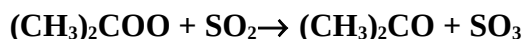


IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet
CGI_18_(CH₃)₂COO + SO₂

Website: <http://www.iupac-kinetic.ch.cam.ac.uk/>. See website for latest evaluated data. Datasheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission. This datasheet created: September 2015; .



(1)

Rate coefficient data

k/cm ³ molecule ⁻¹ s ⁻¹	Temp /K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
(1.32±0.13)× 10 ⁻¹⁰	298	Huang et al., 2015	PLP-LPUVA (a)
$k_1 = \frac{(1.32 \pm 0.02) \times 10^{-10} [M]}{(4.88 \pm 0.32) \times 10^{17} + [M]}$			

Comments

(a) (CH₃)₂COO was generated from pulsed photolysis of a gaseous mixture consisting of 1,1 di-iodoacetone ((CH₃)₂CI₂), O₂, and buffer gas (N₂) at 248 nm (KrF excimer laser) via the established preparation method: (CH₃)₂CI₂ + hν → (CH₃)₂CI + I; (CH₃)₂CI + O₂ → (CH₃)₂COO + IO (2, 30), at 10 - 770 Torr total pressure and 298 K. (CH₃)₂COO was monitored by UV absorption in the region 300 – 450 nm, corresponding to the $\tilde{B}(1A') \leftarrow \tilde{X}(1A')$ electronic transition. A continuous probe light beam multipassed (× 6 to × 8) the long axis of the 76 cm photolysis cell and was detected on a time-gated iCCD spectrometer. (CH₃)₂COO decay kinetics were determined by recording the time-resolved UV absorption spectrum. IO was also detected, [which is formed from “secondary chemistry of the reaction of iodoalkyl radicals with O₂”](#). Linear fit to first order decay plots in presence of varying excess [SO₂] gave the pseudo first order rate constants, k^l; a linear fit to the k^l values vs [SO₂] plots was used to determine the cited value for k₁. The values were independent of total pressure above 100 Torr but at lower pressures the rate constant declined with pressure. This was attributed to participation of an unstable adduct formed in the reaction which can be stabilised by collision with bath gas molecules. The pressure dependence was described by the [empirical](#) expression:

$$k_1 = \frac{(1.32 \pm 0.02) \times 10^{-10} [M]}{(4.88 \pm 0.32) \times 10^{17} + [M]}$$

Preferred Values

Parameter	Value	T/K
k/cm ³ molecule ⁻¹ s ⁻¹	(1.32±0.13)× 10 ⁻¹⁰	298
k/cm ³ molecule ⁻¹ s ⁻¹		

$$\frac{(1.32 \pm 0.02) \times 10^{-10} [M]}{(4.88 \pm 0.32) \times 10^{17} + [M]}$$

Reliability

$\Delta \log k$

0.1

298

Comments on Preferred Values

Quantum chemical studies predict that reaction with SO₂ would first go through a barrierless formation of an energy-rich cyclic intermediate; the near gas-kinetic experimental rate coefficient is consistent with this. The pressure dependence arises from the decomposition of the adduct back to reactants unless collisional stabilisation occurs. In the case of (CH₃)₂COO, the stabilisation is efficient and the adduct proceeds to form products: acetone and SO₃.

The preferred values for (CH₃)₂COO (acetone oxide) reaction with SO₂ are based on the study of Huang et al (2015) which is the only reported direct kinetic study, which used the di-iodide photochemical source of [Criegee Intermediates \(CI\)](#). The rate coefficient at p > 100 Torr is faster than other CI + SO₂ reactions and is exceeded only by the reactions of simple CI with organic acids which are all $\geq 1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. At lower pressure k falls off with pressure; at 10 Torr, $k = 5.6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. However a simple L-H energy transfer model did not give a good fit to the pressure dependence, and the empiracle 'best fit' expression adopted by Huang et al (2015) is accepted in the recommendation. It should not be employed outside the pressure and temperature range. Steady state kinetics studies in which loss of SO₂ (Newlands et al, 2014) and formation of H₂SO₄ (Berndt et al., 2014) were measured give broadly consistent relative rate constants indicating SO₃ formation is the main reaction pathway.

Comments

References

- Liu, F., Beames J. M., Green, A.M., Lester, M. I.; *J. Phys. Chem. A*, 118, 2298, 2014.
 Berndt T., Jokinen, T., Sipila, M., Mauldin III, R.L., Herrmann, H., Stratmann, F., Junninen, H., and Kulmala, M.; *Atmos. Environ.*, 89, 603, 2014.
 Newland, M.J., Rickard, A.R., Alam, M.S., Vereecken, L., Munoz, A., Rodenas, M., and Bloss, W.J.; *Phys. Chem. Chem. Phys.*, 17, 4076, 2015.
 Huang, H-L, Chao, W., and Lin, J Jr.-M., PNAS, early edition, 2015, www.pnas.org/cgi/doi/10.1073/pnas.1513149112
 Vereecken L, Harder H, and Novelli A.; *Phys. Chem. Chem. Phys.*, 14, 14682, 2012.