

## Reduction of Sulfur Dioxide on Carbons Catalyzed by Salts

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**Abstract.** The reduction of SO<sub>2</sub> on different carbons in the presence of the nitrates and sulfides of sodium, potassium and calcium and potassium polysulfides was studied. The presence of salts increased the initial rate 2-5 fold for all of them and did not change the product distribution. The catalysis was not determined by the cation and there was no difference in the catalytic reactivity between nitrates and sulfides. The sulfur content of the activated carbon increased during the reaction on account of the stable reactive intermediates in the reduction of SO<sub>2</sub>. In the presence of NaNO<sub>3</sub> or Na<sub>2</sub>S, the amount of sulfur incorporated was in the molar ratio Na:S = 3 ± 0.3, and the XPS spectra of the residual carbon showed an increase of ca. 9% of the non-oxidized form of sulfur in the intermediates. In the absence of salt, it is proposed that after the adsorption of SO<sub>2</sub> on the carbon, a 1,3,2-dioxathiolane or 1,2-oxathietene 2-oxide are formed and that decompose to produce CO<sub>2</sub> and atomic sulfur. The non-oxidized sulfur intermediate would be an episulfide **3**, formed from the reaction of the atomic sulfur with the nearest double bond and followed by consecutive reactions of insertion of atomic sulfur to form a trisulfide. Extrusion of S<sub>2</sub> from the trisulfide would regenerate the episulfide, establishing a sulfide-disulfide-trisulfide equilibrium that worked as a capture-release cycle of sulfur. In the presence of salt, the results are consistent with the assumption that the episulfide **3** reacts with the corresponding sulfide anion to form a disulfide anion, which upon reaction with atomic sulfur forms a trisulfide anion that decomposes releasing diatomic sulfur S<sub>2</sub>, transporting the sulfur and generating a thiolate that is part of the catalytic cycle.

**Keywords:** sulfur dioxide; carbons; graphite; charcoal; activated carbon; catalysis by salts.

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## Introduction

The reduction of SO<sub>2</sub> on carbons has been intensively studied because sulfur and nitrogen oxides are considered among the worst atmospheric pollutants and precursors of acid rain [1]. The elemental sulfur produced in the reaction is a more desirable product because it is easy to handle and store.

Mechanistic studies of the reduction of SO<sub>2</sub> by carbon have been hampered owing to the use of deficient experimental techniques to allow quantitative measurements of the reactivity and product distribution. The products of the C + SO<sub>2</sub> reaction involve the C-O-S system, and there are 21 reactions that are thermodynamically possible [2, 3].

When different carbons are heated in the presence of sulfur, H<sub>2</sub>S, CS<sub>2</sub> or SO<sub>2</sub>, surface complexes have been observed [4-7] that change the reactivity of the carbon [8]. Several mechanistic proposals have postulated that these surface complexes could act as intermediates, but without any experimental evidence [8-11].

We have studied the reaction C + SO<sub>2</sub> on different carbons (graphite, charcoal, activated carbon, cokes) under strict kinetic conditions and shown that the reaction is first-order with respect to carbon and first-order with respect to SO<sub>2</sub> [12, 13].

Analysis of product distribution showed that the reduction of SO<sub>2</sub> proceeds through the stoichiometric reaction (1) because it is the only reaction of the C-O-S system where the ratio CO<sub>2</sub> : S<sub>2</sub> = 2 : 1.



The reduction of SO<sub>2</sub> on activated carbon showed that the sulfur content on the carbon increased until the reaction reached the steady-state condition. The sulfur content remained constant during this period and it was chemically bound to the carbon matrix [13].

The XPS spectrum of the residual carbon showed that the sulfur was bound as non-oxidized and oxidized sulfur. The superficial complexes behaved as reactive intermediates because, besides the constant concentration during the steady state, the residual carbon reacted with SO<sub>2</sub> at the same rate as the pure activated carbon and also reacted with CO<sub>2</sub> to produce SO<sub>2</sub> alone by the reverse reaction [13]. The non-oxidized sulfur C(S) can be a sulfide or disulfide, while for the oxidized sulfur C(SO) there are several possible derivatives (sulfone, sulfoxide, dioxathiolane, oxathietene oxide).

It is well known that the reactivity of carbons increases with ash, whose content can act as a catalyst [10, 12, 14, 15]. For the C + S<sub>x</sub> reaction the catalytic activity of salts increases by the same order as the metal ion increases in size, and it is able to form polysulfides [4].

We considered that a study of the catalysis by salts of the C + SO<sub>2</sub> reaction might identify the catalytic active species and provide an insight into the mechanism and the relationship among the catalytic species and the intermediates formed in the non-catalytic pathway. In this work, we have studied the effects of the nitrates, sulfides and polysulfides of sodium, potassium and calcium on the reduction of SO<sub>2</sub> with different carbons, characterizing the catalytic species.

## Experimental

All reagents were of analytical grade and were used without further purification. Sulfur dioxide, from White & Martins, was 99.9% pure. The polysulfides were obtained through the reaction of potassium sulfide with stoichiometric amounts of sulfur, at 500 °C, under vacuum, and were characterized by elemental analysis [16]. The graphite, 99.98%, was from Nacional de Grafite Ltda. The charcoal was prepared from coconut shells by pyrolysis at 300, 500 and 1000 °C for 2 hours at each temperature [17]. The activated carbon was from Carbomafra S.A., Santa Catarina, Brazil. It was steam activated at 700 °C, and then demineralized by HCl and HF treatment [18]. It had a particle size of 1.68 mm. All other solids were ground to an average particle diameter of 0.503 mm.

The addition of salt to all carbons was carried out by impregnation of the surface from an aqueous solution of appropriate concentration so as to obtain  $1.2 \times 10^{-3}$  mol metal/g of carbon, and the water was slowly eliminated under vacuum in a rotary evaporator at 60-70 °C. The sodium content of the samples impregnated with sodium salts was determined by flame photometry.

The carbon samples were characterized by proximate analysis. The specific surface area was determined by the static method, using CO<sub>2</sub> at room temperature as adsorbate and the Dubinin-Polanyi isotherm equation [19a] to fit the experimental data (Table 1).

**Table 1.** Characteristics of the carbon samples

Characteristics	Graphite	Charcoal	Demineralized activated carbon
Ash, %	-	1.40	0.31
Volatile, %	-	4.29	7.05
Fix carbon, %	99.98	94.31	92.64
Total sulfur, %	nil	0.70	nil
Surface area, m <sup>2</sup> .g <sup>-1</sup>	21.9	204	384
Mean diameter, mm	0.51	0.71	1.68

X-Ray diffraction analysis showed that graphite was highly crystalline and that charcoal and activated carbon were mainly amorphous.

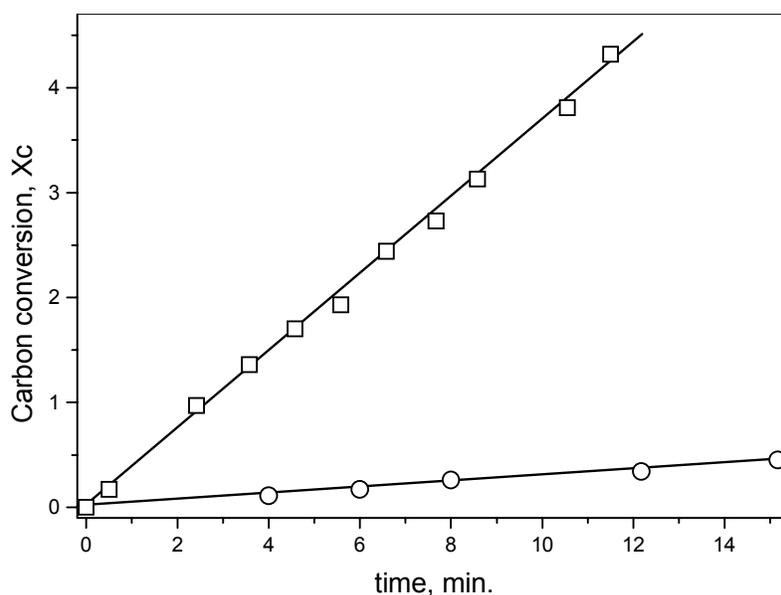
The XPS spectra were obtained using a VG Microtech ESCA 3000 spectrometer operating with a Mg(K $\alpha$ ) source. The base pressure of the system was in the low  $10^{-10}$  mbar range and the operating pressure was maintained below  $10^{-8}$  mbar during the measurements. The calibration was carried out with respect to the main C<sub>1s</sub> peak at 284.6 eV. The concentration of the elements was calculated using the system database. The deconvolution of the various peaks was done using the SDP software from XPS International [19b]. The samples for the XPS spectra were obtained after the kinetic run, allowing the residual carbon to cool under N<sub>2</sub> atmosphere, after shutting off the stream of SO<sub>2</sub>. The samples were extracted in a soxhlet with CS<sub>2</sub> to eliminate physically bound elemental sulfur. The solvent was eliminated by heating under vacuum. No difference in sulfur content was observed before or after the extraction. The sulfur content was determined in a LECO SC132 analyzer.

## Kinetics

The reduction of sulfur dioxide on the carbons was performed in a reaction system similar to that described in detail previously [12]. The samples were placed in a tubular quartz reactor fitted with a temperature controller and heated by an electric oven. The total gas flow and the partial pressure of  $\text{SO}_2$ , diluted in nitrogen, were controlled by two flowmeters, and the gas mixture was pre-heated in a gas mixer before entering the reactor. The reaction products were allowed to flow through two cooled traps to condense the sulfur, and the gaseous products were analyzed by glc using Porapak-Q and 5 Å molecular sieve columns. Pure standards were used to calibrate the response. The gas chromatograph was connected to a computer that contained a program to calculate the areas percentwise. Carbon conversions and product distributions were calculated from the glc analysis.

The reaction conditions such as temperature, gas flow, partial pressure of  $\text{SO}_2$  and particle size were defined through previous experiments without salts in order to eliminate limitations by mass transfer in the rate of reaction.

**Figure 1.** Carbon conversion versus time in the presence of  $\text{KNO}_3$ ,  $1.2 \times 10^{-3}$  mol of metal/g; samples 5.0 g;  $\square$ , charcoal at  $650^\circ\text{C}$ ; total flow  $30 \text{ mL}\cdot\text{min}^{-1}$ ;  $P_{\text{SO}_2}$  1.0 atm;  $\circ$ , graphite at  $900^\circ\text{C}$ ; total flow  $18 \text{ mL}\cdot\text{min}^{-1}$ ;  $P_{\text{SO}_2}$  0.5 atm.



All the experiments were carried out by placing the carbon sample in the reactor which was heated at  $900^\circ\text{C}$  for 3 h under a  $20 \text{ mL}\cdot\text{min}^{-1}$  flow of nitrogen. The temperature of the reactor was then adjusted to the experimental conditions, as well as the flow of  $\text{SO}_2$  and  $\text{N}_2$ . The gaseous products of the reaction were analyzed periodically by gas chromatography. The carbon conversion and the amount of elemental sulfur formed in the reaction were obtained by mass balance. The number of moles of sulfur (as S) was calculated from the difference between [moles of  $\text{SO}_2$  entering the reactor] and [moles of  $\text{SO}_2$  leaving the reactor plus the moles of sulfur-containing products]. Considering the stoichiometry of the reaction, sulfur was expressed as  $\text{S}_2$ . The reactivity of the carbon was calculated as the initial rate  $R_0$  from the slope of the plot of the carbon conversion  $x_C$  vs. time (eq 2)

$$R_o = \left( \frac{dx_c}{dt} \right)_{x_c \rightarrow 0} = \frac{\Delta X_c}{\Delta t} = k_2 C_C P_{SO_2} \quad (2)$$

[12, 13] where  $k_2$  is the second-order rate constant,  $C_C$  is the concentration of reactive carbon sites, and  $P_{SO_2}$  is the partial pressure of  $SO_2$ . Typical plots are shown in Figure 1.

## Results and Discussion

The reactions of  $SO_2$  with all carbons were carried out under steady-state conditions and at a temperature and total flow where the reaction was not diffusion controlled but chemically controlled. The reactor operated under differential conditions. The effect of salts was measured at a constant concentration of 1.2 mM of metal per gram of carbon.

### *Reaction of $SO_2$ with graphite and charcoal in the presence of salts*

The reactivity of graphite in the presence of sodium, potassium and calcium salts increased by a factor of 2-5 and the maximum effect was observed for  $K_2S$  (Table 2).

**Table 2.** Effect of salts on the reaction of graphite with  $SO_2$  at 900 °C <sup>a</sup>

Salt	$10^9 R_o$ , $\text{mol m}^{-2} \cdot \text{s}^{-1} \cdot \text{atm}^{-1}$	Molar fraction, % <sup>b</sup>	
		$CO_2$	$S_2$
None	3.16	68.5±1.5	31.2±2.1
$NaNO_3$	6.79	67.2±1.4	32.6±1.2
$Na_2S$	6.38	67.9±2.3	31.7±2.0
$KNO_3$	5.45	70.3±3.2	29.4±4.5
$K_2S$	17.73	66.5±2.8	30.8±3.2
$Ca(NO_3)_2$	8.46	66.5±2.3	33.3±2.5
$CaS$	11.49	66.3±2.0	33.6±2.6

<sup>a</sup> Samples: 6.0 g; salt:  $1.2 \times 10^{-3}$  mol of metal/g carbon; total flow:  $18 \text{ mL} \cdot \text{min}^{-1}$ ;  $P_{SO_2}$ : 0.5 atm.

<sup>b</sup> Average molar fraction during the stationary period without considering  $SO_2$  and  $N_2$ ;  $COS$ ,  $CO$  and  $CS_2$  less than 1% were not considered.

The average distribution of products, calculated during the steady state period, showed that for the non-catalyzed and catalyzed reaction, the  $CO_2:S_2$  ratio of the products was near two. The molar fraction of the products did not change in the presence of salts. The secondary products  $CO$ ,  $COS$  and  $CS_2$  were ca. 1% or less, suggesting that the catalysis did not involved the secondary reactions that were consecutive to the main reaction [12, 13].

The effect of the addition of salts on charcoal was lesser than it was for graphite. The rate increased only in the range of 30-60 % (Table 3). The same reactivity was observed with respect to the

carbon conversion for both nitrates and sulfides, increasing slightly in the order  $\text{Na}^+ < \text{K}^+ < \text{Ca}^{2+}$ . This absence of effect of the anion on the catalytic activity was also observed in the reaction of charcoal with sulfur [4]. Again, the presence of salts did not change the distribution of products. More than 90% of the molar fraction corresponded to the main products  $\text{CO}_2$  and  $\text{S}_x$ .

**Table 3.** Effect of salts on the reaction of charcoal with  $\text{SO}_2$  at  $650\text{ }^\circ\text{C}^{\text{a}}$

Salt	$10^8 R_0$ , $\text{mol m}^{-2}\cdot\text{s}^{-1}\cdot\text{atm}^{-1}$	Molar Fraction, % <sup>b</sup>			
		$\text{CO}_2$	$\text{S}_2$	$\text{COS}$	$\text{CO}$
None	4.25	62.6±0.5	30.5±0.4	3.4±0.2	2.9±0.5
$\text{NaNO}_3$	5.39	64.2±0.6	31.9±0.4	2.4±0.3	1.6±0.6
$\text{Na}_2\text{S}$	5.39	65.0±0.2	32.6±0.3	1.0±0.1	1.4±0.2
$\text{KNO}_3$	6.21	64.5±1.3	32.1±0.4	1.9±1.0	1.3±0.5
$\text{K}_2\text{S}$	5.88	63.3±0.2	31.5±0.2	2.6±0.2	2.6±0.3
$\text{Ca}(\text{NO}_3)_2$	6.86	62.4±1.0	31.7±0.2	2.0±0.2	4.0±1.2
$\text{CaS}$	6.53	62.8±1.3	31.7±0.4	2.1±0.5	3.5±1.5

<sup>a</sup> Samples: 5.0 g; salt:  $1.2 \times 10^{-3}$  mol of metal/g carbon; total flow:  $30\text{ mL}\cdot\text{min}^{-1}$ ;  $P_{\text{SO}_2}$ : 0.5 atm.

<sup>b</sup> Average molar fraction, without considering  $\text{SO}_2$  and  $\text{N}_2$ ;  $\text{CS}_2$  less than 1% was not considered.

From thermodynamic analysis [20] and experimental data [21], it was concluded that the formation of  $\text{CaS}$  from  $\text{CaO}$  and sulfur-containing gases would occur in the presence of the highly reductive carbon. The calcium sulfide formed might produce a polysulfide again, in contact with  $\text{SO}_2$  or the intermediates of the reduction. Therefore, the role of the catalyst would be to increase the transport of  $\text{S}_x$  from the intermediates, similar to other reactions of carbon, where alkaline and alkaline-earth salts are also effective catalysts. This mechanism will be analyzed in detail below.

**Figure 2.** XPS spectra in the  $\text{S}_{2p}$  region of activated carbon after the reaction with  $\text{SO}_2$  at  $630\text{ }^\circ\text{C}$  and extraction with  $\text{CS}_2$ . Sample: 2.0 g; salt  $1.2 \times 10^{-3}$  mol of metal; total flow  $95\text{ mL}\cdot\text{min}^{-1}$ ;  $P_{\text{SO}_2}$  0.2 atm; a) no salt added; b) in the presence of  $\text{NaNO}_3$ ; c) in the presence of  $\text{Na}_2\text{S}$ .

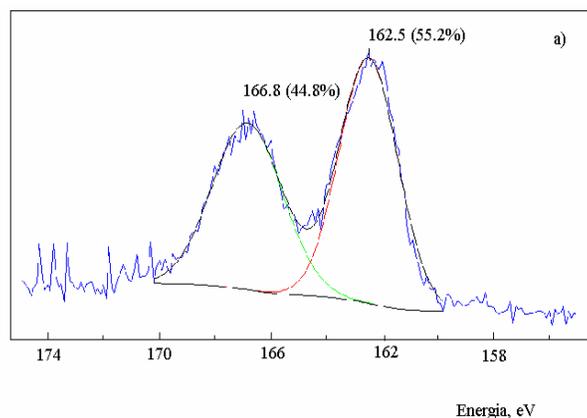
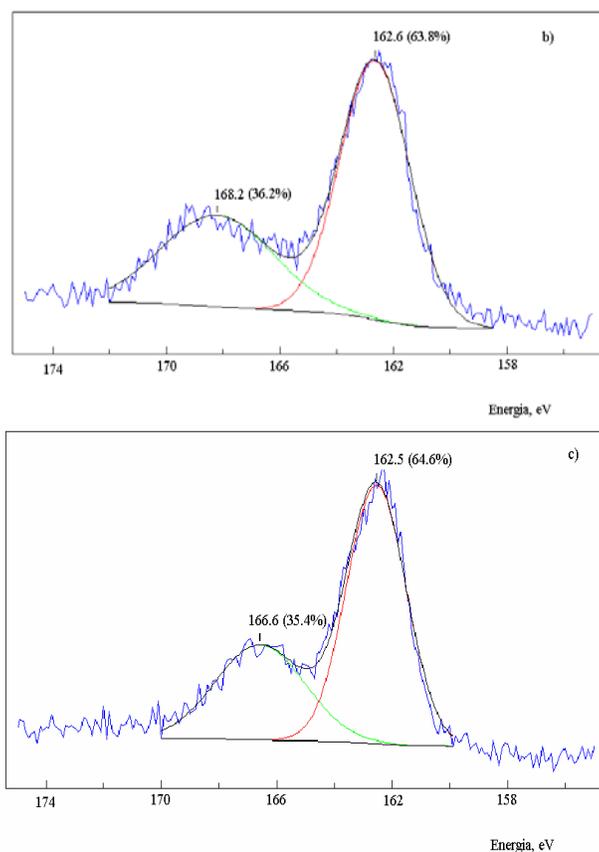


Figure 2. Cont.



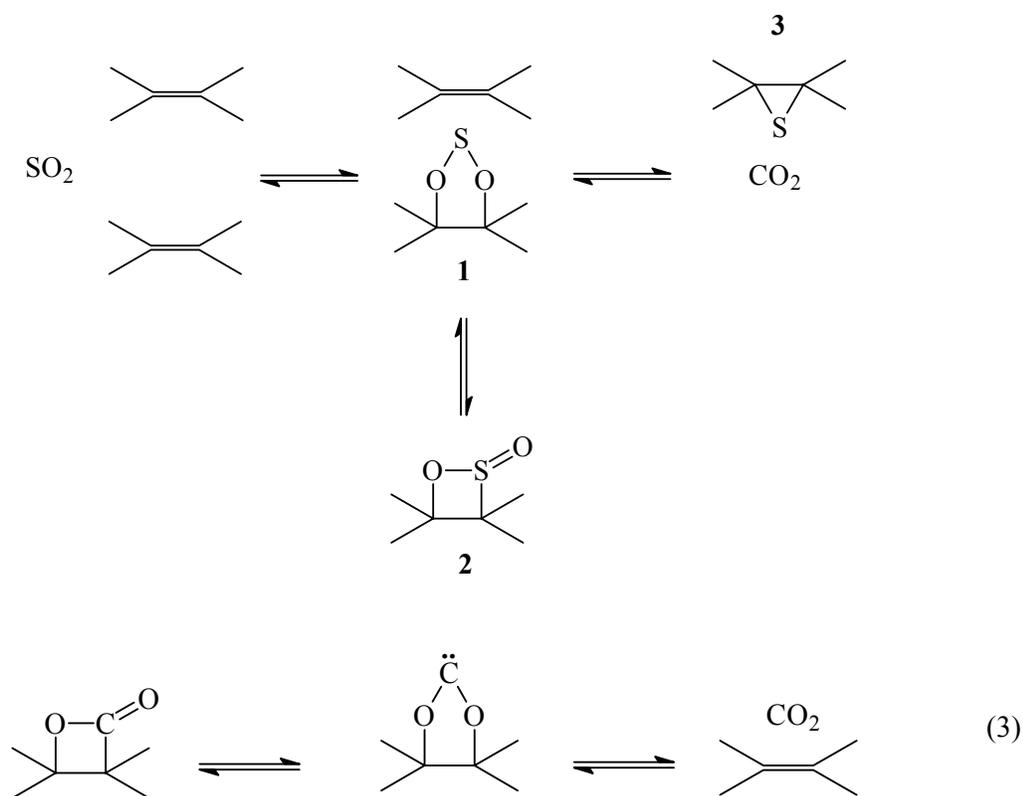
### Reaction of SO<sub>2</sub> with activated carbon

#### In the absence of salts.

The reduction of SO<sub>2</sub> on activated carbon in the absence of salt showed that the sulfur content of the carbon increased until a constant value when the reaction reached the steady-state condition. The XPS spectra in the S<sub>2p</sub> region of the residual carbon after the reaction with SO<sub>2</sub> (Fig. 2a) showed that the band at 162.5 eV assigned to a non-oxidized sulfur C(S) had 55.2% weight of the total sulfur and the band at 166.8 eV related to an oxidized sulfur bond C(SO) had 44.8% weight [13]. Therefore, the ratio C(S): C(SO) was 1.2.

A detailed interpretation of the mechanism of the primary reaction C + SO<sub>2</sub> is shown in Scheme 1. The reaction of SO<sub>2</sub> with a double bond would form a 1, 3, 2-dioxathiolane **1** and/or a 1,2-oxathietene 2-oxide, **2**. This is the reverse reaction of the thermal extrusion of SO<sub>2</sub> from **1** [22] or **2** [23] that has been proposed to occur by a concerted path to form a double bond. The reaction is similar to the thermal decomposition of β-lactones to produce CO<sub>2</sub> and an olefin through a carbene (eq 3) [24].

Scheme 1. Mechanism of the primary reaction

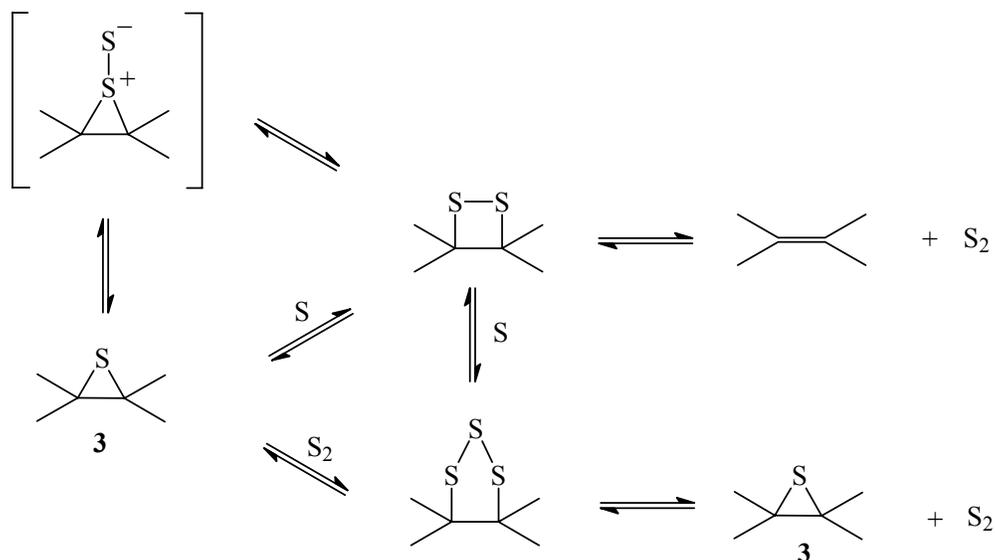


The oxidized intermediates **1** and/or **2** decompose to produce  $\text{CO}_2$  and atomic sulfur. According to this mechanism the non-oxidized sulfur intermediate is an episulfide **3** formed from the reaction of the atomic sulfur with the nearest double bond. It is known that atomic sulfur reacts with olefins producing episulfides and mercaptans [25, 26].

The formation of the episulfide **3** is probably concerted with the formation of  $\text{CO}_2$ . However, the mechanism of formation of  $\text{CO}_2$  is not known and in Scheme 1 the fragment of the residual carbon matrix was not included. The fact that the reaction is reversible [13] imposes the condition that the sulfur should be at the proper place to react with  $\text{CO}_2$  to re-form  $\text{SO}_2$ . In fact, the reversibility of the reaction imposes the condition that the atomic sulfur formed from the oxidized intermediate C(SO) should not go freely into the gas phase, but should remain as the intermediate on the carbon matrix in order to regenerate  $\text{SO}_2$  from  $\text{CO}_2$ . For this reason, monoatomic sulfur extrusion from the episulfide should not be considered [27].

Since sulfur does not accumulate [13] and episulfides inserted in a carbon matrix are very unreactive and thermally stable [4], this reaction, that should occur during the pre-steady-state period, must be followed by consecutive reactions of insertion of atomic sulfur to form intermediate(s) able to liberate free sulfur when the steady-state has been reached (Scheme 2).

Scheme 2. Mechanism of the sulfur transport



The insertion of a second sulfur atom in the episulfide produces a disulfide that can either decompose, to produce a diatomic sulfur  $S_2$  and the original double bond, or accept a third atom forming a trisulfide. Anthracene endodisulfide decomposes to form anthracene and singlet diatomic sulfur  $^1S_2$  [28]. Singlet diatomic sulfur is very reactive and can react with dienes to form episulfides and disulfides.

Formation of episulfides can be understood if  $^1S_2$  reacts with the olefin to form a thiosulfoxide intermediate followed by desulfurization. The reverse reaction would produce a disulfide from the episulfide through the thiosulfoxide intermediate (Scheme 2). However, transport of sulfur through the disulfide to release  $S_2$  would render the reaction irreversible and could only occur after the concentration of episulfide had reached the steady state. Formation of a trisulfide from the disulfide or the episulfide allows the extrusion of a more stable form of sulfur such as  $^1S_2$  [29-32] that would regenerate the sulfide, establishing an equilibrium sulfide-disulfide-trisulfide that would function as a capture-release cycle of sulfur. Trisulfides can result from the insertion of  $S_2$  into a previously formed disulfide, followed by the extrusion of sulfur [31].

Releasing sulfur from the trisulfide as  $S_2$  is reasonable because at the temperature of the reaction the main species is  $S_2$ . At the boiling point, gaseous sulfur consists mainly of species  $S_8$  and  $S_6$ , which dissociate into  $S_2$  when the temperature is raised. At 730 °C and 1 torr,  $S_2$  is almost 99% pure and dissociation to monoatomic sulfur requires a temperature above 1500 °C [33, 34].

For the dioxathiolane intermediate **1** to accumulate, according to Scheme 1, the rate determining step should be the decomposition of the episulfide **3**. The ratio non-oxidized sulfur C(S): oxidized sulfur C(SO) should be one. The XPS spectrum (Figure 2a) showed that the ratio is 1.2, indicating that the most stable intermediate is the episulfide and that the formation of  $S_2$  from the disulfide is not important (Scheme 2).

*In the presence of salts*

Since the mechanism of reduction of SO<sub>2</sub> on different carbons proved to be the same with respect to the stoichiometry of the reaction and the formation of secondary products [12], a more detailed study of the catalysis by salts on activated carbon can provide some important pieces of evidence on the mechanism of the catalytic pathway. It is considered that the addition of salts on a carbon surface forms species that act as catalytic active sites of the reaction [35, 36] and whose concentration depends on the amount of salt deposited.

Nitrates of sodium, potassium or calcium melt and decompose during the thermal pre-treatment [37] producing the corresponding oxide that could be reduced to metallic form in the presence of carbon, and, upon the reaction of the carbon with SO<sub>2</sub>, could generate sulfides which are thermodynamically more stable. At the temperature range used in this work for the reduction reaction, they remained as solids.

Activated carbon impregnated with sulfides and polysulfides of sodium and potassium increased the reactivity by about four times, as shown in Table 4. No difference between Na<sup>+</sup> and K<sup>+</sup> salts was observed, and mono and polysulfides showed the same reactivity, independent of the number of sulfur atoms in the polysulfide. Potassium polysulfides K<sub>2</sub>S<sub>n</sub> (n = 2-4) decompose at the experimental temperature, and the fact that the rate of carbon conversion R<sub>0</sub> was the same for the series of potassium polysulfides indicates that they decomposed to formed the same catalytically-active species.

**Table 4.** Effect of sulfides and polysulfides on the reaction of activated carbon with SO<sub>2</sub> at 700 °C <sup>a</sup>

Salt	None	NaNO <sub>3</sub>	Na <sub>2</sub> S	K <sub>2</sub> S <sub>n</sub> , n = 1-4
10 <sup>9</sup> R <sub>0</sub> , mol m <sup>-2</sup> .s <sup>-1</sup> .atm <sup>-1</sup>	1.08	3.80	4.34	4.07
10 <sup>3</sup> mol S/g carbon	2.2	6.2 <sup>b</sup>	5.4 <sup>b</sup>	

<sup>a</sup> Samples: 5.0 g; salt: 1.2x10<sup>-3</sup> mol of metal/g carbon; total flow: 60 ml.min<sup>-1</sup>; P<sub>SO<sub>2</sub></sub>: 0.5 atm.

<sup>b</sup> Corrected for 1.2x10<sup>-3</sup> mol of metal/g carbon

Sodium nitrate also decomposed during the pre-treatment at 900 °C, producing Na<sub>2</sub>O and NO<sub>x</sub> along with a small amount of CO<sub>2</sub> from the carbon oxidation. No nitrogen was observed in the XPS spectrum, indicating a total decomposition of the nitrate.

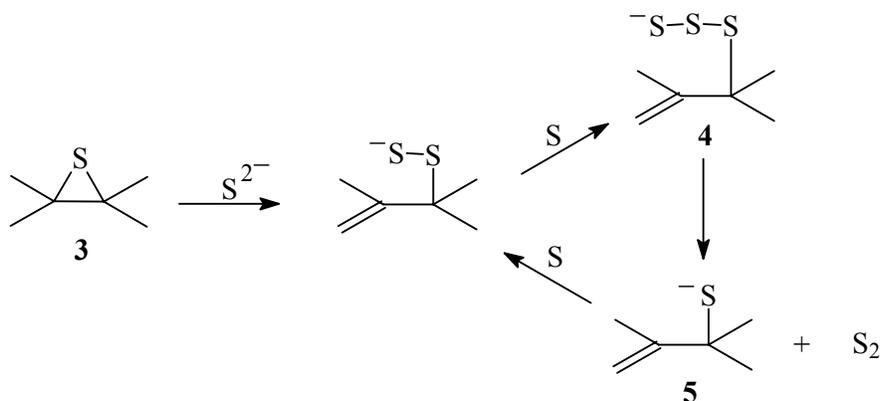
Upon reaction with SO<sub>2</sub>, the sulfur content of the activated carbon increased in the presence of NaNO<sub>3</sub> and Na<sub>2</sub>S to a constant value of 2.2 x 10<sup>-3</sup> mol S/g carbon, while the sodium content after the reaction with SO<sub>2</sub> did not change (Table 4). Considering the sulfur content due to the non-catalyzed reaction, the sulfur excess in the presence of salt with respect to sodium was in the ratio Na : S = 3.0 ± 0.3 (Table 4). A sodium polysulfide Na<sub>2</sub>S<sub>6</sub> with such a ratio would be very unlikely because hexasulfides are very unstable at 700 °C [38].

The residual carbon impregnated with sodium nitrate produced an XPS spectrum (Figure 2b) with a band of oxidized sulfur centered at 168.2 eV (36.2%) [39]. On the other hand, the band of non-oxidized sulfur presented the same energy as it did in the absence of salt, but increased to 63.8% with respect to the oxidized sulfur. The same result was observed for the residual carbon containing Na<sub>2</sub>S

(Figure 2c), also with an increase of the non-oxidized sulfur band to 64.6%. Therefore, there was an increase of the chemically bound non-oxidized sulfur in the presence of salt, and the ratio C(S):C(SO) increased to 1.8.

These results are consistent with the assumption that once the episulfide **3** is formed (Scheme 1), the sulfide anion from the salt produces a disulfide anion upon the reaction with **3** (Scheme 3). Sulfur is known to react with even trace amounts of  $S^{2-}$  to give polysulfide ions [40].

**Scheme 3.** Mechanism of the sulfur transport catalyzed by salts



Reaction of the disulfide anion with the sulfur arising from the decomposition of the dioxathiolane intermediate **1** would form the trisulfide anion **4** that decomposes and releases singlet diatomic sulfur  $^1S_2$ , thus transporting the sulfur and generating the powerful nucleophile thiolate **5** that is part of the catalytic cycle [41, 42]. A catalytic capture-release cycle of sulfur is then established which is similar to the non-catalyzed reaction. These results support the assumption that the transport of sulfur occurs through a trisulfide intermediate. The reaction of organometallic trisulfides in the presence of triphenylphosphine produced  $^1S_2$  through a trisulfide intermediate that extruded  $S_2$  to form a sulfide [30, 32].

Finally, from the XPS spectra and sulfur content, it can be concluded that in the absence of salt the main component of the non-oxidized sulfur intermediate is the episulfide, and therefore its decomposition must be rate determining of the sulfur transport. In the presence of salt on the other hand, since the trisulfide is the main component, the sulfur transport being determined by the decomposition of the trisulfide and consequently the product distribution in the presence of salt does not change.

## Conclusions

There were no important differences between the catalytic effects of nitrates and sulfides on the reduction of  $SO_2$  on carbons, and this similarity was also observed for polysulfides. In general, under differential reactor conditions, the distribution of products did not change in the presence of salts.

It is proposed that the reduction of  $SO_2$  on activated carbon in the absence of salt occurs through a primary mechanism where after the adsorption of  $SO_2$  on the carbon, a 1,3,2-dioxathiolane or 1,2-oxathietene 2-oxide would be formed that decomposes to produce  $CO_2$  and an episulfide **3**. Consecutive reactions of insertion of atomic sulfur form a trisulfide that extrudes  $S_2$ , regenerating the

episulfide and establishing a transport mechanism where a sulfide-disulfide-trisulfide equilibrium works as a capture-release cycle of sulfur. In the presence of salt, the results are consistent with the assumption that the episulfide **3** reacts with the corresponding sulfide to form a disulfide anion, which upon reaction with atomic sulfur, would form a trisulfide anion that decomposes releasing diatomic sulfur S<sub>2</sub>, transporting the sulfur and generating a thiolate that is part of the catalytic cycle.

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### References

1. Steiner, P.; Jüntgen, H.; Knoublauch, K. "Removal and Reduction of Sulfur Dioxides from Polluted Gas Streams". In: *Sulfur Removal and Recovery from Industrial Processes*; Pfeifer, J.B., Ed.; Advances in Chemistry Series 139, American Chemical Society: Washington, DC, **1975**; pp. 180-191.
2. Lepsoe, R. *Ind. Eng. Chem.* **1940**, *32*, 910.
3. Siller, C.W. *Ind. Eng. Chem.* **1948**, *40*, 1227.
4. Humeres, E.; Moreira, R.F.P.M.; Castro, S.C. *J. Braz. Chem. Soc.* **1994**, *5*, 69.
5. Chang, C.H. *Carbon* **1981**, *19*, 175.
6. Panagiotidis, T.; Richter, E.; Juntgen, H. *Carbon* **1988**, *26*, 89.
7. Blayden, H.E.; Patrick, J.W. *Carbon* **1971**, *5*, 533.
8. Panagiotidis, T. *Sci & Tech.* **1988**, *41*, 239.
9. Abramowitz, H.; Insinga, R.; Rao, Y.K. *Carbon* **1976**, *14*, 84.
10. Ratcliffe, C.T.; Pap, G. *Fuel* **1980**, *59*, 244.
11. Macák, J.; Pick, P. *Erdol Kohle Erdgas-P.* **1975**, *26*, 345.
12. Humeres, E.; Moreira, R.F.P.M.; Peruch, M.G.B. *Carbon* **2002**, *40*, 751.
13. Humeres, E.; Peruch, M.G.B.; Moreira, R.F.P.M.; Schreiner, W. *J. Phys. Org. Chem.* **2003**, *16*, 824.
14. Davini P. *Carbon* **1993**, *31*, 47.
15. Alvarez-Merino, M.A.; Carrasco-Marin, F.; Moreno-Castilla, C. *Appl. Catal. B- Environ.* **1997**, *13*, 229.
16. Brauer, G. *Handbook of Preparative Inorganic Chemistry, 2nd edition*; Academic Press: New York, **1965**.
17. Gavalas, GR. "Coal Pyrolysis". In: *Coal Science and Technology*; Anderson, L.L., Ed.; Elsevier: Amsterdam, 1982; Vol. 4.
18. Bimer, J. *Fuel* **1998**, *77*, 519.
19. a) Karr, C. Jr. *Analytical Methods for Coal and Coal Products*; Academic Press: New York, **1978**;  
b) Spectral Data Processor Version 3.2, XPS International: Mountain View, CA, USA.
20. Kellog, H.H. *Metal Trans.* **1970**, *2*, 2161.

21. Torres-Ordoñez, R.; Wall, T.F.; Longwell, J.P.; Sarofim, A.F. *Fuel* **1993**, *72*, 633.
22. Dittmer, D.C.; Levy, G.C.; Kuhlmann, G.E. *J. Am. Chem. Soc.* **1969**, *91*, 2097.
23. Durst, T.; Gimbarzevsky, B.P. *J. Chem. Soc. Chem. Comm.* **1975**, 724.
24. a) Noyce, D.S.; Banitt, E.H. *J. Org. Chem.* **1966**, *31*, 4043; b) Chapman, O.L.; Adams, W.R. *J. Am. Chem. Soc.* **1968**, *90*, 2333.
25. Verkokczy, B.; Sherwood, A.G.; Safarik, I.; Strausz, O.P. *Can. J. Chem.* **1983**, *61*, 2268.
26. Moore, C.G.; Porter, M. *Tetrahedron* **1959**, *6*, 10.
27. Loudon, J.D. "The Extrusion of Sulfur". In *Organic Sulfur Compounds*; Kharasch, N., Ed.; Pergamon: London, **1961**; Vol. 1, Chapter 26.
28. Ando, W.; Sonobe, H.; Akasaka, T. *Tetrahedron Lett.* **1987**, *28*, 6653.
29. Orahovatz, A.; Levinson, M.I.; Carroll, P.J.; Lakshmikantham, M.V.; Cava, M.P. *J. Org. Chem.* **1985**, *50*, 1550.
30. Steliou, K.; Gareau, Y.; Harpp, D.N. *J. Am. Chem. Soc.* **1984**, *106*, 799.
31. Steliou, K.; Salama, P.; Brodeur, D.; Gareau, Y. *J. Am. Chem. Soc.* **1987**, *109*, 926.
32. Steliou, K. *Acc. Chem. Res.* **1991**, *24*, 341.
33. Meyer, B. *Chem. Rev.* **1976**, *76*, 367, and references cited therein.
34. Stull, D.R. *Ind. Eng. Chem.* **1949**, *41*, 1968.
35. Wood, B.J.; Sancier, K.M. *Catal. Re-Sci. Eng.* **1984**, *26*, 233.
36. Wen, W.Y. *Catal. Rev-Sci. Eng.* **1980**, *22*, 1.
37. *CRC Handbook of Chemistry and Physics*, 80th Ed; CRC Press: Boca Raton, **1999-2000**.
38. Chenard, B.L.; Harlow, R.L.; Johnson, A.L.; Vladerchick, S.A. *J. Am. Chem. Soc.* **1985**, *107*, 3871.
39. a) Hittle, L.; Sharkey, A.G.; Honalla, M.; Proctor, A.; Hercules, D.M.; Morsi, B.I. *Fuel* **1993**, *72*, 771; b) Lindberg, B.J.; Hamrin, K.; Johansson, G.; Gelius, U.; Fahlman, A.; Nodling, C.; Siegbahn, K. *Phys. Scripta* **1970**, *1*, 286.
40. Foss, O. "Ionic Scission of the Sulfur-Sulfur Bond". In *Organic Sulfur Compounds*. Kharasch, N., Ed.; Pergamon: London, **1961**; Vol. 1, Chapter 9.
41. Eliel, E.L.; Rao, V.S.; Smith, S.; Hutchins, R.O. *J. Org. Chem.* **1975**, *40*, 524.
42. Barrett, G.C. "Aliphatic Organo-sulphur Compounds, Compounds with Exocyclic Sulphur Functional Groups, and their Selenium and Tellurium Analogues". In *Organic Compounds of Sulfur, Selenium, and Tellurium*; Hogg, D.R., Senior Reporter; The Chemical Society: London, **1977**; Vol. 4, Chapter 1.