

AQUATHERMOLYSIS OF ORGANIC COMPOUNDS IN THE PRESENCE OF HYDROGEN SULFIDE AND SULFATE

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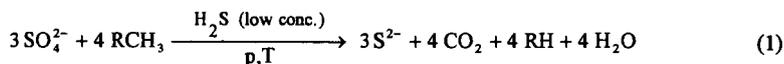
ABSTRACT

Thermal recovery processes are well established enhanced oil recovery techniques. At thermal recovery temperatures in the reservoir can reach 320°C. Under these specific conditions chemical reactions of the reservoir sulfate and hydrogen sulfide easily occur. The conditions at thermal recovery processes allow the thermochemical reduction of sulfate with hydrogen sulfide. In the presence of organic compounds these redox reactions lead to the formation of a variety of inorganic, as well as organic compounds in different oxidation states, including elemental sulfur.

Object of these investigations was to study the thermal induced reactions of organic compounds in the presence of hydrogen sulfide and aqueous solutions of alkali metal- as well as alkaline-earth metal sulfates. *n*-Octane, *n*-hexadecane, and 2-octanone selected as representative organic compounds were allowed to react with the inorganic components in autoclaves at temperatures up to 320°C under variation of the reaction time from 6 hrs. to 500 hrs. The amount of reduced sulfate was estimated by quantitative determination of the residual sulfate in the aqueous layer after each reaction. The organic reaction products were identified by gas chromatography and GC/MS.

INTRODUCTION

Thermal recovery processes are well established enhanced oil recovery techniques and widely applied for recovering heavy oil, heavy oil sands, and shale oil. At thermal recovery temperatures in the reservoirs can reach 320°C. Under these specific conditions decomposition reactions of organic sulfur compounds, which are already present in the crude oil, easily proceed. In addition, reactions of the reservoir sulfate and hydrogen sulfide (H₂S) take place.[1] The conditions, occurring at thermal recovery processes allow the thermochemical reduction of sulfate with H₂S. In the presence of organic compounds these redox reactions lead to the formation of a variety of inorganic and organic sulfur compounds in different oxidation states, including elemental sulfur (or its different radicals). The reduction is autocatalytic with respect to H₂S. Increasing concentrations of elemental sulfur promptly cause its reaction with organic compounds of the crude oil, which consequently leads to the formation of organic sulfur compounds and H₂S.[2-4] Thus, it is obvious that both, consumption and formation of H₂S compete with each other. The net reaction can be given with eq.1:



From eq.1 it becomes evident that only a catalytic amount of H₂S is necessary to initiate the thermochemical reduction of sulfate. It is known that H₂S is very often present in the reservoir. It can be formed under fairly mild conditions by microbial reduction of sulfate.[5] Furthermore, H₂S can be generated by the hydrolysis of inorganic compounds like pyrite, pyrotite, and elemental sulfur.

The pH-value plays an important part in the thermal reduction, since it has a significant influence on both, the formation and the reactivity of the inorganic sulfur compounds.[6] The pH-value is strongly controlled by the metal cation of the used sulfate solutions.

The net reaction (eq.1) reveals that sour gas (CO₂ + H₂S) is formed. These compounds lead to severe problems at the recovery of crude oil, as well as at its manufacturing. Furthermore, the quality of the crude oil will be affected.[7] The changes in the composition of the hydrocarbons and heterocompounds due to aquathermolysis in the absence of sulfate and H₂S are well described in literature.[8] However, only few details

concerning the very complex thermochemical reduction of sulfate in the presence of H_2S and hydrocarbons are available.[1,4,9] On the other hand, sulfate as an oxidizing agent for the synthesis of aromatic carboxylic acids, such as phthalic acids, has been earlier investigated.[10] Moreover, formation of H_2S from the reduction of gypsum has been subject of investigations.[11]

Scope of our research is to better understand the above mentioned reactions and their influences on each other with respect to the different reaction products, which are formed, depending on the reaction time, the reaction temperature, and the employed educts. The reactions were carried out in the presence of aqueous solutions of metal sulfates; moreover, in every reaction only one defined aliphatic hydrocarbon was used serving as a model compound; this was necessary to understand the complex reactions taking place.

EXPERIMENTAL

The experiments were conducted using glass cylinders, which were installed in stainless steel autoclaves. In the case of the reactions with model compounds an aqueous solution of 20 mmol of the corresponding sulfate was used, whereas in the case of crude oil a solution containing 60 mmol of sulfate was employed. Autoclaves of 90 ml and 190 ml content, respectively, were used. Reactions with $CaSO_4$ were carried out in the presence of NaH_2PO_4 (employed in the same molar ratio as $CaSO_4$). The starting pressure at ambient temperature was the steel cylinder pressure of H_2S . The reactions were performed at temperatures between 200°C and 320°C, respectively (Tab.1). After given time intervals the autoclave was cooled to room temperature (RT). The organic layer was separated from the aqueous layer. The decrease of sulfate was determined by quantitative titration, according to the method of SCHÖNINGER.[12] The pH-value of the aqueous phase was determined after the reaction at RT with a pH-meter equipped with a glass electrode. The organic layer was investigated by gas chromatography (GC) and the coupling of gas chromatography with mass spectrometry (GC/MS). GC was performed using a Hewlett Packard Model 5890 Series II instrument, equipped with a Hewlett Packard Flame Ionization Detector (FID) and a Hewlett Packard Photometric Detector (FPD). The organic layer was analyzed by GC/MS using a Hewlett Packard 5890 A Series II GC coupled with a Hewlett Packard 5970 B Series MS Detector, using the same GC program as for the separation. Mass spectra were obtained by electron ionization at 70 eV. The injector system of the GC/MS was a temperature programmable Injector System from Gerstel. The analytical conditions are given in Tab.2. Reactions in the presence of crude oil were worked up in the same manner. However, the recovered crude oil was extracted by liquid sulfur dioxide in order to enrich organic sulfur compounds.[13] The enriched crude oil fractions were investigated by GC (FID, FPD).

RESULTS AND DISCUSSION

In Tab.1 the parameters of the performed reactions are summarized. To rule out artifacts and to make sure that sulfate does not react with the autoclave material, aqueous solutions of the investigated compounds were treated at elevated temperatures under helium or nitrogen pressure in stainless steel autoclaves without H_2S (Tab.1: 1-3). It could be proved that neither reduction of sulfate nor reaction of the organic compound takes place. Sulfate was recovered quantitatively, the organic compound unchanged.

In Fig.1 the amount of reduced sulfate of the reaction of different metal sulfates in the presence of *n*-octane (Fig.1; according to Tab.1: 4, 6-9, 13-17, and 23, 24) is plotted vs. the temperature. In these experiments the reaction time was 72 hrs. It easily can be seen that the reduction rate is strongly controlled by both, reaction temperature and metal cation of the employed sulfate. To attain the same rate of reduction reactions of $MgSO_4$ require higher temperatures than those of $CaSO_4/NaH_2PO_4$. Generally, it can be seen from Fig.1 that the rate of reduction strongly increases at temperatures higher than 250°C. The strong influence of the employed cation becomes evident by comparing the reactions of Na_2SO_4 to those of $Al_2(SO_4)_3$. In the case of sodium sulfate reduction is not as pronounced; after a reaction time of 500 hrs. only about 10% of Na_2SO_4 are reduced at 320°C (Tab.1: 4, 5). In contrast, the reduction in the presence of aluminum ions already starts at 100°C and is almost quantitative at 200°C (Tab.1: 22-24).

In Fig.2 the amount of reduced sulfate of the reactions in the presence of *n*-octane is plotted vs. the reaction time (Fig.2; according to Tab.1: 4, 9-12, 17-21, 24, 25). In this case, the reaction temperature was 320°C. It can be seen from the plots of $MgSO_4$ and $CaSO_4/NaH_2PO_4$ that the rate of reduction increases with increasing reaction time. It is reaching 97% within 144 hrs. for $MgSO_4$; whereas for $CaSO_4/NaH_2PO_4$ only 88% of the

sulfate is reduced within the same reaction time. This indicates that the reaction is controlled by the cation, too; this feature becomes very evident for the reactions of $\text{Al}_2(\text{SO}_4)_3$ and Na_2SO_4 . In the presence of aluminum cations the reduction of sulfate proceeds very fast (see for example Tab.1: 25), whereas the reactivity is very low in the presence of sodium cations (Tab.1: 4, 5). An explanation can be given with the pH-value.

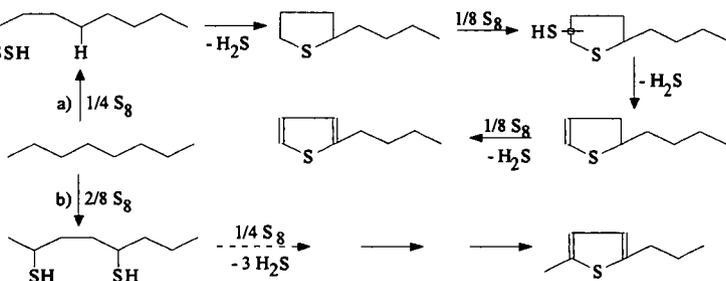
By comparison of the experiments 9, 26, and 27 (Tab.1) it becomes evident that the rate of reduction of sulfate does not only depend on the reaction time and the reaction temperature; it is also influenced by the organic compound which is involved in the reaction. In the presence of *n*-octane 66% of the employed MgSO_4 is reduced; whereas in the presence of *n*-hexadecane or 2-octanone the rate of reduction increases significantly to approximately 80%.

Experiments 28 to 30 (Tab.1) confirm that in the presence of crude oil the rate of reduction of sulfate lies in a similar order of magnitude.

Investigations of the organic layer reveal that preferably organic sulfur compounds are formed. A strong influence of the employed metal salt on the distribution of the different newly formed organic compounds could be shown. Moreover, the reaction conditions, e.g. reaction temperature, as well as time are of main importance.

In Figures 3 to 6 an example of the identification steps of the organic compounds is given. Fig.3 shows the FID chromatogram of the organic layer of reaction 9 (Tab.1); in Fig.4 the corresponding FPD chromatogram is shown. The two chromatograms reveal that a lot of organic compounds are newly formed. In addition, the FPD chromatogram indicates that many organic sulfur compounds are generated. Most of these compounds can be assigned to mono-, as well as dialkylated thiophenes by GC/MS. Moreover, a compound containing two sulfur atoms is observed; 2,2'-bithiophene could be made plausible. The ion chromatogram of the ion mass 111 is shown in Fig.5. It can be seen that a great number of different compounds is formed, the fragmentation of which leads to ion mass 111. Mass 111 is e.g. specific for dialkylated thiophenes containing at least one methylgroup as ring substituent. By comparing the single mass spectra of the total ion current to literature data a specification of 2,5- and 2-alkylsubstituted thiophenes becomes possible. Fig.6 shows one specific example for a typical mass spectrum; it could be shown that 2-ethyl-5-methylthiophene corresponds to this particular spectrum.

The tentative overall reaction is shown in Scheme 1. It can be assumed that at the reduction of sulfate sulfur radicals are generated; these radicals subsequently react with *n*-alkanes as shown in Scheme 1a and 1b, respectively:



Scheme 1.

A series of insertion reactions of sulfur into carbon hydrogen bonds of the alkane, followed by a condensation reaction in the 2,5-position, as well as in the 1,4-position of the alkane lead to ring closure. Thus, 2,5-substituted and 2-substituted tetrahydrothiophene derivatives are formed. Under elimination of H₂S cyclisation may proceed as shown in Scheme 1a or 1b. The thus formed tetrahydrothiophene derivatives react in a cascade of sulfur insertion, as well as H₂S elimination steps to form the corresponding thiophenes.

In addition, other than sulfur containing compounds are formed, too. Some of these could be identified by GC/MS as ketones, e.g. 2-, 3-, and 4-octanone and aromatic compounds, like benzene and ethylbenzene.

Some of the reaction products of experiments 9, 26, and 27 (Tab.1) are identified following published sources [14] and are summarized in Tab.3. The formation of typical

classes of organic compounds, such as substituted thiophenes, ketones and aromatic compounds is clearly indicated.

Furthermore, the GC- and GC/MS-spectra reveal a successive degradation of the alkyl substituents with increasing reaction time and increasing reaction temperature; a tentative overall reaction is already given elsewhere.[4]

CONCLUSIONS

In autoclave experiments the thermal reduction of sulfate in the presence of small amounts of H₂S and aliphatic organic compounds leads to the formation of a great number of organic compounds; many of these contain sulfur as a heteroatom. Alkyl substituted thiophenes are formed in substantial amounts. Evidence is given that the degradation of the alkyl substituents proceeds to form carbon dioxide.

The results of these investigations demonstrate that the conditions at thermal recovery of crude oil are responsible for thermochemical reduction of sulfate. This reaction is catalyzed by H₂S. Inorganic sulfur compounds in different oxidation states, such as elemental sulfur are formed and react with hydrocarbons of the reservoir. These reactions lead to the formation of typical types of organic compounds, such as alkyl substituted thiophenes, ketones, and aromatic compounds, respectively. Thus, at thermal recovery a rapid alteration of crude oil becomes possible and subsequently has a main impact on the quality of the recovered crude oil, as well as the quality of the reservoir.

ACKNOWLEDGMENTS

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 [14] Wiley Database, HP 59943B; a merged Wiley/NBS database.

Table 1. Parameters of the Reactions

No.	sulfate [20 mmol]	organic compounds [5 ml]	pressure [bar]	temperature [°C]	time [h]	reduction [%]	pH-value (after the reaction)
1	(NH ₄) ₂ SO ₄	--	162	350	46	none	7.0
2	MgSO ₄	octane	--	320	72	none	7.0
3	CaSO ₄	toluol	--	290	288	none	5.0
4	Na ₂ SO ₄	octane	126	320	72	3	7.5
5	Na ₂ SO ₄	octane	145	320	500	11	7.5
6	MgSO ₄	octane	74	250	72	4	6.3
7	MgSO ₄	octane	90	270	72	6	6.1
8	MgSO ₄	octane	124	300	72	41	6.7
9	MgSO ₄	octane	156	320	72	66	6.8
10	MgSO ₄	octane	--	320	24	27	6.8
11	MgSO ₄	octane	--	320	48	37	6.8
12	MgSO ₄	octane	--	320	144	97	6.5
13	CaSO ₄	octane	39	200	72	none	2.9
14	CaSO ₄	octane	--	250	72	22	3.8
15	CaSO ₄	octane	--	270	72	46	3.6
16	CaSO ₄	octane	--	290	72	76	5.5
17	CaSO ₄	octane	178	320	72	83	6.2
18	CaSO ₄	octane	159	320	9	54	4.6
19	CaSO ₄	octane	--	320	36	77	6.1
20	CaSO ₄	octane	188	320	144	88	6.6
21	CaSO ₄	octane	174	320	288	89	7.3
22	Al ₂ (SO ₄) ₃	octane	23	100	72	10	3.4
23	Al ₂ (SO ₄) ₃	octane	44	200	72	96	3.5
24	Al ₂ (SO ₄) ₃	octane	160	320	72	99	4.1
25	Al ₂ (SO ₄) ₃	octane	--	320	6	98	3.6
26	MgSO ₄	hexadecane	--	320	72	83	6.4
27	MgSO ₄	2-octanone	--	320	72	79	6.6
28	MgSO ₄	crude oil*	101	290	72	34	7.1
29	CaSO ₄	crude oil*	--	270	72	31	--
30	CaSO ₄	crude oil*	--	320	72	83	6.0

*: 30 g crude oil; 60 mmol of the corresponding sulfate

Table 2a. Analytical Data of GC

Injector temperature	(°C)	280
FID temperature	(°C)	330
FPD temperature	(°C)	250
GC column	DB 5, 30 m x 0.25 mm, film thickness 0.25 µm	
Carrier gas	Helium	
Carrier gas flow	(ml/min.)	1
Sample size	(µl)	1
Split		1:35
Initial oven temp.	(°C)	35
Initial hold	(min.)	5
Program rate	(°C/min.)	5
Final oven temp.	(°C)	310
Final hold	(min.)	10

Table 2b. Analytical Data of GC/MS

Initial Injector temp.	(°C)	40
Program rate	(°C/s)	12
Final Injector temp.	(°C)	300
Final hold	(min.)	10
Purge time	(min.)	5
GC/MS column	DB 1, 30 m x 0.25 mm, film thickness 0.25 µm	
Carrier gas	Helium	
Carrier gas flow	(ml/min.)	1
Sample size	(µl)	0.15
Initial oven temp.	(°C)	35
Initial hold	(min.)	5
Program rate	(°C/min.)	5
Final oven temp.	(°C)	310
Final hold	(min.)	10

Table 3. Products of Reactions at 320°C for 72 hrs. (Tab.1: 9, 26, 27)

Products from <i>n</i> -octane	Products from <i>n</i> -hexadecane	Products from 2-octanone
1. 2-Methyltetrahydro-t.	1. 2-Methylthiophene	1. Heptane
2. Ethylbenzene	2. 2-Methyltetrahydro-t.	2. 2-Methylthiophene
3. 2-Ethylthiophene	3. 2-Ethylthiophene	3. 1-Ethyl-2-methyl-cyclopentane
4. 2,5-Dimethylthiophene	4. 2,5-Dimethylthiophene	4. Octene
5. <i>o</i> -Xylene	5. 2-Propylthiophene	5. Ethylbenzene
6. 2-Propylthiophene	6. 2-Ethyl-5-methyl-t.	6. 2-Ethylthiophene
7. 2-Ethyl-5-methyl-t.	7. 2-Methyl-propyl-t.	7. 2,5-Dimethylthiophene
8. 4-Octanone	8. Benzo[b]thiophene	8. <i>o</i> -Xylene
9. 3-Octanone	9. 3-Hexadecanone	9. 1-Ethyl-5-Methyl-t.
10. 2-Octanone	10. 2-Heptyl-5-pentyl-t.	10. 2,5-Diethylthiophene
11. 2-Methyl-5-propyl-t.	11. 2-Butyl-5-octyl-t.	11. 2-Methyl-5-propyl-t.
12. 2-Butylthiophene	12. 2-Nonyl-5-propyl-t.	12. 2-Butyltetrahydro-t.
13. 2,2-Bithiophene	13. 2-Decyl-5-ethyl-t.	13. Benzo[b]thiophen
	14. 2-Methyl-5-undecyl-t.	
	15. 2-Dodecylthiophene	

t.: abbreviation for thiophene

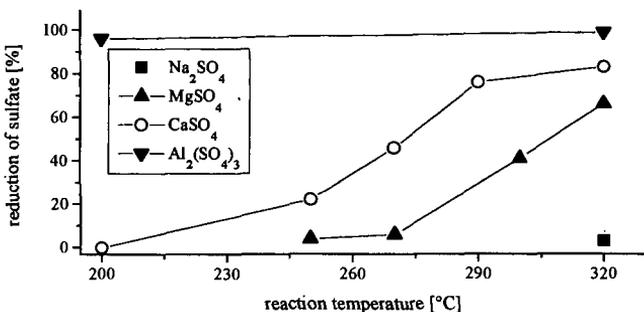


Figure 1. Influence of Temperature and Cation on the Reduction of Sulfate (t = 72 hrs.)

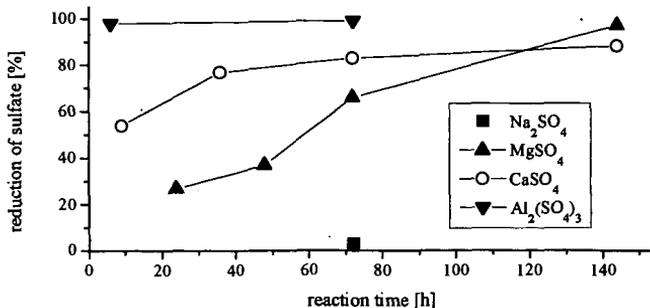


Figure 2. Influence of Reaction Time and Cation on the Reduction of Sulfate (T = 320°C)

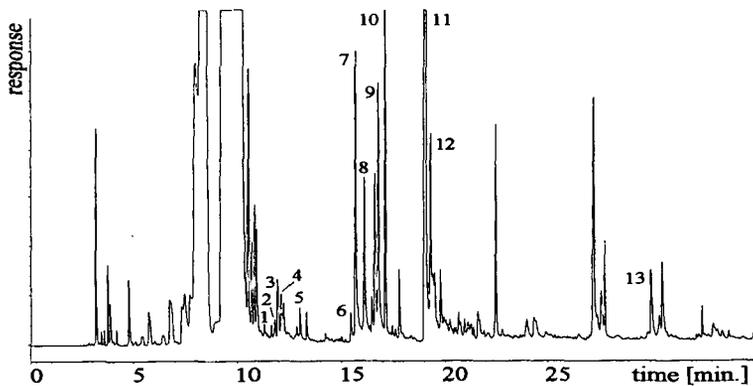


Figure 3. FID Chromatogram of the Reaction of $\text{MgSO}_4/\text{H}_2\text{S}/\text{Octane}$ at 320°C (Tab.1: 9)

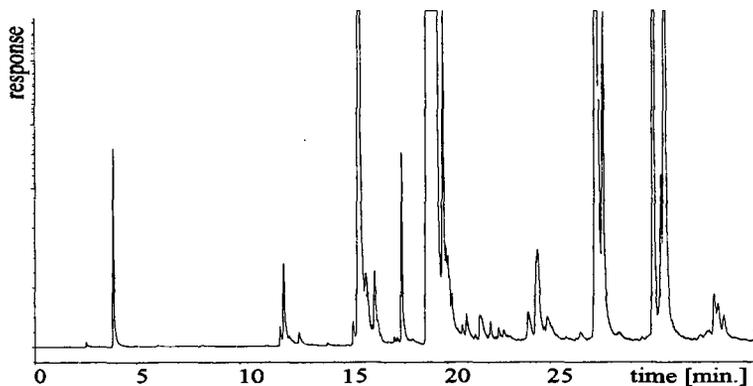


Figure 4. FPD Chromatogram of the Reaction of $\text{MgSO}_4/\text{H}_2\text{S}/\text{Octane}$ at 320°C (Tab.1: 9)

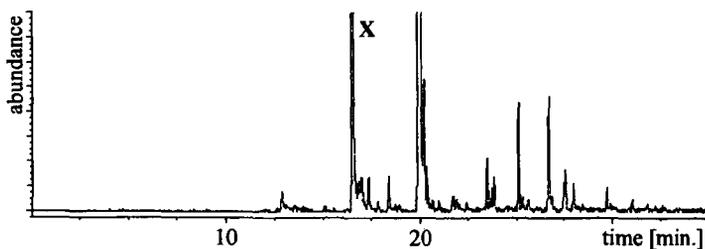


Figure 5. Ion Chromatogram of Ion 111.00 amu.

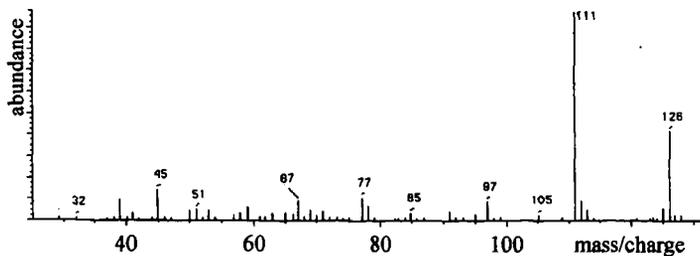


Figure 6. One (Peak Maximum) Scan of Compound X in Fig. 5