

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet O_x_VOC5

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This data sheet last evaluated: December 17th 2007 (with no revisions to the preferred values).

O₃ + C₂H₄ → products

Rate coefficient data

<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
3.3 x 10 ⁻¹⁵ exp[-(2365 ± 101)/ <i>T</i>]	178-233	DeMore, 1969	S-UVA (a)
1.18 x 10 ⁻¹⁸	298*		
(1.55 ± 0.15) x 10 ⁻¹⁸	299	Stedman et al., 1973	S-CL (b)
9.00 x 10 ⁻¹⁵ exp[-(2557 ± 167)/ <i>T</i>]	235-362	Herron and Huie, 1974	(c)
1.69 x 10 ⁻¹⁸	298		
(1.9 ± 0.1) x 10 ⁻¹⁸	299	Japar et al., 1974	S-CL (b)
(1.9 ± 0.1) x 10 ⁻¹⁸	299	Japar et al., 1976	S-CL (b)
(1.69 ± 0.13) x 10 ⁻¹⁸	303	Toby et al., 1976	S-UVA (a)
(1.43 ± 0.19) x 10 ⁻¹⁸	296	Atkinson et al., 1982	S-CL (b)
7.72 x 10 ⁻¹⁵ exp[-(2557 ± 30)/ <i>T</i>]	232-298	Bahta et al., 1984	S-UVA (a)
(1.45 ± 0.10) x 10 ⁻¹⁸	298		
5.1 x 10 ⁻¹⁵ exp[-(2446 ± 91)/ <i>T</i>]	240-324	Treacy et al., 1992	S-CL (b)
(1.37 ± 0.08) x 10 ⁻¹⁸	298		

Comments

- (a) Static system, with UV absorption detection of O₃ at 253.7 nm.
- (b) Static system with chemiluminescence detection of O₃.
- (c) Stopped flow system with MS detection of O₃. Carried out at a total pressure of ~5 mbar but with sufficient O₂ present to minimize the occurrence of secondary reactions removing O₃.

Preferred Values

$k = 1.6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 9.1 \times 10^{-15} \text{ exp}(-2580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 180-360 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

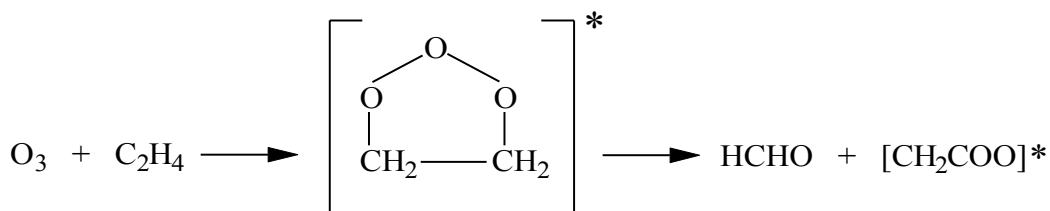
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The temperature dependent kinetic studies of Bahta et al. (1984) and Treacy et al. (1992) are in good agreement. These two studies (Bahta et al., 1984; Treacy et al., 1992) result in rate coefficients which are somewhat lower than many of the previous determinations, including those of Su et al. (1980) and Kan et al. (1981) which are not used in this evaluation. Since Treacy et al. (1992) did not tabulate the individual rate coefficients at the various temperatures studied, only their 298 K value can

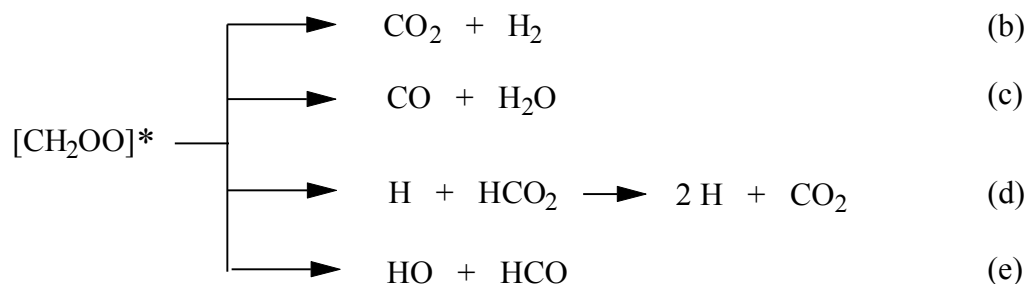
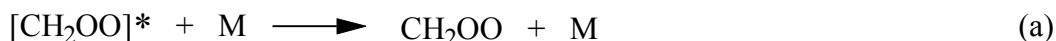
be used in the evaluation of the rate coefficient for this reaction. The preferred values are obtained from a least-squares analysis of the rate coefficients of DeMore (1969), Stedman et al. (1973), Herron and Huie (1974), Japar et al. (1974, 1976), Toby et al. (1976), Atkinson et al. (1982), Bahta et al. (1984) [averaging the rate coefficients at each of the four temperatures studied] and the 298 K rate coefficient of Treacy et al. (1992).

As discussed by Atkinson (1997), the initial reaction forms the energy-rich "primary ozonide" which rapidly decomposes:



to yield HCHO and the energy-rich Criegee intermediate $[\text{CH}_2\text{OO}]^*$. Grosjean and Grosjean (1996) and Grosjean et al. (1996) have measured a formation yield of HCHO of unity at atmospheric pressure of air.

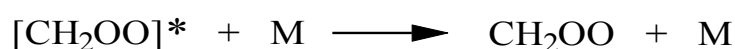
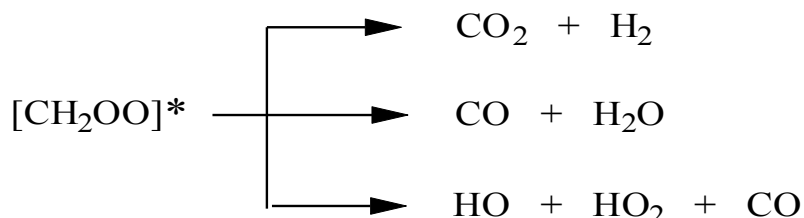
The energy-rich Criegee intermediate can either be stabilized or decompose, with the decomposition channels (b) through (e) having been postulated.



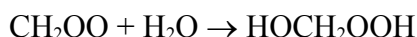
There have been a number of determinations of the yield of the stabilized Criegee intermediate. The values obtained at room temperature and atmospheric pressure of $35 \pm 5\%$ by Su et al. (1980), $37 \pm 2\%$ by Kan et al. (1981), $35 \pm 5\%$ by Niki et al. (1981), $39.0 \pm 5.3\%$ by Hatakeyama et al. (1984, 1986), and $39 \pm 11\%$ by Hasson et al. (2001) are in good agreement (with an average yield of 37%) and are preferred to the slightly higher value of 47% obtained by Horie and Moortgat (1991). The yield of stabilized Criegee intermediate appears to be pressure dependent although a significant fraction have been reported to be formed thermally "cold" at low pressures; by extrapolation of measurements over the range 13 mbar to 1.5 bar, Hatakeyama et al. (1986) found this fraction to be $20 \pm 3\%$ at zero pressure.

The formation of HO radicals has been observed from the reaction of O_3 with ethene at atmospheric pressure of air, with the measured HO radical yield being in the range 12-18% (Atkinson et al., 1992; Paulson et al., 1999; Rickard et al., 1999) [see the data sheet on the reactions of $\text{O}_3 + \text{R}_1\text{R}_2\text{C}=\text{CR}_3\text{R}_4 \rightarrow \text{HO} + \text{products}$ (IUPAC, 2007)]. This observed formation of HO radicals,

presumably via pathway (e), suggests that pathway (d) does not occur, since the low pressure study of Herron and Huie (1974) which invoked pathway (d) could not differentiate between formation of H atoms and HO radicals (any H atoms formed would rapidly react with O₃ in the reaction system used by Herron and Huie (1974, 1977), to produce HO radicals). Hence a possible reaction sequence at atmospheric pressure of air is:



Under typical lower tropospheric conditions, the stabilized Criegee intermediate CH₂OO is expected to react with water vapor to form hydroxymethyl hydroperoxide, HOCH₂OOH (Neeb et al., 1996; Hasson et al., 2001),



which may decompose on surfaces to formic acid plus water vapor (Neeb et al., 1996; Hasson et al., 2001).

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