

Reduction of Sulfur Dioxide on Carbons Catalyzed by Salts

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Abstract. The reduction of SO₂ 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 SO₂. In the presence of NaNO₃ or Na₂S, 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 SO₂ on the carbon, a 1,3,2-dioxathiolane or 1,2-oxathietene 2-oxide are formed and that decompose to produce CO₂ 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 S₂ 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 S₂, 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.

Introduction

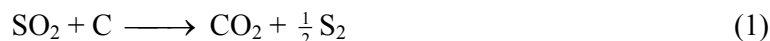
The reduction of SO₂ on carbons has been intensively studied because sulfur and nitrogen oxides are considered among the worst atmospheric pollutants and precursors of acid rain [1]. The elemental sulfur produced in the reaction is a more desirable product because it is easy to handle and store.

Mechanistic studies of the reduction of SO₂ 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 + SO₂ 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, H₂S, CS₂ or SO₂, 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 + SO₂ 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 SO₂ [12, 13].

Analysis of product distribution showed that the reduction of SO₂ proceeds through the stoichiometric reaction (1) because it is the only reaction of the C-O-S system where the ratio CO₂ : S₂ = 2 : 1.



The reduction of SO₂ 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 SO₂ at the same rate as the pure activated carbon and also reacted with CO₂ to produce SO₂ 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_x 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 + SO₂ 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 SO₂ 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 1.2×10^{-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 CO₂ 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 ² .g ⁻¹	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.

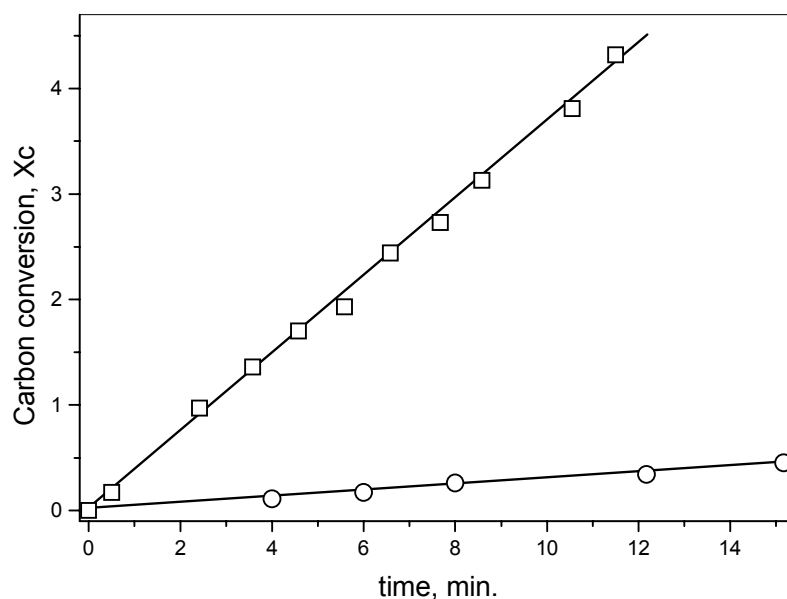
The XPS spectra were obtained using a VG Microtech ESCA 3000 spectrometer operating with a Mg(K α) source. The base pressure of the system was in the low 10^{-10} mbar range and the operating pressure was maintained below 10^{-8} mbar during the measurements. The calibration was carried out with respect to the main C_{1s} 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 N₂ atmosphere, after shutting off the stream of SO₂. The samples were extracted in a soxhlet with CS₂ 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 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 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 KNO_3 , 1.2×10^{-3} mol of metal/g; samples 5.0 g; \square , charcoal at 650°C ; total flow $30 \text{ mL}\cdot\text{min}^{-1}$; P_{SO_2} 1.0 atm; \circ , graphite at 900°C ; total flow $18 \text{ mL}\cdot\text{min}^{-1}$; P_{SO_2} 0.5 atm.



All the experiments were carried out by placing the carbon sample in the reactor which was heated at 900°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 SO_2 and 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 SO_2 entering the reactor] and [moles of SO_2 leaving the reactor plus the moles of sulfur-containing products]. Considering the stoichiometry of the reaction, sulfur was expressed as 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 ^a

Salt	$10^9 R_o$, $\text{mol m}^{-2} \cdot \text{s}^{-1} \cdot \text{atm}^{-1}$	Molar fraction, % ^b	
		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

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

^b 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 CO_2 and S_x .

Table 3. Effect of salts on the reaction of charcoal with 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, % ^b			
		CO_2	S_2	COS	CO
None	4.25	62.6±0.5	30.5±0.4	3.4±0.2	2.9±0.5
NaNO_3	5.39	64.2±0.6	31.9±0.4	2.4±0.3	1.6±0.6
Na_2S	5.39	65.0±0.2	32.6±0.3	1.0±0.1	1.4±0.2
KNO_3	6.21	64.5±1.3	32.1±0.4	1.9±1.0	1.3±0.5
K_2S	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
CaS	6.53	62.8±1.3	31.7±0.4	2.1±0.5	3.5±1.5

^a Samples: 5.0 g; salt: 1.2×10^{-3} mol of metal/g carbon; total flow: $30\text{ mL}\cdot\text{min}^{-1}$; P_{SO_2} : 0.5 atm.

^b Average molar fraction, without considering SO_2 and N_2 ; CS_2 less than 1% was not considered.

From thermodynamic analysis [20] and experimental data [21], it was concluded that the formation of CaS from 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 SO_2 or the intermediates of the reduction. Therefore, the role of the catalyst would be to increase the transport of 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 S_{2p} region of activated carbon after the reaction with SO_2 at $630\text{ }^\circ\text{C}$ and extraction with CS_2 . Sample: 2.0 g; salt 1.2×10^{-3} mol of metal; total flow $95\text{ mL}\cdot\text{min}^{-1}$; P_{SO_2} 0.2 atm; a) no salt added; b) in the presence of NaNO_3 ; c) in the presence of Na_2S .

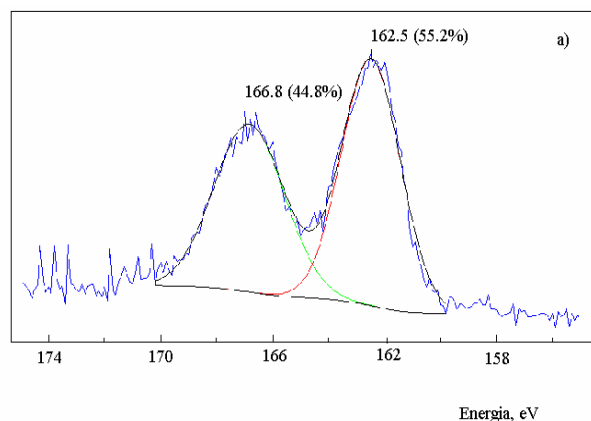
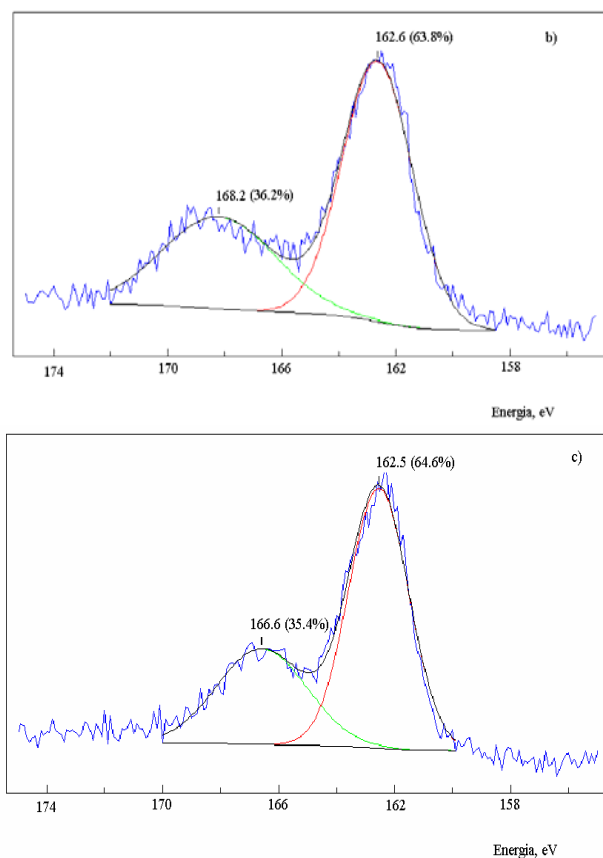


Figure 2. Cont.



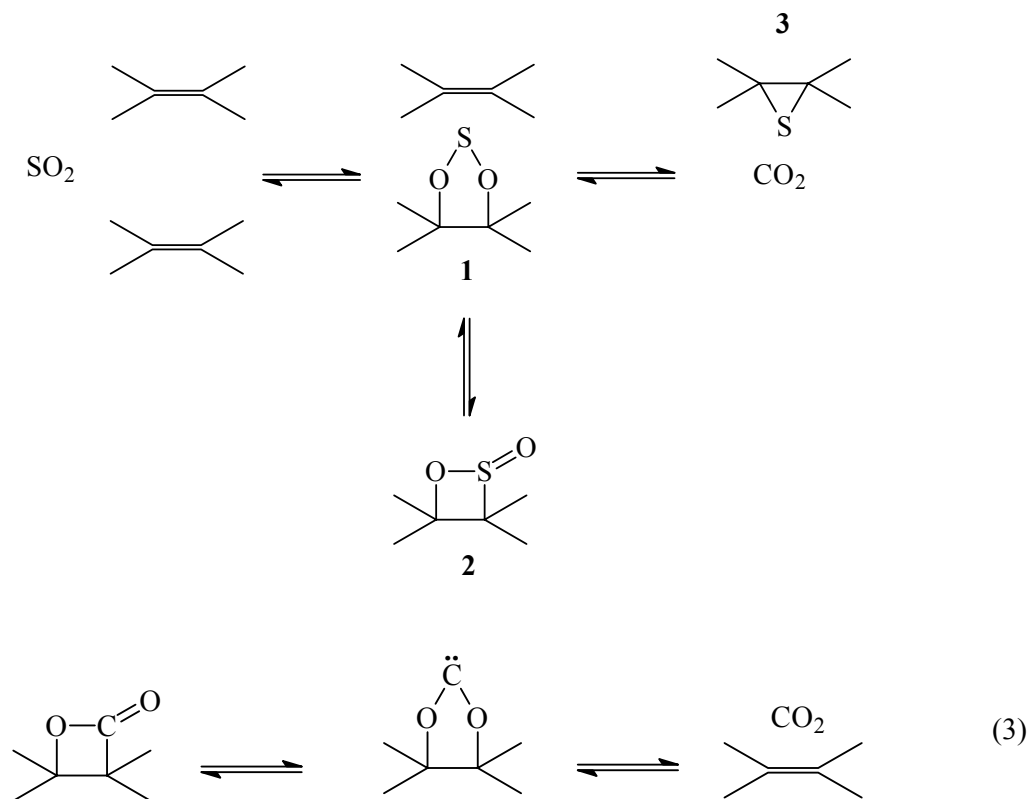
Reaction of SO₂ with activated carbon

In the absence of salts.

The reduction of SO₂ 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_{2p} region of the residual carbon after the reaction with SO₂ (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 + SO₂ is shown in Scheme 1. The reaction of SO₂ 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 SO₂ 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 CO₂ and an olefin through a carbene (eq 3) [24].

Scheme 1. Mechanism of the primary reaction

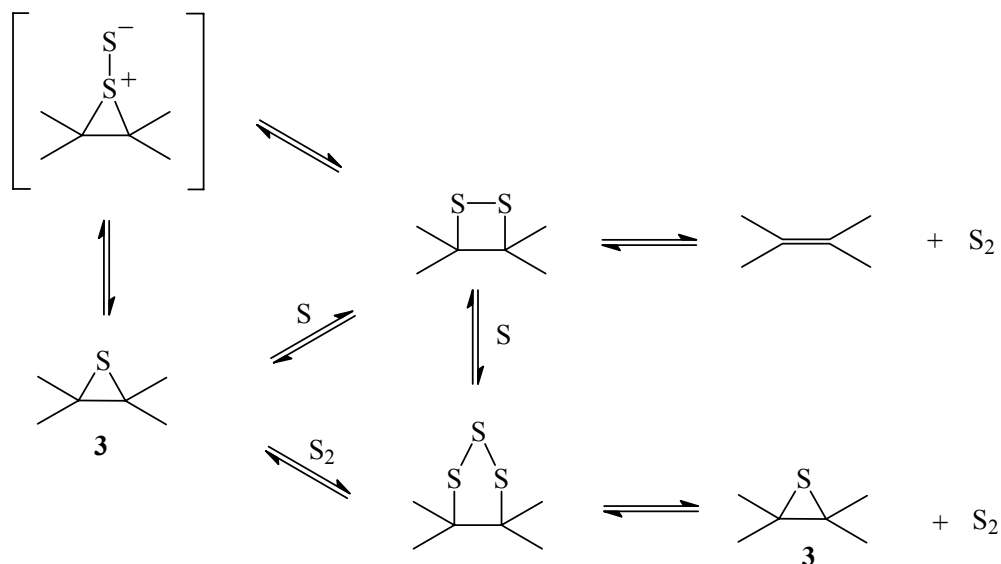


The oxidized intermediates **1** and/or **2** decompose to produce CO_2 and atomic sulfur. According to this mechanism the non-oxidized sulfur intermediate is an episulfide **3** formed from the reaction of the atomic sulfur with the nearest double bond. It is known that atomic sulfur reacts with olefins producing episulfides and mercaptans [25, 26].

The formation of the episulfide **3** is probably concerted with the formation of CO_2 . However, the mechanism of formation of 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 CO_2 to re-form SO_2 . In fact, the reversibility of the reaction imposes the condition that the atomic sulfur formed from the oxidized intermediate $\text{C}(\text{SO})$ should not go freely into the gas phase, but should remain as the intermediate on the carbon matrix in order to regenerate SO_2 from 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 S₂ and the original double bond, or accept a third atom forming a trisulfide. Anthracene endodisulfide decomposes to form anthracene and singlet diatomic sulfur ¹S₂ [28]. Singlet diatomic sulfur is very reactive and can react with dienes to form episulfides and disulfides.

Formation of episulfides can be understood if ¹S₂ 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 S₂ 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 ¹S₂ [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 S₂ into a previously formed disulfide, followed by the extrusion of sulfur [31].

Releasing sulfur from the trisulfide as S₂ is reasonable because at the temperature of the reaction the main species is S₂. At the boiling point, gaseous sulfur consists mainly of species S₈ and S₆, which dissociate into S₂ when the temperature is raised. At 730 °C and 1 torr, S₂ 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 S₂ from the disulfide is not important (Scheme 2).

In the presence of salts

Since the mechanism of reduction of SO₂ 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 SO₂, 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⁺ and K⁺ salts was observed, and mono and polysulfides showed the same reactivity, independent of the number of sulfur atoms in the polysulfide. Potassium polysulfides K₂S_n (n = 2-4) decompose at the experimental temperature, and the fact that the rate of carbon conversion R₀ 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 SO₂ at 700 °C ^a

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

^a Samples: 5.0 g; salt: 1.2x10⁻³ mol of metal/g carbon; total flow: 60 ml.min⁻¹; P_{SO₂}: 0.5 atm.

^b Corrected for 1.2x10⁻³ mol of metal/g carbon

Sodium nitrate also decomposed during the pre-treatment at 900 °C, producing Na₂O and NO_x along with a small amount of CO₂ from the carbon oxidation. No nitrogen was observed in the XPS spectrum, indicating a total decomposition of the nitrate.

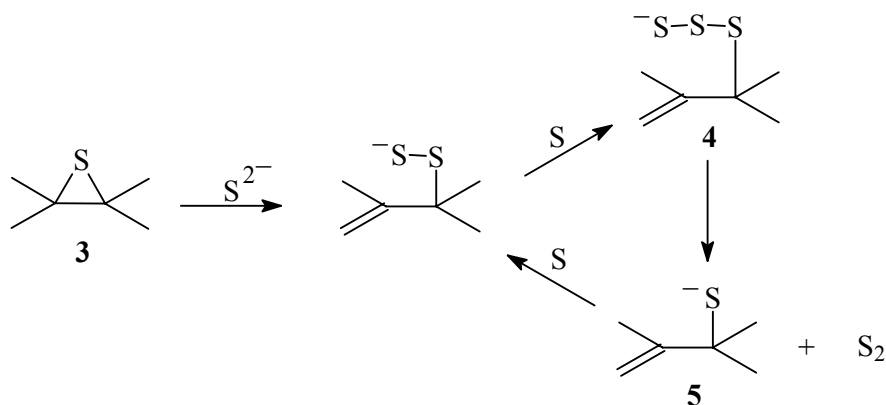
Upon reaction with SO₂, the sulfur content of the activated carbon increased in the presence of NaNO₃ and Na₂S to a constant value of 2.2 x 10⁻³ mol S/g carbon, while the sodium content after the reaction with SO₂ did not change (Table 4). Considering the sulfur content due to the non-catalyzed reaction, 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 Na₂S₆ 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 Na₂S

(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 S₂, 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. Verkozcy, 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.