Kinetics and Mechanisms of the Oxidation of Gaseous Sulfur Compounds

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3.1 INTRODUCTION

The problems associated with global climate change in general, and acid rain in particular, have led to a great deal of research on the atmospheric and combustion chemistry of sulfur. Developments over the last decade have led to significant progress in our understanding of the kinetics and mechanisms of the atmospheric oxidation chemistry of natural and anthropogenic sulfur. Rather less effort, however, has been placed on developing an understanding of sulfur combustion kinetics; the emphasis of mitigation research has instead been placed on removal of sulfur from fuels or development of scrubbing techniques to remove SO₂ from stack gases.

The last major review of the oxidation and combustion chemistry of sulfur, by Cullis and Mulcahy in 1972, still provides an excellent review of the field. It is striking that although their review is a quarter-century old it is only the section on elementary reactions, which deals mostly with low-temperature kinetics studies, that is outdated. In this chapter we update the Cullis and

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Mulcahy review with emphasis on areas that have developed significantly since then, focusing particularly on progress in our understanding of the elementary reactions, diagnostic techniques, and NO\textsubscript{X}–SO\textsubscript{X} interactions in flames.

### 3.2 SULFUR EMISSIONS

Estimates of natural and anthropogenic sulfur emissions vary widely, reflecting the difficulty of establishing accurate inventories (Cullis and Hirschler 1980; Möller 1984; Aneja and Cooper 1989; Aneja 1990; Bates et al. 1992; Spiro et al. 1992). There is general agreement, however, that combustion of fossil fuels accounts for the bulk of the anthropogenic emissions, of which coal combustion accounts for about 60%, petroleum combustion about 30%, and metal smelting the remainder (Spiro et al. 1992). Anthropogenic emissions have been estimated to account for approximately 75% of the total atmospheric sulfur burden in two detailed studies (Bates et al. 1992; Spiro et al. 1992). The anthropogenic emissions, almost exclusively SO\textsubscript{2}, are concentrated in the northern hemisphere. In contrast, biogenic emissions, always in the form of reduced sulfur, consist of a variety of organic and inorganic species, such as H\textsubscript{2}S, CS\textsubscript{2}, COS, dimethyl sulfide (DMS, CH\textsubscript{3}SCH\textsubscript{3}), dimethyl disulfide (DMDS, CH\textsubscript{3}SSCH\textsubscript{3}), and methyl mercaptan (CH\textsubscript{3}SH). Approximately 50% of the biogenic sulfur is emitted in the marine environment. These emissions are dominated by DMS, produced by marine planktonic algae and thought to be the precursor of the sulfate aerosols that act as cloud condensation nuclei in the marine environment and thus play a role in global climate regulation (Charlson et al. 1987).

While coal and petroleum combustion has a single sulfur-containing end product, SO\textsubscript{2}, the chemical nature of bound sulfur in each medium is highly variable, which has important consequences for the detailed mechanism of combustion. Attar and Corcoran (1977) reviewed the literature on the nature of bound sulfur in coal. They noted that sulfur constitutes 0.2 to 10 wt% of coal and includes both organic and inorganically bound species, with an inorganic:organic ratio that is typically 2:1. The nature of the bound organic sulfur is difficult to determine; Attar and Corcoran conclude that most is in the form of thiophenic, aromatic, and aliphatic structures. During pyrolysis a complex mixture of gases is produced, including H\textsubscript{2}S, CS\textsubscript{2}, and thiophene and its derivatives.

### 3.3 ELEMENTARY REACTIONS

There has been a transformation of our understanding of the detailed elementary reaction kinetics of sulfur since the review of Cullis and Mulcahy (1972). At that time, with the exception of reactions of excited atomic sulfur, S\textsuperscript{(\textit{1}D)}, little was known about the elementary reactions of sulfur species; Cullis and Mulcahy presented rate data on only about twenty elementary reactions other than those