

IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet V.A2.10

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This datasheet updated: 5th December 2007.

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

Experimental data

<i>Parameter</i>	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: γ</i> $\gamma_0 = 0.3 \pm 0.1$ (dry CaCO ₃)	298 *	Al-Hosney et al., 2006	Knudsen-MS (a)

**Experimental temperature not given, presumably ambient.*

Comments

- (a) Continuous flow Knudsen experiments using bulk samples of CaCO₃ prepared from an aqueous slurry by allowing H₂O to evaporate under vacuum overnight. The HC(O)OH concentration was 1.9×10^{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.

Preferred Values

No recommendation

Comments on Preferred Values

The only study to date is that of Al-Hosney et al. (2005), who found largely (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 (τ) derived from fitting to the mass dependence of the uptake coefficient was 4, somewhat larger than the maximum value of 3 suggested to be acceptable for powder samples (Boulter and Marschall, 2006).

Exposure of dry CaCO₃ to $\approx 8 \times 10^{15}$ HC(O)OH resulted in formation of formates and carbonic acid via reaction with Ca(OH)(HCO₃) present on CaCO₃ surfaces. Carbonic acid was converted to CO₂ in the presence of moisture, which also results in an enhanced capacity for CaCO₃ 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. Although Al-Hosney et al. (2005) state that the rate of reaction is enhanced by water vapour, this observation was derived from experiments using very high HC(O)OH concentrations. It is likely that under atmospheric conditions the rates of deactivation/reactivation are lower, and that the uptake coefficient obtained under dry conditions and lower [HC(O)OH] is more appropriate. However, until this can be confirmed 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.