

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A2.10 MD10

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SO₂ + mineral oxide (dust) surfaces

Experimental data

Parameter	Temp/K	Reference	Technique/ Comments
<i>Uptake coefficients: γ, γ_0, γ_{ss}</i>			
$\gamma_0 = (8.4 \pm 0.3) \times 10^{-5}$ (Adobe clay)	298*	Judeikis and Stewart, 1976	CRFT-MS (a)
$\gamma_0 = 1 \times 10^{-3}$ (MgO)	298*	Judeikis et al, 1978	CRFT-MS (b)
$\gamma_0 = 5.5 \times 10^{-4}$ (Fe ₂ O ₃)			
$\gamma_0 = 4.0 \times 10^{-4}$ (Al ₂ O ₃)			
$\gamma_0 = (9.5 \pm 0.3) \times 10^{-5}$ (α -Al ₂ O ₃)	296	Goodman et al., 2001	Knudsen-MS/FTIR (c)
$\gamma_0 = (2.6 \pm 0.2) \times 10^{-4}$ (MgO)			
$\gamma_0 = (1.0 \pm 0.2) \times 10^{-4}$ (TiO ₂)	298*	Usher et al. 2002	Knudsen-MS/FTIR (c)
$\gamma_0 = (1.4 \pm 0.7) \times 10^{-4}$ (CaCO ₃)			
$\gamma_0 = (7.0 \pm 2.0) \times 10^{-5}$ (α -Fe ₂ O ₃)			
$\gamma_0 = (5.1 \pm 0.5) \times 10^{-4}$ (MgO)			
$\gamma_0 = (1.6 \pm 0.5) \times 10^{-4}$ (α -Al ₂ O ₃)			
$\gamma_0 < 1 \times 10^{-7}$ (SiO ₂)			
$\gamma_0 = (3 \pm 1) \times 10^{-5}$ (Chinese dust)			
$\gamma = 5 \times 10^{-7}$ (Saharan dust, O ₃)	299	Ullerstam et al., 2002	DRIFTS (d)
$\gamma \approx (1.6 \pm 0.1) \times 10^{-5}$ (Saharan dust)	299	Ullerstam et al., 2003	Knudsen-DRIFTS (e)
$\gamma_0 = (6.6 \pm 0.8) \times 10^{-5}$ (Saharan dust)	298	Adams et al., 2006	CWFT-MS (f)
$\gamma_0 = (6.4 \pm 0.7) \times 10^{-5}$ (Saharan dust, RH \approx 0)	258		
$\gamma_0 = (6.4 \pm 0.7) \times 10^{-5}$ (Saharan dust, RH = 27%)	258		
$\gamma_0 = 0.1$ (CaCO ₃ , powder)	300	Santschi and Rossi, 2006	Knudsen-MS (g)
$\gamma_0 = (7.7 \pm 1.6) \times 10^{-4}$ (CaCO ₃ , O ₃)	293	Li et al., 2006	DRIFTS (h)
$\gamma_{ss} = (8.1 \pm 2.6) \times 10^{-5}$ (CaCO ₃ , O ₃)			
<i>Partitioning coefficients: K_{imc}</i>			
$K_{imc} = (1.2 \pm 0.4)$		Adams et al., 2006	CWFT-MS (f)

*Room temperature assumed to be 298 K (not cited in manuscript).

Comments

- (a) Samples prepared by coating reactor with aqueous slurry before drying in vacuum. γ based on geometric surface area.

- (b) Samples prepared by coating reactor with H₂O/ethanol slurry before drying in vacuum. γ based on geometric surface area.
- (c) Bulk powder samples generated by spraying an aqueous slurry onto the heated sample support. A SO₂ concentration of 1×10^{11} molecule cm⁻³ was employed. The initial uptake coefficients (γ_0) given in the table were calculated using the BET surface area of the sample. Maximum surface coverages of reversibly adsorbed SO₂ of $(1.5 \pm 0.3) \times 10^{14}$ and $(3.5 \pm 0.6) \times 10^{14}$ molecule cm⁻² were obtained by surface spectroscopic methods for α -Al₂O₃ and MgO, respectively.
- (d) The initial SO₂ concentration was $\approx 2\text{-}20 \times 10^{12}$ molecule cm⁻³. Dust samples made from aqueous suspension and were dried at 333 K before use. Uptake coefficient of SO₂ in the presence of O₃ (5.6×10^{12} molecule cm⁻³) was calculated from time dependent IR signals due to the sulphate product. The values of γ listed were obtained using the BET surface area. For comparison, a value of $\approx 10^{-3}$ was obtained using the geometric surface area.
- (e) Dust samples made from aqueous suspension deposited onto sample holder at 373 K (Knudsen reactor experiments) and were dried at 333 K before use. The concentration of SO₂ was $5.4 - 15 \times 10^{12}$ molecule cm⁻³. The value of γ listed was obtained in pulsed valve experiments using the BET surface area. For comparison, a value of $\approx 10^{-3}$ was obtained using the geometric surface area. Values obtained in continuous flow mode were a factor of \approx three lower. No significant change in γ_0 was found when NO₂ was present at $[\text{NO}_2] \approx 1 \times 10^{13}$ molecule cm⁻³.
- (f) Dust samples made from a suspension in ethanol deposited. Initial SO₂ concentration was between 2 and 40×10^{10} molecule cm⁻³. Uptake coefficients were determined using the BET surface area of the sample. Experiments carried out at relative humidity of ≈ 0 (298 K) and 27 % (258 K). No significant change in γ_0 was found when O₃ was added at $\approx 1 \times 10^{13}$ molecule cm⁻³. The partitioning coefficient for reversibly adsorbed SO₂, K_{inc} , was determined from the area of desorption peaks at 298 K and was derived from the published values of $K_{LangC} = (6 \pm 2) \times 10^{-14}$ molecule⁻¹ cm³ and $N_{max} = 2 \times 10^{13}$ molecules cm⁻².
- (g) Powder samples were evacuated for 30 minutes prior to use, which leaves the equivalent ≈ 3 % of one monolayer H₂O on the surface. CO₂ formed promptly with 100% yield and detected in the gas-phase. The uptake coefficient listed in the Table was calculated using the geometric surface area of the powder sample. H₂O (but not CO₂) observed as reaction product. $[\text{HNO}_3]_0 \approx (3 - 7) \times 10^{11}$ molecule cm⁻³. Partial HNO₃ desorption from marble surfaces was observed, suggesting that part of the initial uptake was due to physi-sorption.
- (h) The initial uptake coefficients listed were obtained in the presence of O₃ (4.9×10^{14} molecule cm⁻³) and water vapour (RH = 40 %) and are based on the geometric surface area of the sample. The initial uptake coefficient was independent of SO₂ concentration ($0.6\text{-}9.8 \times 10^{14}$ molecule cm⁻³), RH and O₃ concentration. The steady state uptake coefficient was observed to be dependent on RH and was in the range $1.0\text{-}10.7 \times 10^{-5}$ for RH 5-60 %. Use of the BET surface area resulted in uptake coefficients of $\gamma_0 = (1.4 \pm 0.3) \times 10^{-7}$ and $\gamma_{ss} = (1.5 \pm 0.5) \times 10^{-8}$ at RH = 40%.

Preferred Values

Parameter	Value	T/K
γ (atmospheric dust, RH 0-27 %)	4×10^{-5}	260-300
<i>Reliability</i>		
$\Delta \log(\gamma)$	0.7	

Comments on Preferred Values

Most of the uptake coefficients measured for SO₂ interaction with mineral surfaces obtained using SO_{2(g)} analysis (CWFT, Knudsen) indicate that the process is relatively inefficient, with values of γ_0 close to 10^{-4} – 10^{-5} . The large variability in γ is due to the different mineral sample types used, due to different sample treatments and data analysis (i.e. use of BET or geometric surface area) and due to use of different SO₂ concentrations. The value of $\gamma = 0.1$ on CaCO₃ of Santschi and Rossi (2006) is the exception and is likely due to the use of the geometric rather than BET surface area. Li et al., (2006) and Ullerstam et al. (2002) used DRIFTS to derive much lower uptake coefficients. Uptake coefficients measured using airborne aerosol and at atmospherically relevant conditions of [SO₂], [O₃] and RH are required to reduce the uncertainty.

In the absence of such data, for the purpose of atmospheric modelling, an average uptake coefficient of 4×10^{-5} , independent of relative humidity and based on Saharan (Adams et al., 2006) and Chinese dust (Usher et al., 2002) is presently recommended. The errors associated with this uptake coefficient are likely to be large (>factor of 10) and it is not clear whether the initial or the steady state uptake coefficient is appropriate for atmospheric conditions. The initial uptake coefficient contains components from both reversible and irreversible uptake. The fraction of SO₂ taken up reversibly is however small and dependent on the O₃ concentration. Adams et al. (2006) determined that 86-98 % was taken up irreversibly, the larger fraction obtained when O₃ was present.

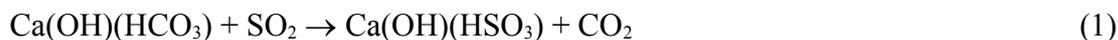
Not only the uptake coefficient, but also the capacity of the mineral surface to convert SO₂ to sulphate depends on the mineral type and humidity. Although the initial uptake coefficient appears to be invariant with humidity on Saharan dust (Adams et al., 2006) CaCO₃ (Li et al., 2006) and clay surfaces (Judeikis and Stewart, 1976; Judeikis, 1978), the steady state uptake coefficient on CaCO₃ was not (Li et al., 2006). In addition, Ullerstam et al. (2002) found that the capacity of Saharan dust increased by ≈ 50 % following treatment with H₂O vapour at high humidity (22 mbar H₂O); Li et al. (2006) also found that the capacity (on CaCO₃) was enhanced by gas phase H₂O.

Adams et al. (2006) report a maximum amount of irreversibly taken up SO₂ as 8×10^{13} molecule cm⁻² of Saharan dust; Al-Hosney et al (2005) found that a CaCO₃ surface saturated at a coverage of 4×10^{13} molecules cm⁻². Santschi and Rossi report a lower capacity of CaCO₃ to take up SO₂ of 7×10^{12} molecules cm⁻², probably related to differences in humidity in their experiments (see above). Using dispersed aerosol samples of CaCO₃, Prince et al. (2007) found that the amount of CO₂ generated and the amount of SO₂ lost both depended strongly on relative humidities between 300 and 90 % but was not influenced by the presence of HNO₃.

Judeikis and Stewart (1976) found that exposure of a pre-reacted clay surface to 95 % RH recovered the reactivity completely. The capacity of MgO increased dramatically (factor 100) going from RH = 0 to 95 %, whereas those of Fe₂O₃ and Al₂O₃ were not substantially changed. Capacities of 25-150 mg of sulphate per gram of clay mineral for 0.86 ppm SO₂ and RH = 86 % (Mamane and Gottlieb (1989) have been measured.

Surface spectroscopy (Goodman et al., 2001; Usher et al, 2002; Ullerstam et al, 2002) has shown that SO₂ can be oxidised to sulphite (SO₃²⁻) and bisulphite (HSO₃⁻) on the dry mineral oxide samples used, probably via reaction with surface-OH and surface-O groups. Contrasting results were found by Li et al. (2006), who only found sulphite formation only in the presence of gas-phase water vapour. Baltrusaitis et al. (2007) found that the extent of reaction of SO₂ with CaCO₃ is enhanced ≈ 5 -fold for particulate CaCO₃ and ≈ 10 -fold for single crystal CaCO₃ in the presence of H₂O vapour at RH between 30 and 85 %.

In order to explain their observations of prompt CO₂ formation, Santschi and Rossi, 2006 suggest that the reaction proceeds via the Ca(OH)(HCO₃) surface species (1). In contrast, Al-Hosney et al., (2005) propose reaction (2) to explain their 296 K surface spectroscopic observations of H₂CO₃ and non-observation of CO₂:



There is clearly some uncertainty regarding the true mechanism and the role of surface water. In the presence of O₃, (or NO₂, Ullerstam et al., (2993)) further oxidation of sulphite to SO₄²⁻ and HSO₄⁻ occurs (Li et al., 2006).

In O₃-free experiments, Judeikis et al. (1978) found, by wet chemical analysis and xray photoelectron spectroscopy, that SO₂ was quantitatively (within a factor of two) converted to sulphate except on Al₂O₃, for which the uptake was found to be reversible. Goodman et al. (2001) found spectroscopic evidence for reversibly adsorbed SO₂, on both α-Al₂O₃ and MgO, and, using calibrated FTIR signals derived adsorption isotherms with maximum coverages listed in the comments above. The reversible component of uptake was however much smaller than reactive uptake to form sulphite.

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