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Dynamics of Autoxidation of Aqueous Sulfur Dioxide in Aqueous Suspensions of Cadmium Oxide

Ashu RANI, D. S. N. PRASAD, Rachna BHARGAVA, and Krishna Swarup GUPTA*
Atmospheric Chemistry Laboratory, Department of Chemistry, University of Rajasthan, Jaipur 302004, India

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Autoxidation of S(IV), in buffered solutions,conforms the rate law (1). The increase in buffer concentration has a

$$R_{\mathrm{obsd}} = k_5[\mathrm{CdO}][\mathrm{S(IV)}]^2[\mathrm{H}^+]^{-1.22} \qquad (1)$$

rate decreasing effect. On the other hand, in unbuffered solutions the kinetics obey a different rate law (2).

$$R_{\mathrm{obsd}} = (k_{10} + k_{11}\,[\mathrm{CdO}])[\mathrm{S(IV)}][\mathrm{H}^+]^{-0.5} \qquad (2)$$

In both situations, the dissolution of CdO accompanies the autoxidation. A heterogeneous catalytic mechanism involving adsorption of both dioxygen and sulfur(IV) on the surface of CdO particle has been proposed.

While investigating heterogeneous photocatalytic oxidation of sulfite in aqueous suspensions of semiconductor powders, Frank and Bard (1977)[1] observed that zinc oxide, in dark, displayed a significant catalysis in suspensions containing 1×10^{-2} mol dm^{-3} acetic acid although the autoxidation was accompanied by a dissolution of ZnO and as a sequel neutralization of the solution also took place, and the experiments with ZnO were not persued further. In view of the fact that cadmium belongs to Zn-subgroup and CdO is more basic than ZnO, it may be expected that surface-pH of CdO particles would be higher than the former and as a consequence CdO would exhibit a stronger catalytic activity, as surface pH is reported to be a dominant factor in determining rates and capacities of SO_2 removal by several metal oxides in systems; aerosol–SO_2(g)–water (Judeikis et al., 1978).[2]

Additional points of interest in studying CdO catalysis were as follows. CdO is found, to a small extent, in suspended particulate matter.[3,4] In an earlier study, the photocatalytic autoxidation of S(IV) in CdS-suspensions has been reported by Gutierrez and Henglein (1983).[5] In this paper, the kinetics of the autoxidation of S(IV), in aqueous suspensions of CdO, is being reported.

Experimental

Materials and Methods. Cadmium oxide in powder form was of Arbha IM make and of 99.5% purity. All other chemicals were of reagent grade and used as received. For obtaining aqueous S(IV) solution, sodium sulfite was used. For study at constant pH, CH_3COOH-CH_3COONa buffer was used. In case of study in unbuffered solutions, the desired initial pH was obtained by adding dilute perchloric acid.

The experimental procedure was essentially the same as used by Brodzinsky et al.[6] The reactions were conducted in an open Erlenmayer flask, which was maintained at desired temperature by circulating thermostated water around it. The reaction was initiated by first adding temperature equilibrated sodium sulfite solution to the buffer solution maintained at the same temperature, followed by the addition of weighed CdO. The reaction mixture was stirred continuously at 1600±100 rpm using a magnetic bar. At this stirring speed, the reaction was shown not to be oxygen mass transfer controlled.

The kinetics were followed by withdrawing 5 ml aliquot, filtering of the solid rapidly with glass wool and analyzing the filterate iodometrically.

The initial rates for kinetics runs were calculated and as the reaction is accompanied by a dissolution of CdO, the initial rates had a slightly higher uncertainty, nevertheless, the rate measurements were reproducible within ±15%. All calculations were done on Apple IIe Computer using Curve Fitter and Scientific Plotter programmes of Interactive Microwave Inc. U.S.A. In the presentation of rate data later, the statistical parameters have been abbreviated as follows: correlation coefficient=CC; coefficient of determination=CD; standard error of estimate=SEE.

Table 1. Estimation of Sulfate in Final Product Solution, [CdO]=0.3 mol dm^{-3}, pH=5.06

$[\mathrm{S(IV)}]\times10^3$ / mol dm^{-3}	$[\mathrm{Sulfate}]\times10^3$ / mol dm^{-3}	$\frac{[\mathrm{Sulfate}]}{[\mathrm{S(IV)}]}$	% Recovery as sulfate
2.0	1.94	0.97	97
3.0	2.89	0.96	96
4.0	3.91	0.98	98

Product Analysis. The quantitative analysis, performed on the final product solution, showed sulfate to be the only product. It was quantitatively estimated in solutions having different initial sulfite concentrations using the standard procedure. The results are given in Table 1. Thus, the stoichiometry of the reaction could be written as,

$$\mathrm{Sulfur(IV)} + 1/2\mathrm{O_2} \xrightarrow{\mathrm{CdO}} \mathrm{Sulfate.}$$

Results

To begin with, the effect of stirring speed on the reaction rate was examined by varying rpm from 300—1800. It was found that the rate increased with increase in rpm attaining a maximal value around 1200 rpm. Hence, all the experiments were carried out at 1600±100 rpm, as at this rpm, reaction is not oxygen mass transfer-controlled.

The initial kinetics experiments, both in buffered and in unbuffered solutions, indicated that CdO has a significant catalytic activity and the standard S(IV) disappearance curves are normal in this case. However, a disturbing and complicating factor, that the reaction is accompanied by a dissolution of CdO powder, also came to light. The same observation was made by Frank and Bard[1)] in case of ZnO-catalyzed reaction. The dissolution was apparent from a visual examination of the reaction mixture and it was observed to be higher in buffered solution than in unbuffered reaction mixtures, presumably owing to the reaction of CdO with CH_3COOH in the former. In case of unbuffered solutions, some CdO was left undissolved at the end of a kinetics run (60% completion). Despite CdO dissolution, the pH in buffered solutions remained effectively constant throughout the course of a kinetics run. This is probably due to interplay of two opposing factors. CdO dissolution tends to increase the pH, while sulfite ion oxidation into sulfate tends to decrease pH and thus, these two factors counter-balance each other leaving pH of the reaction mixtures almost unchanged.

The dissolution of CdO and consequent production of Cd^{2+} ions made us to look for the cause of the catalysis; whether it was due to homogeneous catalysis perpetuated by Cd^{2+} ions or due to CdO particles or due to both. For this reason, influence of 1—2.4×10^{-3} mol dm^{-3} cadmium acetate, $Cd(OAc)_2$, and 2—5×10^{-3} mol dm^{-3} cadmium chloride, in the absence of CdO, was examined. For comparison, the uncatalyzed reaction was also studied under exactly similar conditions. The results given in Table 2 indicate that the rate of autoxidation, in presence of added Cd-salts, is no different than the rate in their absence. This rules out Cd^{2+} being the cause of catalysis.

It may be mentioned that the cadmium acetate used in aforesaid experiments was prepared by dissolving same CdO in acetic acid, as was used in preparing aqueous suspensions for kinetics work. In view of the dissolution of the CdO, the treatment of kinetics results obtained in this study, was based on initial rates, as the initially most of CdO will remain undissolved.

Kinetics in Buffered Suspensions. Influence of Buffer Concentration: The effect of buffer concentration on the reaction rate was studied with twin objectives of finding out a suitable buffer concentration required for maintaining pH for the range of CdO employed, and for examining its influence on the rate itself. The rate increases with decreasing buffer concentrations, while maintaining the ratio $[CH_3COONa]/[CH_3COOH]$ and hence, pH same. However, at buffer concentrations less than $[CH_3COOH]$=6×10^{-2} mol dm^{-3} and $[CH_3COONa]$=1.4×10^{-1} mol dm^{-3}, the pH could not be maintained constant. This led us to select these concentrations of acetic acid and sodium acetate for buffering reaction mixtures. When it was desired to vary pH, $[CH_3COONa]$ was held constant at 1.4×10^{-1} mol dm^{-3}, and $[CH_3COOH]$ was varied.

Table 2. The Influence of $Cd(OAc)_2$ and $CdCl_2$ on S(IV) Autoxidation. [S(IV)]=2×10^{-3} mol dm^{-3}, pH=5.16, t=30 °C

Salt	$[Cd^{2+}]\times10^3$	$R_{obsd}\times10^8$
	mol dm^{-3}	mol dm^{-3}/s^{-1}
$Cd(OAc)_2$	1.0	1.6
$Cd(OAc)_2$	1.7	1.5
$Cd(OAc)_2$	2.3	1.6
$CdCl_2$	2.5	1.5
$CdCl_2$	3.5	1.4
$CdCl_2$	5.0	1.4
Uncatalyzed	—	2.0

CdO-Dependence: Using initial rates, R_{obs}, for CdO variation an order of 0.98±0.02 was determined for CdO. The plots of R_{obsd} vs. [CdO] (Fig. 1) are linear with small intertepts in agreement with the rate law (1). R_{buff} and k_1 values obtained from this figure are collected in Table 3.

$$R_{obsd} = R_{buff} + k_1[CdO], \qquad (1)$$

where R_{buff} is the rate of uncatalyzed reaction in buffered suspensions. k_1 values are seen to vary with S(IV) in accordance with Eq. 2.

$$k_1 = k_2[S(IV)]^2. \qquad (2)$$

From a plot of k_1 and $[S(IV)]^2$, k_2 was determined to be

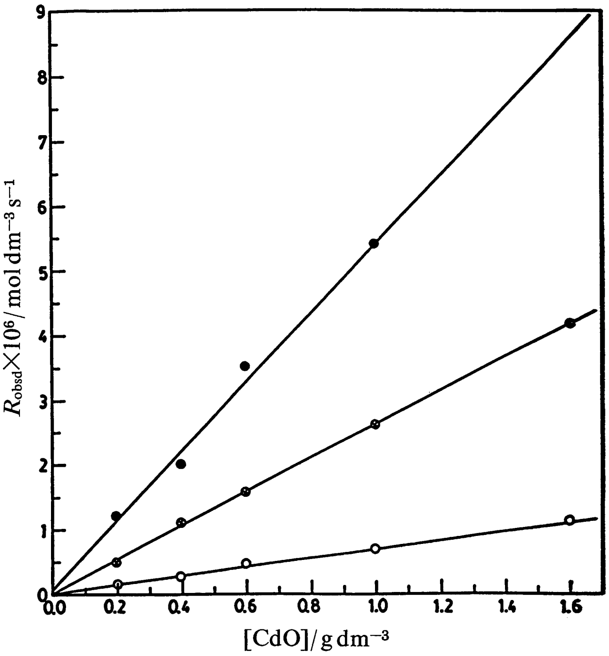

Fig. 1. Variation of CdO at three different S(IV) in buffered solutions at pH 5.06 and 30 °C. [S(IV)]; ○=2.5×10^{-3}, ⊗=5×10^{-3}, ●=7.5×10^{-3} mol dm^{-3}.

Table 3. The Values of R_{buff} and k_1 at Different [S(IV)] at pH=5.06 and 30 °C

$[S(IV)]\times10^3$/mol dm^{-3}	2.5	5.0	7.5
$k_1\times10^7$/mol g^{-1} s^{-1}	7.1	26.2	53.8
$R_{buff}\times10^8$/mol dm^{-3} s^{-1}	0.2	0.4	6.2

$(8.6\pm0.2)\times10^{-2}$ $dm^6\,mol^{-1}\,g^{-1}\,s^{-1}$. The uncatalyzed rate, R_{buff}, is negligible in comparison to catalyzed rate and contribution of the former to the total rate does not exceed more than 6% at the highest [S(IV)], which is well within the uncertainty of present rate measurements and R_{buff} can, therefore, be neglected. In the light of Eq. 2, Eq. 1 then can be modified as Eq. 3.

$$R_{obsd}=k_2[CdO][S(IV)]^2. \quad (3)$$

Sulfur(IV)-Dependence: R_{obsd} values for sulfur(IV) variations yielded an order of 2.05 ± 0.07, in conformity with the rate law (4).

$$R_{obsd}=k_4[S(IV)]^2. \quad (4)$$

The values of k_4, given in Table 4, were determined at various [CdO] from R_{obsd} vs. $[S(IV)]^2$ plots which are given in Fig. 2. A comparison of Eqs. 4 and 3 shows,

$$k_4=k_2[CdO]. \quad (5)$$

Thus, the results of variation of S(IV) also conform Eq. 3. Using Eq. 2, the values of k_2 from sulfur(IV) variations at 0.2, 0.6, and 1.0 $g\,dm^{-3}$ [CdO] were determined to be 0.12 ± 0.02, 0.08 ± 0.01, and 0.07 ± 0.01 $dm^6\,mol^{-1}\,g^{-1}\,s^{-1}$ respectively at pH 5.06 and 30 °C. Similarly, at same pH and temperature, k_2 values of 0.11 ± 0.01, 0.11 ± 0.01, and 0.10 ± 0.01 $dm^6\,mol^{-1}\,g^{-1}\,s^{-1}$ were determined by varying [CdO] at 2.5×10^{-3}, 5.0×10^{-3}, and 7.5×10^{-3} $mol\,dm^{-3}$ [S(IV)], respectively. Some variation is seen in these values which fall in the range 0.07—0.12 $dm^6\,mol^{-1}\,g^{-1}$.

It must be admitted that under varying reaction conditions, such as [S(IV)], [CdO] and pH, the rate of dissolution of CdO will not be same and is likely to vary from one reaction condition to another. Perhaps, this is the reason for variation in k_2 values, although the values fit the same rate law (11) and one gets nearly same values if extracted from a particular variation. We, therefore, ascribe the variation in k_2 values to the phenomenon of differential dissolution.

Table 4. k_4 Values at Different [CdO] at pH=5.06 and 30 °C

$[CdO]/g\,dm^{-3}$	0.2	0.6	1.0
$k_4\times10^2/dm^3\,mol^{-1}\,s^{-1}$	2.9	5.0	6.7

pH-Dependence: The results of pH variation in the range 4.8—5.9, given in Table 5, show the rate to increase with increase in pH. From a log–log plot between R_{obsd} and $[H^+]$, an order of −1.22 in $[H^+]$ was obtained. The complete rate law, including [CdO], [S(IV)] and $[H^+]$-dependences can, therefore, be written as Eq. 6.

$$R_{obsd}=k_5[CdO][S(IV)]^2[H^+]^{-1.22}. \quad (6)$$

Rate laws (3) and (6) are equivalent through $k_2=k_5[H^+]^{-1.22}$.

Temperature-Dependence: The values of R_{obsd}, determined at 25, 30, and 35 °C (Table 6), yielded an energy of activation of 322 $kJ\,mol^{-1}$.

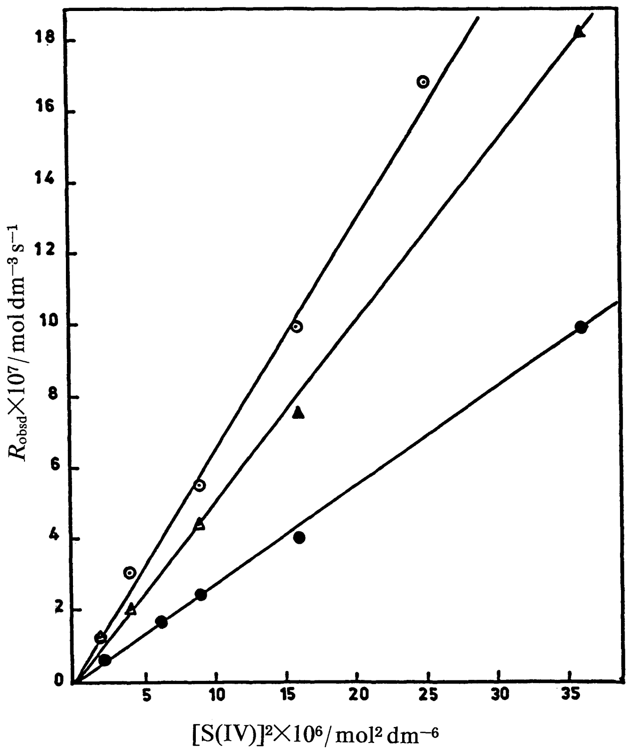

Fig. 2. Dependence of R_{obsd} on [S(IV)] in CdO-catalyzed [S(IV)] autoxidation in buffered solutions at 30 °C and pH=5.06. ●; [CdO]=0.2 $g\,dm^{-3}$, ▲; [CdO]=0.6 $g\,dm^{-3}$; ⊙; [CdO]=1.0 $g\,dm^{-3}$.

Table 5. Values of R_{obsd} and k_2 at Different pH and at 30 °C

Expt. No.	$[S(IV)]\times10^3$ $mol\,dm^{-3}$	[CdO] $g\,dm^{-3}$	pH	$R_{obsd}\times10^6$ $mol\,dm^{-3}\,s^{-1}$	k_2 $dm^6\,mol^{-1}\,g^{-1}\,s^{-1}$
1	2.5	0.6	5.71	3.33	0.89
2	2.5	0.6	5.46	1.65	0.44
3	2.5	0.6	5.30	0.77	0.21
4	2.5	0.6	4.96	0.46	0.12
5	2.5	0.6	4.88	0.29	0.08
6	2.5	0.3	5.71	1.67	0.89
7	2.5	0.3	5.46	0.83	0.45
8	2.5	0.3	5.30	0.38	0.20
9	2.5	0.3	4.96	0.23	0.13
10	2.5	0.3	4.88	0.15	0.08

Table 6. R_{obsd} Values at Temperatures and $[S(IV)]=5\times10^{-3}$ mol dm^{-3}, $[CdO]=0.20$ g dm^{-3}, pH=5.06

Temp/°C	25	30	35
$R_{obsd}\times10^7$/mol dm^{-3} s^{-1}	0.50	5.00	36.4

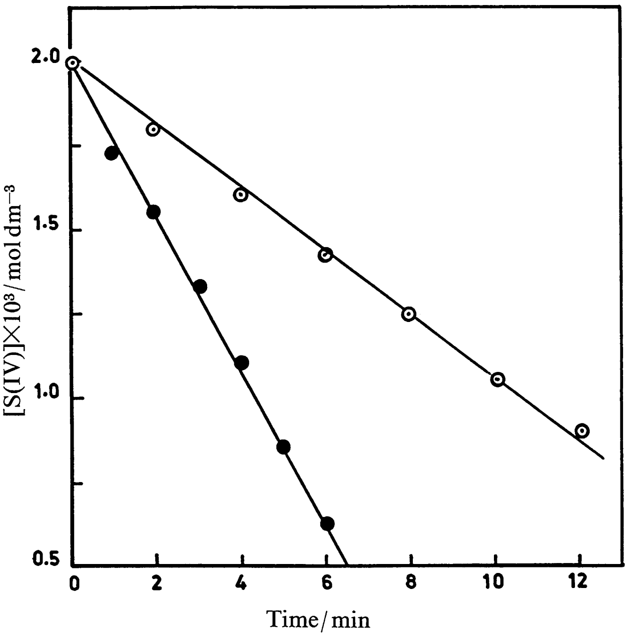

Fig. 3. Rate profiles for CdO-catalyzed [S(IV)] autoxidation in unbuffered solutions at 30 °C. $[S(IV)]=2\times10^{-3}$ mol dm^{-3}, $[CdO]=0.2$ g dm^{-3}, $t=30$ °C. ⊙; pH=4.93, ●; pH=5.80.

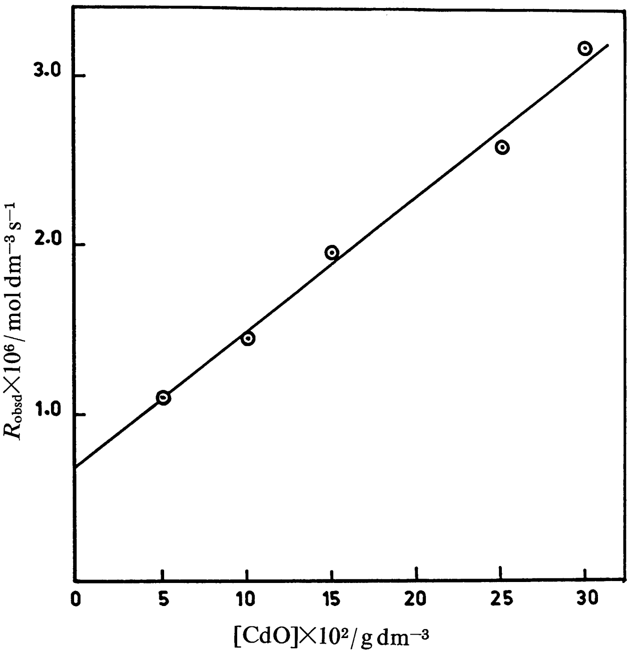

Fig. 4. Variation of R_{obsd} with CdO in unbuffered solutions at $[S(IV)]=2\times10^{-3}$ mol dm^{-3}, pH=5.06, $t=30$ °C.

Kinetics in Unbuffered Suspensions. for studying kinetics in unbuffered solutions, initial pH was adjusted to desired value with the help of dilute perchloric acid. In all these experiments, pH varied with the progress of the reaction. The reaction profiles at different pH values are shown in Fig. 3. For investigating [CdO] and [S(IV)] dependences, a pH value of 5.06±0.02 was selected.

CdO-Dependence: [CdO] was varied from 0.05 to 0.30 g dm^{-3} at $[S(IV)]=2\times10^{-3}$ mol dm^{-3}, pH=5.06 and 30 °C and order in CdO was determined to be 0.6. The fractional order in CdO probably indicates the presence of a term independent of [CdO] in the rate law. In all likelihood, this term corresponds to uncatalyzed reaction. Indeed, the rate measurements, in the absence of CdO, yielded an uncatalyzed rate of 6×10^{-7} mol dm^{-3} s^{-1} under similar reaction conditions. On this premise, a plot between R_{obsd} and [CdO] was drawn and found to be linear (Fig. 4) in agreement with the rate law (7).

$$R_{obsd}=R_{un}+k_6[CdO], \tag{7}$$

where R_{un} is the rate of uncatalyzed reaction in unbuffered suspensions. R_{un} and k_6 values were found to be $(6.8\pm2.1)\times10^{-7}$ mol dm^{-3} s^{-1} and $(8.0\pm1)\times10^{-6}$ mol g^{-1} s^{-1} (CC=0.99; CD=0.99; SEE=3.18×10^{-8}). The presence of uncatalyzed rate term in unbuffered suspensions and its near absence in buffered suspensions deserves an explanation. The uncatalyzed rate has its origin in trace metal ion catalysis.[7,8] In buffered solutions, the acetate ions render these metal ions less reactive by forming complexes with them and, therefore, suppress the uncatalyzed path. Indeed, Cohen et al. (1981)[9] found the autoxidation of S(IV) in fly ash slurries, which incidentally is catalyzed by trace metal ions, is completely seized in acetate buffers, presumably due to masking of trace metal ion catalysts.[9] Moreover, trace organics are also known to inhibit the S(IV) autoxidation and their presence in acetic acid sample used by us can not be denied.[9,10]

S(IV)-Dependence: At a fixed [CdO] of 0.1 g dm^{-3}, pH 5.06 and 30 °C, [S(IV)] was varied from $(1-5)\times10^{-3}$ mol dm^{-3} (Table 7) and order in S(IV) was found to be 0.97 in agreement with Eq. 8,

$$R_{obsd}=k_7[S(IV)]. \tag{8}$$

In view of the fact that a first order dependence of uncatalyzed reaction is well established,[11] it shows the catalyzed reaction to be also of first order in [S(IV)]. On combining Eqs. 7 and 8, one obtains Eq. 9. Comparison of rate laws (7) and (9), and (8) shows,

$$R_{obsd}=(k_8+k_9[CdO])[S(IV)], \tag{9}$$

$$k_7=k_8+k_9[CdO], \tag{10}$$

$$R_{un}=k_8[S(IV)], \tag{11}$$

$$k_6=k_9[S(IV)]. \tag{12}$$

The values of R_{un}, k_6, and k_7 are collected in Table 8 and these values were used for obtaining k_9. The validity of the proposed rate law was tested by calculating the values of k_7 at $[CdO]=0.1$ g dm^{-3} using Eq. 10. The calculated value of 7.4×10^{-4} s^{-1} is in good agreement with the experimental value of $(9.7\pm2.6)\times10^{-4}\,s^{-1}$ obtained from Fig. 5, based on Eq. 10 under similar conditions.

pH-Dependence: A variation in initial pH showed the rate to increase on increasing pH (Table 7). From a log–log plot between rate and $[H^+]$, an order of −0.5 in $[H^+]$ was extracted. On including $[H^+]$-dependence, the rate law (11) is modified to

$$R_{obsd}=(k_{10}+k_{11}[CdO])[S(IV)][H^+]^{-0.5}, \tag{13}$$

where,

$$k_8=k_{10}[H^+]^{-0.5} \text{ and } k_{11}=k_9[H^+]^{-0.5}.$$

Table 7. Values of R_{obsd} at Different [S(IV)], [CdO], and pH at 30 °C in Unbuffered Suspensions

Expt. No.	$[S(IV)]\times10^3$	[CdO]	pH	$R_{obsd}\times10^6$
	$mol\,dm^{-3}$	$g\,dm^{-3}$		$mol\,dm^{-3}\,s^{-1}$
1	2.0	0.05	5.06	1.11
2	2.0	0.10	5.06	1.43
3	2.0	0.15	5.06	1.94
4	2.0	0.20	5.06	2.35
5	2.0	0.25	5.06	2.58
6	2.0	0.30	5.06	3.16
7	1.0	0.10	5.06	1.04
8	2.0	0.10	5.06	1.43
9	3.0	0.10	5.06	2.70
10	4.0	0.10	5.06	3.39
11	5.0	0.10	5.06	4.89
12	2.0	0.20	4.93	1.33
13	2.0	0.20	5.15	1.75
14	2.0	0.20	5.50	2.33
15	2.0	0.20	5.80	3.80

Table 8. Values of R_{un}, k_6, k_8, and k_9 at pH=5.06 and 30 °

$R_{un}\times10^7$	$k_6\times10^6$	$k_7\times10^4$	$k_8\times10^4$	$k_9\times10^3$
$mol\,dm^{-3}\,s^{-1}$	$mol\,g^{-1}\,s^{-1}$	s^{-1}	s^{-1}	$dm^3\,g^{-1}\,s^{-1}$
6.8	8.0	9.7	3.4	4.0

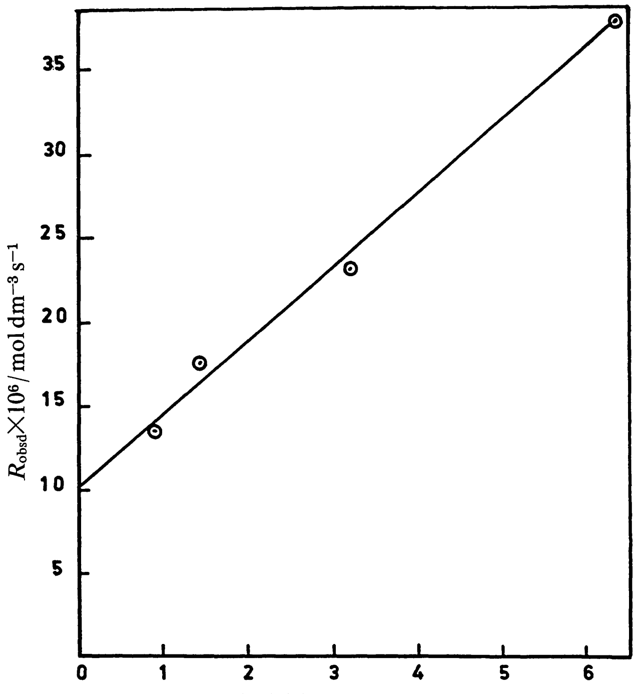

Fig. 5. Variation of [S(IV)] in unbuffered solutions at $[CdO]=0.1\,g\,dm^{-3}$, pH=5.06 and $t=30\,°C$.

Discussion

The most complicating aspect of this study is the dissolution of cadmium oxide, which accompanies the autoxidation of sulfur(IV), as the reaction progresses. However, the observation, that $CdCl_2$ and $Cd(OAc)_2$ do not possess any catalytic activity, is a redeeming feature which renders the system amenable to explanation. It should be mentioned here that the $Cd(OAc)_2$ solution, used for detecting any homogeneous catalysis by Cd^{2+} ions, was prepared by dissolving the same CdO in acetic acid, as was used in aqueous suspensions for studying heterogeneous catalysis. This firmly rules out the possibility of the impurities present in the CdO-sample as a possible cause of catalysis.

Having ruled out the possibility of catalytic activity of CdO-suspensions being due to Cd^{2+} ion, it is attractive to apportion it to the surface provided by CdO-particles. There are two strong points in favor of the heterogeneous nature of the catalysis in the present case. First is the order of two in [S(IV)], as has been found in glass,[12] silica,[13] and ceramic[13] catalyzed reactions. Second is the lack of an alternative explanation.

However, before presenting a mechanism, it is necessary to discuss the apparent difference in $[H^+]$ dependencies in buffered (Eq. 6) and unbuffered (Eq. 13) suspensions. Since, the uncatalyzed reaction, for

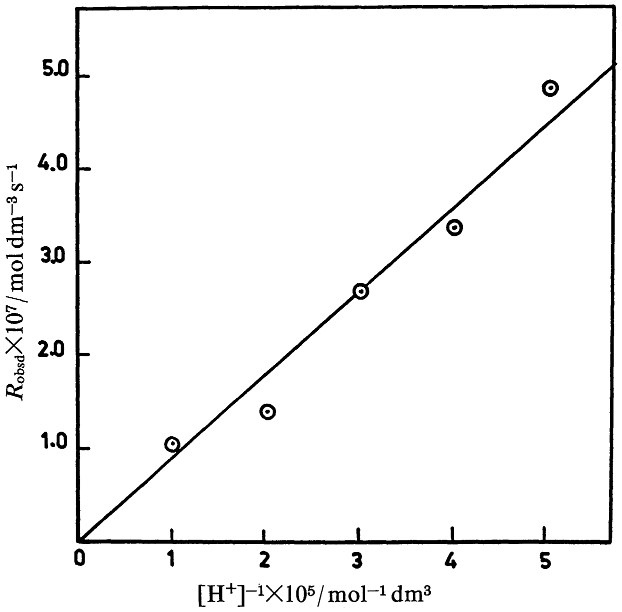

Fig. 6. Variation of R_{obsd} with $[H^+]$ in unbuffered solutions at $[S(IV)]=2\times10^{-3}\,mol\,dm^{-3}$, $[CdO]=0.2\,g\,dm^{-3}$, $t=30\,°C$.

which rate is known to vary as $[H^+]^{-1}$ makes a substantial contribution to overall rate, it is likely that the order of −0.5 in $[H^+]$ in unbuffered study is largely due to this path and the CdO-catalyzed might be $[H^+]$-independent. On this premise, the rate law (13) if written as Eq. 14 fully accounts for observed $[H^+]$-dependence. The plot of R_{obsd} vs. $[H^+]^{-1}$ is straight line with a non-zero intercept (Fig. 6),

$$R_{obsd} = k_{12}[S(IV)][H^+]^{-1} + k_{13}[S(IV)][CdO]. \quad (14)$$

It yielded k_{12} and k_{13} values of $(2.2\pm0.4)\times10^{-9}\ s^{-1}$ and $(2.5\pm0.5)\times10^{-3}\ dm^3\ g^{-1}\ s^{-1}$ respectively at 30 °C.

In buffered study, the uncatalyzed rate is negligible and, therefore, $[H^+]$-dependence can not be ascribed to this path, except nominally. An interpretation in terms of reaction mechanism via involvement of HSO_3^- and SO_3^{2-} ions would be vitiated and obscurred by the fact that the variation in $[H^+]$ also entails a variation in the ratio $[CH_3COONa]/[CH_3COOH]$. Obviously, with increase in pH, $[H^+]$ and $[CH_3COOH]$ both decrease and there is no way to discern whether the rate increases on increasing pH is due to decrease in $[H^+]$ or due to decrease in $[CH_3COOH]$ or both. It should be mentioned that a decrease in $[CH_3COOH]$ would result in decreasing the rate of dissolution of CdO (loc cit) and will thus have a rate increasing effect. CH_3COOH may affect the reaction in another way by getting adsorbed onto particle surface and thus by inhibiting the heterogeneous reaction. In view of this it is best not to consider the $[H^+]$-dependence in the construction of the reaction mechanism.

The kinetics order of unity in bulk [CdO] would result in an order of 1.5 in surface CdO provided all particles are of same radius and the situation would be much more complicated if the particles are not of uniform size as is usually the case.[#] The interpretation of kinetics results obtained in this study is based on bulk concentration of CdO, which is similar to mechanistic treatment resorted to by earlier workers in respect of similar systems.[6]

Now, the results obtained in the present study can be explained by proposing that both S(IV) and O_2 are adsorbed on CdO surface. Subsequently, the reaction is accomplished via interaction between these. Although oxygen dependence could not be studied, it is implicated to account for the observation that no reaction occurs in the absence of O_2 and that if O_2 is not allowed to diffuse rapidly in the suspension, as is evident from the influence of stirring speed on the reaction rate, the rate of autoxidation is quite slow. The kinetics orders of one in bulk [CdO], of two in [S(IV)] in buffered study and of one in unbuffered study would require the formation of at least two activated complexes having the gross compositions—$CdO\cdot O_2\cdot S(IV)$ and $CdO\cdot O_2\cdot(S(IV))_2$ for an unified treatment. The observed kinetics in both types of studies can be explained by the following general mechanism for the CdO-catalyzed path.

$$CdO + O_2 \overset{K_1}{\rightleftarrows} CdO\cdot O_2, \quad (15)$$

$$CdO\cdot O_2 + S(IV) \overset{K_2}{\rightleftarrows} CdO\cdot O_2\cdot S(IV), \quad (16)$$

$$CdO\cdot O_2\cdot S(IV) + S(IV) \overset{K_3}{\rightleftarrows} CdO\cdot O_2\cdot(S(IV))_2, \quad (17)$$

$$CdO\cdot O_2\cdot S(IV) \xrightarrow{k_{14}} \text{Products}, \quad (18)$$

$$CdO\cdot O_2\cdot(S(IV))_2 \xrightarrow{k_{15}} \text{Products}. \quad (19)$$

Assuming that the equilibria (Eqs. 15—17) are rapidly established and that the values of K_1, K_2, and K_3 are low, the rate expression (Eq. 20), at constant atmospheric pressure, can be derived.

$$R_{CdO} = A[CdO][S(IV)]^2 + B[CdO][S(IV)], \quad (20)$$

where R_{CdO} is the rate of CdO-catalyzed path and $A=k_{15}K_1K_2K_3[O_2]$ and $B=k_{14}K_1K_2[O_2]$. It appears that in buffered suspensions path A is dominant and B makes a negligible contribution. The reverse appears to be true in unbuffered suspensions. It is interesting to recall that in carbon-catalyzed sulfur(IV) autoxidation[6] and in nitrite–sulfur(IV)[14] reactions, order in sulfur(IV) was found to vary from zero to two.

An alternative mechanism may also be proposed. CdO due to its basic nature is likely to become hydrated to form $Cd(OH)_2$ and this species may react further with S(IV) and O_2. It may be mentioned here that in Fe(III)-catalyzed reaction above pH 5, and in Cu(II)-catalyzed reaction in alkaline solutions, the possibility of involvement of $Fe(OH)_3$ [15] and $Cu(OH)_2$ [16] has been indicated. Dyson and Quon,[17] while studying the reaction between ZnO fume and SO_2, found that in presence of water vapors $Zn(OH)_2$ is formed. Based on reactive $Cd(OH)_2$, a mechanism similar to (Eq. 15—19) can be written which will reproduce the observed kinetics. The autoxidation in surficial complexes,[18] $CdO_2\cdot O_2\cdot S(IV)$ and $CdO_2\cdot O_2\cdot(S(IV))_2$, is likely to proceed through the formation of peroxomonosulfate[19] and disulfate[20] species. It should be pointed out that in the present study an initial rapid drop in [S(IV)] has not been observed as was the case with carbon particles.[6] This phenomenon was taken as an evidence of adsorption of O_2 on particle surface in a primary step i.e. in Eq. 15 by Brodzinsky et al.[6] So, in the absence of any initial rapid fall in S(IV) in this case, it is possible to formulate the proposed mechanism in an alternative way, which involves the adsorption of S(IV) on CdO first, followed by adosrption or reaction with O_2. At pH=5.06, $[S(IV)]=2\times10^{-3}\ mol\ dm^{-3}$, $[CdO]=0.2\ g\ dm^{-3}$, and $t=30\ °C$. R_{obsd} values of 1.3×10^{-7} and $2.35\times10^{-6}\ mol\ dm^{-3}\ s^{-1}$ have been determined in buffered and unbuffered suspensions respectively. This shows the rate in unbuffered solution to be much faster than in buffered solutions. This could possibly be linked to the difference in the solubility of CdO in two situations. In unbuffered solutions, the solubility of CdO is compara-

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[#] This was pointed by the referee.

tively low and a large amount of solid CdO particles is available for surface catalysis and probably this explains the higher rate in unbuffered solutions.

It is interesting to speculate the possible cause of CdO-catalysis. In our laboratory several transition metal oxides such as CuO,[12) CoO,[13) Co_2O_3,[13) and Ni_2O_3[13) have been found to be effective catalyst for S(IV) autoxidation. However, in all these cases it is possible to ascribe the catalytic activity to the ease of availability of multiple oxidation states and their easy interconvertibility (for example Co(II)/Co(III) in CoO) and adsorption of S(IV) and O_2. In case of CdO, such an explanation does not seem plausible. On the basis of the fact that like CdO, other basic oxides like MgO and ZnO also catalyze the S(IV) autoxidation, the most probable reason for the catalytic activity possessed by CdO particles is its relatively high surface-pH due to its basis nature, which helps in accomplishment of the reaction between sulfur(IV) and O_2.[21)

In the light of the present work, it is desirable that the catalytic activity of other metal oxides, which are found in suspended particulate matter, should also be investigated.

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