$$HO + CH_3O_2 \quad \rightarrow CH_3O + HO_2 \qquad (1)$$
$$\rightarrow CH_2O_2 + H_2O \qquad (2)$$
$$\rightarrow CH_3OH + O_2 \qquad (3)$$
$$+ M \rightarrow CH_3OOOH + M \qquad (4)$$

Rate coefficient data ($k = k_1 + k_2 + k_3 + k_4 + k_5$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	*Reference*	Technique/ Comments
Absolute Rate Coefficients			
$(2.8 \pm 1.4) \times 10^{-10}$	294	Bossolasco et al., 2014	LP-LIF/CRD (a)
$(1.6 \pm 0.4) \times 10^{-10}$	295	Assaf et al., 2016	LP-LIF/CRD (b)
$8.4 \times 10^{-11} (T/298)^{-0.81}$	292-526	Yan et al., 2016	LP-UV (c)
$(8.2 \pm 1.4) \times 10^{-11}$	292		
Branching Ratios			
$k_2 / k < 0.05$	298	Yan et al., 2016	LP-UV (c)
$k_2 / k < 0.05$	295	Assaf et al., 2017	(d)
$k_1 / k = 0.8 \pm 0.2$			

Comments

(a) HO was generated by the 248 nm photolysis of H_2O_2 or O_3 / H_2O, and detected by LIF. CH_3O_2 (excess reactant) was generated by the photolysis of CH_3I in the presence of O_2 and detected by CW- CRDS. This method generates I atoms at the same concentration as CH_3O_2 Bath gas was He and no pressure dependence (67 or 133 mbar) was observed.

(b) All experiments were carried out in 67 mbar He. F atoms (from 248 nm photolysis of XeF_2) reacted with H_2O and CH_4 / O_2 to generate OH and CH_3O_2, respectively. CH_3O_2 ($1-12 \times 10^{12}$ molecule cm^{-3}) was monitored by CRDS, OH ($0.2-38 \times 10^{11}$ molecule cm^{-3}) by LIF.

(c) All experiments were carried out in ≈ 1000 mbar He. 193 nm photolysis of $CH_3(O)CH_3$ / O_2 and N_2O / H_2O was used to generate CH_3O_2 and OH, respectively. Initial radical densities ($0.4-3.7 \times 10^{14}$ molecule cm^{-3} for CH_3 and $4.9-109 \times 10^{12}$ molecule cm^{-3} for HO) were calculated using 193 nm actinometry by observing O_3 formation from photolysis of O_2. The transient absorption of HO was observed at ≈ 308 nm, that of CH_3O_2 at 253.7 nm.

(d) LP-CRD as in comment (b). Sequential CRD detection of HO and HO_2 in back-to-back experiments, both measured simultaneously with CH_3O_2. All experiments were carried

out in 67 mbar He. Broadband cavity enhanced UV spectroscopy (300-450 nm) was used to detect CH_2O_2.

Preferred Values

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.2×10^{-10}	298
k /cm^3 molecule^{-1} s^{-1}	$3.7 \times 10^{-11} \exp(350/T)$	290-530

Reliability

$\Delta \log k$	± 0.3	298
$\Delta E/R$	± 200	290-530

Comments on Preferred Values

There is poor agreement in the three studies of the OH + CH_3O_2 reaction. The first study of this reaction (Bossolasco et al., 2014) reported the largest rate coefficient which was then superseded by a similar study by the same group (Assaf et al., 2016), who reported a value which is lower by a factor 1.75. The early result was suggested to be biased through OH reaction (vibrational energy transfer) with excited I atoms, $I(^2P_{1/2})$, occurring at near collision frequency, though this remains unproven. Both of these studies relied on measurement of the CH_3O_2 concentration via its IR-absorption at 7489.16 cm^{-1} using a cross section of $(3.4 \pm 0.4) \times 10^{-20}$ cm^2 molecule^{-1}. The cross-section was derived from analysis of CH_3O_2 decays kinetics using the rate constant for the self-reaction (Assaf et al., 2016) and is in poor agreement with other literature determinations of the cross-section, which were a factor of two to three lower. In the study of Yan et al., (2016) the rate coefficient was extracted from transient absorption measurements at multiple wavelengths by numerical simulation of a complex mechanism. The authors calculated that the effect of varying critical rate coefficients in the mechanism within their error bounds was to change the derived rate coefficient for HO + CH_3O_2 by just 5%. However, given that the spread in rate coefficients obtained at room temperature is 6.3 to 10.5×10^{-11} cm^3 molecule^{-1} s^{-1} the overall uncertainty is clearly larger than this.
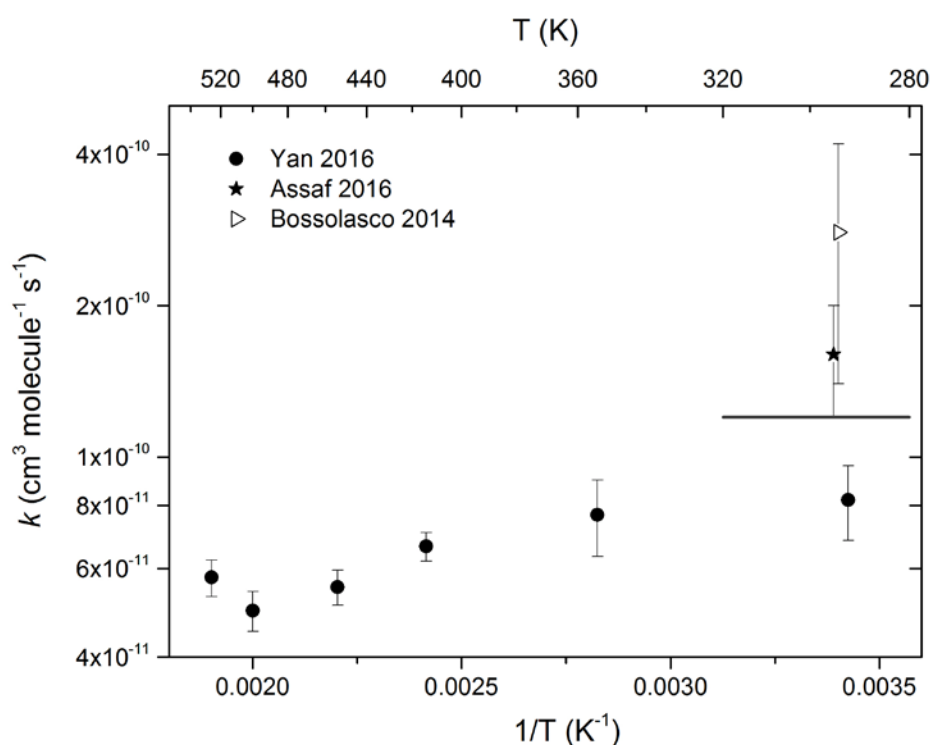
The preferred rate coefficient at 298 K is the average of the studies of Assaf et al (2016) and Yan et al., (2016), with expanded uncertainty. The temperature dependence of the reaction was measured by Yan et al., (2016) in the range 290 to 530 K. As their rate coefficients at 290 and 360 K are, within error bounds identical, we recommend use of the room temperature value for atmospheric modelling.

Both Yan et al., (2016) and Assaf et al (2017) used the absorption spectrum of CH_2O_2 to examine its possible formation. In neither case was CH_2O_2 observed and, following numerical simulation and estimation of errors in cross sections, both set an upper limit of 0.05 for k_2 / k. Measurements of HO_2 formation consistent with the kinetics of its direct and indirect formation (via $CH_3O + O_2$) in channel (1) enabled Assaf et al. (2016) to derive a branching ratio of 0.8 ± 0.2 for k_1 / k. The product studies are in broad agreement with theoretical work (Bian et al, 2015, Müller et al., 2016) which indicates that the reaction proceeds via an activated trioxide association complex that dissociates to CH_3O and HO_2 (channel 1). Formation of CH_2O_2 (channel 2) was found to be insignificant.

Müller et al. (2016) also suggest that weak but significant branching to reactions (3) and (4) is possible, their calculations indicating branching ratios of $k_3/k = 0.07$ and $k_4/k = 0.1$ at atmospheric pressure, though the associated uncertainties are estimated as a factor of ≈ 3.5. Further experimental studies are required to 1) reduce the uncertainty in the rate coefficients, 2) extend the temperature range to those relevant for the atmosphere and 3) to quantify product formation via reactions (3) and (4).

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$k(OH + CH_3O_2)$. The horizontal, solid line represents the IUPAC preferred values.