



# Review on the Interaction Mechanism of Nitrogen/Sulfur Pollutants During Fuel Combustion

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*The formation and control of pollutants emitted from fuel combustion have always been a focal point in combustion chemistry. Key pollutants primarily include nitrogen oxides ( $NO_x$ ) and sulfur oxides ( $SO_x$ ), making it crucial to elucidate the formation processes of nitrogen and sulfur components during combustion for pollutant control. Due to the highly coupled evolution processes of both components, independent reaction mechanisms struggle to describe this process; thus, considering the interactions between them is significant for the evolution of nitrogen and sulfur components. This article investigates the promotional or inhibitory effects between nitrogen and sulfur components in fuel combustion experiments, with the magnitude of this interactive effect varying between 2% and 250%, contingent upon the equivalence ratio and the N/S ratio impacts. Additionally, from a microkinetic perspective, two mechanisms underlying N/S interactions are identified: direct and indirect interactions. Direct interaction involves the formation of NS radicals, primarily through direct reactions of nitrogen species ( $NO_i/HCN/NH_i$ , where  $i$  ranges from 0 to 3) with sulfur constituents ( $SO_x/H_2S$ ). Conversely, indirect interaction alters the radical pool via the intervention of  $NO$  or  $SO_2$ , subsequently influencing each other's reaction pathways. It is noted that the current reaction system is incomplete, lacking key reactions, while the kinetic parameters of some reactions are still contentious. Advanced theoretical calculations are needed to refine the N/S interaction reaction model, to provide more accurate predictions for nitrogen and sulfur pollutant levels. [DOI: 10.1115/1.4065821]*

**Keywords:**  $SO_x$ ,  $NO_x$ , reaction mechanism, interaction, NS radicals, fossil fuel combustion

## 1 Introduction

Amidst the escalating global climate crisis, attaining sustainable development goals and net-zero emissions targets has emerged as a shared objective for the international community. To achieve these goals, fundamental transformations in both energy production and consumption are imperative, alongside urgent demands for effective management and mitigation of pollution issues arising from traditional energy usage. Among these, fuels, as primary carriers of energy, inevitably generate pollutants such as nitrogen oxides ( $NO_x$ ) and sulfur oxides ( $SO_x$ ) during combustion, posing significant threats to atmospheric environments [1,2]. Nitrogen and sulfur oxides react with water vapor and oxygen in the atmosphere to form nitric and sulfuric acids, which contribute to the formation of acid rain. Acid rain directly damages soil and water bodies, impacting the balance of ecosystems. Additionally, nitrogen and sulfur oxides participate in complex photochemical reactions,

leading to the formation of ground-level ozone, which has negative effects on plant photosynthesis and human health. The quality and source of fuel play pivotal roles in determining the level of emitted pollutants. Hoang et al. [3] argue that  $SO_x$  emissions constitute a major cause of environmental pollution, posing significant threats to both ecological systems and human health. In response, the authors employed ultrasonic-assisted technology to develop a novel diesel blend, a strategy that not only enhances the stability and optimizes the spray characteristics of the blended fuel but also markedly reduces its sulfur content. However, Sharma et al. [4] found in a study that the emissions of  $NO_x$  actually increased when B20 fuel (20%/80% of biodiesel/diesel fuel) was mixed with 10%  $H_2O_2$ . Therefore, using low-sulfur and low-nitrogen fuels or adopting appropriate fuel-blending strategies has a very positive effect on mitigating environmental pollution [5,6]. Furthermore, fuel produced through clean processes can effectively circumvent impurities introduced during industrial procedures like oil refining [7]. Conversely, inexpensive and subpar fuels may harbor more impurities, leading to heightened pollutant emissions. To reduce the emission of pollutants, the formation mechanisms and inhibition effects of nitrogen oxides and sulfur oxides have been extensively studied [8,9]. Despite significant progress being made, the chemical interactions between nitrogen/sulfur

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components in combustion remain an area of considerable uncertainty and continue to be a focal point in nitrogen and sulfur chemistry research [10].

The interdependence between nitrogen and sulfur components on each other's evolution has been well established. Jeffries and Crosley [11] first observed the presence of NS radicals in flames of methane mixed with H<sub>2</sub>S and NH<sub>3</sub>, demonstrating a direct correlation between nitrogen and sulfur components. Subsequent conclusions from experiments conducted by Hampartsoumian et al. in the combustion of liquid (gasoline) and solid fuels (coal) indicated that the presence of SO<sub>2</sub> significantly affects the emission of NO<sub>x</sub> [12,13]. Furthermore, numerous studies have confirmed that the interaction between the two alters their respective evolution mechanisms [14–16], highlighting the importance of understanding the interaction mechanism between them for predicting the concentration distribution of NO<sub>x</sub> and SO<sub>x</sub> as well as pollution control.

In general, nitrogen oxides and sulfur oxides produced during the combustion of solid and liquid fuels result from the interaction between the fuel and oxidizer [17]. In contrast, gaseous fuels such as methane, ethane, and other hydrocarbons do not inherently contain sulfur or nitrogen elements and therefore do not produce sulfur oxides during combustion. The generation of nitrogen oxides primarily stems from the oxidation of N<sub>2</sub> in the air [18,19]. Based on this fact, it appears that the interaction between nitrogen and sulfur components is more significant in the combustion of solid and liquid fuels compared to gaseous fuels. However, in large fixed facilities (boilers) burning solid fuels (coal), these complex compound fuels rapidly decompose into smaller hydrocarbons and other light gases, leading to the interaction of nitrogen and sulfur components primarily in the gas phase [20]. Therefore, studying the sulfur/nitrogen component interaction mechanism during the combustion of gaseous fuels is also meaningful. This review outlines the impact of nitrogen and sulfur pollutants on each other's evolution under different combustion conditions, summarizes the micro-reaction mechanisms of N/S interaction, and provides guidance and reference for further research on the interaction of N/S during combustion processes.

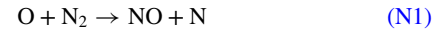
## 2 The Formation Mechanism of Nitrogen and Sulfur Pollutants

In the combustion system, the formation of NO<sub>x</sub> is primarily influenced by fuel characteristics (such as fuel type, nitrogen content, and its form), combustion organization (the mixing mode of fuel and oxygen), and reaction conditions (including equivalence ratio, reaction time, etc.). Conversely, the formation of SO<sub>x</sub> is more significantly governed by fuel characteristics and typically remains unaffected by combustion conditions [2,5]. Considering this, the suppression of NO<sub>x</sub> generation can be approached by both optimizing fuel properties and improving combustion organization. For example, Bui et al. [21] enhanced engine performance and reduced greenhouse gas emissions by adjusting the injection strategy of syngas (mainly composed of CO and H<sub>2</sub>). Compared to pure diesel combustion, the blending of syngas with diesel significantly reduces NO<sub>x</sub> emissions by altering fuel properties. Additionally, optimizing combustion organization through adjusting injection strategies also contributes to NO<sub>x</sub> reduction. Research on this control strategy may also provide ideas for reducing SO<sub>x</sub> emissions. To comprehend this process and the interaction between nitrogen and sulfur components during combustion, this section focuses on the reaction kinetics model of the independent evolution of NO<sub>x</sub> and SO<sub>x</sub> in combustion and analyzes the mechanism of pollutant formation.

**2.1 NO<sub>x</sub> Formation Mechanism.** During the combustion of fuel, nitrogen in the air and nitrogen elements in the fuel will be transformed into nitrogen-containing components, such as NO, NO<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub>, and HCN. Subsequently, under the action of the oxidant, mainly NO, N<sub>2</sub>O, and NO<sub>2</sub> are formed, with the latter

two being present in low concentrations and generally not considered [22,23]. This is due to the fact that in typical NO<sub>x</sub> emissions from methane or coal powder combustion systems, NO usually accounts for over 90%, NO<sub>2</sub> typically ranges between 5% and 10%, while N<sub>2</sub>O typically constitutes less than 2%. There are three mechanisms for the formation of nitrogen oxides: thermal type, prompt type, and fuel type NO<sub>x</sub>, and Fig. 1 summarizes these three mechanisms of NO<sub>x</sub> formation.

The formation of thermal NO<sub>x</sub> originates from the oxidation of N<sub>2</sub> in the air. Under high temperature (typically above 1500 K) and fuel-lean conditions, N<sub>2</sub> in the air reacts with atomic O to form NO, which exhibits strong temperature dependence [24]. This process is widely described using the Zeldovich mechanism [24]:



In the fuel-rich flame region, the chemical bonds of N<sub>2</sub> in the air are cleaved by highly reactive hydrocarbon radicals (CH<sub>x</sub>), leading to rapid oxidation and the generation of NO, known as prompt NO<sub>x</sub>. The most significant reaction involved is [25]



In combustion systems, the contribution of prompt NO to total NO emissions is relatively small and is typically neglected [26].

Fuel NO<sub>x</sub> is formed by the oxidation of nitrogen bound to solid and liquid fuels, accounting for over 80% of NO emissions and serving as its main source [27]. Nitrogen bound to fuel is typically connected to other species through N–C bonds and N–H bonds, making the formation of fuel NO easier compared to the thermal NO formation process that requires breaking N≡N bonds. Many scholars have studied the formation and reduction mechanisms of fuel NO. Pels et al. [28] constructed a detailed mechanism model for HCN evolution, Xu et al. [29] established a detailed reaction model for NH<sub>3</sub> conversion, and Zhou et al. [30] proposed migration and conversion pathways for fuel nitrogen. In numerical simulations, the generation of fuel NO and homogeneous reduction reactions of NO with NH<sub>3</sub>/HCN are usually calculated using the DeSoete mechanism model [31]. In this model, nitrogen within the fuel is oxidized, taking the form of NH<sub>3</sub>/HCN, to generate

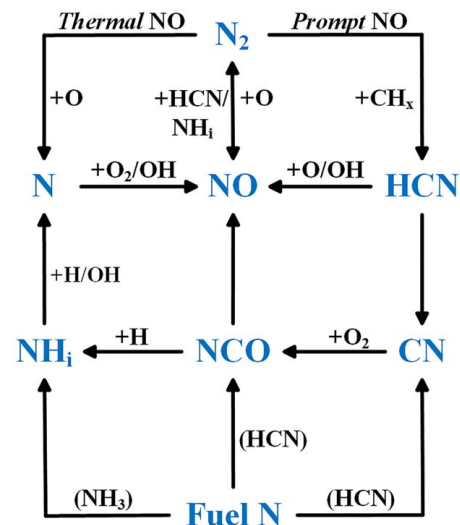
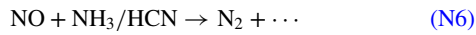
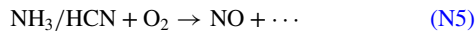


Fig. 1 The evolution pathways of thermal, prompt, and fuel NO<sub>x</sub>. Reproduced with permission from Ref. [16]. © 2007 Elsevier.

fuel NO. Concurrently, a competing reaction occurs, resulting in a reduction in  $N_2$ . The pivotal reactions are as follows [31]:



**2.2 SO<sub>x</sub> Formation Mechanism.** Unlike nitrogen oxides, the formation of sulfur oxides is entirely derived from the sulfur element in the fuel. Therefore, gaseous fuels (such as methane, ethane, and other hydrocarbons) do not produce sulfur oxides during combustion. However, solid fuels, especially coal, produce SO<sub>2</sub> during combustion, leading to severe pollution. Hence, the following sections elaborate on the formation of SO<sub>2</sub> during the combustion of coal dust.

The evolution of sulfur components is divided into two stages: the precipitation of sulfur components from coal pyrolysis and the gas-phase reactions of sulfur components [32,33]. Since the N/S interaction mainly occurs in the gas phase, this article focuses on the latter stage [12]. In the gas-phase reactions, the main sulfur-containing components are H<sub>2</sub>S and SO<sub>2</sub> produced from coal pyrolysis, which interconvert under different combustion atmospheres, with SO<sub>2</sub> being abundantly generated in oxidizing atmospheres. The University of Leeds proposed a detailed reaction mechanism model to describe this process, widely cited by many scholars [34], with the sulfur component evolution mechanisms shown by the black arrows in Fig. 2 of the model. Additionally, although in smaller quantities, COS and CS<sub>2</sub> cannot be overlooked, as indicated by the yellow arrows in Fig. 2 outlining their reaction pathways. Glarborg et al. [35] established a kinetic model for CS<sub>2</sub> oxidation using ab initio methods, and the author also conducted a detailed study on COS oxidation models [36], both of which are oxidized to SO<sub>2</sub>. Building on the research of the aforementioned scholars, Ma et al. [37] constructed a detailed kinetic model including four components: H<sub>2</sub>S/SO<sub>2</sub>/COS/CS<sub>2</sub>, which matched well with experimental values. Furthermore, a small portion of SO<sub>2</sub> will further oxidize to SO<sub>3</sub> under conditions of sufficient oxygen, but this process can lead to severe corrosion issues. Hindiyarti et al. [38] developed a detailed model for this process.

### 3 The Influence of Sulfur Components on the Formation of NO<sub>x</sub>

The sulfur content can have an impact on the formation of NO<sub>x</sub> during fuel combustion, and this process depends on factors such as equivalence ratio and N/S ratio [12,39–41]. For thermal NO<sub>x</sub>, sulfur components inhibit NO<sub>x</sub> formation across all equivalence ratios. However, for fuel NO<sub>x</sub>, sulfur components facilitate NO<sub>x</sub> formation at equivalence ratios greater than 1 while exerting the opposite effect at ratios below 1. Alterations in the N/S ratio intensify or diminish this effect. Due to the different mechanisms of NO<sub>x</sub> formation during the combustion process, the influence of sulfur components on it will also change accordingly; therefore, they need to be discussed separately. In addition, the impact of sulfur components on the formation of prompt NO<sub>x</sub> is often overlooked.

**Reaction paths between sulfur species:**

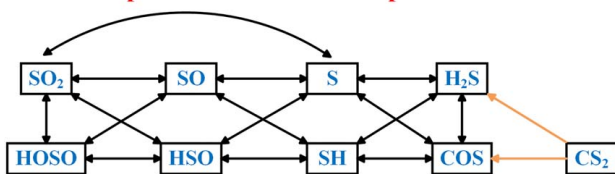
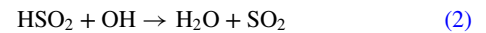
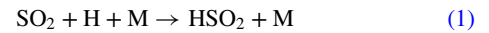


Fig. 2 Detailed schematic diagram of gas-phase reaction mechanisms for sulfur species [34–37]

**3.1 Influence on Thermal NO<sub>x</sub> Generation.** Thermal NO is formed by the oxidation of N<sub>2</sub> in the air, so this section analyzes the combustion results of fuels without nitrogen content.

Wendt and Ekmann [42] found that the NO emissions from methane flames were reduced by up to 36% when doping with a 4.9% volume fraction of SO<sub>2</sub> at equivalence ratios of 0.8–1.2, as shown in Fig. 3. Simultaneously, the authors used inert gas N<sub>2</sub> as a fuel diluent and observed that the NO emissions caused by the addition of N<sub>2</sub> to the fuel were less than 7 ppm. Therefore, based on Fig. 3, the change in NO due to the addition of SO<sub>2</sub> to the fuel is not a result of physical dilution, but rather a consequence of chemical kinetic interactions. This chemical interaction is explained as SO<sub>2</sub> catalyzing the integration of OH and H radicals, thereby reducing radical concentrations through the following reactions [42]:



As the equivalence ratio increases, the extent of this effect decreases. Additionally, when the volume fraction of SO<sub>2</sub> is less than 1%, this influence can be considered negligible.

The influence of H<sub>2</sub>S on thermal NO generation was studied in the combustion of ethane. Pfefferle and Churchill [43] investigated the impact of sulfur components on thermal NO<sub>x</sub> emissions in pre-mixed ethane–air flames with H<sub>2</sub>S added to a hot-stable piston combustion chamber at equivalence ratios of 0.8–1.6. The results indicated that the addition of 0.06 wt% and 0.03 wt% of H<sub>2</sub>S resulted in similar NO<sub>x</sub> emissions, and the sulfur component led to a 5–10% reduction in NO<sub>x</sub> produced at the outlet of the combustion chamber. Consistent with Wendt’s conclusion, the reduction in NO<sub>x</sub> emissions is also attributed to the catalytic integration of free radicals by SO<sub>2</sub> [42], indicating that H<sub>2</sub>S needs to be converted to SO<sub>2</sub> to achieve the inhibitory effect on NO<sub>x</sub>.

The combustion conclusions of liquid fuel (kerosene) are essentially consistent with those of gaseous fuel [13,44]. Hampartsoumian and Nimmo [13] increased the sulfur content in the fuel from 0.2% (initial sulfur content in the fuel) to 4.6% by adding tetrahydrothiophene and studied the impact of the primary zone equivalence ratio  $\Phi_1$  and sulfur content on thermal NO formation under staged air conditions, with a secondary zone equivalence ratio  $\Phi_2$  maintained at 0.85. The research results, as shown in Fig. 4, indicated a decrease in thermal NO formation at all equivalence ratios studied, with the impact becoming less significant as the

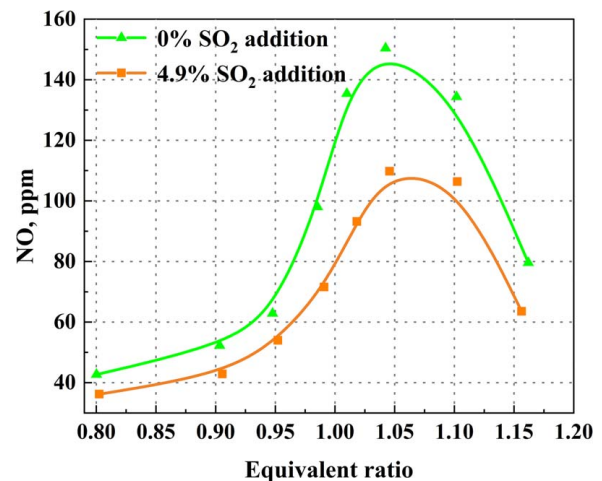
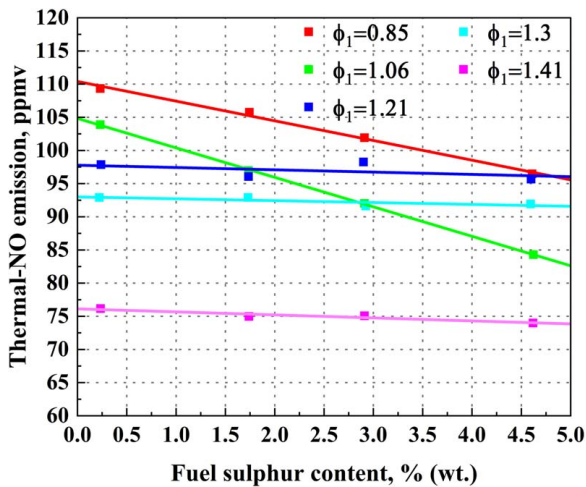


Fig. 3 The influence of SO<sub>2</sub> on thermal NO generation. The equivalence ratio ranges from 0.8 to 1.2. Reproduced with permission from Ref. [42]. © 1975 Elsevier.





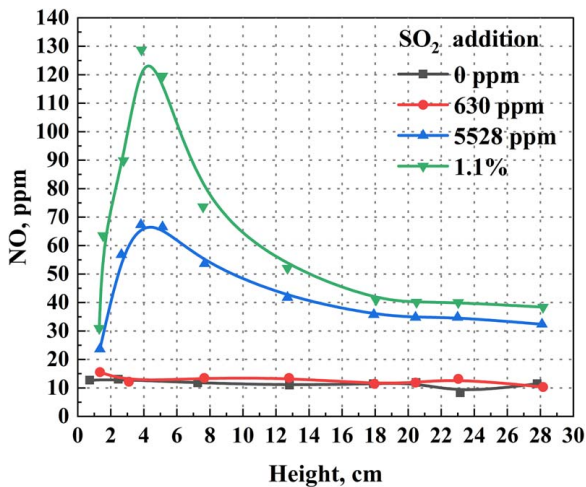
**Fig. 4** The influence of sulfur component concentrations on NO emissions at various equivalence ratios. The equivalence ratio varies from 0.85 to 1.41, while the sulfur component content ranges from 0.2% to 4.6%. Reproduced with permission from Ref. [13]. © 1995 Taylor & Francis.

equivalence ratio increased. It seems that the primary zone equivalence ratio is the main parameter controlling the effect of sulfur on thermal NO.

The combustion experiments described earlier all indicate that in the presence of sulfur components, the formation of thermal  $\text{NO}_x$  at various equivalence ratios is inhibited, and this phenomenon can be explained by the catalytic integration of  $\text{SO}_2$  with active free radicals. Additionally, the sulfur component content can influence this effect, but when the content is below a certain threshold, sulfur components have almost no impact on the generation of thermal  $\text{NO}_x$ .

**3.2 Influence on Fuel  $\text{NO}_x$  Generation.** Fuel  $\text{NO}_x$  is formed by the oxidation of nitrogen in the fuel, so this section analyzes the combustion results of hydrocarbon gas fuels and coal doped with both nitrogen and sulfur components.

The influence of different  $\text{SO}_2$  contents on fuel  $\text{NO}_x$  was studied under rich fuel conditions [45].  $\text{C}_2\text{N}_2$  was added to methane to simulate fuel nitrogen, and the results are shown in Fig. 5. At an



**Fig. 5** The influence of  $\text{SO}_2$  content on fuel  $\text{NO}_x$  under rich combustion conditions. The respective amounts of  $\text{SO}_2$  added are 0 ppm, 630 ppm, 5528 ppm, 1.1%. Reproduced with permission from Ref. [45]. © 1979 Elsevier.

**Table 1** The flame conditions for the influence of  $\text{SO}_2$  levels on NO emissions.

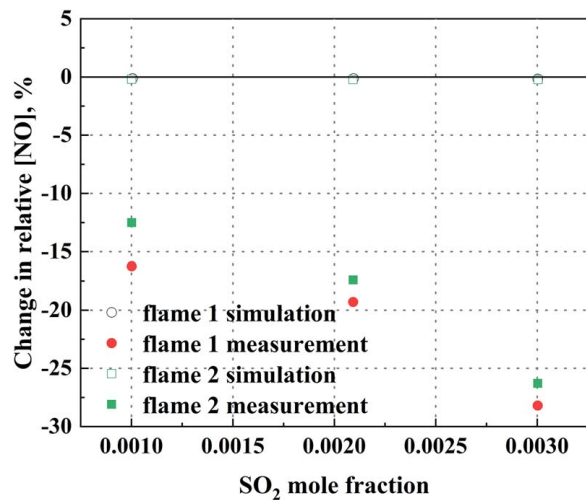
Flame	$\Phi$	$P$ (Torr)	Mass flow rate ( $\text{g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ )	Composition (%)				
				Ar	$\text{CH}_4$	$\text{O}_2$	$\text{NH}_3$	$\text{SO}_2$
1	0.7	40	0.004301	65.66	8.75	24.88	0.3	0–0.3
2	1.0	40	0.004252	65.68	11.23	22.49	0.3	0–0.3

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equivalence ratio of 2.17, the addition of 630 ppm of  $\text{SO}_2$  had little effect on NO emissions, but at  $\text{SO}_2$  addition levels greater than 5528 ppm, there was a significant impact on fuel nitrogen formation. In the absence of sulfur components, the NO content rapidly increased to 10 ppm and then remained constant, while with increasing  $\text{SO}_2$  content, NO formation became significantly evident.

Corley and Wendt [46] introduced  $\text{HCN}/\text{SO}_2$  into a  $\text{CH}_4/\text{He}/\text{O}_2$  flame under rich fuel conditions to investigate the influence of fuel sulfur on the distribution of nitrogen-containing components in the flame. The study results indicated that at an equivalence ratio of 1.71, the addition of sulfur promoted the substantial formation of NO and proposed the possible reaction  $\text{N} + \text{SO} \rightarrow \text{NO} + \text{S}$  to explain the production of NO under this condition but failed to account for the significant increase in NO. Therefore, this model was considered unsuccessful by Jeffries and Crosley [11] due to the exclusion of important reactions and intermediates from the model. Consequently, the authors conducted a study on rich methane flames with the addition of  $\text{H}_2\text{S}$  and  $\text{NH}_3$  for the first time and detected NS radicals in an atmospheric pressure flame through the laser-induced fluorescence (LIF) technique. These results indicated that NS radicals are important intermediates in the flame and directly interconnect with the mechanisms of  $\text{NO}_x$  and  $\text{SO}_x$  formation.

Under lean fuel conditions, the impact of sulfur components on  $\text{NO}_x$  differs from that under rich fuel conditions. Hughes et al. [47] conducted experiments on methane flames with mixed  $\text{SO}_2/\text{NH}_3$  under high percentage argon dilution (lean fuel conditions) to investigate the influence of various  $\text{SO}_2$  contents on NO in the combustion zone using LIF, as depicted in Table 1. Figure 6 shows the measurement and simulation results. The experimental results indicated a significant reduction in NO emissions after the



**Fig. 6** The measured and simulated values of the impact of added  $\text{SO}_2$  on NO emissions in flames 1 and 2. Reproduced with permission from Ref. [47]. © 2002 Faraday Division, Royal Society of Chemistry.

addition of  $\text{SO}_2$ , with a greater decrease in NO levels observed as the  $\text{SO}_2$  content increased. Additionally, simulations using the CHEMKIN program were performed to analyze the experiments, and sensitivity analysis identified sulfur-containing species-related reactions important for NS and NO radicals, demonstrating the significance of nitrogen–sulfur direct interaction reactions. However, the aforementioned simulations were based on predicted rates under the experimental conditions, and parameters such as key elementary reactions and reaction pathways in the mechanism were uncertain, lacking relevant data, leading to significant discrepancies between the simulated results and experimental values [48–50].

Building upon the results of gaseous fuel combustion, the combustion process of solid fuel coal has been extensively investigated. Hampartsoumian et al. [12] measured the NO emissions from a 20-kW coal powder furnace with and without the addition of  $\text{SO}_2$  at various equivalence ratios. Figure 7 illustrates the impact of adding  $\text{SO}_2$  on NO emissions at excess air ratios of 1.3 and 0.84 (the excess air ratio and the equivalence ratio are reciprocal to each other). It was observed that under rich fuel conditions, the addition of sulfur increased NO emissions by 20%, while under lean fuel conditions, it led to a decrease in NO emissions. Clearly, two distinct mechanisms exist, with the dominant mechanism determined by stoichiometry, a conclusion consistent with previous reports on gaseous fuel combustion [42,43,45,47]. The interactions of sulfur-enhancing NO and reduction mechanisms occur simultaneously in coal powder flames, dependent on local atmospheres, and the overall NO emissions result from the competition between these mechanisms.

Furthermore, Fig. 8 illustrates the impact of  $\text{SO}_2$  addition on NO emissions in coal-fired furnaces under both rich and lean fuel conditions [12]. Various coal types were utilized in the experiment. It can be observed that under rich fuel conditions, the relationship between  $\text{SO}_2$  addition and the increase in NO emissions is nonlinear, with the curve gradually flattening. Conversely, under lean fuel

conditions, there is a linear negative correlation between  $\text{SO}_2$  addition and the reduction in NO emissions. This suggests that there may be an upper limit to the promoting effect of increasing  $\text{SO}_2$  content on NO emissions, while the inhibitory effect seems to be absent. Variations in the N/S ratio under different atmospheres influence the extent of the interaction, thereby resulting in either an increase or decrease in the amount of NO change.

Table 2 provides a summary of the fuel combustion results discussed earlier, with the equivalence ratio being the primary influencing factor. From Table 2, it can be observed that the thermal  $\text{NO}_x$  content decreases at each equivalence ratio due to the catalytic integration of  $\text{SO}_2$  on radicals, leading to a reduction in the concentration of active radicals and consequently inhibiting the reactions N1–N4, thereby lowering the thermal  $\text{NO}_x$  formation. The fuel  $\text{NO}_x$  content also decreases under lean fuel conditions for the same reason as thermal  $\text{NO}_x$ . However, under rich fuel conditions, the direct reaction of sulfur components with intermediate nitrogen-containing species promotes fuel  $\text{NO}_x$  formation. This result suggests the existence of two distinct mechanisms, with the equivalence ratio determining which mechanism predominates. Therefore, for combustion systems requiring load variations (such as boilers and gas turbines), changes in the equivalence ratio

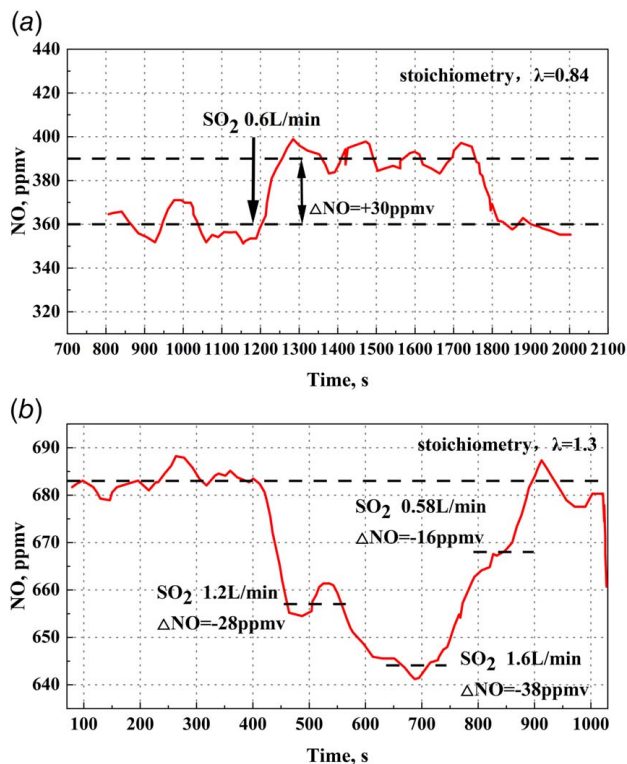


Fig. 7 The impact of  $\text{SO}_2$  addition on NO emissions under different equivalence ratios: (a) fuel-rich condition (excess air ratio  $\lambda = 0.84$ ) and (b) fuel-lean condition (excess air ratio  $\lambda = 1.3$ ). Reproduced with permission from Ref. [12]. © 2001 Elsevier.

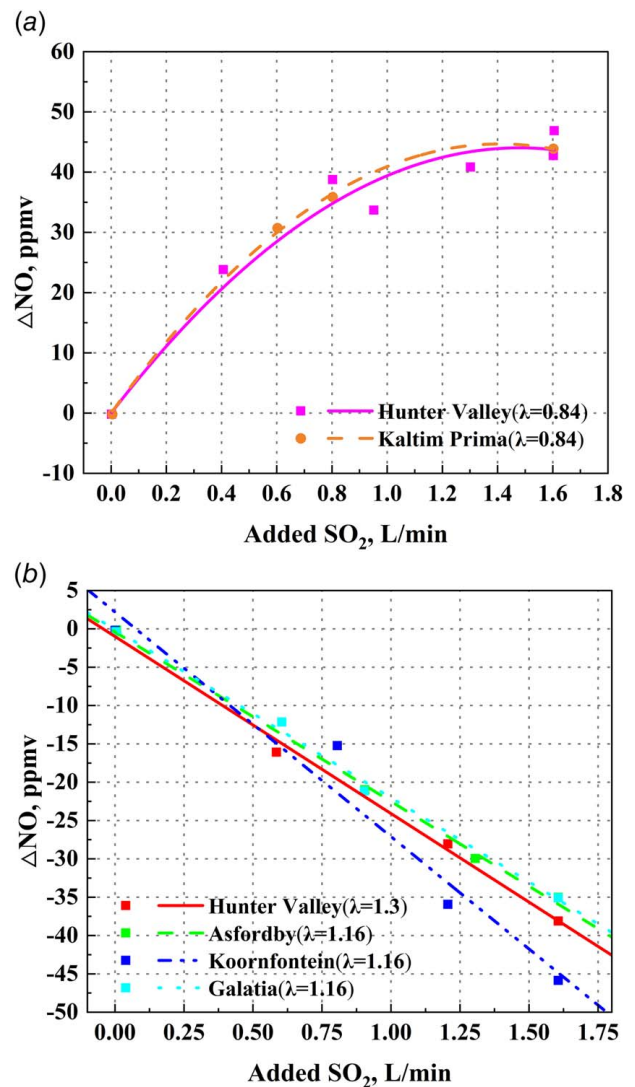


Fig. 8 Influence of  $\text{SO}_2$  addition quantity from different coal types on NO variation under various equivalence ratios: (a) fuel-rich condition and (b) fuel-lean condition. Reproduced with permission from Ref. [12]. © 2001 Elsevier.

**Table 2 Summary of the impact of sulfur components on NO<sub>x</sub> formation**

Fuel	Sulfur additive	Nitrogen additive	Equivalence ratio $\Phi$	Effect on thermal NO <sub>x</sub> emission	Effect on fuel NO <sub>x</sub> emission	Ref.
CH <sub>4</sub>	SO <sub>2</sub>	–	0.8–1.2	Decreased by up to 36%	–	[42]
C <sub>2</sub> H <sub>6</sub>	H <sub>2</sub> S	–	0.8–1.6	Decreased by 5–10%	–	[43]
Gas oil	SO <sub>2</sub>	–	0.85–1.41	Decreased by up to 21%	–	[13]
CH <sub>4</sub>	SO <sub>2</sub>	C <sub>2</sub> N <sub>2</sub>	2.17	–	Increased by 200%	[45]
CH <sub>4</sub>	SO <sub>2</sub>	HCN	1.71	–	Increased by up to 250%	[46]
CH <sub>4</sub>	SO <sub>2</sub>	NH <sub>3</sub>	0.7/1.0	–	Decreased by 12–30%	[47]
Coal	SO <sub>2</sub>	–	1.20 ( $\lambda=0.84$ )	–	Increased by 8%	[12]
			0.77 ( $\lambda=1.30$ )	–	Decreased by 2–6%	

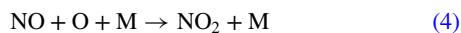
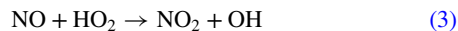
make the interaction between nitrogen and sulfur components non-negligible. It necessitates the incorporation of an N/S interaction reaction system to further enhance the nitrogen–sulfur evolution mechanism model.

#### 4 The Influence of Nitrogen Components on the Formation of SO<sub>x</sub>

While much research has focused on the impact of interactions on the formation of NO<sub>x</sub>, the interaction between the two is mutual, and therefore, the interaction on the evolution of sulfur components cannot be ignored. This section primarily focuses on coal combustion and explores the interactions in the evolution process of SO<sub>x</sub>.

To mitigate nitrogen oxide emissions, coal powder is typically burned under rich fuel conditions [51]. Jiang et al. [52] investigated the impact of nitrogen–sulfur interactions on sulfur component evolution in coal powder furnaces under air-staged combustion. The study results indicate that in a reducing atmosphere, during the process of SO<sub>2</sub> reduction to H<sub>2</sub>S, NO facilitates the conversion of SH radicals to SO radicals through the reactions NO + SH → NS + OH and NS + NO → N<sub>2</sub> + SO, leading to an increase in SO<sub>2</sub> concentration and a decrease in H<sub>2</sub>S concentration. Additionally, as the reducing atmosphere strengthens, the NO concentration decreases, and the interactions become less significant. Furthermore, there is limited research on the influence of NH<sub>3</sub> on the SO<sub>2</sub> reduction process; it is speculated that NH<sub>3</sub> may promote the reduction of SO<sub>2</sub> through the reactions NH + SO → NS + OH and NS + NH → N<sub>2</sub> + SH.

In an oxidizing atmosphere, sulfur components typically convert to SO<sub>2</sub>, and the influence of nitrogen components on this process is rarely reported in the literature reviewed by the author. However, in this atmosphere, some of the SO<sub>2</sub> will further oxidize to SO<sub>3</sub> [53,54], prompting some scholars to investigate the impact of nitrogen components on this process. Fleig et al. [55] conducted a study on SO<sub>3</sub> generation under coal powder oxy-fuel combustion technology, and the results indicate that SO<sub>3</sub> formation is favored when the NO concentration is typically greater than 50 ppm, with the enhancing effect reaching a maximum at 100 ppm, while higher NO concentrations tend to decrease SO<sub>3</sub> formation. The authors attribute this result to the indirect effect of NO on the radical pool through the following reactions [55]:



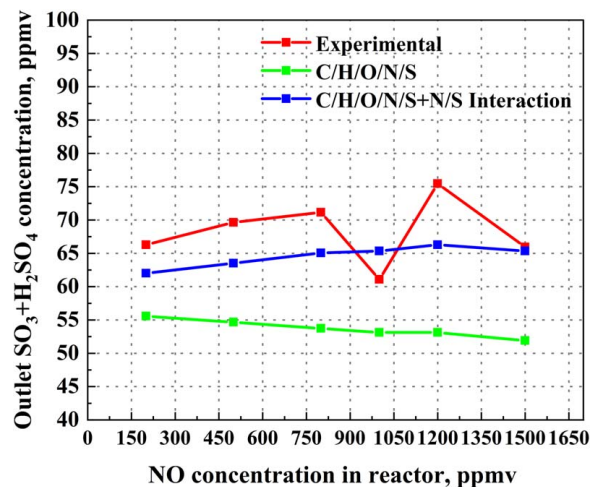
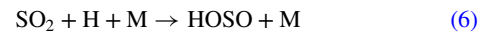
Reaction (3) enhances the concentration of OH radicals at lower NO concentrations, promoting the formation of SO<sub>3</sub>, while reactions (4) and (5) consume available OH and H radicals at higher NO concentrations, reducing the formation of SO<sub>3</sub>. In subsequent studies, the authors consider the reaction NO<sub>2</sub> + SO<sub>2</sub> → SO<sub>3</sub> + NO to be the most significant direct reaction between SO<sub>x</sub> and NO<sub>x</sub> [56]. However, due to considerable controversy surrounding the

interaction between nitrogen and sulfur, the direct interaction between nitrogen and sulfur was not considered in the model. Choudhury and Padak [57], after incorporating the direct interaction between NO<sub>x</sub> and SO<sub>x</sub>, conducted kinetic simulations and sensitivity analyses of methane oxy-fuel combustion experiments using the CHEMKin software. Figure 9 illustrates the impact of NO concentration on the outlet SO<sub>3</sub> concentration under the conditions of equivalence ratio  $\Phi=0.85$  and SO<sub>2</sub> concentration = 2500 ppm. It can be observed that the standalone C/H/O/N/S mechanism simulation exhibits significant deviations from experimental values, but the addition of reactions involving direct interactions between N and S significantly improves the model’s predictions.

#### 5 N/S Interaction Mechanism

The interaction between nitrogen and sulfur components in the combustion process has been summarized earlier, revealing the presence of two distinct mechanisms of nitrogen–sulfur interaction: indirect interaction and direct interaction.

**5.1 Indirect Interaction.** The nitrogen and sulfur components alter their respective evolutions by changing the radical pool, a mechanism that has been described by many scholars. For example, Dagaut et al. [58] proposed the following reactions in their study on the effects of SO<sub>2</sub> and NO on the oxidation of CO/H<sub>2</sub> mixtures:

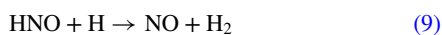
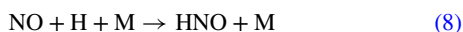


**Fig. 9** The relationship between the simulated and experimental values of outlet SO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub> concentration from the reactor and the concentration of NO. The NO concentration varies from 300 ppm to 1500 ppm, with an equivalence ratio of 0.85 and an SO<sub>2</sub> concentration of 2500 ppm. Reproduced with permission from Ref. [57]. © 2017 American Chemical Society.



**Table 3 Comparison of the proposed nitrogen–sulfur interaction mechanisms in selected literature with the results of this study**

Nitrogen–sulfur interaction mechanism		Ref.
Equivalence ratio > 1 (reducing atmosphere)	Equivalence ratio < 1 (oxidizing atmosphere)	
$\text{NO}_x/\text{HCN}/\text{NH}_i (i=0-3) + \text{SO}_x/\text{H}_2\text{S} \rightarrow \text{NS} + \dots$	$\text{NO}/\text{SO}_2 + \text{X} + \text{M} \rightarrow \text{XNO}/\text{XSO}_2 + \text{M}$	This article
$\text{NH} + \text{SO} \rightarrow \text{NO} + \text{SH}$	$\text{NO}/\text{XSO}_2 + \text{Y} + \text{M} \rightarrow \text{NO}/\text{SO}_2 + \text{XY} + \text{M}$	[12]
	$\text{SO}_2 + \text{H} + \text{M} \rightarrow \text{HSO}_2 + \text{M}$	[42]
	$\text{HSO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{SO}_2$	[42]
$\text{N} + \text{SO} \rightarrow \text{NO} + \text{S}$	–	[46]
$\text{NO} + \text{SH} \rightarrow \text{NS} + \text{OH}$	–	[52]
$\text{NS} + \text{NO} \rightarrow \text{N}_2 + \text{SO}$		
–	$\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$	[55]
	$\text{NO} + \text{O} + \text{M} \rightarrow \text{NO}_2 + \text{M}$	
	$\text{NO} + \text{OH} + \text{M} \rightarrow \text{HONO} + \text{M}$	

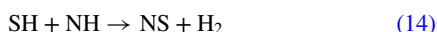


The aforementioned reactions result in a decrease in the concentration of H radicals through the interaction of NO and SO<sub>2</sub>. Cerru et al. [59,60] similarly proposed the integrating effect of SO<sub>2</sub> on H radicals in their study of sulfur mechanisms. Additionally, SO<sub>2</sub> has a similar integrating effect on O and OH radicals [10,61]. The aforementioned reactions can be summarized as follows:



In this reaction, X and Y represent O, OH, or H active radicals. This mechanism predominates in the nitrogen–sulfur interaction under lean fuel conditions, affecting the evolution of each component by reducing the concentration of active radicals (O/OH/H).

**5.2 Direct Interaction.** Compared to indirect interactions, direct reactions of nitrogen–sulfur intermediates play a major role under rich fuel conditions. The presence of NS radicals has been shown to directly impact the evolution of nitrogen and sulfur components [11,62]. In early studies, many scholars proposed possible reactions based on flame combustion experiments for qualitative analysis. For example, Pfefferle and Churchill [43] proposed the following reactions:



Furthermore, other scholars have proposed similar reactions to simulate the nitrogen–sulfur interaction in flames. However, many of these reactions only provide estimated parameters without specific kinetic parameters [63]. Therefore, it is particularly important to accurately calculate the kinetic parameters for direct nitrogen–sulfur reactions.

Table 3 provides a comparison between this study and selected literature regarding the chemical reaction mechanisms. Some of the literature is limited to investigating the interaction in a single

atmosphere [42,46,52,55]. Specifically, under reducing atmospheres, the nitrogen–sulfur interaction manifests as a direct reaction between the two components, while under oxidizing atmospheres, the interaction is primarily characterized by the catalytic integration or consumption of radicals by SO<sub>2</sub>/NO. It is worth noting that although Hampartsoumian et al. [12] considered both atmospheres and reached conclusions similar to those for a single atmosphere, their focus was solely on the impact of sulfur on NO<sub>x</sub> formation. Furthermore, in examining direct interactions, they did not adequately consider reactions between nitrogen-containing intermediates such as NO<sub>x</sub>/HCN, beyond NH radicals, and sulfur components. Due to the complexity and diversity exhibited by nitrogen and sulfur components in actual combustion processes, a comprehensive investigation into the interactions between various nitrogen and sulfur components is crucial. Building upon previous literature, this study proposes new reaction mechanisms for nitrogen–sulfur interactions under different atmospheric conditions. Under oxidizing atmospheres, nitrogen and sulfur components tend to participate in the form of stable oxides through NO and SO<sub>2</sub>, thereby altering the composition and distribution within the radical pool as indicated by the reaction formulas in the table. Conversely, under reducing atmospheres, nitrogen and sulfur components lean toward direct reactions in the form of NO<sub>x</sub>/HCN/NH<sub>i</sub> (i=0–3) and SO<sub>x</sub>/H<sub>2</sub>S, with specific reaction mechanisms depending on the combustion conditions.

With the advancement of computer technology, computational chemistry methods have become a powerful tool for studying the dynamic models of chemical reactions. Hu et al. [64] utilized the Gaussian 09 quantum chemistry software, based on density functional theory and transition state theory, to calculate the rate constants of reactions between NO/NO<sub>2</sub> and sulfur-containing small molecules (SH/S/SO/NS) during combustion processes. Hassani et al. [65] employed the same software to compute the kinetic parameters of the reaction NH + SO within the temperature range of 300–3000 K, enhancing the integrity of the N/S direct interaction reaction system and the accuracy of the kinetic parameters. However, there remains debate over certain reaction pathways and kinetic parameters [66], and the precision of reaction kinetic parameters depends on the development of theoretical calculation levels, which may have limitations. Therefore, perfecting the N/S interaction reaction system is of significant importance for the accurate prediction of nitrogen and sulfur pollutants [67,68].

## 6 Summary and Outlook

Against the backdrop of addressing climate change and achieving sustainable development goals, the formation and control of key pollutants, namely, nitrogen oxides (NO<sub>x</sub>) and sulfur oxides (SO<sub>x</sub>), from fuel combustion have emerged as a central focus in combustion chemistry research. Given the highly coupled evolution of nitrogen and sulfur species during the combustion process, single

reaction mechanisms fall short in adequately elucidating this complexity. Consequently, this article delves into a detailed exposition of the interplay between nitrogen and sulfur components. The article summarizes experimental combustion studies on different fuels and elucidates the impact of nitrogen and sulfur components on each other's evolution under varying equivalence ratios and N/S ratios. Furthermore, a microkinetic analysis of the reaction mechanisms governing N/S interactions was conducted, leading to the following conclusions.

In rich fuel combustion, the presence of SO<sub>2</sub> typically promotes the generation of NO<sub>x</sub>, while under lean fuel conditions, it inhibits NO<sub>x</sub> formation. Similarly, the evolution of nitrogen components is also influenced by equivalence ratios. Under rich fuel conditions, NO promotes the formation of SO<sub>2</sub>, whereas, under lean fuel conditions, small amounts of NO promote the formation of SO<sub>3</sub>, but high NO concentrations inhibit SO<sub>3</sub> formation. Generally, the equivalence ratio determines whether the interaction is promotive or inhibitory, while the extent of change in the N/S ratio can adjust the intensity of this effect. Notably, this effect becomes particularly pronounced when the N/S ratio reaches higher levels, with variations in its impact ranging from 2% to 250%, indicating that the N/S ratio is also a significant influencing factor. However, when the nitrogen or sulfur content is at a low threshold, its intervention in the overall reaction process can be considered secondary and does not constitute a significant impact.

From the perspective of reaction kinetics at the microscopic level, there are two different interaction mechanisms between nitrogen and sulfur, with the actual reaction pathway depending on the equivalence ratio conditions during combustion. Specifically, when the equivalence ratio is greater than 1, the direct reaction of nitrogen–sulfur intermediates plays a dominant role. The primary pathway involves interactions between nitrogen–sulfur intermediates such as HCN/NO/NH<sub>i</sub> (where *i* ranges from 0 to 3) and H<sub>2</sub>S/SO<sub>x</sub>, with the NS radical being the direct product linking the two. Conversely, when the equivalence ratio is less than 1, nitrogen and sulfur components tend to react in the form of stable oxides like NO and SO<sub>2</sub>. The specific reactions can be represented as NO/SO<sub>2</sub> + X + M → XNO/XSO<sub>2</sub> + M and subsequent reactions XNO/XSO<sub>2</sub> + Y + M → NO/SO<sub>2</sub> + XY + M. These reactions alter the concentration distribution of active radicals such as H, OH, and O in the radical pool, thereby affecting the formation mechanisms of nitrogen and sulfur compounds.

Although significant progress has been made, current research tends to focus more on the effects of interactions on the evolution of nitrogen components, with fewer studies dedicated to sulfur components. Therefore, research on the interactions in the evolution of sulfur components is needed. Additionally, the calculation of kinetic parameters for direct reactions is limited by the computational capabilities at the time, resulting in low accuracy and a narrow temperature range of applicability. This limitation makes it challenging to accurately describe the interactions between nitrogen and sulfur species during combustion processes. Therefore, improvements to the N/S interaction mechanism model are necessary. It is expected that enhancing the understanding of nitrogen–sulfur component interactions will lead to more reliable computational results in numerical simulations, providing stronger theoretical support for predicting and reducing nitrogen and sulfur pollutants in fuel combustion.

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## Conflict of Interest

There are no conflicts of interest.

## Data Availability Statement

The datasets generated and supporting the findings of this article are obtainable from the corresponding author upon reasonable request.

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