

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet O_x_VOC17

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This data sheet created on April 2009.

O₃ + *cis*-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>			
3.32×10^{-16}	303	Bufalini and Altshuller, 1965	(a)
1.41×10^{-16}	296	Cox and Penkett, 1972	S-CA
$(1.61 \pm 0.07) \times 10^{-16}$	299 ± 2	Japar et al., 1974	S-CL
$3.11 \times 10^{-15} \exp[-(956 \pm 54)/T]$	225-364	Huie and Herron, 1975	SF-MS (b)
1.26×10^{-16}	298		
$(1.38 \pm 0.16) \times 10^{-16}$	297 ± 1	Atkinson et al., 1983	S-CL
$3.4 \times 10^{-15} \exp[-(979 \pm 22)/T]$	240-324	Treacy et al., 1992	S-UVA
$(1.23 \pm 0.18) \times 10^{-16}$	298		
<i>Relative Rate Coefficients</i>			
$(1.23 \pm 0.08) \times 10^{-16}$	296 ± 2	Greene and Atkinson, 1992	RR (c)

Comments

- (a) Reactions were carried out in a stirred flow reactor, with analysis of *cis*-2-butene by GC and of O₃ by chemical analysis involving oxidation of iodide to tri-iodide with colorimetric analysis.
- (b) 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.
- (c) 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, and 1,4-cyclohexadiene and *cis*-2-butene) were measured by GC. The rate coefficient ratio of $k(\text{O}_3 + \textit{cis}\text{-2-butene})/k(\text{O}_3 + \textit{propene}) = 12.8 \pm 0.8$, derived from the measured values of $k(\text{O}_3 + 1,4\text{-cyclohexadiene})/k(\text{O}_3 + \textit{propene}) = 4.75 \pm 0.23$ and $k(\text{O}_3 + 1,4\text{-cyclohexadiene})/k(\text{O}_3 + \textit{cis}\text{-2-butene}) = 0.372 \pm 0.014$, 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).

Preferred Values

$k = 1.25 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 3.2 \times 10^{-15} \exp(-965/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220-370 K.

Reliability

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

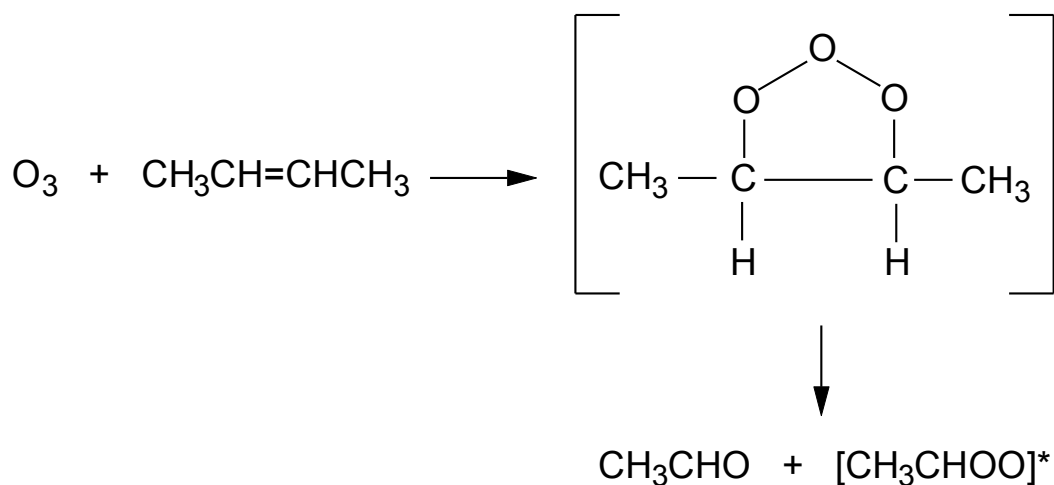
$$\Delta(E/R) = \pm 200 \text{ K.}$$

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, 2-methylpropene, *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 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.

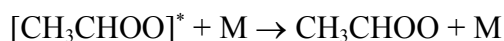
The room temperature rate coefficients of Cox and Penkett (1972) and Atkinson et al. (1983) are in good agreement with the preferred value.

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

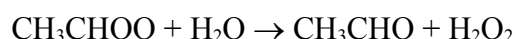


Tuazon et al. (1997) measured a molar formation yield of CH₃CHO of 1.19 ± 0.14 (GC analyses) and 1.08 ± 0.08 (FTIR spectroscopic analyses) in dry air (≤5% relative humidity), in agreement with that of 1.150 ± 0.104 measured by Grosjean et al. (1996) at 55 ± 10% relative humidity for a *cis*-/*trans*- mixture of 2-butene (both studies being in the presence of an HO radical scavenger). These data suggest that 10-20% of the measured CH₃CHO arises from reactions of the [CH₃CHOO]^{*} Criegee 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., 2000). The [CH₃CHOO]^{*} Criegee intermediate can be collisionally stabilized,



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

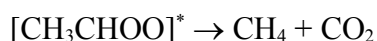


Niki et al. (1977) determined a yield of stabilized Criegee intermediate (CH₃CHOO) of 0.18 at room temperature and atmospheric pressure, consistent with the higher than unit molar yield of CH₃CHO measured by Grosjean et al. (1996) and Tuazon et al. (1997). This stabilized CH₃CHOO intermediate is likely *anti*- CH₃CHOO.

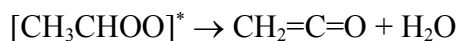
The chemically activated [CH₃CHOO]* intermediate in the *syn*- form can undergo isomerization and decomposition, yielding HO radicals.



Atkinson and Aschmann (1993), Gutbrod et al. (1997), McGill et al. (1999) and Orzechowska and Paulson (2002) derived HO radical formation yields of 0.41 (uncertain to a factor of ~1.5), 0.17, 0.33 ± 0.07 and 0.32 ± 0.05, respectively, at room temperature and atmospheric pressure. Tuazon et al. (1997) also observed formation of CH₄ and ketene [CH₂=C=O] with molar yields of 0.190 ± 0.025 and 0.074 ± 0.019, respectively, indicating the occurrence of the decomposition reactions:



and



Additional reaction pathways must account for the remaining ~25% loss processes of the [CH₃CHOO]* intermediate.

References

- Atkinson, R.: J. Phys. Chem. Ref. Data, Monograph 2, 1, 1994.
Atkinson, R. and Aschmann, S. M.: Environ. Sci. Technol., 27, 1357, 1993.
Atkinson, R., Aschmann, S. M., Carter, W. P. L. and Pitts Jr., J. N.: Int. J. Chem. Kinet., 15, 721, 1983.
Bufalini, J. J. and Altshuller, A. P.: Can. J. Chem., 43, 2243, 1965.
Cox, R. A. and Penkett, S. A.: J. Chem. Soc. Faraday Trans. 1, 68, 1735, 1972.
Fenske, J. D., Hasson, A. S., Ho, A. W. and Paulson, S. E.: J. Phys. Chem. A, 104, 9921, 2000.
Greene, C. R. and Atkinson, R.: Int. J. Chem. Kinet., 24, 803, 1992.
Grosjean, E., de Andrade, J. B. and Grosjean, D.: Environ. Sci. Technol., 30, 975, 1996.
Gutbrod, R., Meyer, S., Rahman, M. M. and Schindler, R. N.: Int. J. Chem. Kinet., 29, 717, 1997.
Huie, R. E. and Herron, J. T.: Int. J. Chem. Kinet., Symp. 1, 165, 1975.
IUPAC: <http://iupac.pole-ether.fr>, 2013.
Japar, S. M., Wu, C. H. and Niki, H.: J. Phys. Chem., 78, 2318, 1974.
McGill, C. D., Rickard, A. R., Johnson, D. and Marston, G.: Chemosphere, 38, 1205, 1999.

Niki, H., Maker, P. D., Savage, C. M. and Breitenbach, L. P.: Chem. Phys. Lett., 46, 327, 1977.

Orzechowska, G. and Paulson, S. E.: Atmos. Environ., 36, 571, 2002.

Treacy, J., El Haag, M., O'Farrell, D. and Sidebottom, H.: Ber. Bunsenges. Phys. Chem., 96, 422, 1992.

Tuazon, E. C., Aschmann, S. M., Arey, J. and Atkinson, R.: Environ. Sci. Technol., 31, 3004, 1997.

- Recommendation
- Treacy et al. (1992), Arrhenius expression
- Bufalini and Altshuller (1965)
- ▼ Cox and Penkett (1972)
- Japar et al. (1974)
- ◆ Huie and Herron (1975)
- ▲ Atkinson et al. (1983)
- ◆ Treacy et al. (1992), at 298 K
- Greene and Atkinson (1992)

