of the compound. The first H_2S maximum at 470 °C could result from the reduction of SO_2 to some extent. The second H_2S maximum is attributed to the reduction of troilite (FeS) into metallic iron and H_2S . This compound can be formed either by reduction of FeSO_4 or by reaction of FeO with H_2S . As the reduction efficiency of CaSO_4 is extremely low (only 6 %), only a small H_2S signal can be detected (fig. not shown). However, the combustion of the tar and char residue

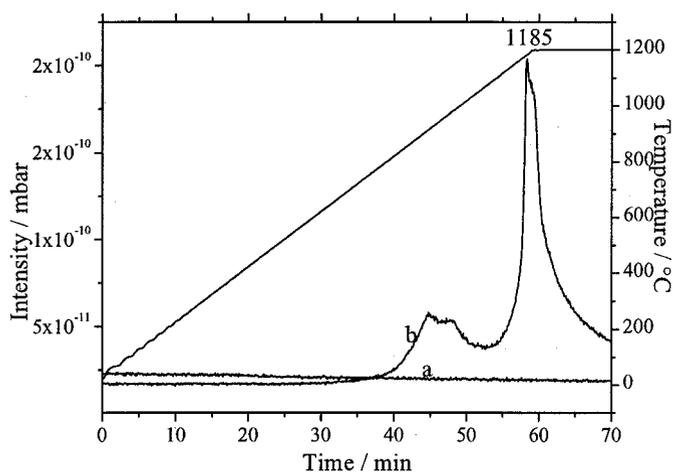


Figure 5. Evolution of SO_2 ($m/z = 48 + m/z = 64$) during combustion of tar and char residue of (a) FeSO_4 and (b) CaSO_4

of CaSO_4 shows clearly a substantial release of SO_2 (fig. 5b). For FeSO_4 , no SO_2 (fig. 5a) could be detected during combustion, indicating all sulphur is released during the reductive pyrolysis either as H_2S or as SO_2 .

Conclusions

This study focussed on the pyrolysis reactions of some sulphur model compounds. Two side reactions in regard to the reduction to H_2S could be identified: the evolution of volatile sulphur

species that are not completely reduced into H_2S at relatively low temperatures, and the incorporation of sulphur into the matrix during the charring of the sample. Even though these results are based upon the pyrolysis of pure model compounds, experiments on coal and elastomer samples indicate similar behaviour.

References

1. J. Yperman, I.I. Maes, H. Van den Rul, S. Mullens, J. Van Aelst, D.V. Franco, J. Mullens and L.C. Van Poucke, *Analytica Chimica Acta*, 395 (1999) 143-155
2. J. Van Aelst, J. Yperman, D.V. Franco, L.C. Van Poucke, A.C. Buchanan III and P.F. Britt, *Energy & Fuels*, 14 (2000) 1002-1008