

# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet O<sub>x</sub>\_VOC41

Datasheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission. The citation for this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, (<http://iupac.pole-ether.fr>).

This datasheet last evaluated: August 2020; last change in preferred values: July 2018

## O<sub>3</sub> + 2,3-dimethylbut-2-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>			
$(1.51 \pm 0.08) \times 10^{-15}$	299 ± 2	Japar et al., 1974	S-CL/GC-FID (a)
$2.82 \times 10^{-15} \exp[-(294 \pm 196)/T]$	227-363	Huie and Herron, 1975	MS/MS (a)
$1.05 \times 10^{-15}$	298*		
$(1.0 \pm 0.2) \times 10^{-15}$	295 ± 0.5	Witter et al., 2002	S-UVA/FTIR (b)
<i>Relative Rate Coefficients</i>			
$(1.24 \pm 0.11) \times 10^{-16}$	296 ± 2	Greene and Atkinson, 1992	RR/GC-FID (c)

### Comments

- (a)  $k$  determined from the observed first-order rate of ozone decay (measured by the first technique shown) in the presence of known excess concentrations of 2,3-dimethylbut-2-ene (measured by the second technique shown) in air.
- (b) Experiments carried out with comparable concentrations of each reagent, in the absence of an HO radical scavenger. The system was simulated using an explicit chemical mechanism, with  $k$  optimized to recreate the observed decays in the concentrations of ozone (measured by the first technique shown) and 2,3-dimethylbut-2-ene (measured by the second technique shown).
- (c) Relative rate study, with *n*-octane present to scavenge HO radicals. The concentrations of 2,3-dimethylbut-2-ene and propene (the reference compound) were measured by GC. The measured value of  $k(\text{O}_3 + 2,3\text{-dimethylbut-2-ene})/k(\text{O}_3 + \text{propene}) = 123 \pm 11$  is placed on an absolute basis using  $k(\text{O}_3 + \text{propene}) = 1.01 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 296 K (IUPAC, current recommendation).

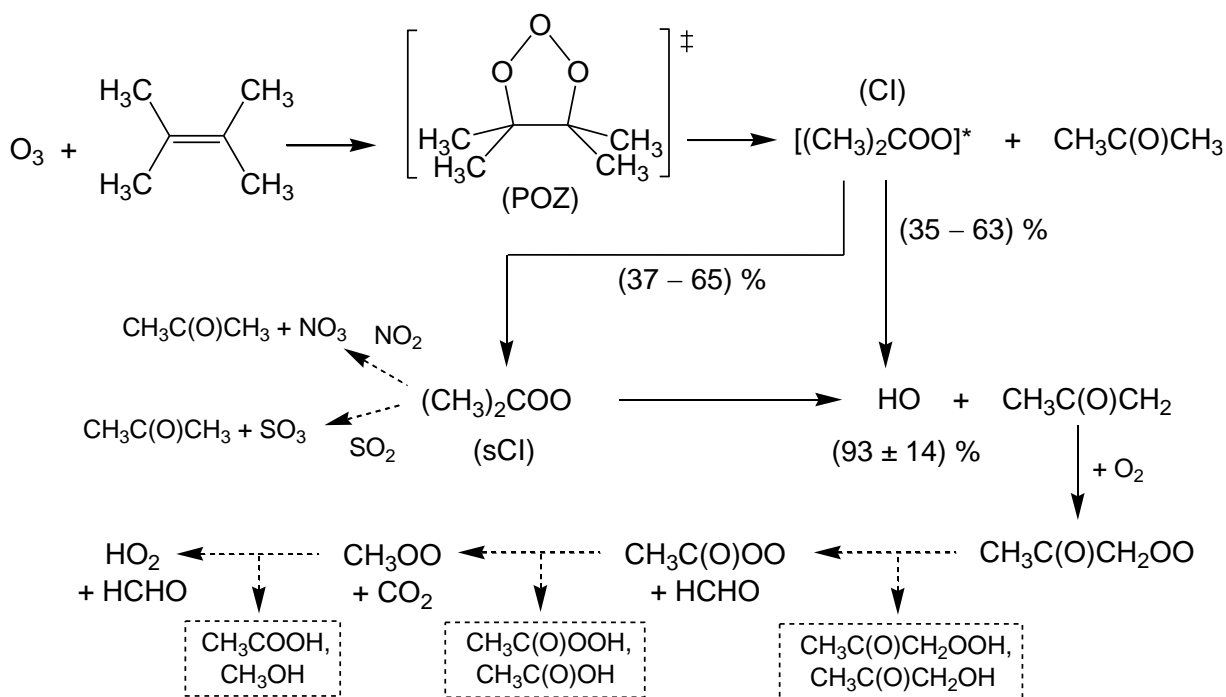
### Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.1 \times 10^{-15}$	298
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$3.0 \times 10^{-15} \exp(-300/T)$	220-370
<i>Reliability</i>		
$\Delta \log k$	± 0.08	298
$\Delta E/R$	± 200	220-370

### Comments on Preferred Values

The preferred value of  $E/R$  is based on the approximate, sole determination of Huie and Herron (1975). The preferred value of  $k$  at 298 K is based on the average of the direct determinations of Huie and Herron (1975) and Witter et al. (2002), and the relative rate determination of Greene and Atkinson (1992), corrected to 298 K, where necessary, using the preferred value of  $E/R$ . These values are in good agreement, lying within  $\pm 15\%$  of the preferred value. Japar et al. (1974) report a comparable value of  $k$ , lying about 35% higher than the preferred value.

It is well established that the reaction proceeds by initial addition of  $O_3$  to form an energy-rich “primary ozonide (POZ)” which rapidly decomposes to form an (excited) Criegee intermediate (CI),  $[(CH_3)_2COO]^*$ , and acetone,  $CH_3C(O)CH_3$ , as represented in the schematic shown below. The schematic also shows some established features of the further chemistry of  $[(CH_3)_2COO]^*$ , with suggested approximate contributions of the product pathways at 298 K and atmospheric pressure inferred from reported end product studies.



$[(CH_3)_2COO]^*$  may either decompose, or be collisionally deactivated to form the stabilized Criegee intermediate  $(CH_3)_2COO$  (sCI). The yield of sCI has been determined in a number of studies, based on scavenging with added  $SO_2$ , and quantification of the product  $H_2SO_4$  or  $CH_3C(O)CH_3$ . The yield has been shown to be dependent on pressure (Drodz et al., 2011; Hakala and Donahue, 2016; Campos-Pineda and Zhang, 2017), suggesting a small nascent yield of sCI, 12–15%, at zero pressure. There is some disagreement in the yields measured at higher pressures, although more recent studies (Berndt et al., 2014; Newland et al., 2015, 2020; Hakala and Donahue, 2016) report relatively consistent values in the range 31–45% at atmospheric pressure (preferred value  $38 \pm 10\%$ ).

The dominant decomposition route for both the excited and stabilized Criegee intermediates is expected to form HO radicals by an accepted decomposition mechanism involving abstraction of a  $\beta$ -hydrogen via a vinyl hydroperoxide intermediate (Fenske et al., 2000; Kroll et al., 2001), also forming the methylvinoxy or acetyl radical ( $CH_3C(O)CH_2$ ) as a co-product. Direct and indirect evidence for the formation of HO radicals has been reported in numerous studies (e.g. Chew and Atkinson, 1996; Rickard et al., 1999; Fenske et al., 2000; Siese et al., 2001; Orzechowska and Paulson, 2002; Aschmann et al., 2003; Berndt and Böge, 2006; Alam et al., 2013), with yields in the range 80–107% at close to atmospheric pressure (preferred value,  $93 \pm 14\%$ ). This suggests that decomposition is almost the

exclusive fate for  $(\text{CH}_3)_2\text{COO}$  under typical experimental conditions, with only a minor fraction removed by bimolecular reaction. Consistent with this, reported yields of acetone ( $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ ) in experiments employing an HO radical scavenger are close to unity (e.g. Grosjean and Grosjean, 1996; Tuazon et al., 1997; Wedian and Atkinson, 2010; Newland et al., 2020) indicating that its secondary formation from bimolecular reactions of  $(\text{CH}_3)_2\text{COO}$  is limited. Based on reported kinetic data (summarised and evaluated in datasheets CGI\_14 and CGI\_18 to CGI\_20), decomposition is also the major fate of  $(\text{CH}_3)_2\text{COO}$  under tropospheric conditions.

The acetyl radical ( $\text{CH}_3\text{C}(\text{O})\text{CH}_2$ ) reacts with  $\text{O}_2$  under atmospheric conditions. This is expected to form a stabilized peroxy radical, which can undergo conventional bimolecular reactions (e.g. with NO,  $\text{HO}_2$  and other peroxy radicals) initiating reaction sequences forming a large number of potential products, with examples shown in the schematic. These include formaldehyde (HCHO), methyl glyoxal ( $\text{CH}_3\text{C}(\text{O})\text{CHO}$ ), hydroxyacetone ( $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OH}$ ), methanol ( $\text{CH}_3\text{OH}$ ) and  $\text{CO}_2$ , which have been reported to be formed in experimental studies employing HO scavengers (e.g. Grosjean and Grosjean, 1996; Tuazon et al., 1997; Wedian and Atkinson, 2010). The approximate reported yields are 29-43 % for HCHO, 30 % for methyl glyoxal and hydroxyacetone collectively, 6 % for  $\text{CH}_3\text{OH}$  and 28 % for  $\text{CO}_2$ .

## References

- Alam, M. S., Rickard, A. R., Camredon, M., Wyche, K. P., Carr, T., Hornsby, K. E., Monks, P. S. and Bloss, W. J.: *J. Phys. Chem.*, 117, 12468, 2013.
- Aschmann, S. M., Tuazon, E. C., Arey, J. and Atkinson, R.: *J. Phys. Chem. A*, 107, 2247, 2003.
- Berndt, T. and Böge, O.: *Phys. Chem. Chem. Phys.*, 8, 1205, 2006.
- Berndt, T., Jokinen, T., Sipilä, M., Mauldin, R. L., Herrmann, H., Stratmann, F., Junninen, H. and Kulmala, M.: *Atmos. Environ.*, 89, 603, 2014.
- Campos-Pineda, M. and Zhang, J.: *Chem. Phys. Lett.*, 683, 647, 2017.
- Chew, A. A. and Atkinson, R.: *J. Geophys. Res.*, 101, 28649, 1996.
- Drozd, G. T., Kroll, J. and Donahue, N. M.: *J. Phys. Chem. A*, 115, 161, 2011.
- Fenske, J. D., Hasson, A. S., Paulson, S. E., Kuwata, K. T., Ho, A. and Houk, K. N.: *J. Phys. Chem. A*, 104, 7821, 2000.
- Greene, C. R. and Atkinson, R.: *Int. J. Chem. Kinet.*, 24, 803, 1992.
- Grosjean, E. and Grosjean, D.: *Environ. Sci. Technol.* 30, 2036, 1996.
- Hakala, J. P. and Donahue, N. M.: *J. Phys. Chem. A*, 120, 2173, 2016.
- Huie, R. E. and Herron, J. T.: *Int. J. Chem. Kinet., Symp.* 1, 165, 1975.
- Japar, S. M., Wu, C. H. and Niki, H.: *J. Phys. Chem.*, 78, 2318, 1974.
- Kroll, J. H., Sahay, S. R., Anderson, J. G., Demerjian, K. L. and Donahue, N. M.: *J. Phys. Chem. A*, 105, 4446, 2001.
- Newland, M. J., Rickard, A. R., Alam, M. S., Vereecken, L., Muñoz, A., Ródenas, M. and Bloss, W. J.: *Phys. Chem. Chem. Phys.*, 17, 4076, 2015.
- Newland, M. J., Nelson, B. S., Muñoz, A., Ródenas, M., Vera, T., Tárrega, J., and Rickard, A. R.: *Phys. Chem. Chem. Phys.*, 22, 13698, 2020.
- Orzechowska, G. and Paulson, S. E.: *Atmos. Environ.*, 36, 571, 2002.
- Rickard, A. R., Johnson, D., McGill, C. D. and Marston, G.: *J. Phys. Chem. A*, 103, 7656, 1999.
- Siese, M., Becker, K. H., Brockmann, K. J., Geiger, H., Hofzumahaus, A., Holland, F., Mihelcic, D. and Wirtz, K.: *Environ. Sci. Technol.*, 35, 4660, 2001.
- Tuazon, E. C., Aschmann, S. M., Arey, J. and Atkinson, R.: *Environ. Sci. Technol.*, 31, 3004, 1997.
- Wedian, F. Z. and Atkinson, D. B.: *J. Atmos. Chem.*, 66, 65, 2010.
- Witter, M., Berndt, T., Böge, O., Stratmann, F. and Heintzenberg, J.: *Int. J. Chem. Kinet.*, 34, 394, 2002.

