

## Article

# The Chemical Behaviors of Nitrogen Dioxide Absorption in Sulfite Solution

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**Abstract:** The simultaneous removal of nitrogen oxides ( $\text{NO}_x$ ) and sulfur dioxide ( $\text{SO}_2$ ) by absorption is considered to be one of the most promising technologies for flue gas treatment, and sulfite is the main component of the absorption solution. To understand the chemical behaviors of the  $\text{NO}_2$  absorption in sulfite solution, the absorption time dependences of concentrations of nitrogen and sulfur compositions in both gas phase and liquid phases were investigated by flue gas analyzer, Ion chromatography (IC), Gas chromatography (GC), and Fourier transform infrared spectrometry (FTIR) methods using a bubbling reactor. The mass equilibrium of the N and S compositions were also studied. The results indicate that sulfite concentration plays a vital role in  $\text{NO}_2$  absorption. The main absorption products are  $\text{NO}_3^-$  and  $\text{NO}_2^-$ , and  $\text{NO}_2^-$  can be converted into  $\text{NO}_3^-$  in the presence of oxygen. Besides, about 4% to 9% by-products of S compositions are formed, and 4% to 11% by-products of N compositions such as NO,  $\text{N}_2$ ,  $\text{N}_2\text{O}_5$ ,  $\text{N}_2\text{O}$ , and  $\text{HNO}_3$  in the gas phase were detected in the emissions from the bubbling reactor. On the basis of N and S compositions, a possible pathway of  $\text{NO}_2$  absorption in sulfite solution was proposed.

**Keywords:** absorption; nitrogen oxides; sulfite solution; chemical behaviors; product analysis

## 1. Introduction

As major poisonous air pollutants, nitrogen oxides ( $\text{NO}_x$ ) and sulfur dioxide ( $\text{SO}_2$ ) from the fossil fuel combustion are key contributors to acid deposition, photochemical smog and hazy weather, and bring out a great harm to the environment and human health [1].  $\text{NO}_x$  and  $\text{SO}_2$  removal technologies, therefore, have been the research focus of air pollution control in recent decades. It is well known that the commonly practiced technologies of removing  $\text{NO}_x$ , such as low  $\text{NO}_x$  burners, selective non-catalytic reduction (SNCR), and selective catalytic reduction (SCR), have been widely developed and used.  $\text{SO}_2$  emissions have also been effectively controlled by wet flue gas desulfurization (WFGD), circulated fluid bed flue gas desulfurization (CFB-FGD), and so on. Although the combination of the commonly practiced de- $\text{NO}_x$  and de- $\text{SO}_2$  processes can meet the limitations of  $\text{SO}_2$  and  $\text{NO}_x$  emissions stipulated by environmental legislation, traditional  $\text{NO}_x$  and  $\text{SO}_2$  removal technologies in a stepwise manner have some drawbacks, such as the requirement for large construction site, high capital investment, and high operation costs. Thus, the emerging technologies for the simultaneous removal of  $\text{NO}_x$  and  $\text{SO}_2$  are to be extensively developed [2,3].

The integrated oxidation-absorption process using chemical reagents for simultaneous removal of  $\text{NO}_x$  and  $\text{SO}_2$  is considered as a cost-effective and environmental friendly technology for flue gas treatment and has gained increasing interest [4]. However, nitric oxide (NO), accounting for more than 95% of  $\text{NO}_x$  in typical flue gas, is almost insoluble and low active. Thus, NO has to be oxidized into soluble nitrogen dioxide ( $\text{NO}_2$ ) at the first step. Recently, a few studies related to the NO

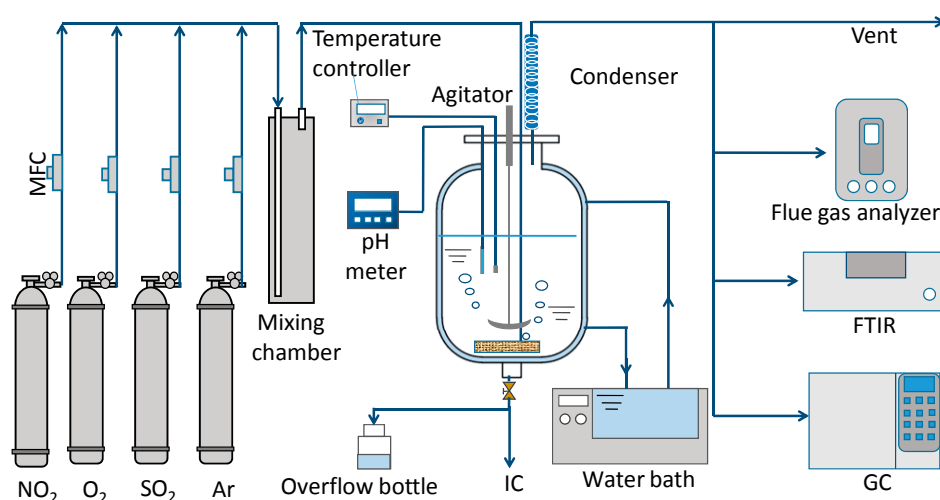
oxidation have been reported [5–12], including gas phase catalytic oxidation, ozone oxidation, corona discharge oxidation, and liquid oxidation. After oxidation, the soluble  $\text{NO}_2$  can be further removed with  $\text{SO}_2$  in the subsequent absorption process [13]. Till now, the  $\text{NO}_2$  absorption process using chemical reagents have widely been studied to develop the industrial scale process. Many absorbents such as  $\text{Ca}(\text{OH})_2$ ,  $\text{CaCO}_3$ ,  $\text{Na}_2\text{SO}_3$ ,  $(\text{NH}_4)_2\text{SO}_3$ , and  $\text{CaSO}_3$  have been tested and the reaction mechanism have been probed [1,14–22]. Among them, sulfite solutions have been considered as a cost-effective absorbent because of their high removal efficiency, their desulphurization byproduct characteristics, and their capacity of simultaneous removal of mercury and chlorine [23–25]. However,  $\text{NO}_2$  and  $\text{SO}_2$  absorption into sulfite absorbents involves complex chemical behaviors. Consequently, and the chemical behavior of absorption has not been widely generalized up to now. Furthermore, there are few reports on the analysis of the gas products from the  $\text{NO}_2$  and  $\text{SO}_2$  absorption in absorbents. Thus it is absolutely necessary to further understand the chemical behaviors of the absorption process to promote  $\text{NO}_2$  and  $\text{SO}_2$  removal by adsorption.

In this study,  $\text{Na}_2\text{SO}_3$  solution was selected as sulfite absorbent. The time-dependences of concentrations of main nitrogen and sulfur (N and S) compositions in both gas phase and liquid phase were investigated by flue gas analyzer, Ion chromatography (IC), Gas chromatography (GC) and Fourier transform infrared spectrometry (FTIR). The mass equilibrium of the N and S compositions of  $\text{NO}_2$  absorption into absorbent through mass balance calculation were also carried out. Moreover, a possible reaction pathway of  $\text{NO}_2$  removal was proposed.

## 2. Experimental Section

### 2.1. Experimental Setup

A scheme of the experimental setup is shown in Figure 1. It consists of a reaction gas feeding unit, an absorption reactor, and a set of gas analytical instruments. A stirred bubbling device with an effective volume of 5 L (150 mm inner diameter and 300 mm in height) was used as the absorption reactor. A mechanical agitator provided continuous stirring at a speed of 105 rpm. The temperature of the reactor was maintained with the help of a thermostatic water bath. A condenser was used to cool and dehydrate the outlet flue gas and reduce the influence of  $\text{H}_2\text{O}$  on products analysis.



**Figure 1.** Schematic diagram of the experimental setup. MFC: Mass flow controller; IC: Ion chromatography; FTIR: Fourier transform infrared spectrometry; GC: Gas chromatography.

### 2.2. Experimental Methods

All experiments were performed at atmospheric pressure and the temperature of  $325 \pm 5$  K. The simulated flue gas, which was supposed to be outlet flue gas after NO oxidation, was simulated by mixing proper amount of  $\text{NO}_2$ ,  $\text{O}_2$ ,  $\text{SO}_2$ , and Ar from compressed gas cylinders. The basic simulated flue gas compositions were 260 ppm  $\text{NO}_2$ , 300 ppm  $\text{SO}_2$ , 6%  $\text{O}_2$  and Ar. The gas flow rate

was adjusted by mass flow controller (MFC), and the four gas streams with a total flow rate of 4 L min<sup>-1</sup> were completely mixed in a mixing chamber before being fed into the absorption reactor. The volume of Na<sub>2</sub>SO<sub>3</sub> solution (0.02 M) stored in the stirred bubbling device was 2 L. pH of absorption solution was maintained at 6–7 by adding 1 M HCl or 1 M NaOH solution. The liquid samples at different times for IC analysis were attained from the sampling port. Qualitative analysis of liquid phase (NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>) was carried out by ion chromatography (IC, Metrohm 792, Herisau, Switzerland). The concentrations of NO<sub>2</sub>, NO, SO<sub>2</sub>, and O<sub>2</sub> in the tail gas were monitored by a flue gas analyzer (Testo350-pro, Schwarzwald, Germany). Sulfite ions (SO<sub>3</sub><sup>2-</sup>) in the liquid phase were measured by an iodometric titration method. N<sub>2</sub> formed in the absorption reaction was monitored using gas chromatography (GC, Agilent 7890, Santa Clara, CA, USA) with a Thermal conductivity detector (TCD, Agilent, Santa Clara, CA, USA), and 5 Å molecular sieve chromatographic column (Agilent, Santa Clara, CA, USA), and the temperature of column oven and detector were 40 and 180 °C, respectively. Other N compositions of outlet gas were analyzed by Fourier transform infrared spectrometry (FTIR, Nicolet 6700, Waltham, MA, USA) equipped with a high-sensitivity mercury cadmium telluride detectors (MCT, Nicolet, Waltham, MA, USA) cooled by liquid nitrogen. The outlet gas stream passed through a 2.5 L gas cell, which had optical path length of 10 m, accordingly averaged spectra after 32 scans at 4cm<sup>-1</sup> resolution were collected in the 3000–650 cm<sup>-1</sup> ranges.

In the current system, inlet NO<sub>2</sub>, SO<sub>2</sub> concentrations, and initial sulfite concentration were previously set, without other sources of nitrogen and sulfur compositions. The molar quantity of N and S compositions in a closed loop system from absorption reaction could be calculated by graphical integration during a fixed period, and the theoretical values in this loop-locked system were expressed as follows:

$$TN_t = \int_0^t \frac{Q(C_0 - C_t) \times 10^{-6}}{V_m} dt \quad (1)$$

$$TS_t = \int_0^t \frac{Q(C_0 - C_t) \times 10^{-6}}{V_m} dt + 0.04 \quad (2)$$

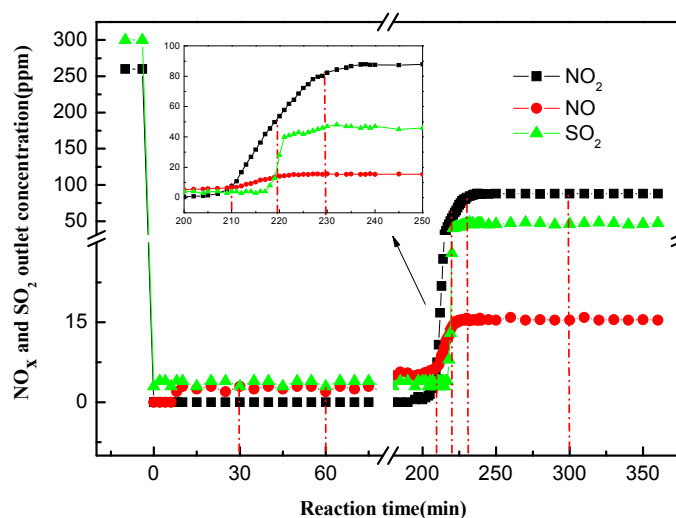
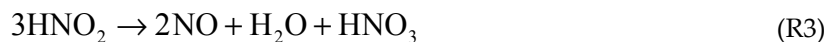
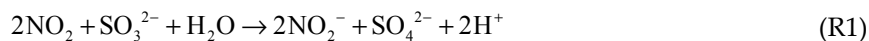
where  $TN_t$  and  $TS_t$  are the total molar quantity of N and S compositions absorbed into reaction system during  $t$  absorption time (mol).  $C_0$  and  $C_t$  are inlet and outlet concentrations of NO<sub>2</sub> or SO<sub>2</sub> (ppm), respectively.  $Q$  is the total flow rate of the flue gas (L min<sup>-1</sup>).  $V_m$  is the molar volume of NO<sub>2</sub> or SO<sub>2</sub> in 325 K (L mol<sup>-1</sup>), and  $t$  is the absorption time (min). Meanwhile, 0.04 in Equation (2) is the original molar quantity of SO<sub>3</sub><sup>2-</sup> in stirred bubbling device (mol).

### 3. Results and Discussion

#### 3.1. Quantitative Analysis of N and S Compositions in Gaseous and Liquid Phases

In order to analyze the distribution of N and S compositions in closed loop reaction system, the dependence of outlet NO<sub>2</sub> and SO<sub>2</sub> concentrations with the absorption time were investigated, and the results are shown in Figure 2. Due to the high sulfite concentration, both NO<sub>2</sub> and SO<sub>2</sub> were not detected in the outlet flue gas during the initial absorption period of about 200 min, which suggests that nearly all of NO<sub>2</sub> and SO<sub>2</sub> are absorbed. The outlet NO<sub>2</sub> and SO<sub>2</sub> concentrations rapidly increase from 210 min to 230 min and are almost unchanged after 230 min. It is clear that the absorption equilibrium is established after a certain absorption time. These results also show that the reaction between NO<sub>2</sub> and sulfite may be mainly controlled by diffusion in the initial reaction period, which is due to the sulfite concentration makes reaction rate is much faster than the diffusion rate [22,26]. Figure 2 also shows that NO, as one of the absorption products, has similar time dependence to NO<sub>2</sub> and SO<sub>2</sub> concentrations. It was found that hardly any NO was detected during initial absorption period of about 200 min. NO concentration gradually increases from about 210 min to 230 min and almost keeps unchanged after 230 min. This can be explained as follows: in the initial absorption period, NO<sub>2</sub> can oxidize sulfite solutions directly (R1). However, with the depletion of

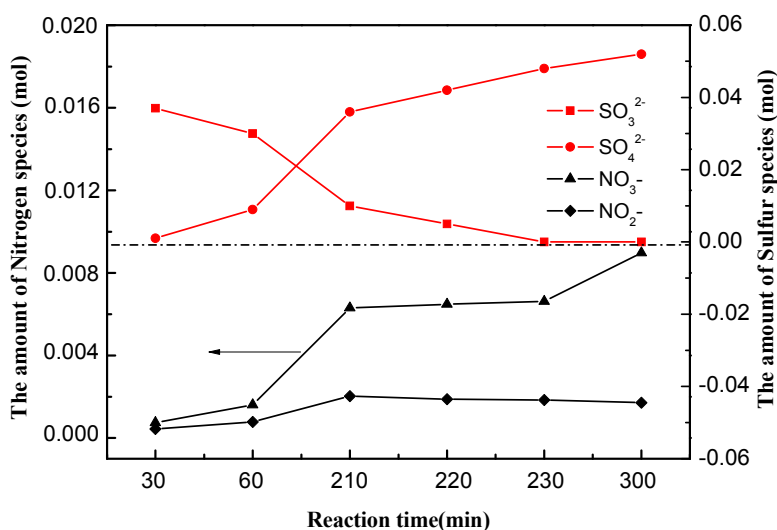
sulfite solutions,  $\text{NO}_2$  absorption in  $\text{H}_2\text{O}$  (R2) occurs, and  $\text{HNO}_2$  may be formed. Generally,  $\text{HNO}_2$  is unstable in its liquid phase and can decompose into  $\text{NO}$  as R3 [22,27].



**Figure 2.** The dependence of outlet  $\text{NO}_2$ ,  $\text{SO}_2$ , and  $\text{NO}$  concentrations with the absorption time.

$\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{SO}_3^{2-}$ , and  $\text{SO}_4^{2-}$ , which are main reactants or products of liquid phase, are synchronously analyzed by IC at the absorption times of 30 min, 60 min, 210 min, 220 min, 230 min and 300 min to better understand the chemical behaviors of  $\text{NO}_2$  and  $\text{SO}_2$  absorption in sulfite solution. As shown in Figure 3,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{SO}_4^{2-}$  concentrations in absorption solution increase as the absorption proceeds. Compared with  $\text{NO}_2^-$ , more  $\text{NO}_3^-$  was formed at the same absorption time, which can be ascribed to the oxidation of  $\text{NO}_2^-$  and the decomposition of unstable  $\text{HNO}_2$  [22,28]. After the absorption time of about 300 min,  $\text{NO}_2^-$  concentration is almost unchanged although  $\text{NO}_3^-$  ions still increase, which is attributed to the fact that nitrite ions are further oxidized into nitrate ions.

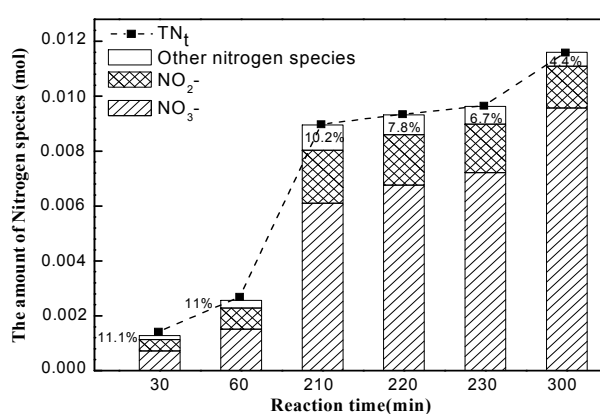
Figure 3 also shows that the sulfite concentration gradually decreases as the absorption proceeds and are almost unavailable after 220 min, which results in a sharp decrease of  $\text{NO}_2$  absorption performance. It indicates that sulfite concentration is closely related with the performance of the removal of  $\text{NO}_2$ , which agrees well with the findings shown in Figure 2. The sulfite is consumed because of its reaction with  $\text{NO}_2$  or  $\text{O}_2$ . For  $\text{NO}_2$  absorption in sulfite solution, the sulfate is formed through the reaction between  $\text{NO}_2$  or  $\text{O}_2$  and sulfite (R1) [29].



**Figure 3.** The dependence of  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NO}_2^-$  contents with the reaction time.

### 3.2. Equilibrium Analysis of N and S Compositions

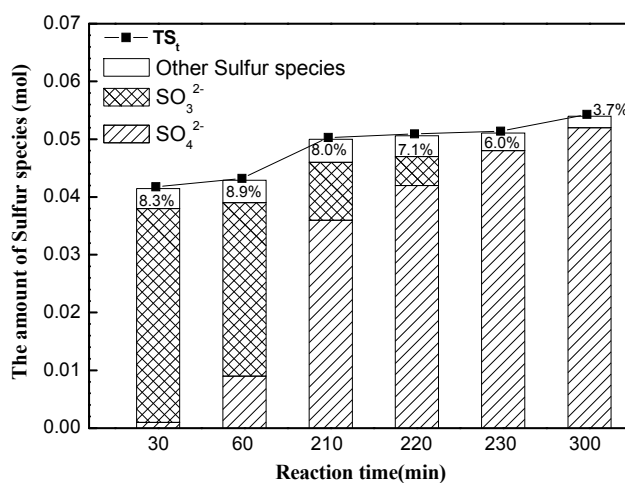
Figures 4 and 5 present the N and S equilibrium of  $\text{NO}_2$  and  $\text{SO}_2$  absorption in sulfite solution, respectively. It can be seen from Figure 4 that the sum of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  ions in the absorption solution is lower than the calculated  $\text{TN}_t$  for almost all the reaction times, which suggests that other N compositions of about 4% to 11%, are formed in the absorption process. Some researchers have confirmed the existence of other N compositions. Siddiqi et al. [30] studied the effect of nitrogen dioxide on the absorption of sulfur dioxide in wet flue gas cleaning processes and pointed out that nitrogen–sulfur compounds could be formed and further decomposed into gaseous products in the co-existence condition of  $\text{NO}_2$  and  $\text{SO}_2$  absorption process. Yan, et al. [31] also reported that the reaction of sulfite with  $\text{NO}$  could produce  $\text{N}_2$ . However, few quantitative researches about gas phase products have been previously reported. In addition, Figure 4 also shows that the amount of other N compositions is almost kept constant before 210 min, and then decreases as the absorption proceeds, which means that sulfite plays a dominant role in the formation of other N compositions. These results are consistent with the dependence of  $\text{NO}_2$  removal (Figure 2) and  $\text{SO}_3^{2-}$  amount (Figure 3) with the reaction time.



**Figure 4.** The equilibrium analysis of N compositions for  $\text{NO}_2$  absorption in sulfite solution.

Similarly, the calculated  $\text{TS}_t$  is also more than the sum of detected  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$ , as shown in Figure 5. Other S compositions besides  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$  account for about 4% to 9% in the reaction system. Besides the above-mentioned nitrogen–sulfur compounds, Chen et al. [32] and Zhuang et al. [32,33] thought that the sulfite radicals could be formed by the reaction between  $\text{NO}_2$  and sulfite, the sulfite radicals could undergo either recombination or reaction with oxygen. By comparing Figure 4 with Figure 5, it can be seen that the amount of other S compositions is much lower than that of other

N compositions, which suggests that not all other S compositions participate in the formation of other N compositions.



**Figure 5.** The equilibrium analysis of S compositions for SO<sub>2</sub> absorption in sulfite solution.

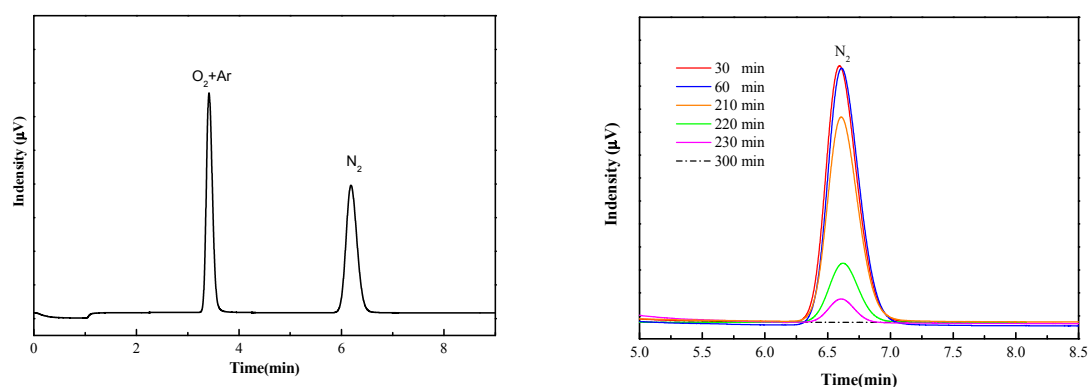
### 3.3. Qualitative Analysis of N Compositions

Besides NO<sub>2</sub>, NO, NO<sub>2</sub><sup>−</sup>, and NO<sub>3</sub><sup>−</sup>, the nitrous products such as N<sub>2</sub>O, N<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, and N<sub>2</sub>, can form during the NO<sub>2</sub> absorption into sulfite solution [10,30]. IC, GC, and FTIR were used to detect these products in this study. Figures 6 and 7 present the GC and FTIR spectra of the gaseous products, respectively.

It can be seen from Figure 6 that the gaseous N<sub>2</sub> is formed mainly in the initial absorption period, declines as the absorption proceeds, and finally disappears after 230 min. N<sub>2</sub> formation can be explained by the following reactions [31],



The sulfite plays an important role in N<sub>2</sub> formation according to Reactions (4) and (5). Thus N<sub>2</sub> concentration decrease is due to the fact that sulfite concentration in reaction system gradually declines and finally disappears. Although N<sub>2</sub> concentration cannot contribute to the equilibrium analysis of nitrogen, the observed declining tendency of N<sub>2</sub> peaks with the absorption time indicates that N<sub>2</sub> is one of other nitrogen compositions.



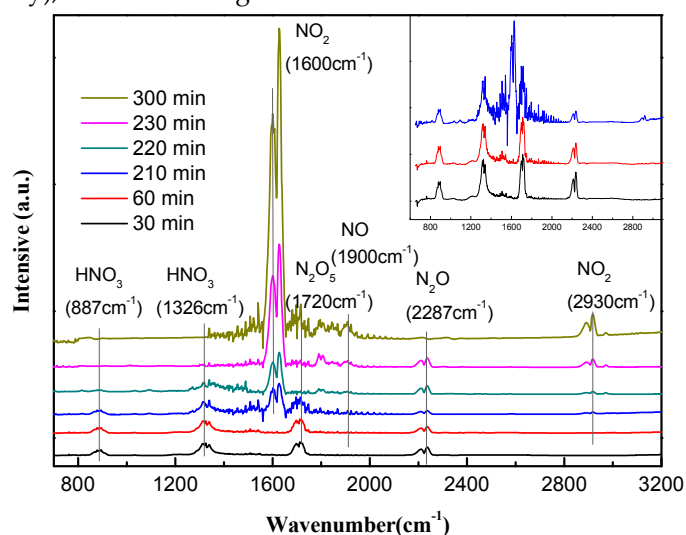
**Figure 6.** GC spectra of gaseous N-products during NO<sub>2</sub> absorption.

Based on the FTIR analysis, the effect of absorption time on the gaseous N-product distribution can be seen, as shown in Figure 7. Six distinct absorbance peaks are observed at 2930 cm<sup>−1</sup>, 2287 cm<sup>−1</sup>, 1720 cm<sup>−1</sup>, 1600 cm<sup>−1</sup>, 1326 cm<sup>−1</sup>, and 887 cm<sup>−1</sup>, and the bands are assigned to NO<sub>2</sub>, N<sub>2</sub>O, N<sub>2</sub>O<sub>5</sub>, NO<sub>2</sub>, HNO<sub>3</sub>, and HNO<sub>3</sub>, respectively [34]. In the initial absorption period, the intensities of bands at 2287

$\text{cm}^{-1}$ ,  $1720\text{ cm}^{-1}$ ,  $1326\text{ cm}^{-1}$ , and  $887\text{ cm}^{-1}$  almost keep unchanged, which shows that  $\text{N}_2\text{O}$ ,  $\text{N}_2\text{O}_5$ , and  $\text{HNO}_3$  as gaseous products are continuously generated from the absorption reactions. Then the amounts of  $\text{N}_2\text{O}$ ,  $\text{N}_2\text{O}_5$ , and  $\text{HNO}_3$  rapidly decrease after the absorption time of about 210 min and finally disappear after about 230 min, which indicates that the absorption equilibrium is established, and no sufficient sulfite is used to react with  $\text{NO}_2$  to produce gaseous  $\text{N}_2\text{O}$ ,  $\text{N}_2\text{O}_5$ , and  $\text{HNO}_3$ . These results are consistent with the equilibrium analysis of sulfur compositions (see Figure 5). In fact, not all sulfite would be converted to sulfate ions, nitrogen–sulfur compounds, and sulfite radical may exist in reaction system. In addition, the occurrence of  $\text{N}_2\text{O}_5$  is due to the reaction between  $\text{NO}_2$  and  $\text{O}_2$  in gas phase, or the decomposition of nitrogen–sulfur compounds. Furthermore, the gaseous  $\text{HNO}_3$  is not only attributed to the fact that  $\text{HNO}_3$  in absorption liquid enters gas phase, but also that gas phase reaction happens, which can be described by the following Reaction (6):



Figure 7 also shows that the peak at  $1600\text{ cm}^{-1}$ , assigned to  $\text{NO}_2$ , gradually increases and the peak at  $1900\text{ cm}^{-1}$ , assigned to  $\text{NO}$ , gradually decreases after the absorption time of about 210 min. The results are also in accordance with those of gas phase composition analysis by flue gas analyzer (Testo350-pro, Germany), as shown in Figure 2.



**Figure 7.** FTIR spectra of the gaseous N-products during  $\text{NO}_2$  absorption.

Figure 8 shows the distribution of nitrogen products for  $\text{NO}_2$  absorption into sulfite solution, based on mass balance for a typical inlet gas with 260 ppm  $\text{NO}_2$ , as the sole N source. Because  $\text{NO}_2$  is hardly detected in the outlet flue gas of the reactor before 60 min,  $\text{NO}_2$  absorbed into the liquid phase is 2.56 mmol during initial absorption time of 60 min.  $\text{NO}_3^-$  and  $\text{NO}_2^-$  concentrations in the absorption solution, based on IC results, are 1.511 and 0.766 mmol, respectively. Because both  $\text{NH}_3$  and  $\text{NH}_4^+$  have not been found by FTIR and IC, the other N compositions is calculated as 0.283 mmol according to mass balance, account for 11% of the total N compositions, and the calculated values of other N compositions content are in good agreement with the experimental values.



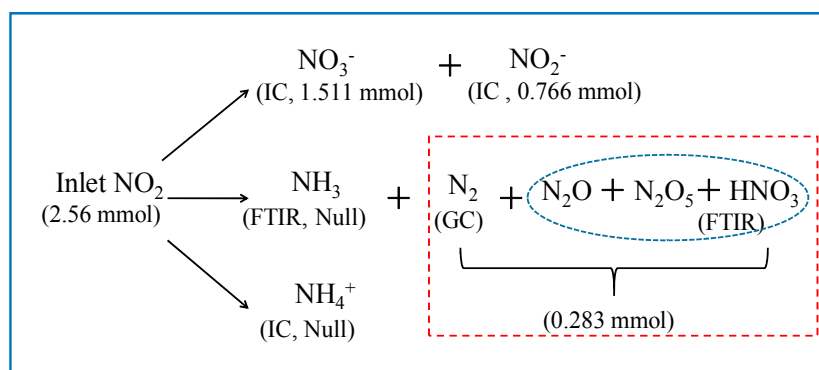


Figure 8. The nitrogen balance of  $\text{NO}_2$  absorption in sulfite solution.

### 3.4. $\text{NO}_2$ Absorption Pathway

According to the above-mentioned analyses, a possible  $\text{NO}_2$  absorption pathway can be proposed, as depicted in Figure 9.

The main reactants in the gas phase include  $\text{NO}_2$ ,  $\text{SO}_2$ , and  $\text{O}_2$ . The sole N source in the inlet flue gas is  $\text{NO}_2$ . When  $\text{NO}_2$  laden gas contacts with sulfite solution, the transfer of the  $\text{NO}_2$  into absorption solution occurs, meanwhile, reactions take place in the liquid phase, and the main products of  $\text{NO}_2$  absorption in flue gas are  $\text{NO}_3^-$  and  $\text{NO}_2^-$ , especially  $\text{NO}_3^-$  in absorption solution dramatically increases due to the absorption of  $\text{NO}_2$  and the oxidation of  $\text{NO}_2^-$ .  $\text{HNO}_3$  is considered to involve gas and liquid states existing in reaction system, and the gaseous  $\text{HNO}_3$  in outlet flue gas is from both  $\text{HNO}_3$  escape in absorption solution and the reaction between  $\text{NO}_2$  and  $\text{H}_2\text{O}$  in the gas phase.  $\text{HNO}_2$  may be produced by  $\text{NO}_2^-$  combining with  $\text{H}^+$ , and  $\text{HNO}_2$  is unstable in liquid phase and easily decomposes, which leads to  $\text{HNO}_3$  formation and  $\text{NO}$  release. As  $\text{NO}$  increasing, a homogeneous reaction of  $\text{NO}$  and  $\text{NO}_2$  results in an increase of the  $\text{N}_2\text{O}_3$  to a smaller extent, the  $\text{NO}$  or  $\text{N}_2\text{O}_3$  can react with  $\text{SO}_3^{2-}$  to form hydroxylamine-disulfonate (HADS), which is a precursor of numerous N-S compounds. In addition, the existence of  $\text{SO}_2$  in the gas phase is in favor of the sulfite and bisulfate formation, and  $\text{HNO}_2$  can also react with  $\text{HSO}_3^-$  to form HADS. The intermediate products of N-S compounds finally decompose to  $\text{N}_2\text{O}_5$ ,  $\text{N}_2\text{O}$ , and  $\text{N}_2$  in gas phase.

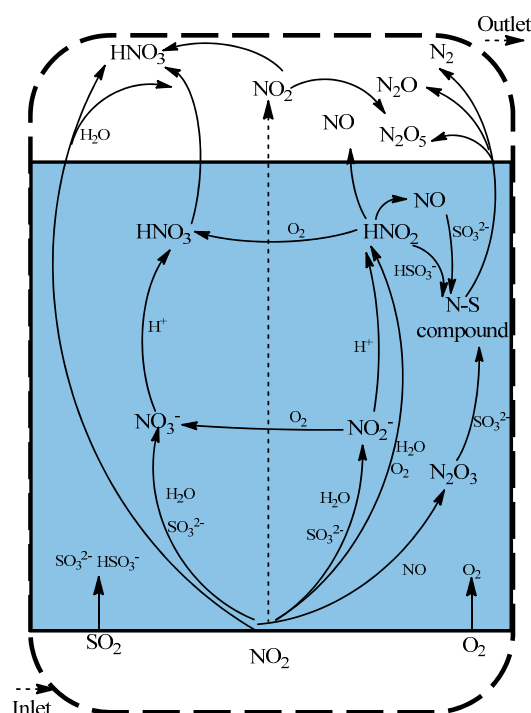


Figure 9. A possible  $\text{NO}_2$  absorption pathway.



#### 4. Conclusions

A series of experiments were performed to study the chemical behaviors for the NO<sub>2</sub> and SO<sub>2</sub> absorption in sulfite solution, and a possible NO<sub>2</sub> absorption pathway was proposed. The main findings can be summarized as follows: The performance of NO<sub>2</sub> absorption is closely related with sulfite concentration. The main N and S compounds generated in the NO<sub>2</sub> absorption process are NO<sub>3</sub><sup>−</sup>, NO<sub>2</sub><sup>−</sup>, and SO<sub>4</sub><sup>2−</sup>. Moreover the NO<sub>3</sub><sup>−</sup>, NO<sub>2</sub><sup>−</sup>, and SO<sub>4</sub><sup>2−</sup> concentrations change with absorption times. Besides, about 4% to 9% by-products of S compositions are formed, and 4% to 11% by-products of N compositions, such as NO, N<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>, N<sub>2</sub>O, and HNO<sub>3</sub> in gas phase, were detected in the emissions. Meanwhile, N<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>, and N<sub>2</sub>O could be ascribed to the decomposition of sulfur–nitrogen compounds as intermediate products exited from the redox reaction between sulfite solutions and NO<sub>2</sub>.

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**Author Contributions:** Tianle Zhu conceived and designed the experiments; Ye Sun performed the experiments; Ye Sun, Xiaowei Hong, Xiaoyan Guo and Deyuan Xie analyzed the data; Ye Sun and Tianle Zhu wrote the paper.

**Conflicts of Interest:** The authors declare no conflict of interest.

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