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Topic 05.
Reaction mechanisms and kinetics / modelling and experimentation

Theoretical study on the mechanism of sulfur migration to gas in the pyrolysis of benzothiophene

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Introduction

- The release and control of sulfur species in the pyrolysis of fossil fuels and certain solid wastes are hot research issues. Particularly, thiophene derivatives are important intermediates for sulfur gases release from organic sulfur, while the related mechanisms still remain unclear.
- Herein, the sulfur migration mechanism for the release of sulfur-containing radicals in benzothiophene pyrolysis was explored through density functional theory calculation (DFT) and wave function analysis.

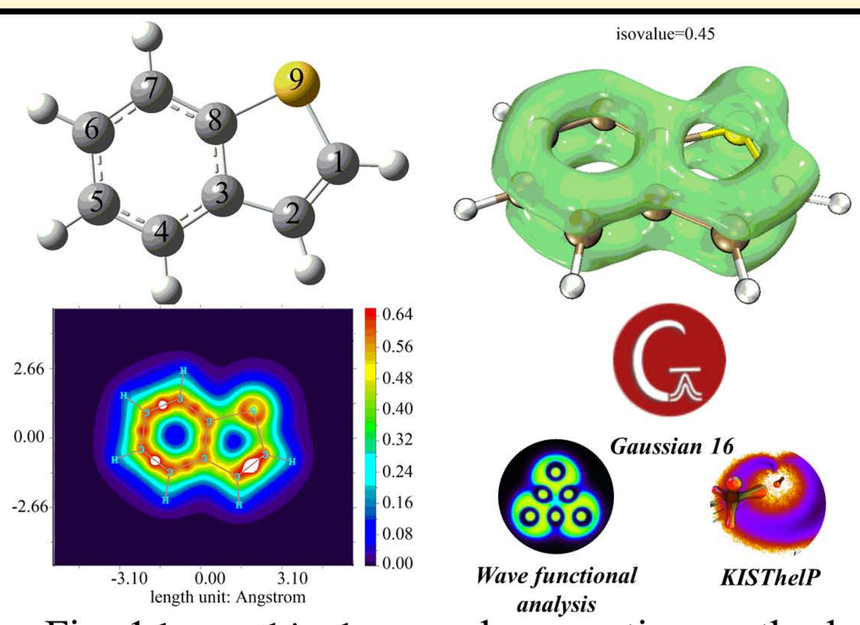

Fig. 1 benzothiophene and computing method

Results and discussion

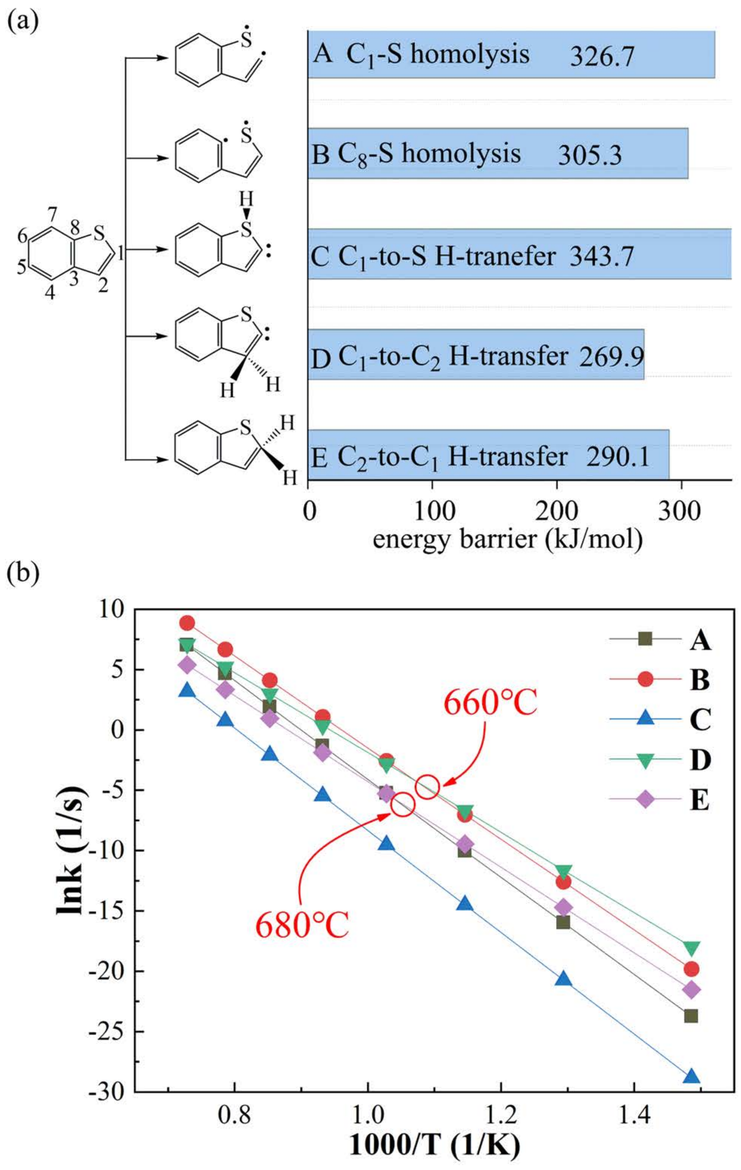

Fig. 2 Initial reaction steps for the pyrolysis of benzothiophene

- C_1-to-C_2 H-migration has the highest reaction rates at low temperatures and the lowest energy barrier (269.9 kJ/mol). When temperature exceeds 680°C, the reaction rates of homolysis reaction exceed H-transfer.

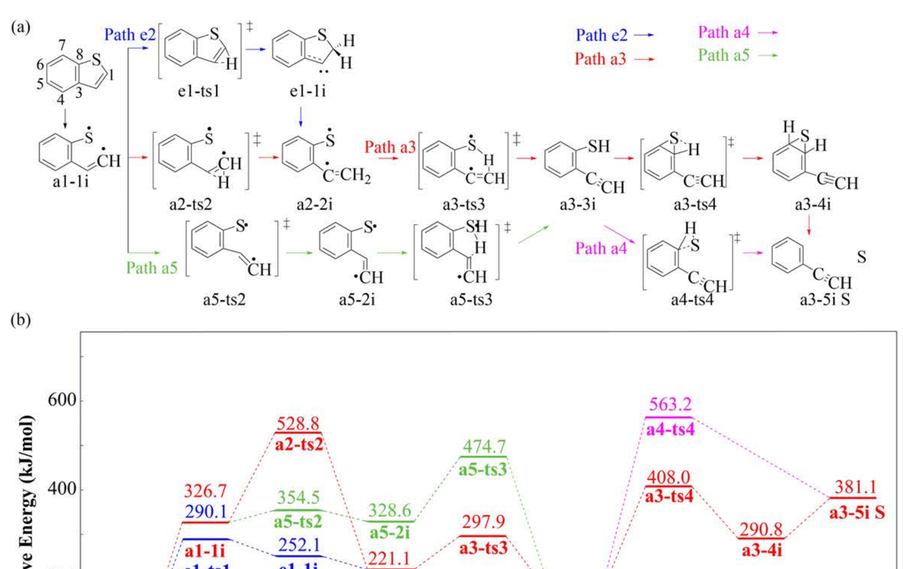

Fig. 3 Pathways to generate S radicals and corresponding energy diagrams

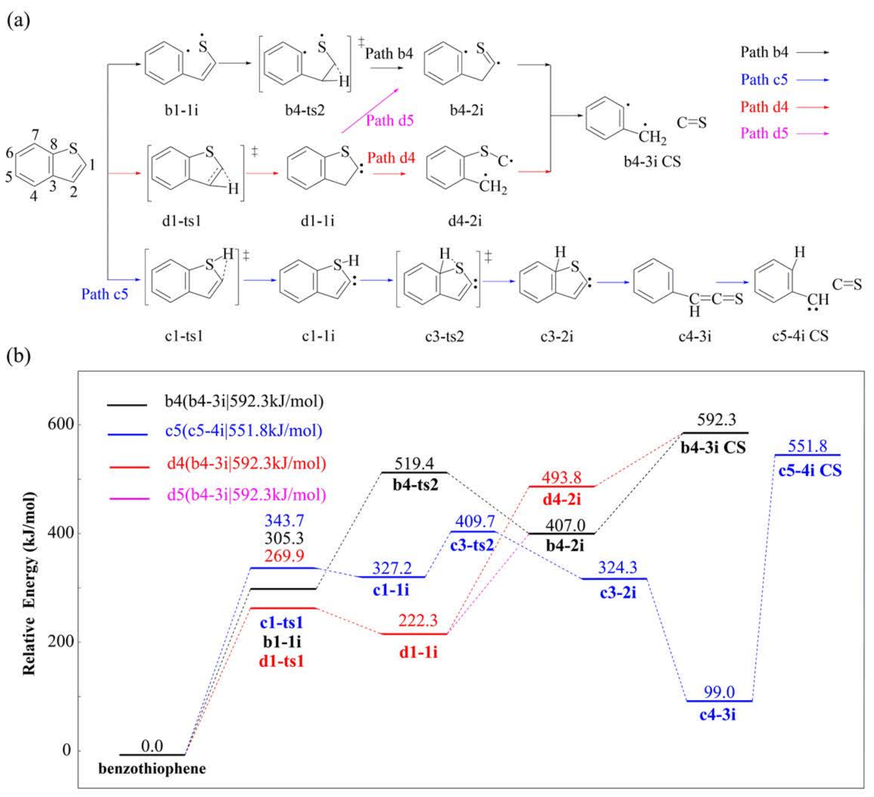

Fig. 5 Pathways to generate CS radicals and corresponding energy diagrams

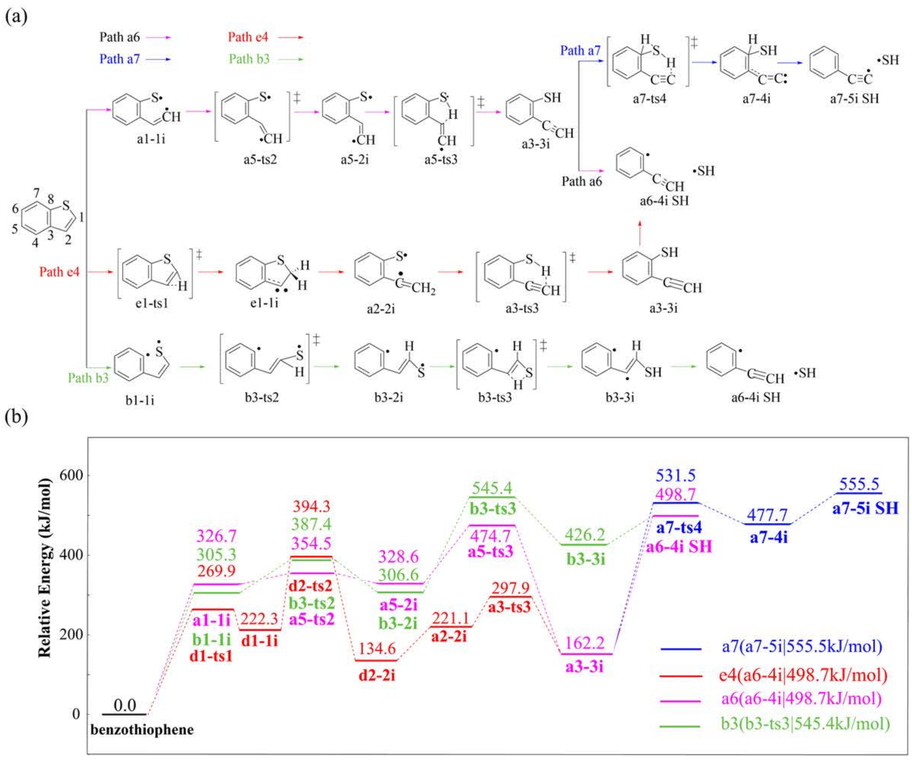

Fig. 4 Pathways to generate SH radicals and corresponding energy diagrams

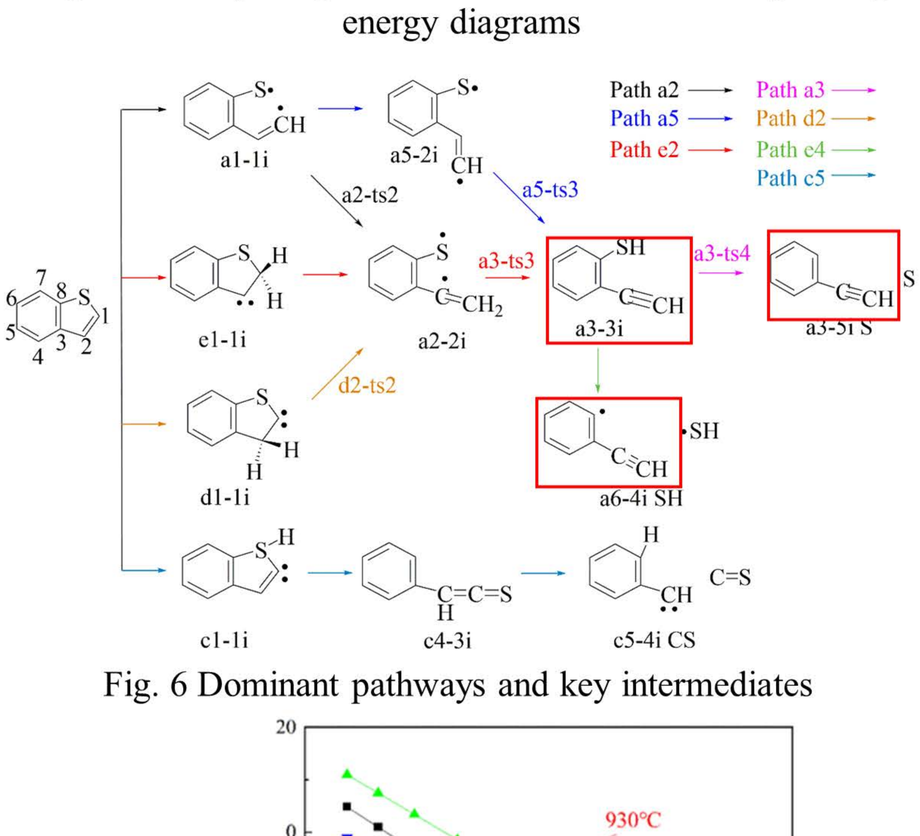

Fig. 6 Dominant pathways and key intermediates

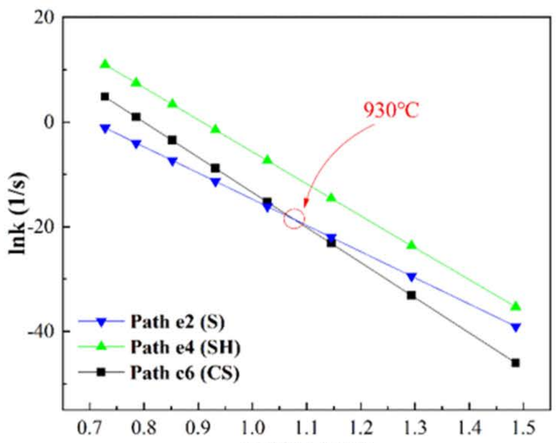

Fig. 7 Rate constants of the rate-determining steps

- There are totally 10, 12, and 4 pathways to generate S, SH, and CS radicals with dominant pathways shown in Fig. 6. The overall energy barriers for the generation of S, SH and CS radicals are 408.0, 498.7, 551.8 kJ/mol, respectively.
- CS radical generation is more difficult than S and SH radicals, while the rate constant of CS radical exceeds that of S radical when the temperature is over 930°C.

Conclusion

- The C_1-to-C_2 H-migration is the most favorable to induce the decomposition of benzothiophene at low temperatures while the increase of temperature promotes the homolysis of the C–S bond.
- 2-Ethynylbenzenethiol, which is favorablly formed by C_2-to-C_1 H-transfer, is the key intermediate for the generation of S and SH radicals.
- The strong competitiveness of S and SH radicals results in the most abundant H_2S. The rise of temperature is more beneficial for CS generation and thus promotes the formation of CS_2.