IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC15

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

O_3 + 2-methylpropene $\rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
1.8×10^{-17}	283 ± 2	Becker et al., 1974	S-UVA (a)
$(1.36 \pm 0.02) \times 10^{-17}$	299 ± 2	Japar et al., 1974	S-CL/GC-FID (a)
$3.17 \times 10^{-15} \exp[-(1671 \pm 23)/T]$	225-363	Huie and Herron, 1975	MS/MS (a)
1.16×10^{-17}	298*		
1.45×10^{-17}	295 ± 1	Grimsrud et al., 1975	F-CL (a)
1.2×10^{-17}	294 ± 2	Adeniji et al., 1981	S-CL (a)
$2.5 \times 10^{-15} \exp[-(1592 \pm 115)/T]$	240-324	Treacy et al., 1992	S-CL (a)
$(1.09 \pm 0.18) \times 10^{-17}$	298		
1.24×10^{-17}	296 ± 2	Neeb and Moortgat, 1999	S-FTIR (b)
$(1.11 \pm 0.12) \times 10^{-17}$	298	Wegener et al., 2007	S-UVA/GC-FID (c)
$3.39 \times 10^{-15} \exp[-(1697 \pm 52)/T]$	295.6-349.8	Shi et al., 2011	S-UVA (a)
$(1.09 \pm 0.02) \times 10^{-17}$	295.6		
Relative Rate Coefficients			
$(1.15 \pm 0.04) \times 10^{-17}$	296 ± 2	Greene and Atkinson, 1992	RR/GC-FID (d)
$1.89 \times 10^{-15} \exp[-(2122 \pm 102)/T]$	278-353	Avzianova and Ariya, 2002	RR/GC-FID (e)
$(1.10 \pm 0.07) \times 10^{-17}$	298		

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-methylpropene (measured either by the second technique shown, or with the initial concentration determined by quantified dilution of the pure gas).

(b) k determined from the observed first-order rate of propene decay in the presence of known excess concentrations of ozone, with both reagents measured by FTIR. Cyclohexane added to scavenge HO radicals.

(c) Experiments carried out with comparable concentrations of each reagent, in the presence of excess CO as 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-methylpropene (measured by the second technique shown).

(d) Relative rate study, with *n*-octane present to scavenge HO radicals. The concentrations of 2-methylpropene and propene (the reference compound) were measured by GC. The measured value

of $k(O_3 + \text{2-methylpropene})/k(O_3 + \text{propene}) = 1.14 \pm 0.04$ is placed on an absolute basis using $k(O_3 + \text{propene}) = 1.01 \times 10^{-17}$ cm^3 molecule^{-1} 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 O_3 + propene. The measured rate coefficient ratios were not tabulated, except at room temperature, assumed to be 298 K. The rate coefficient ratio $k(O_3 + \text{2-methylpropene})/k(O_3 + \text{propene}) = 0.327 \exp[-(242 \pm 102)/T]$, derived from the data provided in Avzianova and Ariya (2002), is placed on an absolute basis using $k(O_3 + \text{propene}) = 5.5 \times 10^{-15} \exp(-1880/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation). The 298 K rate coefficient calculated from the Arrhenius expression (1.52×10^{-18} cm^3 molecule^{-1} 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 O_3 + 2-methylpropene is similar to that for O_3 + but-1-ene (E/R = 1750 K). The Arrhenius expression cited by Avzianova and Ariya (2002) is clearly in error.

Preferred Values

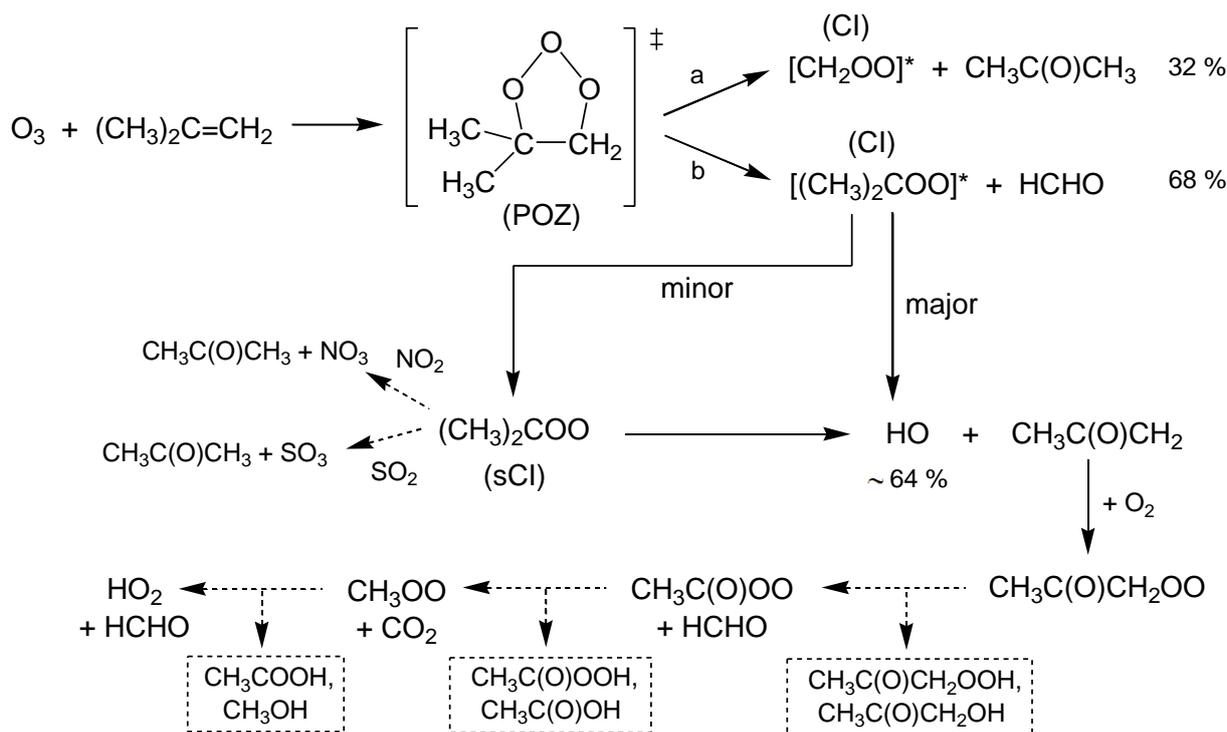| Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.15×10^{-17}	298
k /cm^3 molecule^{-1} s^{-1}	$2.92 \times 10^{-15} \exp(-1650/T)$	220-370

Reliability

$\Delta \log k$	± 0.05	298
$\Delta E/R$	± 200	220-370

Comments on Preferred Values

The preferred value of E/R is based on the average of those reported by Huie and Herron (1975), Treacy et al. (1992) and Shi et al. (2011), which are in good agreement. The Arrhenius parameters given by Avzianova and Ariya (2002) are inconsistent with the reported room temperature value of k (see comment (e)), and their value of E/R is significantly greater than the preferred value.

The preferred value of k at 298 K is based on the average of the direct determinations of Huie and Herron (1975), Treacy et al. (1992), Wegener et al. (2007) and Shi et al. (2011) and the relative rate determinations of Greene and Atkinson (1992) and Avzianova and Ariya (2002), corrected to 298 K, where necessary, using the preferred value of E/R. These values are in very good agreement, lying within ± 5 % of the preferred value. The absolute determinations of Japar et al. (1974), Adeniji et al. (1981) and Neeb and Moorgat (1999) are also consistent with the preferred value, lying 12-16 % higher. Grimsrud et al. (1975) and Becker et al. (1983) report values of k lying about 30 % and a factor of two higher, respectively.

It is well established that the reaction proceeds by initial addition of O_3 to form an energy-rich "primary ozonide" which rapidly decomposes to form two sets of primary carbonyl product plus (excited) Criegee intermediate, as shown in the schematic below. Reported yields of acetone ($CH_3C(O)CH_3$) and formaldehyde (HCHO) suggest important contributions from both decomposition channels, (a) and (b), with HCHO also expected to have secondary sources (see below). Values of $k_a/(k_a+k_b)$ lying in the range 0.28-0.35 can be inferred from the reported molar yields of acetone (Grosjean et al., 1996; Tuazon et al., 1997; Neeb and Moortgat, 1999; Newland et al., 2020), consistent with the value given in the schematic.

$$O_3 + (CH_3)_2C=CH_2 \longrightarrow \left[\begin{array}{c} O \\ O \quad O \\ H_3C \\ \overset{|}{C} - CH_2 \\ H_3C \end{array} \right]^{\ddagger}$$

(POZ)

a → (CI) $[CH_2OO]^* + CH_3C(O)CH_3$ 32 %

b → (CI) $[(CH_3)_2COO]^* + HCHO$ 68 %

minor

major

$CH_3C(O)CH_3 + NO_3$ NO_2

$CH_3C(O)CH_3 + SO_3$ SO_2 ←---- $(CH_3)_2COO$ (sCI) → $HO + CH_3C(O)CH_2$ ~ 64 %

$+ O_2$

$HO_2 + HCHO$ ←---- $CH_3OO + CO_2$ ←---- $CH_3C(O)OO + HCHO$ ←---- $CH_3C(O)CH_2OO$

$CH_3COOH,$ CH_3OH | $CH_3C(O)OOH,$ $CH_3C(O)OH$ | $CH_3C(O)CH_2OOH,$ $CH_3C(O)CH_2OH$

The further chemistry of $[CH_2OO]^*$ is expected to follow the pathways described in the data sheet for the $O_3 + C_2H_4$ reaction (Ox_VOC5), although their relative importance is not necessarily the same. The schematic above 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 total yield of stabilized Criegee intermediates (i.e. CH_2OO and $(CH_3)_2COO$) has been determined by scavenging with added SO_2 and quantifying the associated products, H_2SO_4 (Hatekayama et al., 1986) or HCHO and $CH_3C(O)CH_3$ (Newland et al., 2020). The recommended total yield, based on these studies, is 21 ± 5 %. Newland et al. (2020) report that CH_2OO and $(CH_3)_2COO$ account for about 70 % and 30 % of the total sCI yield, respectively. Consistent with this, Neeb et al. (1997) inferred a yield of 13 % specifically for CH_2OO, based on scavenging with added H_2O and quantification of the product $HOCH_2OOH$. This suggests that the major fate of $[(CH_3)_2COO]^*$ formed from 2-methylpropene ozonolyis is decomposition, with only a minor fraction stabilized to form $(CH_3)_2COO$.

The dominant decomposition route for both $[(CH_3)_2COO]^*$ and $(CH_3)_2COO$ is expected to form HO radicals by an accepted decomposition mechanism involving abstraction of a β-hydrogen via a vinyl hydroperoxide intermediate (Fenske et al., 2000; Kroll et al., 2001), also forming the 1-methylvinoxy or acetonyl 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. Atkinson and Aschmann, 1993; Neeb and Moortgat, 1999; Paulson et al., 1999; Rickard et al., 1999; Wegener et al., 2007; Alam et al., 2013), with yields in the range 60–84 % (preferred value, 69 %). A minor contribution to HO formation may also result from decomposition of $[CH_2OO]^*$. Assuming that the relative importance of the reaction pathways for $[CH_2OO]^*$ formed from 2-methylpropene are similar to those for $[CH_2OO]^*$ formed from ethene, this contribution is estimated to be about 5 %, suggesting that decomposition of $[(CH_3)_2COO]^*$ and $(CH_3)_2COO$ contributes about 64 %. Based on reported kinetic data (summarised and evaluated in datasheets CGI_14 and CGI_18 to CGI_20), decomposition is also expected to be the major fate of $(CH_3)_2COO$ under tropospheric conditions.

The acetonyl radical ($CH_3C(O)CH_2$) reacts with O_2 under atmospheric conditions. This is expected to form a stabilized peroxy radical, which can undergo conventional bimolecular reactions (e.g. with NO, HO_2 and other peroxy radicals) initiating reaction sequences forming a large number of potential products, with examples shown in the schematic. These include methyl glyoxal ($CH_3C(O)CHO$), hydroxyacetone ($CH_3C(O)CH_2OH$), methanol (CH_3OH) and CO_2, which have been reported to be formed with respective yields of about 15 %, 7 %, 5 % and 28 % (Neeb and Moortgat, 1999; Tuazon et al., 1997). CO_2 may also be formed from the decomposition of $[CH_2OO]^*$, with an estimated yield of about 7 % (assuming the relative importance of the pathways is similar to those in the ethene system). The chemistry also results in significant secondary formation of HCHO. Total molar yields in the range 95−119 % have been reported by Grosjean et al. (1996), Tuazon et al. (1997), Neeb and Moortgat (1999) and Newland et al. (2020), which is consistent with major primary and secondary sources in the system.

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