IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet

CGI_18_$(CH_3)_2COO$ + SO2

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(1) $$(CH_3)_2COO + SO_2 \rightarrow (CH_3)_2CO + SO_3$$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp /K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.32 \pm 0.13) \times 10^{-10}$	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) $(CH_3)_2COO$ was generated from pulsed photolysis of a gaseous mixture consisting of 1,1 di-iodoacetone ($(CH_3)_2CI_2$), O_2, and buffer gas (N_2) at 248 nm (KrF excimer laser) via the established preparation method: $(CH_3)_2CI_2 + h\nu \rightarrow (CH_3)_2CI + I$; $(CH_3)_2CI + O_2 \rightarrow (CH_3)_2COO + IO$ (2, 30), at 10 - 770 Torr total pressure and 298 K. $(CH_3)_2COO$ was monitored by UV absorption in the region 300 – 450 nm, corresponding to the $\tilde{B}$ (1A′) ← $\tilde{X}$(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. $(CH_3)_2COO$ 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 O_2. Linear fit to first order decay plots in presence of varying excess [SO_2] gave the pseudo first order rate constants, k^I; a linear fit to the k^I values vs [SO_2] plots was used to determine the cited value for k_1. 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 stablised 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}	$(1.32 \pm 0.13) \times 10^{-10}$	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 SO_2 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 stablisation occurs. In the case of $(CH_3)_2COO$, the stablisation is efficient and the adduct proceeds to form products: acetone and SO_3

The preferred values for $(CH_3)_2COO$ (acetone oxide) reaction with SO_2 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 + SO_2 reactions and is exceeded only by the reactions of simple CI with organic acids which are all ≥ 1 x 10^{-10} cm^3s^{-1}. At lower pressure k falls off with pressure; at 10 Torr, $k = 5.6 \times 10^{-11}$ cm^3s^{-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 SO_2 (Newlands et al, 2014) and formation of H_2SO_4 (Berndt et al., 2014) were measured give broadly consistent relative rate constants indicating SO_3 formation is the main reaction pathway.

Comments

References

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