

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet O_x_VOC15

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O₃ + 2-Methylpropene → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.4 \times 10^{-15} \exp[-(1409 \pm 202)/T]$	303-373	Bufalini and Altshuller, 1965	(a)
$(2.32 \pm 0.34) \times 10^{-17}$	303		
1.8×10^{-17}	283 ± 2	Becker et al., 1974	(b)
$(1.36 \pm 0.02) \times 10^{-17}$	299 ± 2	Japar et al., 1974	S-CL
$3.17 \times 10^{-15} \exp[-(1671 \pm 23)/T]$	225-363	Huie and Herron, 1975	SF-MS (c)
1.16×10^{-17}	298		
1.45×10^{-17}	295 ± 1	Grimsrud et al., 1975	F-CL
1.2×10^{-17}	294 ± 2	Adeniji et al., 1981	S-CL
$2.5 \times 10^{-15} \exp[-(1592 \pm 115)/T]$	240-324	Treacy et al., 1992	S-UVA
$(1.09 \pm 0.18) \times 10^{-17}$	298		
<i>Relative Rate Coefficients</i>			
$(1.09 \pm 0.04) \times 10^{-17}$	296 ± 2	Greene and Atkinson, 1992	RR (d)
$1.80 \times 10^{-15} \exp[-(2122 \pm 102)/T]$	278-353	Avzianova and Ariya, 2002	RR (e)
$(1.09 \pm 0.07) \times 10^{-17}$	~298		

Comments

- (a) Reactions were carried out in a stirred flow reactor, with analysis of 2-methylpropene by GC and of O₃ by chemical analysis involving oxidation of iodide to tri-iodide with colorimetric analysis.
- (b) Reactions were carried out using a static reaction system, in a 220 m³ volume stainless steel reactor. Ozone decays, in the presence of excess 2-methylpropene, were monitored by UV absorption at 253.7 nm.
- (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.
- (d) Relative rate study, with *n*-octane present to scavenge HO radicals formed from the O₃ reactions. The concentrations of 2-methylpropene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{O}_3 + \text{2-methylpropene})/k(\text{O}_3 + \text{propene}) = 1.14 \pm 0.04$ is placed on an absolute basis by use of a rate coefficient of $k(\text{O}_3 + \text{propene}) = 9.6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- (e) Relative rate method carried out at 760 Torr (1.013 bar) of air diluent in a 3 L volume Pyrex reactor, with 1,3,5-trimethylbenzene being present to scavenge the HO radicals formed. The concentrations of 2-methylpropene and propene (the reference compound) were monitored by

GC. The measured rate coefficient ratios were placed on an absolute basis by Avzianova and Ariya (2002) using the Arrhenius expression of Treacy et al. (1992) for O₃ + propene. The measured rate coefficient ratios were not tabulated, except at room temperature, assumed to be 298 K. The rate coefficient ratio $k(\text{O}_3 + 2\text{-methylpropene})/k(\text{O}_3 + \text{propene}) = 0.327 \exp[-(242 \pm 102)/T]$, derived from the data provided in Avzianova and Ariya (2002), is placed on an absolute basis by use of $k(\text{O}_3 + \text{propene}) = 5.5 \times 10^{-15} \exp(-1880/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation). The 298 K rate coefficient calculated from the Arrhenius expression ($1.45 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is a factor of 7 lower than the room temperature rate coefficient cited by Avzianova and Ariya (2002), and their Arrhenius plots indicate that the temperature dependence for O₃ + 2-methylpropene is similar to that for O₃ + 1-butene ($B = 1745 \text{ K}$). The Arrhenius expression cited by Avzianova and Ariya (2002) is clearly in error.

Preferred Values

$k = 1.1 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.7 \times 10^{-15} \exp(-1630/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220-370 K.

Reliability

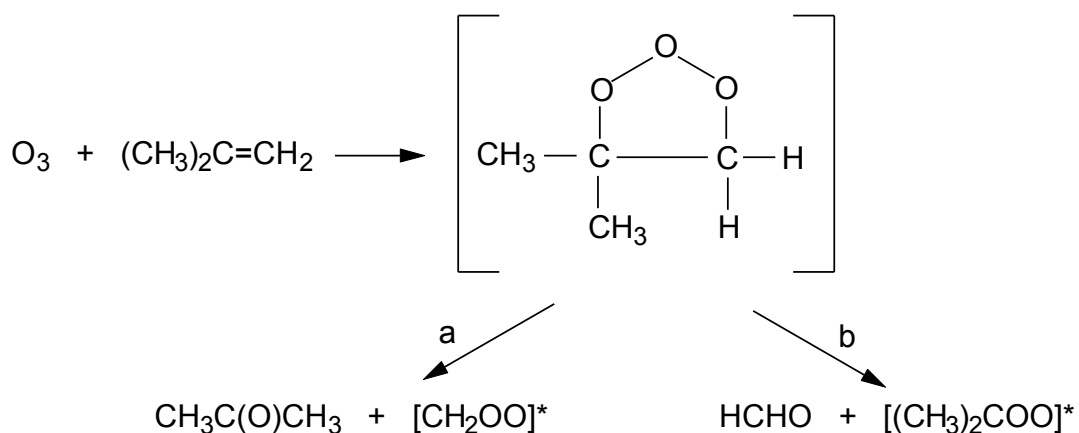
$\Delta \log k = \pm 0.08$ at 298 K.

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

Comments on Preferred Values

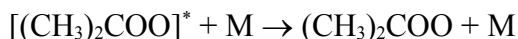
The room temperature rate coefficients from the absolute rate studies of Huie and Herron (1975) and Treacy et al. (1992) and the relative rate study of Greene and Atkinson (1992) are in excellent agreement, and this is the case for the reactions of O₃ with 1-butene, *cis*-2-butene, *trans*-2-butene and 2-methyl-2-butene (Atkinson, 1994). In general the room temperature rate coefficients of Japar et al. (1974) tend to be slightly higher than those of Huie and Herron (1975) and Treacy et al. (1992), especially for the more reactive alkenes, suggesting that this may have been due to insufficiently rapid mixing of the reactants. The preferred temperature dependence is the average of those determined by Huie and Herron (1975) and Treacy et al. (1992). The preferred 298 K rate coefficient is the average of the rate coefficients of Huie and Herron (1975), Treacy et al. (1992) and Greene and Atkinson (1992), the latter being adjusted to 298 K using the preferred temperature dependence. The preferred temperature dependence is combined with the preferred rate coefficient at 298 K to obtain the pre-exponential factor. The room temperature rate coefficients of Japar et al. (1974) and Avzianova and Ariya (2002) are in good agreement with the preferred value.

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

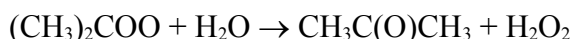


Molar formation yields of HCHO and acetone have been measured in the presence of an HO radical scavenger by Grosjean et al. (1996) and Tuazon et al. (1997), with HCHO yields of 0.950 ± 0.098 (Grosjean et al., 1996) and 1.01 ± 0.07 (Tuazon et al. (1997) and with acetone yields of 0.340 ± 0.031 (Grosjean et al., 1996) and 0.323 ± 0.030 and 0.294 ± 0.030 (Tuazon et al., 1997). It is likely that HCHO is also formed from the $[(\text{CH}_3)_2\text{COO}]^*$ intermediate, and assuming the acetone yield is that for primary formation, then $k_a/(k_a + k_b) \sim 0.32$ at room temperature and 1 bar of air.

In the absence of other information, it is assumed that the reactions of the energy-rich Criegee intermediate $[\text{CH}_2\text{OO}]^*$ formed from 2-methylpropene are similar to those for $[\text{CH}_2\text{OO}]^*$ formed from ethene (see IUPAC, 2009). The $[(\text{CH}_3)_2\text{COO}]^*$ Criegee intermediate can be collisionally stabilized,



and the stabilized Criegee intermediate can then react with water vapor to form acetone + H_2O_2 .



Hatakeyama et al. (1984) derived an overall stabilized Criegee intermediate $(\text{CH}_2\text{OO} + (\text{CH}_3)_2\text{COO})$ yield of 0.174 ± 0.032 at room temperature and atmospheric pressure. The majority of this stabilized Criegee intermediate yield can be accounted for by using the above rate coefficient ratio of $k_a/(k_a + k_b)$ and assuming that the $[\text{CH}_2\text{OO}]^*$ stabilization yield is 0.37 (see $\text{O}_3 + \text{ethene}$ data sheet, IUPAC, 2009).

The major fate of chemically activated $[(\text{CH}_3)_2\text{COO}]^*$ is isomerization and decomposition, yielding HO radicals.



Atkinson and Aschmann (1993), Rickard et al. (1999), Paulson et al. (1999) and Neeb and Moortgat (1999) derived HO radical formation yields of 0.84 (uncertain to a factor of ~ 1.5), 0.60 ± 0.15 , 0.72 ± 0.12 and $0.60^{+0.05}_{-0.07}$, respectively, at room temperature. This HO radical yield of ~ 0.65 accounts for essentially all of the $[(\text{CH}_3)_2\text{COO}]^*$ formed from decomposition of the primary ozonide, and further indicates that there is little or no stabilized $(\text{CH}_3)_2\text{COO}$ intermediate formed.

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- Recommendation
- Treacy et al. (1992), Arrhenius expression
- - - Bufalini and Altshuller (1965), Arrhenius expression
- Bufalini and Altshuller (1965)
- ▼ Japar et al. (1974)
- Huie and Herron (1975)
- ◆ Adeniji et al. (1981)
- ▲ Treacy et al. (1992), at 298 K
- ◆ Greene and Atkinson (1992)
- Avzianova and Ariya (2002), at 298 K

