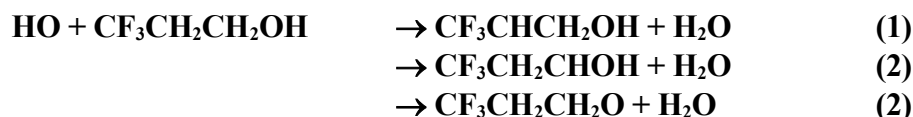


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet of FOx87; VII.A5.4

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(0.89 \pm 0.03) \times 10^{-12}$	298	Kelly et al. (2005)	PLP-LIF (a)
$(0.97 \pm 0.11) \times 10^{-12}$	298	Jimenez et al. (2010)	PLP-LIF (b)
$2.82 \times 10^{-12} \exp[-(302 \pm 139)/T]$	263-358	Antinolo et al. (2011)	PLP-LIF (c)
$(1.03 \pm 0.11) \times 10^{-12}$	287		
<i>Relative Rate Coefficients</i>			
$(1.06 \pm 0.04) \times 10^{-12}$	298	Kelly et al. (2005)	RR (d)
$(1.05 \pm 0.05) \times 10^{-12}$			RR (d)
$(1.43 \pm 0.03) \times 10^{-12}$			RR (d)
$(0.68 \pm 0.07) \times 10^{-13}$	296	Hurley et al (2005)	RR (e)
$(0.70 \pm 0.08) \times 10^{-13}$			RR (e)

Comments

- (a) HO radicals were generated by the 248 nm (KrF eximer laser) photolysis of H_2O_2 in 100 Torr (133 mbar) of helium diluent at 298 K.
- (b) HO radicals were produced by 248 nm (KrF eximer laser) photolysis of H_2O_2 in 47-211 Torr (63-281 mbar) of helium diluent at 298 K. HO radicals were monitored by LIF.
- (c) HO radicals were produced by 248 nm (KrF eximer laser) photolysis of H_2O_2 in 46-95 Torr (61-127 mbar) of helium diluent at 263-358 K. HO radicals were monitored by LIF.
- (d) HO radicals were generated by the 254 nm (Hg lamp) photolysis of either H_2O_2 or O_3 (in the presence of H_2O vapor) in one atmosphere of air. Rate coefficient ratios of $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CH}_2\text{OH})/k(\text{HO}+\text{HC}(\text{O})\text{OC}_4\text{H}_9) = 0.30 \pm 0.01$, $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CH}_2\text{OH})/k(\text{HO}+n\text{-hexane}) = 0.20 \pm 0.01$, and $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CH}_2\text{OH})/k(\text{HO}+\text{CF}_3\text{CH}_2\text{OH}) = 0.95 \pm 0.02$ were determined. Placing these ratios on an absolute basis using $k(\text{HO}+\text{HC}(\text{O})\text{OC}_4\text{H}_9) = 3.54 \times 10^{-12}$ (Le Calvé et al., 1997), $k(\text{HO}+n\text{-hexane}) = 5.27 \times 10^{-12}$ (Calvert et al., 2008), and $k(\text{HO}+\text{CF}_3\text{CH}_2\text{OH}) = 1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2009) gives $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CH}_2\text{OH}) = (1.06 \pm 0.04) \times 10^{-12}$, $(1.05 \pm 0.05) \times 10^{-12}$, and $(1.43 \pm 0.03) \times 10^{-12}$, respectively.
- (e) HO radicals were generated by the photolysis of CH_3ONO in 700 Torr (933 mbar) of air. Rate coefficient ratios of $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CH}_2\text{OH})/k(\text{HO}+\text{C}_2\text{H}_2) = 0.87 \pm 0.09$ and $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CH}_2\text{OH})/k(\text{HO}+\text{C}_2\text{H}_4) = 0.089 \pm 0.010$ were reported. Using $k(\text{HO}+\text{C}_2\text{H}_2) = 7.8 \times 10^{-13}$ and $k(\text{HO}+\text{C}_2\text{H}_4) = 7.9 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CH}_2\text{OH}) = (6.79 \pm 0.70) \times 10^{-13}$ and $(7.03 \pm 0.79) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	9.6×10^{-13}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$2.72 \times 10^{-12} \exp(-305/T)$	250-430
<i>Reliability</i>		
$\Delta \log k$	0.10	298
$\Delta E/R$	± 100	260-460

Comments on Preferred Values

There is significant scatter in the room temperature rate coefficients reported in the relative rate studies by Kelly et al. (2005) and Hurley et al. (2005). The room temperature rate coefficients reported in the absolute rate studies by Kelly et al. (2005) and Jiménez et al. (2010) are in good agreement. The absolute rate determinations at 298 K by Kelly et al. (2005) and Jiménez et al. (2010) lie in the center of the scatter in the results from the relative rate studies of Kelly et al. (2005) and Hurley et al. (2005). The recommended rate coefficient at 298 K is an average from the results of the absolute rate studies by Kelly et al. (2005) and Jiménez et al. (2010). An interpolation of the absolute rate data at 263 – 358 K reported by Antinolo et al. (2011) is in good agreement with the recommended rate coefficient at 298 K. The recommended temperature dependence is taken from a fit to the data from Antinolo et al. (2011). The A factor has been adjusted to be consistent with the recommended rate coefficient at 298K. The majority of reaction is believed to occur via hydrogen abstraction from the $-\text{CH}_2-$ group bearing the alcohol functionality (Calvert et al., 2010). Subsequent reaction of the $\text{CF}_3\text{CH}_2\text{CHOH}$ with O_2 will give $\text{CF}_3\text{CH}_2\text{CHO}$. The HO radical initiated oxidation of $\text{CF}_3\text{CH}_2\text{CH}_2\text{OH}$ is expected to give $\text{CF}_3\text{CH}_2\text{CHO}$ in a yield close to 100%. Consistent with this expectation, Hurley et al. (2005) observed the formation of $\text{CF}_3\text{CH}_2\text{CHO}$ as the sole product of the chlorine atom initiated oxidation of $\text{CF}_3\text{CH}_2\text{CH}_2\text{OH}$ in one atmosphere of air.

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