**IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet V.A2.11**

The citation for this datasheet is: IUPAC Subcommittee for Gas Kinetic Data Evaluation, http://www.iupac-kinetic.ch.cam.ac.uk
This datasheet last evaluated: March 2010; last change in preferred values: March 2010.

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## $HC(O)OH$ + mineral oxide (dust) surfaces

### Experimental data

| *Parameter* | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| $\gamma_0$ | | | |
| $(3 \pm 1) \times 10^{-3}$ (dry $CaCO_3$) | 298 * | Al-Hosney et al., 2006 | Knudsen-MS (a) |
| $1.7 \times 10^{-5}$ (Na-Montmorillonite, RH = 0 %) | 212 | Hatch et al., 2007 | Knudsen-MS (b) |
| $1.7 \times 10^{-5}$ (Na-Montmorillonite, RH = 29 %) | | | |
| $2.3 \times 10^{-5}$ (Na-Montmorillonite, RH = 45 %) | | | |

**Experimental temperature not given, presumably room temperature***.**

### Comments

(a) Continuous flow Knudsen experiments using bulk samples of $CaCO_3$ prepared from an aqueous slurry by allowing $H_2O$ to evaporate under vacuum overnight. The $HC(O)OH$ concentration was $1.9 \times 10^{11}$ molecule $cm^{-3}$. The mass of substrate was varied (≈ 2 –70 mg) to enable a pore diffusion correction to be carried out (all uptake coefficients were derived in this manner). Transmission-FTIR and ATR-FTIR analysis of the substrate were used to obtain mechanistic information.

(b) Bulk samples of Na-montmorillonite prepared from an aqueous slurry. Concentration of $HC(O)OH$ was varied between ~ $2\text{-}30 \times 10^{11}$ molecule $cm^{-3}$. The initial uptake coefficient (based on the BET surface area) obtained in first two seconds of exposure was not influenced by slowly changing surface area due to swelling of the clay mineral at non-zero RH and was independent of the formic acid concentration. FTIR sample analysis indicated that the interaction is (at least in part) irreversible.

### Preferred Values

none.

*Comments on Preferred Values*

Al-Hosney et al. (2005) found dominantly (98 %) irreversible uptake of $HC(O)OH$ to calcite. Time and mass dependent uptake coefficients were observed and a pore diffusion correction was performed to derive the “true” uptake coefficient. The tortuosity coefficient ($\tau$) derived from fitting to the mass dependence of the uptake coefficient was 4, slightly larger than the maximum value of 3 suggested to be acceptable for powder samples (Boulter and Marschall, 2006).

Exposure of dry $CaCO_3$ to ≈ $8 \times 10^{15}$ $HC(O)OH$ resulted in formation of formates and carbonic acid via reaction with $Ca(OH)(HCO_3)$ present on $CaCO_3$ surfaces. Carbonic acid was converted to $CO_2$ in the presence of moisture, which also results in an enhanced capacity for $CaCO_3$ to take up $HC(O)OH$ and an enhanced rate of formate formation. This is explained in terms of surface reorganisation (reactivation) and involvement of underlying layers so that no surface saturation is observed at high relative humidity. Hatch et al. (2007) observed that the initial uptake of formic acid to Na-montmorillonite increased only slightly as RH increased and that the uptake HC(O)OH saturated at calculated coverages that varied between <0.1 and $0.5 \times 10^{14}$ molecule $cm^{-2}$, which are sub-monolayer. Al Hosney et al derived a saturation surface coverage of $\sim 3 \times 10^{14}$ molecules $cm^{-2}$ for $CaCO_3$.

The initial uptake coefficients of formic acid to calcite and Na-montmorillonite are vastly different (factor 100), thus uptake to atmospheric dust would be dominated by the calcite fraction. As the uptake of HC(O)OH to calcite was observed to cease at coverages of $\sim 3 \times 10^{14}$ molecules $cm^{-2}$ the initial uptake coeffcient is not appropriate for modelling the interaction of HC(O)OH and mineral dust in the atmosphere. Assuming $\sim 3 \times 10^{14}$ reactive sites per $cm^2$, and a HC(O)OH mixing ratio of 350 ppt, the initial uptake coefficient would be reduced by a factor of ~ 10 following one hour of exposure. This may be offset by reorganisation of the particle surface at high humidities, but until quantitative kinetic data are available at RH other than zero, we make no recommendation.

## References

Al-Hosney, H. A., Carlos-Cuellar, S., Baltrusaitis, J. and Grassian, V. H.: Phys. Chem. Chem. Phys. 7, 3587-3595, 2005.
Boulter, J. E. and Marschall, J.: J. Phys. Chem. A 110, 10444-10455, 2006.
Hatch, C. D., Gough, R. V. and Tolbert, M. A.: Atmos. Chem. Phys. 7, 4445-4458, 2007.