

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet O_x_VOC16

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This datasheet last evaluated: September 2013; last change in preferred values: September 2013

O₃ + but-1-ene → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
1.03×10^{-17}	303	Bufalini and Altshuller, 1965	(a)
1.41×10^{-17}	298 ± 2	Bufalini and Altshuller, 1965	(b)
$(1.23 \pm 0.04) \times 10^{-17}$	299 ± 2	Japar et al., 1974	S-CL
$2.93 \times 10^{-15} \exp[-(1686 \pm 20)/T]$	225-363	Huie and Herron, 1975	SF-MS (c)
1.03×10^{-17}	298		
5.3×10^{-18}	260 ± 2	Adeniji et al., 1981	S-CL
1.24×10^{-17}	294 ± 2		
$3.7 \times 10^{-15} \exp[-(1801 \pm 155)/T]$	240-324	Treacy et al., 1992	S-UVA
$(8.8 \pm 0.6) \times 10^{-18}$	298		
<i>Relative Rate Coefficients</i>			
$(9.36 \pm 0.29) \times 10^{-18}$	296 ± 2	Greene and Atkinson, 1992	RR (d)
$3.82 \times 10^{-15} \exp[-(1754 \pm 46)/T]$	278-353	Avzianova and Ariya, 2002	RR (e)
$(1.10 \pm 0.01) \times 10^{-17}$	~298		

Comments

- (a) Reactions were carried out in a stirred flow reactor, with analysis of but-1-ene 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 12 L reactor with analysis of but-1-ene by GC and of O₃ by chemical analysis involving oxidation of iodide to tri-iodide with colorimetric analysis.
- (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 but-1-ene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{O}_3 + \text{but-1-ene})/k(\text{O}_3 + \text{propene}) = 0.975 \pm 0.030$ is placed on an absolute basis using $k(\text{O}_3 + \text{propene}) = 9.6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 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 1-butene 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 $k(\text{O}_3 + \text{but-1-ene})/k(\text{O}_3 + \text{propene}) = 0.694 \exp[(126 \pm 46)/T]$, derived from the data provided in Avzianova and Ariya (2002), is placed on an absolute basis using $k(\text{O}_3 + \text{propene}) = 5.5 \times 10^{-15} \exp(-1880/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

Preferred Values

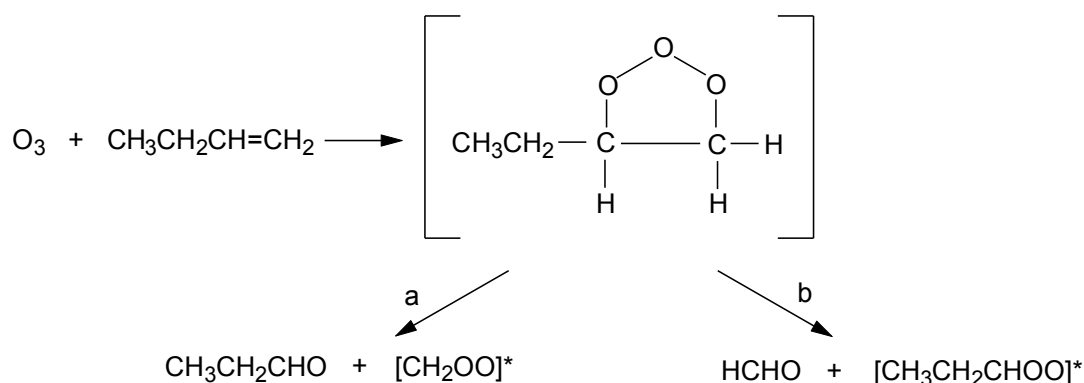
Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	9.6×10^{-18}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$3.35 \times 10^{-15} \exp(-1745/T)$	220-370
<i>Reliability</i>		
$\Delta \log k$	± 0.08	298
$\Delta E/R$	± 200	220-370

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 2-methylpropene, *cis*-but-2-ene, *trans*-but-2-ene and 2-methylbut-2-ene (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 in the work of Japar et al (1974). 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 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.

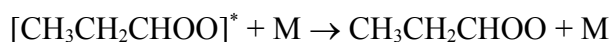
The rate expression of Avzianova and Ariya (2002) obtained from relative rate measurements yields rate coefficients ~10% higher than the preferred values over the temperature range studied (278-353 K), with an almost identical temperature dependence.

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

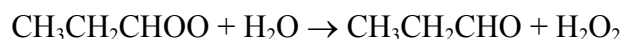


Grosjean et al. (1996) measured molar formation yields of HCHO and propanal of 0.630 ± 0.031 and 0.350 ± 0.031 , respectively, in the presence of an HO radical scavenger (see below) at $55 \pm 10\%$ relative humidity, while Paulson et al. (1999) obtained a propanal yield of 0.45 ± 0.02 in the presence of an HO radical scavenger in air at $\sim 10\%$ relative humidity (Hasson et al., 2001). Subsequently, Hasson et al. (2001) observed that the propanal formation yield, in the presence of an HO radical scavenger, increased from 0.36 ± 0.03 at $<0.5\%$ relative humidity to 0.52 ± 0.05 at $>50\%$ relative humidity.

The energy-rich Criegee intermediates are believed to be carbonyl oxides, and the Criegee intermediate $[\text{CH}_3\text{CH}_2\text{CHOO}]^*$ can exist in the *anti*- or *syn*- configuration (Fenske et al., 2000a). 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 1-butene are similar to those for $[\text{CH}_2\text{OO}]^*$ formed from ethene (see IUPAC, 2009). The $[\text{CH}_3\text{CH}_2\text{CHOO}]^*$ Criegee intermediate can be collisionally stabilized,

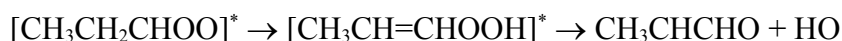


and the stabilized Criegee intermediate can then react with water vapor to form propanal + H_2O_2 .



Hasson et al. (2001) determined an overall stabilized Criegee intermediate ($\text{CH}_2\text{OO} + \text{CH}_3\text{CH}_2\text{CHOO}$) yield of 0.27 at room temperature and atmospheric pressure, and their measured yields of propanal and H_2O_2 as a function of relative humidity (with H_2O_2 yields of 0.013 ± 0.003 at $<0.5\%$ relative humidity and 0.11 ± 0.03 at $>50\%$ relative humidity) suggest that the reaction $\text{CH}_3\text{CH}_2\text{CHOO} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{H}_2\text{O}_2$ accounts for much, if not all, of the increase in propanal formation yield as the relative humidity increases from $<0.5\%$ to $>50\%$. The propanal and H_2O_2 data suggest a stabilized $\text{CH}_3\text{CH}_2\text{CHOO}$ yield (relative to but-1-ene reacted) of 0.10-0.16. Using a rate coefficient ratio of $k_b/(k_a + k_b) \sim 0.65$ (consistent with the Hasson et al. (2001) propanal yield at low water vapor concentrations) 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 total stabilized Criegee intermediate yield obtained by Hasson et al. (2001) leads to a stabilized $\text{CH}_3\text{CH}_2\text{CHOO}$ yield of ~ 0.13 (relative to but-1-ene reacted). These two estimates of the amount of stabilized $\text{CH}_3\text{CH}_2\text{CHOO}$ formed are in agreement and suggest that the fraction of the $[\text{CH}_3\text{CH}_2\text{CHOO}]^*$ intermediate which is stabilized at ~ 298 K and 1 bar of air is ~ 0.20 . This stabilized $\text{CH}_3\text{CH}_2\text{CHOO}$ intermediate is likely *anti*- $\text{CH}_3\text{CH}_2\text{CHOO}$.

The chemically activated $[\text{CH}_3\text{CH}_2\text{CHOO}]^*$ intermediate in the *syn*- form can undergo isomerization and decomposition, yielding HO radicals.



Atkinson and Aschmann (1993), Paulson et al. (1999) and Fenske et al. (2000b) derived HO radical formation yields of 0.41 (uncertain to a factor of ~ 1.5), 0.29 ± 0.04 and 0.26 at room temperature, independent of pressure (Fenske et al., 2000b). Additional decomposition pathways presumably account for the remaining loss processes of the $[\text{CH}_3\text{CH}_2\text{CHOO}]^*$ intermediate.

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- Recommendation
- Treacy et al. (1992), Arrhenius expression
- Avzianova and Ariya (2002), 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

