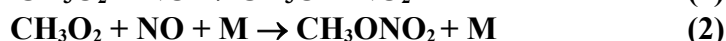


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet II.A6.120 ROO\_1

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This data sheet last evaluated: June 2013; last change in preferred values: July 2005.



$$\Delta H^\circ (1) = -48.8 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ (2) = -218.3 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(8.0 \pm 2.0) \times 10^{-12}$	295	Plumb et al., 1979	DF-MS (a)
$(3.0 \pm 1.7) \times 10^{-12}$	298	Adachi and Basco, 1979	FP-AS
$(7.1 \pm 1.4) \times 10^{-12}$	298	Sander and Watson, 1980	FP-AS (b)
$(6.5 \pm 2.0) \times 10^{-12}$	298	Cox and Tyndall, 1979 / 1980	MMS-AS (c)
$(8.1 \pm 1.6) \times 10^{-12}$	240-339	Ravishankara et al., 1981	LP-LIF (d)
$2.1 \times 10^{-12} \exp[(380 \pm 250)/T]$	218-365	Simonaitis and Hecklen, 1981	FP-AS (e)
$(7.7 \pm 0.9) \times 10^{-12}$	298		
$(8.6 \pm 2.0) \times 10^{-12}$	295	Plumb et al., 1981	DF-MS (f)
$(7 \pm 2) \times 10^{-12}$	298	Zellner et al., 1986	LP-AS (g)
$(8.8 \pm 1.4) \times 10^{-12}$	295	Sehested et al., 1993	PR-UV (h)
$(11.2 \pm 1.4) \times 10^{-12}$	298	Masaki et al., 1994	LP-MS (i)
$2.8 \times 10^{-12} \exp[(285 \pm 60)/T]$	199-429	Villalta et al., 1995	F-CIMS (j)
$(7.5 \pm 1.3) \times 10^{-12}$	298		
$(7.5 \pm 1.0) \times 10^{-12}$	298	Helleis et al., 1996	DF-MS (k)
$9.2 \times 10^{-13} \exp[(600 \pm 140)/T]$	203-295	Scholtens et al., 1999	F-CIMS (l)
$(7.8 \pm 2.2) \times 10^{-12}$	298		
$1.75 \times 10^{-12} \exp[(435 \pm 35)/T]$	193-300	Bacak et al., 2004	F-CIMS (m)
$(7.42 \pm 0.27) \times 10^{-12}$	298		
$(9.9 \pm 2.1) \times 10^{-12}$	298	Xing et al., 2004	LP-MS (n)
<i>Branching ratios</i>			
$k_2/k < 0.003$ (100 Torr)	295	Scholtens et al., 1999	F-CIMS (l)
$k_2/k = 0.0039 \pm 0.0011$ (100 Torr)	298	Butkovskaya et al., 2012	DF-CIMS (o)
$k_2/k$ (P) see below	223-298		

## Comments

- (a) Flow tube at  $11 \pm 2.6$  mbar He. Direct detection of  $\text{CH}_3\text{O}_2$  (generated in  $\text{O} + \text{C}_2\text{H}_4 + \text{O}_2$ ) via electron impact mass spectrometry.
- (b) Data obtained at 100, 467 and 933 mbar He, and 933 mbar  $\text{N}_2$ .  $\text{CH}_3\text{O}_2$  formed by  $\text{Cl} + \text{CH}_4 + \text{O}_2$ .
- (c) Data obtained at 720 mbar  $\text{N}_2 / \text{O}_2$ .  $\text{CH}_3\text{O}_2$  formed by  $\text{Cl} + \text{CH}_4 + \text{O}_2$ .
- (d)  $\text{CH}_3\text{O}_2$  generated by photolysis of  $\text{CH}_3\text{N}_2\text{CH}_3$  in presence of  $\text{O}_2$ . Rate data obtained via LIF detection of  $\text{NO}_2$ .
- (e) Pressures of 93 to 800 mbar  $\text{CH}_4$ .  $\text{CH}_3\text{O}_2$  formed by  $\text{Cl} + \text{CH}_4 + \text{O}_2$ .
- (f) Flow tube at 7.7 mbar He, direct detection of  $\text{CH}_3\text{O}_2$  (generated in  $\text{Cl} + \text{CH}_4 + \text{O}_2$ ) via electron impact mass spectrometry.
- (g) Experiments conducted at 13.3 mbar He or  $\text{N}_2$ .  $\text{CH}_3\text{O}_2$  generated by photolysis of  $\text{CH}_3\text{N}_2\text{CH}_3$  in presence of  $\text{O}_2$ . Rate data obtained by measuring  $\text{CH}_3\text{O}_2$  by absorption spectroscopy, LIF used to observe formation of  $\text{CH}_3\text{O}$ .
- (h) Experiments conducted in 1013 mbar  $\text{SF}_6/\text{O}_2$ .  $\text{CH}_3\text{O}_2$  generated in  $\text{F} + \text{CH}_4 (+\text{O}_2)$  and  $\text{NO}_2$  formation monitored to derive kinetic information.
- (i) Experiments conducted in 4–8 mbar  $\text{N}_2/\text{O}_2$ . Mass spectrometry using photo-ionisation detection of  $\text{CH}_3\text{O}_2$ , which was formed in the 193 nm photo-dissociation of acetone in the presence of  $\text{O}_2$ .
- (j) Experiments conducted in 2.7- 7.3 mbar He.  $\text{CH}_3\text{O}_2$  generated by thermal decomposition of  $\text{CH}_3\text{CH}_2\text{ONO}$  in the presence of  $\text{O}_2$ . Mass spectrometry using chemi-ionisation detection of  $\text{CH}_3^+$  generated in  $\text{O}_2^+ + \text{CH}_3\text{O}_2$ .
- (k) Experiments conducted in 2.3 mbar He,  $\text{CH}_3\text{O}_2$  generated in  $\text{F} + \text{CH}_4 (+\text{O}_2)$ . Electron impact detection of  $\text{CH}_3\text{O}_2$  in excess  $\text{NO}$ . Measurements using deuterated methyl peroxy gave  $k(\text{CD}_3\text{O}_2 + \text{NO}) = (8.6 \pm 1.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.
- (l) Turbulent flow reactor at 133 mbar  $\text{N}_2$  total pressure.  $\text{CH}_3\text{O}_2$  generated in  $\text{F} + \text{CH}_4 (+\text{O}_2)$  and detected as  $\text{CH}_3\text{OOH}^+(\text{H}_2\text{O})_n$  following proton transfer from  $\text{H}_3\text{O}^+$ .
- (m) Turbulent flow reactor at 133 or 266 mbar  $\text{N}_2$  total pressure.  $\text{CH}_3\text{O}_2$  generated in  $\text{F} + \text{CH}_4 (+\text{O}_2)$  and detected as  $\text{FO}_2^-$  following reaction with  $\text{SF}_6^-$ . Yield of  $\text{NO}_2$  was found to be  $1 \pm 0.1$  at 298 K.
- (n)  $\text{CH}_3\text{O}_2$  generated by reaction of  $\text{CH}_3$  with  $\text{O}_2$ , whereby  $\text{CH}_3$  radicals were generated in the 193 nm photolysis of  $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ , or the 248 nm photolysis of  $\text{CH}_3\text{I}$ . The data obtained using  $\text{CH}_3\text{I}$  are reported to be more reliable.  $\text{CH}_3\text{O}_2$  was detected as the negative parent ion following electron transfer from high Rydberg state rare gas atoms. The bath gas was 5.3 mbar (He) and 2.7 mbar  $\text{O}_2$ .
- (o) Turbulent flow reactor operated at pressures between 50 and 500 Torr  $\text{N}_2$  at 298 K and at temperatures between 223 and 298 K at 100 or 200 Torr  $\text{N}_2$ .  $\text{CH}_3\text{O}_2$  was generated in the reaction of  $\text{CH}_3$  (from  $\text{F} + \text{CH}_4$ ) with  $\text{O}_2$ .  $\text{CH}_3\text{ONO}_2$  was detected following  $\text{H}^+$  or  $\text{D}^+$  transfer from  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  or  $\text{D}_3\text{O}^+(\text{D}_2\text{O})_n$ . Branching ratios to  $\text{CH}_3\text{ONO}_2$  formation were calculated from formation rates of  $\text{CH}_3\text{ONO}_2$  relative to  $\text{HCHO}$  and/or  $\text{CH}_3\text{ONO}$  which are the end products from further reactions of  $\text{CH}_3\text{O}$  (channel 1) with  $\text{O}_2$  and  $\text{NO}$ .

## Preferred Values

$k = 7.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 2.3 \times 10^{-12} \exp(360/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200 K to 430 K.

### Reliability

$\Delta \log k = \pm 0.05$  at 298 K.

$\Delta(E/R) = \pm 100$  K.

### Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$7.7 \times 10^{-12}$	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$2.3 \times 10^{-12} \exp(360/T)$	200-430

### Reliability

$\Delta \log k$	$\pm 0.05$	298
$\Delta(E/R)$	$\pm 100$	200-500

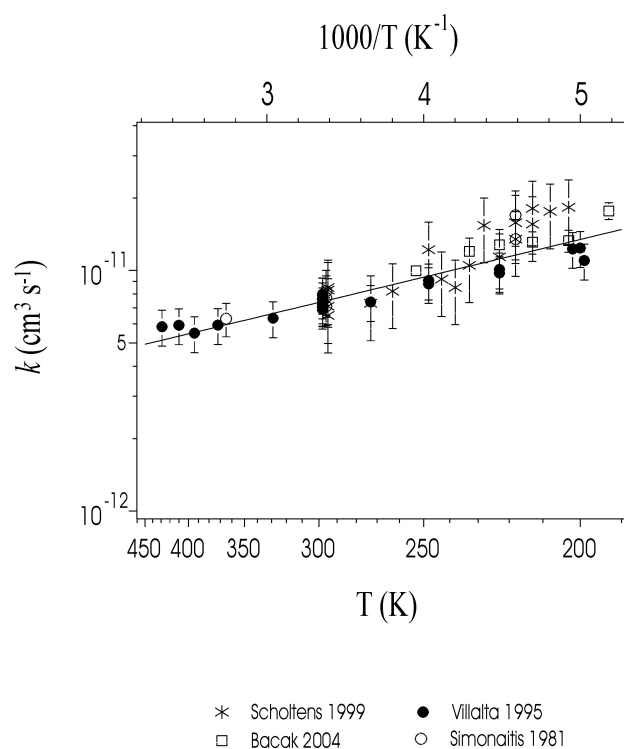
### Comments on Preferred Values

This reaction has been subject of intensive investigation using several different experimental techniques. With the exception of the data of Adachi and Basco (1979), Masaki et al. (1994) and Xing et al. (2004), the remaining eleven datasets at room temperature are in good agreement. The recommended value of the rate coefficient at 298 K is the average of the results from Scholtens et al. (1999), Helleis et al. (1996), Villalta et al. (1995), Ravishankara et al. (1981) and Bacak et al. (2004). The temperature dependence of the rate coefficient is described by four sets of data which are in good agreement at temperatures above 230 K. At lower temperatures there is some deviation, with the datasets of Scholtens et al. (1999) and Simonaitis and Hecklen (1981) deviating from Arrhenius behaviour. These data sets were obtained at higher pressures than that of Villalta et al. (1995) and the possibility of a pressure dependence in the rate coefficient at low temperatures has been discussed (Scholtens et al., 1999). The latest data on this reaction (Bacak et al., 2004) do not, however, support this. The datasets of Villalta et al. (1999) and Bacak et al. (2004) which cover the largest temperature range, provide the basis of the recommended temperature dependence, which has been adjusted for the average 298 K rate coefficient.

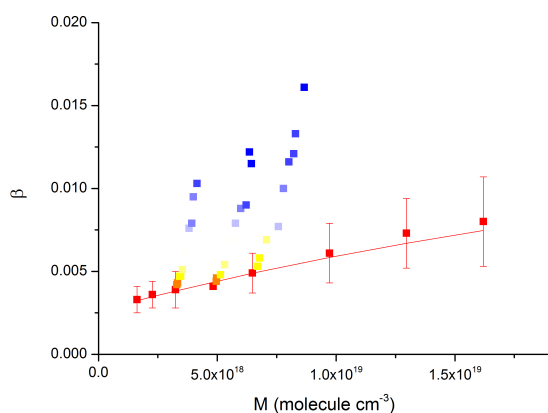
The  $\text{CH}_3\text{O}$  and  $\text{NO}_2$  products of channel (1) are formed at yields close to unity (Ravishankara et al., 1981; Zellner et al., 1986; Bacak et al., 2004). Butkovskaya et al. (2012) measured  $\text{CH}_3\text{ONO}_2$  yields ( $\beta = k_2/k$ ) between 0.0033 and 0.016, which were largest at high pressures and low temperatures, consistent with  $\text{CH}_3\text{ONO}_2$  formation in a termolecular reaction. Their yield of  $0.0039 \pm 0.0011$  at 100 Torr  $\text{N}_2$  and 295 K is consistent with the upper limit of 0.03 determined by Scholtens et al. (1999). Butkovskaya et al. did not provide a parameterisation of their branching ratios but a simple expression,  $\beta(T,P) = \beta_0\beta_\infty/(\beta_0 + \beta_\infty)$ , with  $(\beta_\infty) = 0.022$  and  $\beta_0 = 0.00295 + 5.15 \times 10^{-22} M^*(T/298)^{7.4}$  adequately reproduces their dataset. Further data is necessary to confirm the formation of  $\text{CH}_3\text{ONO}_2$  at these yields, identify the origin of an apparent non-zero  $\text{CH}_3\text{ONO}_2$  yield at zero pressure and to derive the pressure dependence at low temperatures to enable more detailed fall-off expressions to be used. Finally, we note that the branching ratios measured by Butkovskaya et al. (2012) at low temperature and pressure are at least an order of magnitude larger than those derived from field-observations in the lower stratosphere (Flocke et al., 1998) or theory (Barker et al., 2003).

## References

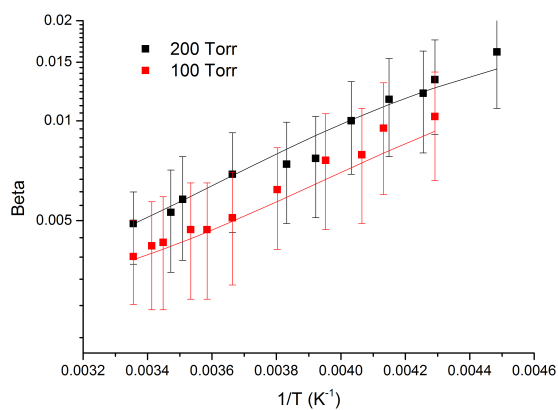
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Temperature dependence of  $k$ . Solid line represents the IUPAC preferred values



Pressure dependence of  $\beta$  at 298 K (red data points). The solid line is from the parameterisation above. The temperature dependence, colour coded from 223 (blue) to 298 K (red) was investigated at 100, 150 and 200 Torr  $N_2$ .



Temperature dependence of  $\beta$  at 100 Torr (red data points) and 200 Torr (blue data points). The solid line represents the parameterised branching ratio using the expression above and the low- and high-pressure limiting values given in the text.