

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet O_x_VOC6

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This datasheet last evaluated: 17th December 2007 (with no revision of the preferred values).

O₃ + C₃H₆ → products

Rate coefficient data

<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
6.14 × 10 ⁻¹⁵ exp[-(1897 ± 109)/ <i>T</i>]	235-362	Herron and Huie, 1974	(a)
1.06 × 10 ⁻¹⁷	298		
4.9 × 10 ⁻¹⁵ exp[-(1858 ± 70)/ <i>T</i>]	240-324	Treacy et al., 1992	S-CL (b)
(9.4 ± 0.4) × 10 ⁻¹⁸	298		

Comments

- (a) 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. Due to a typographical error, the lowest temperature studied was 235.0 K and not 250.0 K as originally stated.¹
- (b) Static system, with chemiluminescence detection of O₃. C₃H₆ in large excess over O₃.

Preferred Values

$k = 1.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 5.5 \times 10^{-15} \exp(-1880/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230-370 K.

Reliability

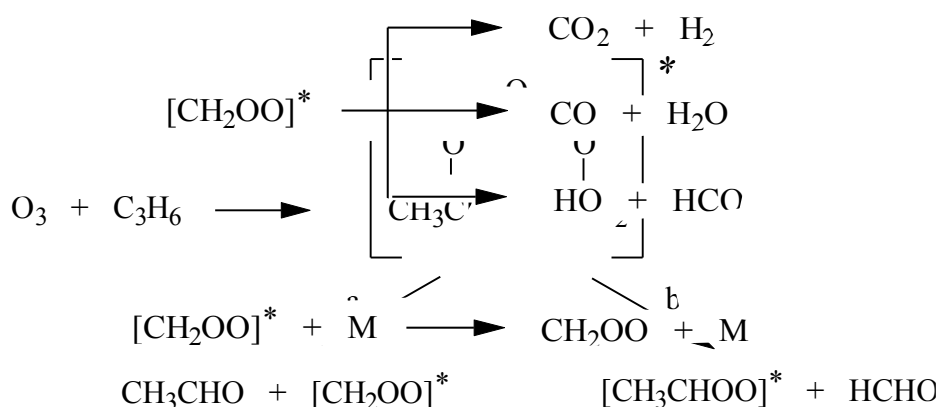
$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

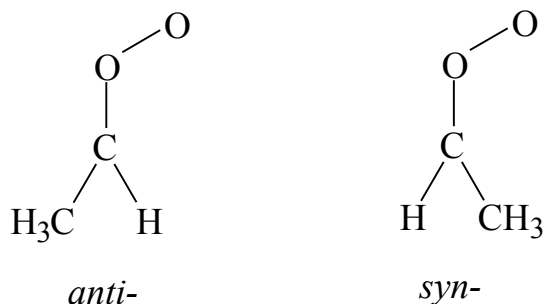
Comments on Preferred Values

The absolute rate coefficients of Herron and Huie (1974) (note that the lowest temperature studied was 235.0 K and not 250.0 K as given by Herron and Huie, 1974) and Treacy et al. (1992) are in excellent agreement for propene, 1-butene, *cis*- and *trans*-2-butene, 2-methylpropene and 2-methyl-2-butene over the temperature ranges common to both studies. Accordingly, the 298 K rate coefficients and temperature dependencies of Herron and Huie (1974) and Treacy et al. (1992) have been averaged to yield the preferred Arrhenius expression (note that the individual rate coefficients at the various temperatures studied by Treacy et al. (1992) were not tabulated).

The reaction proceeds via the initial formation of the “primary ozonide” (Atkinson, 1997), which rapidly decomposes to two sets of “primary” carbonyl plus Criegee intermediate:



For 1-alkenes measured product yields suggest that the rate coefficient ratio $k_b/(k_a + k_b)$ is in the range 0.65-0.50 at room temperature (Grosjean et al., 1996; Tuazon et al., 1997; Atkinson, 1997; Rickard et al., 1999). For propene, yields of CH₃CHO have been measured in the presence of an HO radical scavenger (see below), of 0.520 ± 0.026 at $55 \pm 10\%$ relative humidity by Grosjean et al. (1996), 0.446 ± 0.092 at $\sim 5\%$ relative humidity by Tuazon et al. (1997), and 0.34 ± 0.01 in dry air by Rickard et al. (1999). Higher yields of HCHO were obtained by Grosjean et al. (1996) and Tuazon et al. (1997), but these include any formation of HCHO from subsequent reactions of the [CH₃CHOO]^{*} intermediates. The energy-rich Criegee intermediates are believed to be carbonyl oxides, and the Criegee intermediate [CH₃CHOO]^{*} can exist in the *anti*- or *syn*- configuration (Fenske et al., 2000a).



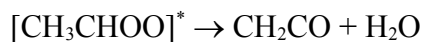
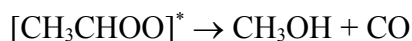
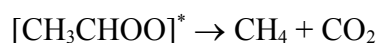
In the absence of other information, it is assumed (Rickard et al., 1999) that the reactions of the energy-rich Criegee intermediate [CH₂OO]^{*} formed from propene are similar to those for [CH₂OO]^{*} formed from ethene. Hence, as for the O₃ + C₂H₄ reaction at room temperature and 1 bar of air (IUPAC, 2007):

Less data are available concerning the stabilization and decomposition reactions of the $[\text{CH}_3\text{CHOO}]^*$ intermediate. Based upon the SO_2 to H_2SO_4 conversion yield in an O_3 + propene reaction system, Hatakeyama et al. (1984) determined an overall stabilized Criegee intermediate ($\text{CH}_2\text{OO} + \text{CH}_3\text{CHOO}$) yield of 0.254 ± 0.023 at room temperature and atmospheric pressure, while Horie and Moortgat (1991) obtained a stabilized Criegee intermediate yield of 0.44. Rickard et al. (1999) measured the acetaldehyde yield in the presence and absence of 0.002 bar SO_2 and ascribed the observed increase in the acetaldehyde yield to the reaction $\text{SO}_2 + \text{CH}_3\text{CHOO} \rightarrow \text{SO}_3 + \text{CH}_3\text{CHO}$ (similar to the assumptions made by Hatakeyama et al., 1984) which corresponds to a yield of stabilized CH_3CHOO of 0.12-0.16 for rate coefficient ratios $k_b/(k_a + k_b)$ of 0.65-0.50. For rate coefficient ratios $k_b/(k_a + k_b)$ of 0.65-0.50 and assuming that the $[\text{CH}_2\text{OO}]^*$ stabilization yield is 0.37, the data of Hatakeyama et al. (1984) lead to a fraction of the $[\text{CH}_3\text{CHOO}]^*$ intermediate which is stabilized at ~ 298 K and 1 bar of air of 0.14-0.19, reasonably consistent with the study of Rickard et al. (1999). While the stabilization/decomposition yields are expected to depend on the individual alkene reacting with O_3 (and on the total pressure and temperature), this fraction of $[\text{CH}_3\text{CHOO}]^*$ intermediate which is stabilized at 298 K and 1 bar of air (0.12-0.19) is similar to the measured yields of stabilized CH_3CHOO from *trans*-2-butene, of 0.185 (Hatakeyama et al., 1984) and 0.13 (Rickard et al., 1999), and *cis*-2-butene, of 0.18 (Niki et al., 1977) and 0.19 (Rickard et al., 1999). A yield of stabilized CH_3CHOO from $[\text{CH}_3\text{CHOO}]^*$ of 0.16 at 298 K and 1 bar of air is recommended, with it being likely that this stabilized CH_3CHOO intermediate is *anti*- CH_3CHOO .

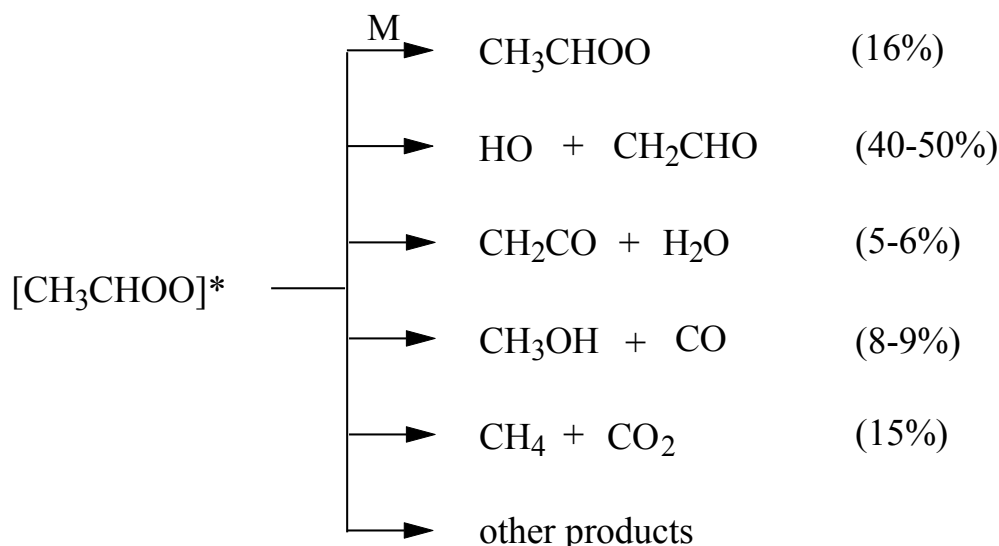
The $[\text{CH}_3\text{CHOO}]^*$ decomposition pathways include the formation of HO radicals through the “hydroperoxide” channel; see the data sheet on the reactions of $\text{O}_3 + \text{R}_1\text{R}_2\text{C}=\text{CR}_3\text{R}_4 \rightarrow \text{HO} + \text{products}$ (IUPAC, 2007).



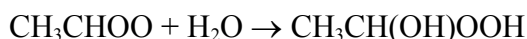
and this reaction pathway is believed to occur for both the initially energy-rich Criegee intermediate and for the stabilized *syn*- CH_3CHOO intermediate (Fenske et al., 2000a; Kroll et al., 2001). At atmospheric pressure, the measured HO radical formation yield is in the range 0.32-0.37 (Atkinson and Aschmann, 1993; Paulson et al., 1999; Rickard et al., 1999; Neeb and Moortgat, 1999; Fenske et al., 2000b). Other decomposition pathways include (Atkinson, 1997; Tuazon et al., 1997):



with measured methane, methanol and ketene yields at atmospheric pressure and in the presence of an HO radical scavenger of 0.096 ± 0.010 , 0.055 ± 0.007 and 0.036 ± 0.008 , respectively (Tuazon et al., 1997). The subsequent reaction of the vinoxy (CH_2CHO) radical in air may lead to some small formation of HO radicals (Atkinson, 1997), and a possible overall reaction sequence involves the initial formation of 35-40% ($[\text{CH}_2\text{OO}]^* + \text{CH}_3\text{CHO}$) and 65-60% ($[\text{CH}_3\text{CHOO}]^* + \text{HCHO}$). The subsequent reactions of the $[\text{CH}_2\text{OO}]^*$ intermediate have been shown above, therefore leading to an HO radical yield, relative to the propene reacted, of ~ 0.05 from the $[\text{CH}_2\text{OO}]^*$ intermediate. The following reactions of the $[\text{CH}_3\text{CHOO}]^*$ intermediate are then plausible.



Under lower tropospheric conditions, the stabilized Criegee intermediate CH₃CHOO (expected to be in the *anti*-configuration) is anticipated to react with water vapor to form the hydroxyhydroperoxide (Neeb and Moortgat, 1999; Sauer et al., 1999; Baker et al., 2002).



This hydroxyhydroperoxide may decompose (possibly heterogeneously) to CH₃C(O)OH + H₂O or to CH₃CHO + H₂O₂ ((Neeb and Moortgat, 1999; Sauer et al., 1999).

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