

# Kinetic Study on the Oxidation of 2, 2, 4-Trimethylpentane by MgSO<sub>4</sub>

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**Abstract:** Some organic sulfur compounds (OSCs) in crude oil may be derived from thermochemical interactions between petroleum and sulfates in deep buried sedimentary basins. In the present study, experiments on the system of 2, 2, 4-trimethylpentane–MgSO<sub>4</sub>–H<sub>2</sub>O were operated at elevated temperatures and elevated pressures. Properties of the products were characterized and the reaction kinetics was tentatively investigated. The results demonstrated that the oxidation of 2, 2, 4-trimethylpentane by MgSO<sub>4</sub> occurs above 425 °C to produce a series of organic sulfur compounds, including mercaptans, sulfoethers and thiophenes. The calculated activation energy of the reaction between 2, 2, 4-trimethylpentane and MgSO<sub>4</sub> is 50.236 kJ/mol.

**Keywords:** Organic sulfur compounds, crude oil, 2, 2, 4-trimethylpentane, MgSO<sub>4</sub>, reaction kinetics.

## INTRODUCTION

The origin and distribution of organic sulfur compounds (OSCs) are important in the discussion of the origin of sulfur rich oils, and could give useful insights to sulfur cycle in geologic body. Direct cracking or biodegradation of kerogen and oil is routinely assumed as the main natural source of OSCs, and the thermochemical origin of OSCs has not yet been given enough attentions. It is noteworthy that several organosulphur species, such as mercaptans and thiophene compounds, have been detected in some deep buried carbonate reservoirs in the last decade, which suggested possibilities of thermochemical origin of OSCs [1-3]. However, experiments regarding the TSR origin of OSCs are seldom reported, although a series of thermal experiments with n-alkanes were conducted to discuss TSR in previous studies [4-14]. Especially, Ding *et al.* reported that some n-alkanes may provide hydrogen source for OSCs generation [15, 16]; however, the reactivity of isoalkanes for the formation of OSCs and the related kinetics have been seldom investigated. In this paper, thermal simulation experiments on the system of 2, 2, 4-trimethylpentane–MgSO<sub>4</sub>–H<sub>2</sub>O were carried out at high temperatures and high pressures. Detailed analyses were performed on the generated gas, residual oil and solids, and the reaction kinetics was tentatively studied. The results of these experiments could provide important insights to the origin of OSCs in crude oil.

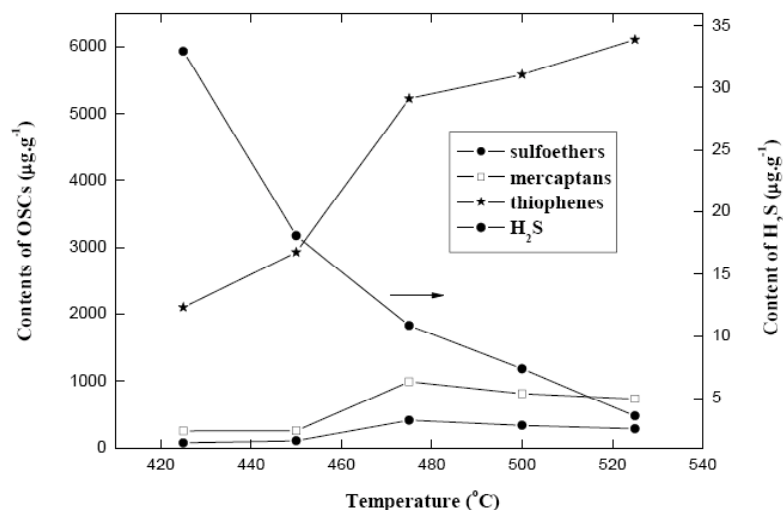
## EXPERIMENTAL

All thermal simulation experiments were operated using an autoclave (200 ml) at high temperatures and high pressures. Each runtime, 10.000 g MgSO<sub>4</sub> powder was put into the reactor, then the reactor was vacuumed, and 20 mL of 2, 2, 4-trimethylpentane and 10mL of distilled water were loaded into the autoclave through a feed regulator of the autoclave. 2, 2, 4-trimethylpentane and MgSO<sub>4</sub> used in the experiments were analytical pure. It is hard to detect the reaction products under the temperature of less than 300 °C. Therefore, the reactor was first heated to 340 °C directly and then to the final temperatures by a program control. The final temperatures were 425 °C, 450 °C, 475 °C, 500 °C and 525 °C, and the heating times were 48 h, 36 h, 24 h, 12 h and 6 h, respectively. After experiments, the solid products were put into a ceramic crucible, heated at 120 °C for 2 h in an oven to remove water, and then calcinated at 550 °C in the muffle. The weight change of solid reactant and solid products after calcinations was measured by an electronic balance. Oil products and solid products were analyzed by capillary gas chromatography combined with a pulsed flame photometric detector (Agilent 6890) and X-ray diffraction (Rigaku).

### Gas Chromatography-Pulsed Flame Photometric Detector

An Agilent 6890 series gas chromatograph with a RIPP PONA column (50 m × 0.2 mm i.d. × 0.5 μm film thickness), electronic pressure controller and an automatic sample injector with a model of Agilent 7683 was used with ultra-high purity nitrogen as a carrier gas. The injector temperature was kept at 250 °C and

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**Figure 1:** Contents of OSCs and H<sub>2</sub>S in oil phase with different reaction temperature.

its pressure is kept at 14 psi. A pulsed flame photometric detector (PFPD, O.I. Analytical 5380) was used for GC-PFPD analysis and its temperature was kept at 250 °C. The injection volume was 1.0 µl and the split ratio is 30:1. For the oil products, the column temperature was set at 35 °C for the first minute, 1.5 °C/min from 35 °C to 100 °C, and then to 250 °C at the rate of 10 °C/min, and stayed at this temperature for 15 minutes. The detector response signals were integrated using computer software (Star Workstation 5.0, Varian).

### XRD

The products were mechanically crushed and ground to size of < 200 mesh. X-ray diffraction (XRD) data were collected at room temperature with a RIGAKU D/max-rB automatic X-ray diffractometer under a voltage of 50 kV, a current of 150 mA at a scanning speed of 2 °/min, using graphite monochromated Cu-Kα radiation. The experiment parameters were as follows: DS = 1 °, SS = 1 °, RS = 0.3 mm.

### RESULTS

Contents of OSCs and H<sub>2</sub>S in oil phase with different reaction temperature were given in Figure 1. With the increasing temperature, contents of H<sub>2</sub>S in oil phase were decreasing, which could be explained by the further reaction between H<sub>2</sub>S and the remained hydrocarbons in the autoclave. The contents of mercaptans and sulfoethers increased at 425 °C-500 °C, but then declined when temperatures increased further due to the low thermal stability of mercaptans and sulfoethers at elevated temperatures. The positive

correlation between the contents of thiophenes and different reaction temperatures was given in Figure 1, indicating that thiophenes are thermally more stable than mercaptans or sulfoethers. According to the analysis above, OSCs were produced in the system of 2, 2, 4-trimethylpentane-MgSO<sub>4</sub>-H<sub>2</sub>O above 425 °C. After calcinations at 550 °C in the muffle, X-ray powder diffraction patterns of solid products at 475 °C were shown in Figure 2. From the patterns, two distinct crystallographic phases, MgO and MgSO<sub>4</sub> were found to coexist in the products. These results suggested that MgO was produced in the reduction of MgSO<sub>4</sub> by 2, 2, 4-trimethylpentane. The reaction of 2, 2, 4-trimethylpentane and MgSO<sub>4</sub> was assumed as n order reaction, and its kinetic equation was written as follows:

$$\frac{dx}{dt} = k(1-x)^n = A e^{-E/RT} (1-x)^n \quad (1)$$

Where  $dx/dt$  is reaction rate,  $x$  is reaction conversion,  $t$  is reaction time,  $k$  is the reaction rate constant,  $n$  is reaction order,  $A$  is the apparent frequency factor,  $E$  is apparent activation energy,  $R$  is the gas constant, and  $T$  is absolute temperature.

For  $n \neq 1$ , the approximate integration of equation (1) will give

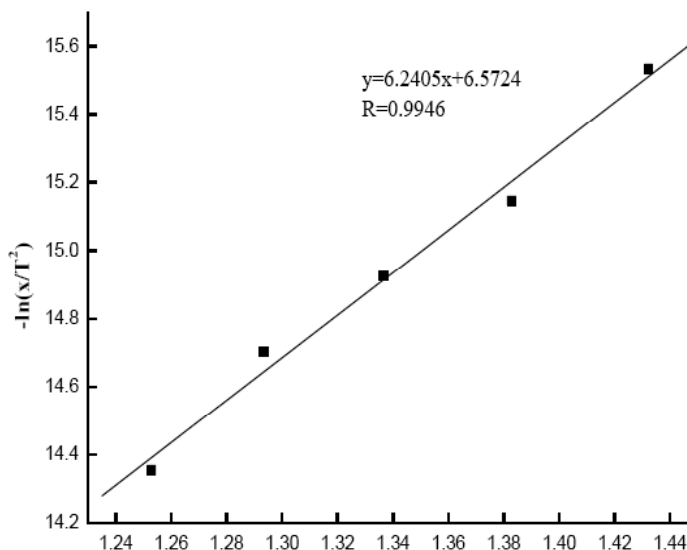
$$\ln \frac{1-(1-x)^{1-n}}{(1-n)T^2} = \ln \frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right) - \frac{E}{RT} \quad (2)$$

Where  $\beta$  is the heating rate.

For  $n=1$ , equation (1) after taking the approximate integration became:

**Table 1: The Linear Regression Coefficients for the Reaction of 2,2,4-Trimethylpentane and MgSO<sub>4</sub>**

Reaction Order	0	0.2	0.4	0.6	0.8	1.0
Regression Coefficient	0.9946	0.9944	0.9942	0.9939	0.9936	0.9932

**Figure 2:** The regression line for the reaction between 2, 2, 4-trimethylpentane and magnesium sulfate.

$$\ln \left[ \frac{-\ln(1-x)}{T^2} \right] = \ln \frac{AR}{\beta E} \left( 1 - \frac{2RT}{E} \right) - \frac{E}{RT} \quad (3)$$

Based on the conversions at different temperatures, and taking different  $n$  values (0-1), the linear regression coefficients of lines for  $-\ln \frac{1-(1-x)^{1-n}}{(1-n)T^2}$  vs.  $10^3/T$  and

$\ln \frac{-\ln(1-x)}{T^2}$  vs.  $10^3/T$  can be drawn. When the linear

regression coefficient is closest to 1, the corresponding value of  $n$  is the reaction order. In the kinetic model for the reaction of 2, 2, 4-trimethylpentane and MgSO<sub>4</sub>, the molar conversion was calculated from the weight change of the reactants and the solid products (after calcinations). The conversions are 8.75 %, 13.83 %, 18.44 %, 24.62 % and 37.15 % at temperatures of 425 °C, 450 °C, 475 °C, 500 °C, 525 °C, respectively. The linear regression coefficients for the reaction between 2, 2, 4-trimethylpentane and magnesium sulfate were listed in Table 1, and it can be concluded that the reaction order is zero.

This means that reaction rate is independent of the volume of 2, 2, 4-trimethylpentane or the weight of MgSO<sub>4</sub>, and it becomes only function of temperature. For  $n=0$ , equation (2) became:

$$\ln \frac{x}{T^2} = \ln \frac{AR}{\beta E} \left( 1 - \frac{2RT}{E} \right) - \frac{E}{RT} \quad (4)$$

By using the linear regression of  $-\ln \frac{x}{T^2}$  vs.  $10^3/T$  in equation(4), the apparent activation energy  $E$  and apparent frequency factor  $A$  can be determined by the slope and intercept of regressed line respectively (Figure 2).

The apparent activation energy is 50.236 kJ/mol and apparent frequency factor is  $4.11 \times 10^{-2} \text{ s}^{-1}$ . The kinetic model for the reaction between 2, 2, 4-trimethylpentane and magnesium sulfate then can be written as

$$\frac{dx}{dt} = 4.11 \times 10^{-2} e^{-6042.338/T} \quad (5)$$

## CONCLUSIONS

In the presence of water the reaction between 2, 2, 4-trimethylpentane and MgSO<sub>4</sub> produced a series of organic sulfur compounds, such as mercaptans, sulfoethers and thiophenes. The apparent activation energy of the reaction between 2, 2, 4-Trimethylpentane and magnesium sulfate is 50.236 kJ/mol. The oxidation of petroleum by sulfates may be another important source for the origin of OSCs besides the traditional sources from direct cracking or biodegradation of kerogen and oil, and could provide important insights to sulfur cycle in the geologic body.

## ACKNOWLEDGEMENTS

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