

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet O_x_VOC18

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O₃ + *trans*-2-Butene → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$6.03 \times 10^{-16} \exp[-(101 \pm 151)/T]$	303-373	Bufalini and Altshuller, 1965	(a)
$(4.32 \pm 0.67) \times 10^{-16}$	303		
3.32×10^{-16}	298 ± 2	Bufalini and Altshuller, 1965	(b)
2.57×10^{-16}	296	Cox and Penkett, 1972	S-CA
$(2.75 \pm 0.23) \times 10^{-16}$	299 ± 2	Stedman et al., 1973	S-CL
$(2.60 \pm 0.09) \times 10^{-16}$	299 ± 2	Japar et al., 1974	S-CL
$5.96 \times 10^{-15} \exp[-(1051 \pm 43)/T]$	225-364	Huie and Herron, 1975	SF-MS (c)
1.76×10^{-16}	298		
$(2.56 \pm 0.15) \times 10^{-16}$	299	Japar et al., 1976	S-CL (d)
2.88×10^{-16}	294 ± 2	Adeniji et al., 1981	S-CL
$6.7 \times 10^{-15} \exp[-(1066 \pm 115)/T]$	240-324	Treacy et al., 1992	S-UVA
$(1.81 \pm 0.06) \times 10^{-16}$	298		
<i>Relative Rate Coefficients</i>			
$(2.02 \pm 0.10) \times 10^{-16}$	297 ± 2	Nolting et al., 1988	RR (e)
$(2.06 \pm 0.15) \times 10^{-16}$	296 ± 2	Greene and Atkinson, 1992	RR (f)
$5.57 \times 10^{-15} \exp[-(1144 \pm 54)/T]$	278-353	Avzianova and Ariya, 2002	RR (g)
$(1.79 \pm 0.12) \times 10^{-16}$	~298		

Comments

- Reactions were carried out in a stirred flow reactor, with analysis of *trans*-2-butene by GC and of O₃ by chemical analysis involving oxidation of iodide to tri-iodide with colorimetric analysis.
- Reactions were carried out using a static reaction system, in a 12 L reactor with analysis of 1-butene by GC and of O₃ by chemical analysis involving oxidation of iodide to tri-iodide with colorimetric analysis.
- 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.
- Experiments carried out in air and helium diluent gas. The rate coefficient in the table is that measured in air. A slightly higher rate coefficient of $(2.83 \pm 0.07) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was measured in helium diluent, consistent with data from a comprehensive study of the effects of O₂ on the measured rate coefficients for O₃ + propene, which showed that secondary reactions occurred in the absence of O₂.

- (e) The concentrations of *trans*-2-butene and *cis*-2-butene (the reference compound) were measured in the presence of O₃ by GC. It appears from the publication that an HO radical scavenger was not present. The measured rate coefficient ratio $k(\text{O}_3 + \textit{trans}\text{-2-butene})/k(\text{O}_3 + \textit{cis}\text{-2-butene})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{O}_3 + \textit{cis}\text{-2-butene}) = 1.24 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K (IUPAC, current recommendation).
- (f) Relative rate study, with *n*-octane present to scavenge the HO radicals formed from the O₃ reactions. The concentrations of pairs of alkenes (1,4-cyclohexadiene and propene, 1,4-cyclohexadiene and *cis*-2-butene, *cis*-2-butene and 2-methyl-2-butene, and *trans*-2-butene and 2-methyl-2-butene) were measured by GC. The rate coefficient ratio of $k(\text{O}_3 + \textit{trans}\text{-2-butene})/k(\text{O}_3 + \textit{propene}) = 21.5 \pm 1.5$, derived from the measured values of $k(\text{O}_3 + 1,4\text{-cyclohexadiene})/k(\text{O}_3 + \textit{propene}) = 4.75 \pm 0.23$, $k(\text{O}_3 + 1,4\text{-cyclohexadiene})/k(\text{O}_3 + \textit{cis}\text{-2-butene}) = 0.372 \pm 0.014$, $k(\text{O}_3 + 2\text{-methyl-2-butene})/k(\text{O}_3 + \textit{cis}\text{-2-butene}) = 3.30 \pm 0.06$, and $k(\text{O}_3 + \textit{trans}\text{-2-butene})/k(\text{O}_3 + 2\text{-methyl-2-butene}) = 0.510 \pm 0.010$, is placed on an absolute basis by use of a rate coefficient of $k(\text{O}_3 + \textit{propene}) = 9.6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- (g) 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 *trans*-2-butene and *cis*-2-butene (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 + *cis*-2-butene. The measured rate coefficient ratios were not tabulated, except at room temperature, assumed to be 298 K. The rate coefficient ratio $k(\text{O}_3 + \textit{trans}\text{-2-butene})/k(\text{O}_3 + \textit{cis}\text{-2-butene}) = 1.74 \exp[-(179 \pm 54)/T]$, derived from the data provided in Avzianova and Ariya (2002), is placed on an absolute basis by use of $k(\text{O}_3 + \textit{cis}\text{-2-butene}) = 3.2 \times 10^{-15} \exp(-965/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation). The 298 K rate coefficient calculated from the Arrhenius expression ($1.20 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is a factor of 1.5 lower than the room temperature rate coefficient cited by Avzianova and Ariya (2002), indicating that the Arrhenius expression cited by Avzianova and Ariya (2002) is in error.

Preferred Values

$k = 1.9 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 6.6 \times 10^{-15} \exp(-1060/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220-370 K.

Reliability

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

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

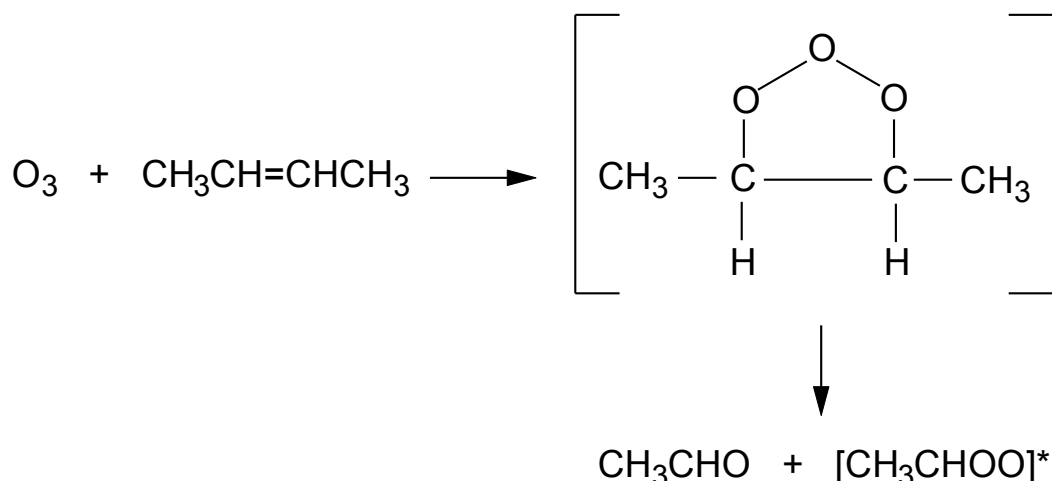
Comments on Preferred Values

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 good agreement, and this is the case for the reactions of O₃ with 1-butene, 2-methylpropene, *cis*-2-butene and 2-methyl-2-butene (Atkinson, 1994). In general the room temperature rate coefficients of Japar et al. (1974), and of Stedman et al. (1973) and Japar et al. (1976), 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 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 preferred rate expression is almost identical to that of Treacy et al. (1992).

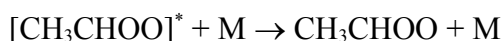
The room temperature rate coefficients of Nolting et al. (1988) and Avzianova and Ariya (2002) are in excellent agreement with the preferred values.

The reaction proceeds via the initial formation of a “primary ozonide”, which in the case of *trans*-2-butene rapidly decomposes to a “primary” carbonyl plus Criegee intermediate:

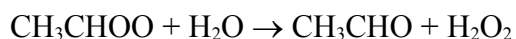


Tuazon et al. (1997) measured a molar formation yield of CH₃CHO of 1.14 ± 0.14 (GC analyses) and 1.09 ± 0.09 (FTIR spectroscopic analyses) in dry air (≤5% relative humidity), in agreement with that of 1.150 ± 0.104 measured by Grosjean et al. (1996) at 55 ± 10% relative humidity for a *cis*-/*trans*- mixture of 2-butene (both studies being in the presence of an HO radical scavenger). Subsequently, Hasson et al. (2001) observed that the CH₃CHO formation yield, in the presence of an HO radical scavenger, increased from 0.97 in dry air to a maximum of 1.17 at ~80% relative humidity, indicating that secondary formation of CH₃CHO from the [CH₃CHOO]^{*} Criegee intermediate accounts for ~15-20% of the reactions of the [CH₃CHOO]^{*} intermediate.

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). The [CH₃CHOO]^{*} Criegee intermediate can be collisionally stabilized,



with the stabilized Criegee intermediate then reacting with water vapor to form CH₃CHO + H₂O₂:



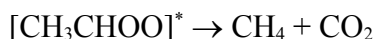
Hatakeyama et al. (1984), Horie and Moortgat (1991) and Hasson et al. (2001) reported yields of stabilized Criegee intermediate (CH₃CHOO) of 0.185 ± 0.028, 0.42 and 0.24, respectively, at atmospheric temperature and pressure, with the values of Hatakeyama et al. (1984) and Hasson et al. (2001) being consistent with the additional CH₃CHO formation in the presence

of water vapor (Hasson et al., 2001). This stabilized CH₃CHOO intermediate is likely *anti*-CH₃CHOO.

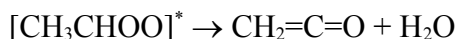
The chemically activated [CH₃CHOO]* intermediate in the *syn*- form can undergo isomerization and decomposition, yielding HO radicals.



Atkinson and Aschmann (1993), Gutbrod et al. (1997), McGill et al. (1999), Fenske et al. (2000b), Siese et al. (2001) and Orzechowska and Paulson (2002) derived HO radical formation yields of 0.64 (uncertain to a factor of ~1.5), 0.24, 0.54 ± 0.11 , 0.61, 0.75 ± 0.19 and 0.64 ± 0.12 , respectively, at room temperature and atmospheric pressure. The HO radical formation yield determined by Gutbrod et al. (1997) from the conversion of CO to CO₂ is significantly lower than the other literature yields, and the data of McGill et al. (1999), Fenske et al. (2000b), Siese et al. (2001) and Orzechowska and Paulson (2002) indicate an HO radical formation yield of ~0.64. Tuazon et al. (1997) observed formation of CH₄ and ketene [CH₂=C=O] with molar yields of 0.113 ± 0.018 and 0.045 ± 0.009 , respectively, indicating the occurrence of the decomposition reactions:



and



HO radical formation (~64%), decomposition to CH₄ + CO₂ and ketene + H₂O (~16%) and collisional stabilization (~20%) then account for essentially all of the loss processes of the [CH₃CHOO]* intermediate.

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- Recommendation
- Treacy et al. (1992), Arrhenius expression
- - - Bufalini and Altshuller (1965), Arrhenius expression
- Bufalini and Altshuller (1965), 303 K
- ▼ Cox and Penkett (1972)
- Stedman et al. (1974)
- ◆ Japar et al. (1974, 1976)
- ▲ Huie and Herron (1975)
- ◆ Adeniji et al. (1981)
- Treacy et al. (1992), at 298 K
- ▽ Nolting et al. (1988)
- Greene and Atkinson (1992)
- ◆ Avzianova and Ariya (2002)

