



Thermal fixation of sulfur dioxide

as elemental sulfur or sulfate with sodium oxalate

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Summary

In a new thermal reaction, gaseous SO₂ is reduced to elemental S₈ over powdered Na₂C₂O₄ at 370 °C. Mixtures of SO₂ and dry air gave oxidation to sodium sulfate.

Introduction

Sulfur dioxide is a troublesome pollutant arising from volcanic activity but also formed in many combustion processes. Human activities account for the release of as much as 2×10^8 tonnes y⁻¹. This release contributes to acid precipitation and the consequent degradation of forest. SO₂ decomposes thermally at very high temperatures, photochemically by irradiation with UV light, radiochemically by γ-rays, in electrical discharges and electrolytically.¹ In these reactions, SO₂ is believed to react *via* reduction to SO₂⁻ and then SO. Since SO (detected spectroscopically) rapidly disproportionates to S₈ and SO₂, the observed products are S₈, O₂ and SO₃.¹

Large quantities of sulfur dioxide, emitted into the atmosphere by the combustion of fossil fuels and the smelting of sulfide ores,² become oxidized to sulfuric acid and contribute to acid rain. The average lifetime of sulfur dioxide in the atmosphere has been estimated to be in the range of 3–10 h.^{3a,b} Measurements of the acidity of snow and rain have shown that in parts of the eastern US and western Europe precipitation has changed from a nearly neutral pH 200 years ago to pH 4–5 today;^{3a} in extreme cases, (Scotland, 1974) the rain had a pH of 2.4, equivalent to the acidity of vinegar.^{3a} Taller stacks have been constructed to relieve local pollution problems.^{3a} However, this has turned local problems into regional ones.

Removal of SO₂ from gas streams is possible by absorption of this acid gas by bases such as NaOH,^{4c} but the resulting sulfites are not innocuous because disposal is needed and inadvertent acid treatment releases the SO₂ once again. Air oxidation of aqueous solutions of sulfites is possible and it has been extensively studied, but this adds a second step and the need for an external oxidant, a solvent and a catalyst.^{4d} Methods for the recovery and removal of SO₂ from effluent gases involve reduction to elemental sulfur.⁵

Allied Signal⁵ commercialized a method for converting SO₂ into S₈ in 1970 as an emission control system for a Canadian sulfide ore roasting facility. It can be applied for gas streams containing 4–100% SO₂, and for concentrations below 4%, a preliminary concentrating process is combined. Although the whole process is complex and involves eleven different elements and compounds, the main reductant is methane. Other reduction processes for the reduction of SO₂ to S₈ involves the use of H₂S (Claus process) or CO (Bureau of Mines) as reducing agents.⁵

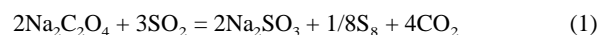
The oxidation of SO₂ to SO₃ is, by far, the most important reaction in the chemistry of the oxides of sulfur.² In the presence of Pt, the reaction begins at 200 °C.^{6a} In practical operations, the reaction is carried out at 450 °C using Pt or V₂O₅ as catalyst. V₂O₅ is preferred as catalyst because it is cheaper than Pt and less susceptible to poisoning by selenium and arsenic.⁷ A scheme has also been proposed⁸ for the oxidation of SO₂ to SO₃, with V₂O₅ on silica as catalyst.

In this paper we describe a new and convenient thermal method for the reduction of SO₂ to elemental S₈. When the reaction is used for the removal of SO₂ from air mixtures, oxidation of SO₂ to Na₂SO₄ takes place instead.

Results

We previously reported that powdered sodium oxalate at 450–460 °C is an efficient selective reducing agent for highly unreactive species such as fluorocarbons, converting perfluorodecalin to perfluoronaphthalene, for example.⁹ The ready availability of the reagent (\$8/kg in bulk) permits the method to be considered for commercial application. We therefore examined it for the reduction of SO₂.

Passing SO₂ over a packed bed of powdered Na₂C₂O₄ at 370 °C led to the production of elemental sulfur by reduction of SO₂. Not all the SO₂ was destroyed in this one-pass apparatus, but in a multipass apparatus with trap-to-trap distillation using dry ice cooling of the sink trap, three passes were found to be sufficient to reduce the whole charge of SO₂ (5.23 g, 81.7 mmol, 95%) according to the following equation.



The expected amount of sulfur was removed from the oxalate bed by extraction with CS₂ to constant weight. The unreacted Na₂C₂O₄ was determined by titration with KMnO₄ solution and the Na₂SO₃ product by titration with NaI₃ solution. In the titration of Na₂SO₃ with I₂, Na₂SO₃ is oxidized to Na₂SO₄ and we also

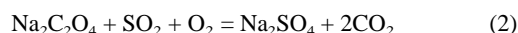
Green Context

The conversion of sulfur dioxide from a pollutant into a useful raw material such as elemental sulfur or sulfate is a valuable achievement. This paper describes such conversions using reactants such as sodium oxalate. This is a new reaction—under non-aerobic conditions the product is sulfur, under oxidative conditions, sulfate is formed. DJM

determined the amount of Na_2SO_4 formed by precipitation with BaCl_2 and gravimetric determination of the resulting BaSO_4 . We found that the moles of Na_2SO_3 determined by titration and the Na_2SO_4 determined gravimetrically were identical, indicating that no Na_2SO_4 was formed when SO_2 was passed through the oxalate bed. After the SO_2 was consumed, the CO_2 formed gave an acid soluble precipitate (CaCO_3) from $\text{Ca}(\text{OH})_2(\text{aq})$ but was not determined quantitatively.

To examine potential applications for removing SO_2 from air, we moved to mixtures of SO_2 and dry air and found that neither sulfite nor sulfur were now formed. Since these two species were found to be stable to air at the temperatures of the reaction, they are not being formed and then subsequently oxidized by air. Therefore, a different pathway must be involved.

A 1:1 (v/v) SO_2 /dry air mixture was passed over powdered sodium oxalate in a single-pass reactor. The stoichiometry of eqn. (2) was determined for this new reaction as follows. The sulfate was determined gravimetrically with BaCl_2 . Sodium sulfite was absent because the bed residue showed no reaction with aq. NaI_3 . Finally, one mole of oxalate, determined by titration with KMnO_4 of the oxalate remaining, was found to be consumed per mole of sulfate formed.



We have applied this reaction to the removal of SO_2 from air mixtures using single pass and multiple pass apparatus. In the single pass apparatus, where excess air is present, we found that as the length of $\text{Na}_2\text{C}_2\text{O}_4$ bed increases, so does the % SO_2 removed (Fig. 1). The percentage of SO_2 removed was

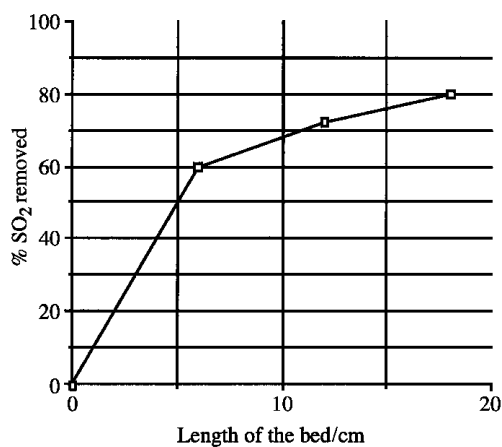


Fig. 1 Efficiency of SO_2 removal versus bed length.

determined by measuring the different amounts of SO_2 absorbed in a solution of NaI_3 when identical gas flow was passed through a cold and a hot oxalate bed.

We have also used the trap to trap multipass apparatus in the presence of dry air by passing a 1:1 (v/v) SO_2 /air mixture through the bed and condensing the unreacted SO_2 . The condensed SO_2 was passed back and forth from trap to trap in a stream of excess dry air until the reaction finished. By connecting the exit of the apparatus to a 0.05 M NaI_3 solution, we were able to determine the amount of SO_2 that escapes the apparatus because of imperfect cooling of the trap. We found that 89% of SO_2 was retained in the bed as Na_2SO_4 and ca. 10% escapes. There is no significant SO_2 absorption in the cold bed.

Other substrates were not reduced under these conditions. For example, $(\text{C}_6\text{H}_5)_3\text{PO}$, $(\text{C}_6\text{H}_5)_3\text{PO}$, $(\text{CH}_3)_2\text{SO}_2$ and $(\text{CH}_3)_2\text{SO}$

were unchanged when passed through the sodium oxalate bed at temperatures of 370 °C to 450 °C.

Mechanism

The main point of this paper is to report the results, but some preliminary mechanistic discussion is presented here.

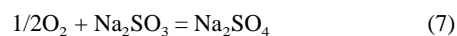
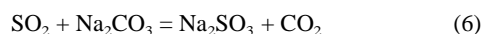
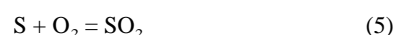
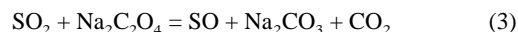
Sulfur formation

A number of possible mechanisms might operate for the reduction of SO_2 to S_8 . The most plausible intermediates seem to be $\text{SO}_2^{\cdot-}$ and then SO , as previously proposed.¹ The known disproportionation of SO to give S_8 and SO_2 , followed by absorption of the acidic SO_2 by the basic Na_2CO_3 formed on oxidation of oxalate, is expected to yield the other observed product Na_2SO_3 .

Sulfate formation

The SO_2 oxidation with air raised the question whether SO_2 or O_2 or even CO_2 (300 ppm in air) was reacting with oxalate. Passing pure dry air over the oxalate bed at the reaction temperature produced no change in the bed instead of the oxidation of the oxalate to Na_2CO_3 that we had originally expected, so neither CO_2 nor O_2 react directly. Other work^{9b} shows that even pure CO_2 does not react with hot sodium oxalate. It might seem remarkable that a reagent that reduces such inert substrates as perfluorocarbons and even CFCs^{10} fails to react with O_2 , but an important caveat is that the temperature used here (370 °C) is far lower than in the fluorocarbon work (465 °C) and mechanistic work on the fluorocarbon reaction shows that incipient decomposition of the oxalate to carbon is required for reaction with the fluorocarbons. Given that O_2 does not react with the oxalate, the most likely possibility is that O_2 intercepts a reduction product from the SO_2 . The three most plausible candidates are the 1-, 2- and 4-electron reduction products of SO_2 : $\text{SO}_2^{\cdot-}$, SO and S atoms.

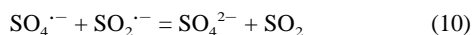
Eqn. (3)–(7) illustrate a proposed mechanism *via* SO as intermediate. Sulfur monoxide, which can be formed when SO_2 is reduced with sulfur vapor in a glow discharge,^{6b} has been considered as an intermediate in other reduction reactions of SO_2 to S_8 .⁶ Since it is unstable at all temperatures it disproportionates into S_8 and SO_2 . However S atoms readily react with oxygen to give SO_2 .¹¹ Another difficulty with this mechanism is that the oxygen atom removed from the SO_2 by sodium oxalate to generate SO , would be expected to initially appear in the product in the form of Na_2CO_3 as shown in eqn. (3). In the presence of SO_2 this carbonate would be converted to Na_2SO_3 . For the observed product to be Na_2SO_4 , the initially formed Na_2SO_3 would have to be oxidized by air. We find, however, that Na_2SO_3 is stable to dry air under our reaction conditions. Therefore a mechanism involving SO and S atoms as intermediates seems unlikely.



This made us suspect that the radical¹² $\text{SO}_2^{\cdot-}$ was the more likely intermediate that reacts with O_2 . Its formation would involve a single electron transfer (SET) from the surface of the crystal. A SET mechanism is also consistent with our earlier observation⁹ that $\text{Cl}_3\text{C}-\text{CCl}_3$ is formed when CCl_4 is passed over

$\text{Na}_2\text{C}_2\text{O}_4$ at a similar temperature (320 °C), since this product is most easily rationalized by recombination of two $\text{CCl}_3\cdot$ radicals formed by SET to CCl_4 . Of course, CCl_4 is a different class of substrate, so this may not be relevant.

The $\text{SO}_2^{\cdot-}$ radical was previously observed in dithionite solutions by electron paramagnetic resonance.¹³ Prior mechanistic studies¹⁴ suggest that air oxidation of dithionite solutions to SO_4^{2-} goes *via* the pathway of eqn. (8)–(10).



Our data are consistent with a similar mechanism operating in the sodium oxalate reaction. If so, it is an unusual case of an O_2 oxidation where the substrate and not O_2 is reductively activated.

Conclusions

In this paper, we describe a simple thermal method for the reduction of SO_2 to S_8 using hot sodium oxalate. When the reaction was used for the removal of SO_2 from air mixtures, we found that oxidation of SO_2 to Na_2SO_4 took place instead of reduction to S_8 . A mechanism is discussed.

Experimental

Reduction of sulfur dioxide

Trap to trap multipass (TM) or single pass (SP) experiment

The apparatus, consisting of a glass tube wrapped with a heating tape, was connected either to a pair of cold traps on each end (TM) or to the gas source *via* a flow meter (SP) and loaded with powdered sodium oxalate (40.0 g, 298.5 mmol). The substrate was passed (70 mL min^{-1} for 2.5 h) through the heated (370 °C) oxalate bed (SP) or passed through the oxalate bed (70 mL min^{-1} for 2.5 h) and condensed in the trap (TM) and subsequently passed from trap to trap by heating the source trap and cooling the sink trap (acetone/dry ice, -78 °C).

The unreacted sodium oxalate was determined by titration with 0.15 M KMnO_4 . Sulfur (0.85 g, 26.56 mmol) was isolated from the bed by extraction with carbon disulfide to constant weight. Sodium sulfite (6.69 g, 51.08 mmol) was also found in the bed which was determined by titration with 0.2 M NaI_3 solution and the sodium sulfate thus formed was determined gravimetrically using BaCl_2 . Only three passes were required to convert the full sample (5.23 g, 81.72 mmol, 95%) into sulfur and sodium sulfite.

Attempted reaction with oxygen

A flow of O_2 (33.3 mL h^{-1}) was passed through a $\text{Na}_2\text{C}_2\text{O}_4$ bed (40.0 g, 298.5 mmol) at 370 °C. After 3 h flow, the $\text{Na}_2\text{C}_2\text{O}_4$ in the bed was determined by titration with 0.15 M KMnO_4 solution showing that no reaction had occurred. We repeated this experiment, but after 3 h, the O_2 flow was closed and a flow of SO_2 (10 mL min^{-1}) was passed through the bed. After a few minutes, condensation of S_8 was observed in the air cooled condenser placed at the exit of the bed. This indicates, that at the temperature of eqn. (3), SO_2 was reduced to S_8 , while O_2 did not react with the bed.

Reaction with sulfur dioxide and dry air

Single pass (SP) experiment

Sodium oxalate (40.4 g, 301.9 mmol) was placed in the reactor and a 1:1 mixture of SO_2 (flow: 14.0 mL min^{-1}) and dry air was passed through the hot bed (370 °C) for 10 h. The solid mixture

in the bed was dissolved in water and the unreacted sodium oxalate (19.26 g, 143.73 mmol) was determined by titration with 0.15 M KMnO_4 solution. The solution failed to react with an aqueous solution of NaI_3 , indicating the absence of sodium sulfite. However, Na_2SO_4 (22.4 g, 158.0 mmol) was found in the bed as determined gravimetrically with BaCl_2 . We found that one mole of sodium oxalate (21.2 g, 158.0 mmol) was consumed per mole of Na_2SO_4 (22.4 g, 158.0 mmol) formed.

Removal of sulfur dioxide from air

Single pass experiment

A stream of dry air (flow 13.7 mL min^{-1}) was passed through a dilute solution of Na_2SO_3 (0.05 M) which was acidified with an excess of HCl (10 mL $\text{HCl}_{(c)}$). The gas stream was then passed through the hot $\text{Na}_2\text{C}_2\text{O}_4$ cylindrical bed (40.0 g, 0.30 mol per bed) with the following dimensions: 6.0 cm and 1.7 cm. The removing efficiency increases with the retention time of SO_2 in the bed (number of beds used). We measured the results for one, two and three beds. The percentage of SO_2 removed was calculated by running identical experiments with cold $\text{Na}_2\text{C}_2\text{O}_4$ bed(s). The SO_2 unretained in the bed was trapped in 500 mL solution of NaI_3 (0.05 M), reacted with a known amount of Na_2SO_3 and titrated by return with NaI_3 . The data obtained are reported in Table 1. The average concentration of SO_2 in the stream was in the range 1.5–3.0% v/v as determined by measuring the volume of air and the absorbed SO_2 in a 0.2 M NaI_3 solution.

Table 1 Removal of SO_2 from air

Number of beds	Length of the bed/cm	% SO_2 removed
1	6	60
2	12	72
3	18	80

Trap to trap multipass experiment in the presence of air

The apparatus, consisting of a glass tube wrapped with a heating tape, was connected to a pair of cold traps on each end (TM) loaded with powdered sodium oxalate (40.0 g, 298.5 mmol). A mixture of 1:1 SO_2 /dry air was passed (30 mL min^{-1} for 3.5 h) through the heated (370 °C) oxalate bed. The unreacted SO_2 was condensed in the trap (TM) and subsequently passed from trap to trap in a stream of dry air by heating the source trap and cooling the sink trap (acetone/dry ice, -78 °C). The exit of the apparatus was connected to a trap containing 500 mL 0.05 M NaI_3 in order to capture the SO_2 that escapes from the trap due to imperfect cooling (0.30 g, 4.68 mmol). Unreacted sodium oxalate was determined by titration with 0.15 M KMnO_4 and the Na_2SO_4 (5.55 g, 39.1 mmol) gravimetrically determined by precipitation with BaCl_2 , showing that 89% of the SO_2 (2.5 g, 39.1 mmol) was retained in the bed.

Acknowledgment

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