This datasheet created: September 2015; last change in preferred values: 2016.

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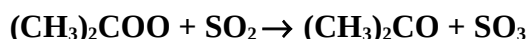
(1)

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp /K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.32 \pm 0.13) \times 10^{-10}$ (k_∞)	298	Huang et al., 2015	PLP-LPUVA (a)
$k_1 = \dfrac{(1.32 \pm 0.02) \times 10^{-10}[M]}{(4.88 \pm 0.32) \times 10^{17} + [M]}$			
$(1.90 \pm 0.19) \times 10^{-10}$ (300 Torr)	283	Smith et al, 2016	PLP-LPUVA (b)
$(1.53 \pm 0.15) \times 10^{-10}$ (300 Torr)	293		
$(1.26 \pm 0.13) \times 10^{-10}$ (300 Torr)	303		
$(0.73 \pm 0.5) \times 10^{-10}$ (4 Torr He)	293	Chhantal Pun et al., 2017	PLP-PIMS (c)
$(1.5 \pm 0.5) \times 10^{-10}$ (10 Torr He)			
$(1.37 \pm 1.2) \times 10^{-10}$ (10 Torr He (CD$_3$)$_2$COO)			
$(2.2 \pm 0.1) \times 10^{-10}$ (k_∞)	293	Chhantal Pun et al., 2017	PLP-CRDS-UVA (c) (c)
$(1.84 \pm 0.12) \times 10^{-10}$ (10 Torr N$_2$)			
$(1.90 \pm 0.07) \times 10^{-10}$ (20 Torr N$_2$)			
$(2.01 \pm 0.25) \times 10^{-10}$ (30 Torr N$_2$)			
$(2.13 \pm 0.03) \times 10^{-10}$ (40 Torr N$_2$)			
$(2.15 \pm 0.05) \times 10^{-10}$ (50 Torr N$_2$)			
$(2.29 \pm 0.08) \times 10^{-10}$ (75 Torr N$_2$)			
$(2.24 \pm 0.06) \times 10^{-10}$ (100 Torr N$_2$)			

Comments

(a) (CH$_3$)$_2$COO was generated from pulsed photolysis of a gaseous mixture consisting of 2,2 di-iodopropane ((CH$_3$)$_2$CI$_2$), O$_2$, and buffer gas (N$_2$) at 248 nm , at 10 - 770 Torr total pressure and 298 K. (CH$_3$)$_2$COO was monitored by UV absorption in the region 300 – 450 nm, corresponding to the $\tilde{B}$ (1A′) ← $\tilde{X}$(1A′) electronic transition. (CH$_3$)$_2$COO decay kinetics were determined by recording the time-resolved UV absorption spectrum, after correction for other absorbers. IO, which is formed from

secondary chemistry of the reaction of iodoalkyl radicals with O_2, was also detected. The rate coefficients obtained 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 (activated complex ??) formed in the reaction which can be stablised by collision with bath gas molecules. However a simple L-H energy transfer model did not give a good fit to the pressure dependence, and the authors they gave an empirical 'best fit' expression which is cited in the table, together with a value for the high pressure limiting value, (k_∞).

(b) $(CH_3)_2COO$ was generated from pulsed photolysis of a gaseous mixture consisting of 2,2- diiodopropane, $(CH_3)_2CI_2$, O_2, and buffer gas (N_2) at 248 nm At a total pressure of 395 mbar. $(CH_3)_2COO$ was monitored by time-resolved UV absorption at 340 nm. The amount of $(CH_3)_2COO$ formed was estimated using a cross-section $\sigma = 1.6 \times 10^{-17}$ cm^2 at 340 nm. The values of k^{II} at 396mbar exhibited a weak negative temperature dependence, (E/R = 1761 K).

(c) $(CH_3)_2COO$ was formed by laser photolysis of 2,2- diiodopropane in the presence of O_2 and characterized by synchrotron photoionization mass spectrometry (He buffer gas) and by cavity ring-down ultraviolet absorption spectrometry (N_2 buffer gas). The CRD measurement of the rate coefficient at 293 K and slightly higher pressures (between 10 Torr and 100 Torr in N_2) yielded even larger rate coefficients, in the range $(1.84 \pm 0.12) \times 10^{-10}$ to $(2.29 \pm 0.08) \times 10^{-10}$ cm^{3}s^{-1}.

Preferred Values

Parameter	Value	T/K
k_∞/cm^3 molecule^{-1} s^{-1}	4.2×10^{-13} exp(1761/T)	280 – 310
k (M) (<100Torr)	$\dfrac{1.5 \times 10^{-10}[M]}{4.9 \times 10^{17} + [M]}$	298

Reliability

$\Delta \log k_\infty$	0.15	298
Δ (E/R)	500 K	280 - 303

Comments on Preferred Values

The preferred values for $(CH_3)_2COO$ (acetone oxide) reaction with SO_2 are based on the studies of Huang et al (2015), Smith et al (2016) and Chhantyal-Pun et al (2017), in which the rate coefficients were measured by direct kinetic methods. At pressures above ~100 Torr the rate constant is independent of pressure and there is reasonable consistency in the results from the three studies. The temperature dependence is that reported by Smith et al 2016. The recommended value for k_∞ is the average from the 3 studies, corrected for temperature differences using the Arrhenius expression from Smith et al. (see Fig 1). However, rate coefficients measured by Chhantyal-Pun et al., using both cavity ring-down and photoionization methods, are larger than measurements at similar conditions reported by Huang et al. and Smith et al.; this is reflected in the uncertainty indicated in the stated $\Delta \log k_\infty$ value.

Huang et al. (2015) report a decrease in the rate coefficient for this reaction with decreasing pressure below about 100 Torr (N_2/O_2 buffer). The measurement of Chhantyal-Pun et al (using PIMS) at 4 Torr He, ($k = (7.3 \pm 0.5) \times 10^{-11}$ cm^3 s^{-1}), is similar to Huang et al.'s measurement at 20 Torr N_2, $(7.0 \pm 0.4) \times 10^{-11}$ cm^3 s^{-1}). PIMS measurements at 10 Torr yield a larger rate coefficient, $(1.5 \pm 0.5) \times 10^{-10}$ cm^3 s^{-1}, which agrees within <u>combined</u> uncertainties with the value of $(1.84 \pm 0.12) \times 10^{-10}$ cm^3 s^{-1}), obtained at 10 Torr N_2 using the cavity ring-down method. As this reaction shows pressure dependence a difference in energy transfer efficiency between He and N_2 may account for these differences in k at 10 Torr. The recommend<u>ed</u> expression for the pressure dependence uses the <u>empirical</u> formulation of Huang et al, with adjustment of the parameters to force the expression to give the mean value of k_∞ in the pressure independent region at 298K.

Measurements of k at 4 Torr of the reaction $(CD_3)_2COO + SO_2$ using PIMS, show an inverse kinetic isotope effect with the deuterated rate coefficient, $(1.37 \pm 0.12) \times 10^{-10}$ cm^3 s^{-1}, approximately twice the rate coefficient for the undeuterated reaction. This inverse kinetic isotope effect, $k_H/k_D = 0.53 \pm 0.06$, could reflect more effective collisional stabilization of the deuterated association complex because of the increased density of vibrational states. At 10 Torr total pressure, measurements were also taken at high photon energies (13 eV) to follow the formation of SO_3 product. The rise time of the SO_3 agrees reasonably well with the observed decay of $(CH_3)_2COO$ confirming that SO_3 is a direct product of the reaction of $(CH_3)_2COO$ with SO_2. 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 in the ozonolysis of tetramethyl ethylene, give broadly consistent relative rate constants indicating SO_3 formation is the main reaction pathway.

Quantum chemical studies predict that reaction with SO_2 would first go through a barrierless formation of an energy-rich cyclic intermediate (Vereecken et al 2014); 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 overall rate coefficients are similar in magnitude to directly measured rate coefficients of anti-CH_3CHOO with SO_2, indicating a similar mechanism is involved.

References

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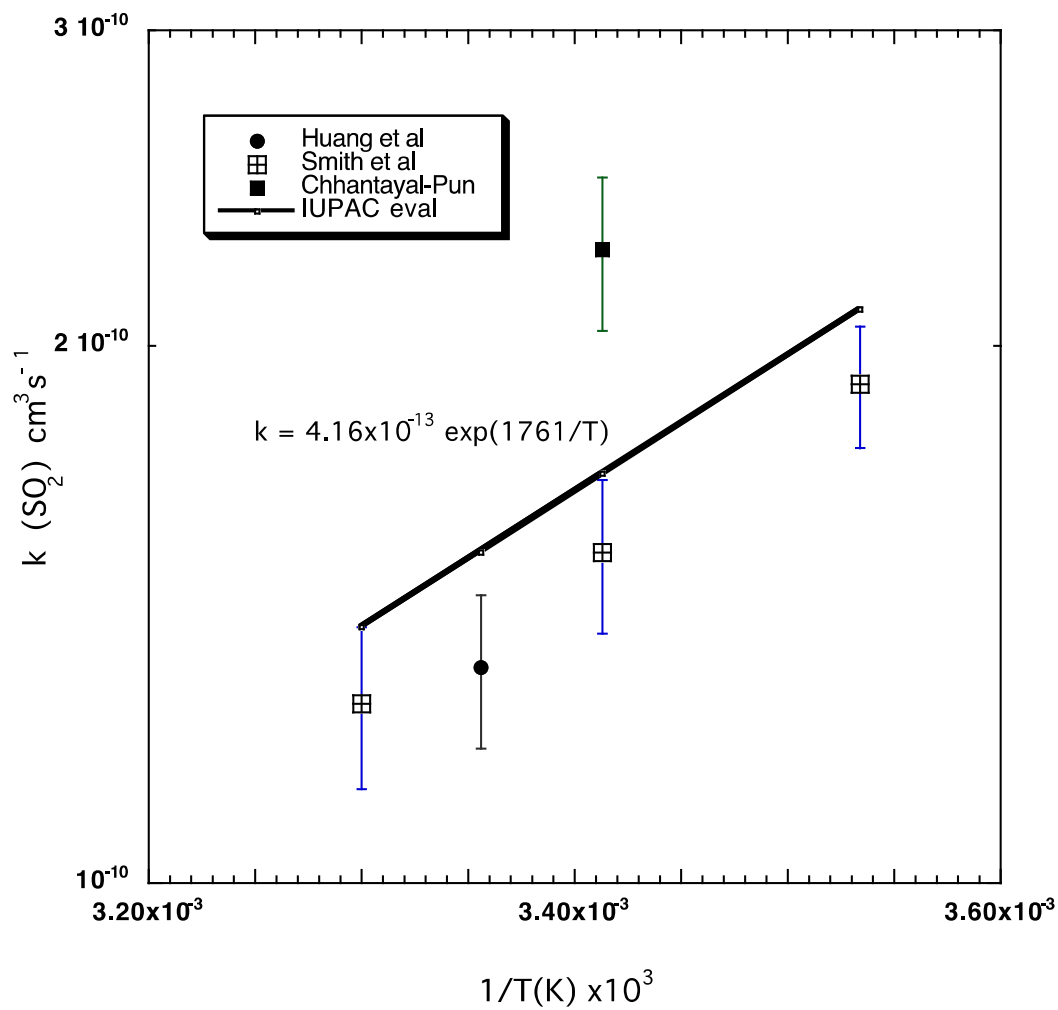
Fig 1: Temperature dependence of limiting high pressure rate constants k_∞ for reaction: $(CH_3)_2COO + SO_2$. Line shows IUPAC recommended Arrhenius expression for $k(T)$, based on results of Smith et al, 2016.
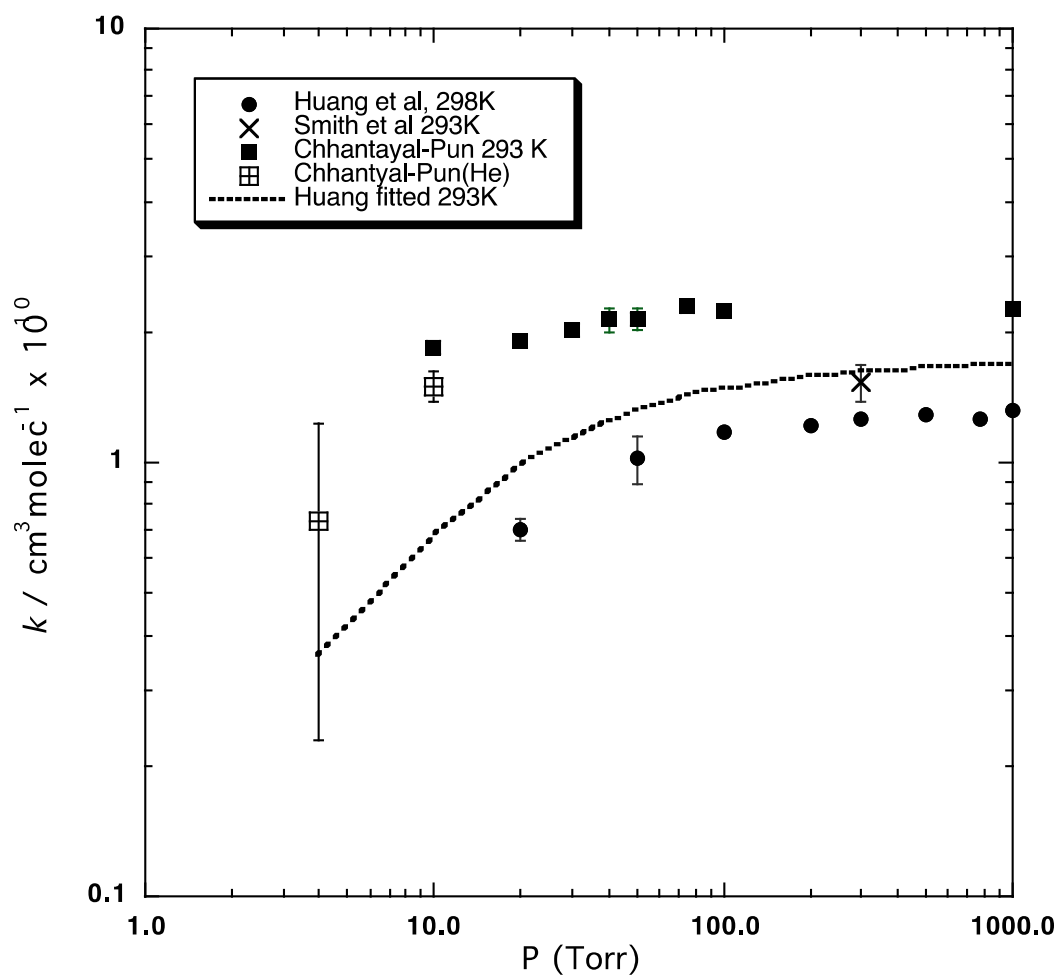
Fig 2: Pressure dependence of rate constants for $(CH_3)_2COO + SO_2$. Line shows IUPAC recommended for k(p) at 298 K, based on results of Smith et al, 2016.