

Surface-mediated autoxidation of aqueous SO₂ in ceramic powder suspensions

Rachna Bhargava, Ashu Rani & K S Gupta*

Atmospheric Chemistry Laboratory, Department of Chemistry, University of Rajasthan, Jaipur 302 004, India

Received 18 November 1991; revised and accepted 10 March 1992

In acetate buffered ceramic suspensions, if the ceramic concentration is not too high, the kinetics of autoxidation conforms to the rate law

$$R_{\text{obs}} = R_{\text{un}} + k_s [\text{H}^+]^{-1} [\text{Ceramic}] [\text{S(IV)}]^2$$

where R_{un} is the rate of uncatalyzed reaction and k_s is the rate constant for the surface catalyzed path. The rate of autoxidation is unaffected by oxygen partial pressure. Interestingly, the rate versus [ceramic] profile passes through a maximum indicating that the autoxidation mechanism involves the adsorption of both sulphur(IV) and dioxygen on particle surface.

So far most of the work on the studies of autoxidation of sulphur(IV) is limited to homogeneous metal ion catalysis¹, aerosol studies², catalysis by metal oxides³⁻⁴, e.g., CoO³, Ni₂O₃⁴, CdO⁵, CuO⁶ and some other solid materials like fly ash^{7,8} dust⁹, glass¹⁰, carbonaceous particles¹¹ and minerals and rocks¹². These studies intend to delineate relative importance of these materials in atmospheric acid generation. These studies are also useful in searching new desulphurization catalysts.

Recently, the kinetics of S(IV)-autoxidation in silica⁶ suspensions have been investigated in our laboratory. Our desire to carry out a comparative rate analysis made us to look into the chemistry of the aqueous suspension of ceramic powder. The other motivating factor was to assess the efficacy of this material in promoting conversion of S(IV) into S(VI) and its relevance to atmospheric processes because ceramic, which is largely a man-made material, is being released to the atmosphere as fine dust by its industrial users.

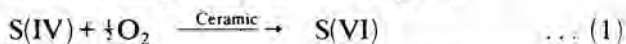
Materials and Methods

Ceramic powder was prepared by grinding thoroughly the small pieces of broken tea cups (Bharat make), washed with acid dichromate, water, EDTA-NaOH mixture and doubly distilled water, and using sieves the powder was separated into four fractions having different particle sizes, *r*, viz. $r \leq 53$; $53 \leq r \leq 75$; $75 \leq r \leq 120$; $120 \leq r \leq 180$ μm . pH was maintained with acetate buffer. Kinetics were followed by estimating S(IV) iodometrically^{3,4,9,10}. Reaction mixtures were continuously

stirred at 1500 ± 100 rpm, as at this stirring speed the reaction was shown, by varying stirring speed between 200-1800 rpm, not to be oxygen mass transfer-controlled. The treatment of kinetic results was based on the initial rates. The reproducibility of duplicate rate measurements was better than $\pm 10\%$. All calculations were done on APPLE IIe computer using curve fitter and scientific plotter programmes of Interactive Microwave Inc. In the presentation of rate data later the statistical parameters have been abbreviated as follows: CC = correlation coefficient, CD = coefficient of determination and SEE = standard error of estimate.

Product analysis

Sulphate was estimated gravimetrically by precipitating it as BaSO₄ using standard procedure. Stoichiometry was found as in Eq. (1).



There was no evidence for the formation of dithionate.

Results

Chemical analysis of ceramic powder (done in CGCRI, Calcutta) revealed the following percentage of substances: SiO₂-69.42; Al₂O₃-20.64; Fe₂O₃-0.81; TiO₂-0.69; CaO-2.75; MgO-0.40; K₂O-3.69, CoO-0.02, MnO-0.01, ZnO-0.15 and with Cr₂O₃, CuO and NiO in traces.

In line with practically insoluble nature of ceramic powder, its recovery from final product so-

lution, under varying pH was more than 99%, the rest being lost. Uncatalysed and leachate reactions, which are trace metal ion catalysed¹³, are completely seized by an EDTA concentration of $5 \times 10^{-6} \text{ mol dm}^{-3}$, whereas the reaction in suspension, in the presence of the same amount of EDTA, is only slowed down slightly but not seized.

The kinetics were studied in suspension and in corresponding leachate solution in otherwise identical conditions. In a suspension ($[\text{ceramic}] = 1.0 \text{ g dm}^{-3}$, $[\text{S(IV)}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $pH = 5.06$ and $t = 30^\circ$) initial rate of autoxidation, R_{obs} , was determined to be $8.0 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$. Now the leachate of the same amount of ceramic was prepared and keeping all other conditions same as in previous experiment, the kinetic measurements yielded a R_{obs} value of $2.0 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$ which is the same as the uncatalysed rate ($2.5 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$) determined separately. Had the catalysis in the suspension been wholly due to trace metal ion catalysis, the rates in suspension and in leachate would have been of the same magnitude. However this is not so. This leads us to conclude that in suspension the catalysis is not due to trace metal ions and is most likely surface-mediated.

In a few kinetic runs, the reaction was studied in nitrogen atmosphere excluding O_2 completely. No perceptible reaction occurred over a period of one hour.

At a fixed pH , on increasing buffer concentration the rate of autoxidation decreased. A plot of $[R_{\text{obs}}]^{-1}$ versus $[\text{CH}_3\text{COONa}]$ is linear passing through the origin. In all further experiments overall $[\text{CH}_3\text{COONa}]$ was maintained at 0.14 mol dm^{-3} and wherever needed $[\text{CH}_3\text{COOH}]$ was changed for obtaining desired pH . Since the particle size, affects the rate of reaction in all experiments, unless otherwise stated, ceramic powder fraction, $r \leq 53 \mu\text{m}$, was used.

Kinetic results

The effect of $[\text{ceramic}]$ on R_{obs} is shown in Fig. 1. On increasing $[\text{ceramic}]$ upto 4 g dm^{-3} the rate increases and thereafter a further increase in $[\text{ceramic}]$ leads to a continuous decrease in the rate of reaction. However, the results of $[\text{ceramic}]$ variation between 0.5 to 4.0 g dm^{-3} displayed a linear relationship between R_{obs} and $[\text{ceramic}]$. The plots of R_{obs} versus $[\text{ceramic}]$ were found to be linear with a non-zero intercept (Fig. 2). The intercept is ascribed to the uncatalysed reaction and thus the results are in agreement with the rate law (2).

$$R_{\text{obs}} = R_{\text{un}} + k_2[\text{ceramic}] \quad \dots (2)$$

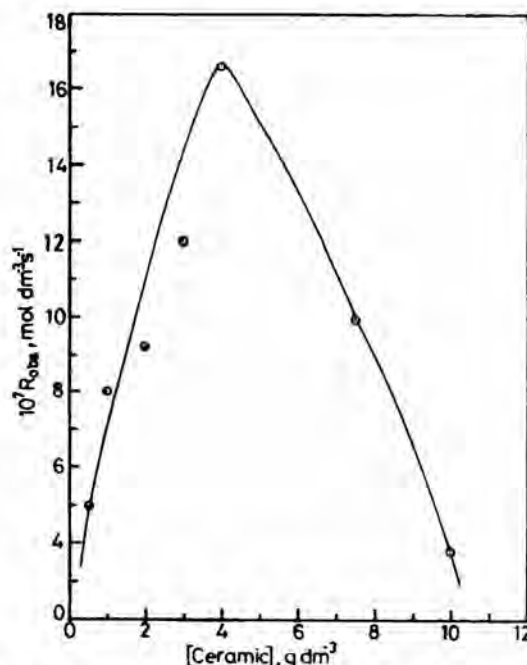


Fig. 1 – The variation of R_{obs} with $[\text{ceramic}]$ over its full concentration range at $pH = 5.06$, $[\text{S(IV)}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$ and 30°C

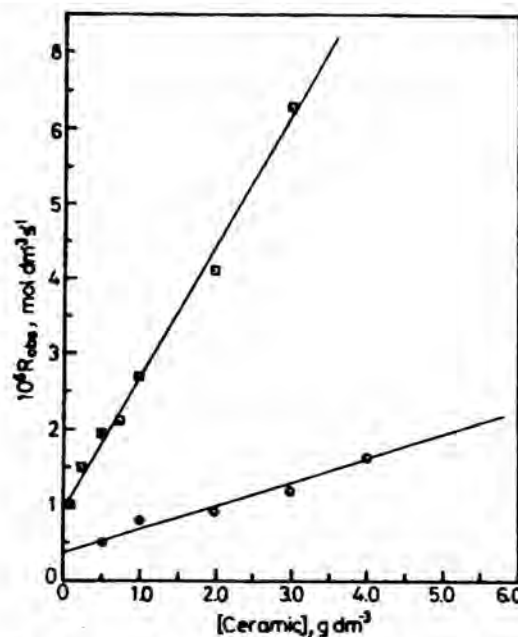


Fig. 2 – The plot of R_{obs} with $[\text{ceramic}]$ in the autoxidation of sulphur(IV) at 5.06 pH and 30°C . $\odot$, $[\text{S(IV)}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$; $\square$, $[\text{S(IV)}] = 4 \times 10^{-3} \text{ mol dm}^{-3}$.

where R_{un} represents the rate of uncatalysed path and k_2 is the rate constant of the catalysed path.

The results of S(IV) variation at fixed $[\text{ceramic}]$ and pH showed an order of 1.6 ± 0.05 in S(IV) . The kinetic data pertaining to both $[\text{S(IV)}]$ and

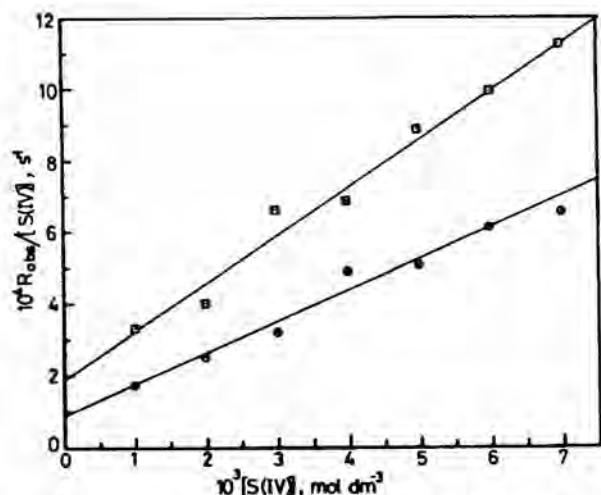


Fig. 3—The plot of $R_{\text{obs}}/[S(\text{IV})]$ versus $[S(\text{IV})]$ at $\text{pH}=5.06$ and at 30° . $\odot$, $[\text{ceramic}]=0.5 \text{ g dm}^{-3}$, $\square$, $[\text{ceramic}]=1.0 \text{ g dm}^{-3}$

$[\text{ceramic}]$ variations fitted rate law (3) as shown in Fig. 3.

$$R_{\text{obs}} = k_1[S(\text{IV})] + k_4[\text{ceramic}][S(\text{IV})]^2 \quad \dots (3)$$

The values of k_1 and k_4 are given in Table 1. A comparison of k_4 values shows these to vary in the range $0.08\text{--}0.16 \text{ dm}^6 \text{ mol}^{-1} \text{ g}^{-1} \text{ s}^{-1}$. This variation in k_4 is probably due to the inhomogeneity of the powder sample itself. Sulphur(IV) autoxidation, even in homogeneous studies, shows invariably a large scatter leading to relatively higher uncertainty¹⁴.

Like k_4 , the values of k_1 (Table 1) also display variation in their magnitude. This is probably due to the fact that the contribution of uncatalyzed rate, except at low $[\text{ceramic}]$, is not sizeable and one does not expect to extract k_1 values with a high degree of precision. However, it is gratifying to note that the average value of k_1 (Table 1) is in good agreement with the value of $2.0 \times 10^{-4} \text{ s}^{-1}$ determined independently using same reagent samples and reaction conditions. The dependence of k_1 on pH is of interest to us. In general the rate of uncatalyzed S(IV) autoxidation based on the reactive SO_3^{2-} species is described by rate law (4)¹⁵.

$$R_{\text{un}} = k_{\text{SO}_3}[\text{SO}_3^{2-}] \quad \dots (4)$$

In the pH range (4.65–5.91), S(IV) would be present largely as HSO_3^- with some SO_3^{2-} . In terms of S(IV), which represents the analytical concentration of all sulphur(IV) species, Eq. (4) takes the form (5).

$$R_{\text{un}} = \frac{k_0[S(\text{IV})]}{[H^+]} \quad \dots (5)$$

Rate law (5)^{15,16} has generally been found to be valid for uncatalysed reaction. On comparing Eqs (3) and (5)

$$k_1 = \frac{k_0}{[H^+]} \quad \dots (6)$$

Using the k_1 value of 1.8×10^{-4} at $\text{pH}=5.06$ and 30° , we obtained $k_0 = 1.57 \times 10^{-9} \text{ s}^{-1}$ at 30° . This value of k_0 has been used in estimating R_{un} values at different pH and $[S(\text{IV})]$ in terms of rate law (5).

The $[H^+]$ dependence of the reaction was investigated by varying pH in the range 4.65 to 5.91. The rate increases with increase in pH . However, for an analysis of $[H^+]$ dependence of the ceramic catalysed reaction, the values of R_{un} (Rate law 3) at different pH are required. These values were obtained at $[S(\text{IV})] = 4 \times 10^{-3} \text{ mol dm}^{-3}$ using Eqs (5) and (6).

Rate law (3) can be written as (7).

$$R_{\text{obs}} - R_{\text{un}} = R_{\text{cat}} = k_4[\text{ceramic}][S(\text{IV})]^2 \quad \dots (7)$$

The values of R_{cat} are given in Table 2 and these values were used for obtaining k_4 at different pH . The plot of k_4 versus $[H^+]^{-1}$ was found to be linear with negligible intercept showing that

$$k_4 = \frac{k_5}{[H^+]} \quad \dots (8)$$

Rate law (8), therefore, can be written as

$$R_{\text{obs}} = R_{\text{un}} + \frac{k_5}{[H^+]}[\text{ceramic}][S(\text{IV})]^2 \quad \dots (9)$$

At 30° , k_5 was determined to be $9.28 \times 10^{-7} \text{ dm}^6 \text{ mol}^{-1} \text{ g}^{-1} \text{ s}^{-1}$.

Table 1—Values of k_1 and k_4 obtained from $[S(\text{IV})]$ and $[\text{Ceramic}]$ variation at $\text{pH}=5.06$, $\text{temp.}=30^\circ$

$10^4 k_1$ (s^{-1})	k_4 ($\text{dm}^6 \text{ mol}^{-1} \text{ g}^{-1} \text{ s}^{-1}$)	Method
1.92	0.08	[Ceramic] variation
2.46	0.10	[Ceramic] variation
0.94	0.16	[S(IV)] variation
1.88	0.13	[S(IV)] variation
Av = 1.8 ± 0.43 Av = 0.117 ± 0.027		

Table 2 – The values of k_4 at various pH values and at 30°

pH	$10^6 R_{\text{obs}}^*$ (mol dm ⁻³ s ⁻¹)	$10^6 R_{\text{un}}^{**}$ (mol dm ⁻³ s ⁻¹)	$10^6 R_{\text{cat}}$ (mol dm ⁻³ s ⁻¹)	k_4 (dm ⁶ mol ⁻¹ g ⁻¹ s ⁻¹)
5.91	17.12	5.12	12.0	0.75
5.60	7.78	2.50	5.28	0.33
5.38	4.55	1.51	3.04	0.19
5.28	3.27	1.19	2.08	0.13
5.18	2.71	0.95	1.76	0.11
5.06	2.16	0.72	1.44	0.09
4.86	1.57	0.45	1.12	0.07
4.65	0.92	0.28	0.64	0.04

* Average of two independent measurements at [Ceramic] = 1.0 g dm⁻³, [S(IV)] = 4×10^{-3} mol dm⁻³.

** Calculated from the rate law (5) using $k_0 = 1.5 \times 10^{-9}$ s⁻¹ at 30°.

The catalytic activity of the ceramic powder decreases with increase in particle size, r . The log-log plots of R_{obs} and r were linear with a slope of -1 indicating an inverse first order in particle size.

The rate of reaction was unaffected on varying O_2 partial pressure by passing $O_2:N_2$ mixtures in varying proportions showing a zero order in O_2 .

A value of 110 kJ mol⁻¹ for overall energy of activation was determined by studying the reaction in the temperature range 30–40°C.

Reaction profiles in unbuffered suspensions

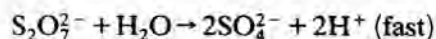
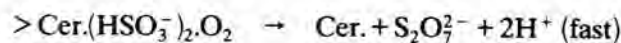
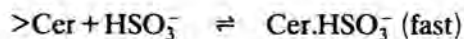
The reaction profiles for unbuffered suspensions, in which the initial pH was adjusted by addition of dilute HClO₄, showed the occurrence of the reaction in two stages; the first of which is rapid and the second a slower one. Similar rate profiles have been obtained in carbon¹¹, CoO³, and CaSO₃¹⁷ suspensions.

Discussion

There are several lines of arguments which suggest the mechanism of autoxidation to involve the adsorption of dioxygen and S(IV) on the particle surface as has been assumed by several previous workers^{3,4,10,18,19}. Surface area decreases with increase in particle size. The fact that the rate decreases with increase in particle size points to the surface nature of the autoxidation. Autoxidation occurs only in the presence of oxygen. The adsorption of both oxygen and S(IV) on particle surface is also indicated by the rate profile which passes through a maximum; the observance of which can be explained if the operation of a Langmuir-Hinshelwood type of mechanism²⁰ is assumed. This, in effect, requires that both S(IV)

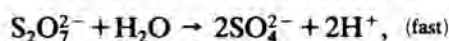
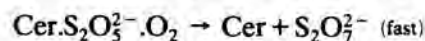
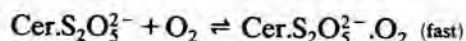
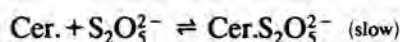
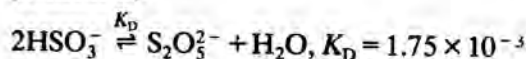
and O_2 must be adsorbed on the adjacent sites on the ceramic surface to facilitate the oxidation. When [catalyst] is very high, a large number of active sites are available for adsorption of S(IV) and O_2 on remote sites. The inhibitory effect of buffer also points to the catalysis being surface mediated. The adsorption of one or more of the buffer constituents on the particle surface results in the reduced availability of the active sites for the adsorption of O_2 and S(IV).

Although, on increasing pH the rate increases, the observed effect may not be real and may have its origin in variation of [acetic acid] (cf. buffer effect) which accompanies a variation in pH. Hence, it is considered advisable not to take [H⁺]-dependence into consideration in proposing the mechanism. In the pH range of this study, S(IV) will be largely present as HSO₃⁻ (dissociation constant values of 1.26×10^{-2} for $K_{d(1)}$ and 6.24×10^{-8} for $K_{d(2)}$ ²². The nature of the kinetics, which is first order in ceramics, second order in S(IV) and zero order in O_2 may be explained by following mechanism in Scheme 1.



Scheme 1

The results can also be explained by involving metabisulphite ion in an alternative mechanism (Scheme 2).



Scheme 2

The formation of disulphate ion in Schemes 1 and 2 has been proposed in the light of the work of Batterton and Hoffmann²³. Both the proposed mechanisms will lead to the same experimental rate law (9).

It is of interest to compare the results of this study with those of silica¹², glass¹⁰, CdO⁵ and carbon suspensions¹¹. In CdO⁵, silica⁶ and glass¹⁰ a clear-cut second order dependence in S(IV), as in the present study, was noted. In case of carbon¹¹, the order varied from two to zero. However, a distinctive feature of this study, same as in the case of glass, is the observance of rate maximum in rate profile on varying [ceramic]. This phenomenon was absent in other studies and probably supports the operation of a Hinshelwood-Langmuir mechanism²⁰. An initial rapid drop in [S(IV)] in unbuffered suspensions has been found in all these studies except CdO⁵. The phenomenon of induction period, which was observed in glass catalyzed reaction¹⁰ below pH 5, was absent in all other cases.

The results obtained in this study have relevance to the environmental chemistry of SO₂. Ceramic is mainly composed of such material which is an important constituent of suspended particulate matter. These materials are, therefore, likely to catalyze the atmospheric transformation of S(IV) into S(VI) in various forms of atmospheric water. Moreover, in real atmosphere the size of suspended particles is much smaller ($1 \times 10^{-2} - 10^{-1} \mu\text{m}$)²⁴ and so the rate of autoxidation is expected to be much higher due to large surface area, in agreement with the inverse relationship between rate and particle size.

Acknowledgement

The work was supported by an Indo-US Sub-commission Research project CE-2.

References

- Hoffmann M R & Boyce S D in *Trace atmospheric constituents: properties, transformations and fates*, edited by S E Schwartz (John Wiley, New York) (1983) pp. 147-189.
- Berresheim H & Jaeschke W, *J Atmos Chem*, 4 (1986) 311-334.
- Prasad D S N, Ashu Rani, Madnawat P V S, Bhargava R & Gupta K S, *J mol Catal*, 69 (1991) 393-405.
- Bhargava R, Prasad D S N, Rani A, Bhargava P, Jain U & Gupta K S, *Transition met Chem*, accepted (1991).
- Ashu Rani, Prasad D S N, Bhargava R & Gupta K S, *Bull chem Soc Japan*, 64 (1991) 1956.
- Prasad D S N, Rani A & Gupta K S, *Environ Sci Technol* Accepted (1991).
- Cohen S, Chang S G, Markowitz S S & Novakov T, *Environ Sci Technol*, 15 (1981) 1498-1502.
- Madnawat P V S, Prasad D S N, Rani A, Sharma M & Gupta K S, Unpublished work.
- Rani Ashu, Prasad D S N, Madnawat P V S & Gupta K S, *Atmos Environ*, 26A (1992) 667-673.
- Rani A, Prasad D S N, Jain U & Gupta K S, *Indian J Chem Sect A*, 30 (1991) 756-764.
- Brodzinsky R, Chang S G, Markowitz S S & Novakov T, *J phys Chem*, 84 (1980) 3354-3358.
- Gupta K S, Madnawat P V S, Bhargava R, Prasad D S N, Sharma M & Rani A in *Proc V int. conf on precipitation scavenging and atmosphere surface exchange processes*, edited by S E Schwartz (Hemisphere, New York) accepted (1991).
- Huss Jr A, Lim P K & Eckert C A, *J Am chem Soc*, 100 (1978) 6252-6253.
- Martin L R in *SO₂, NO and NO₂ oxidation mechanisms: Atmospheric considerations* edited by J G Calvert (Butterworth, Boston) (1984), pp. 70-71.
- Beilke S, Lamb D & Miller J, *Atmos Environ*, 9 (1975) 1083-1090.
- Hoather R C & Goodeve C F, *J phys Chem*, 30 (1934) 1149.
- Weisnicht W L, Overman J, Wang C C, Wang H J, Erwin J & Hudson J L, *Chem engng Sci*, 35 (1980) 463-468.
- Faust B C, Hoffmann M R & Bahnemann D W, *J phys Chem*, 93 (1989) 6371-6381.
- Hong A P, Boyce S D & Hoffmann M R, *Environ Sci Technol*, 23 (1989) 533-540.
- Laidler K J, *Chemical kinetics*, (Harper & Row, New York) (1987) pp. 229-275.
- van Eldik R & Harris G M, *Inorg Chem*, 19 (1980) 880.
- Tartar H V & Garretson H H, *J Am chem Soc*, 63 (1941) 808.
- Batterton E A & Hoffmann M R, *J phys Chem*, 92 (1988) 3962-3965.
- Spedding D J, *Air pollution* (Oxford University Press, London) (1974) p. 8.