

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC29

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This data sheet updated: 24th October 2007 (with revision of preferred values).

OH + (CH₃)₂C(OH)CH=CH₂ → products

Rate coefficient data

<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
8.2 x 10 ⁻¹² exp[(610 ± 50)/T]	231-300	Rudich et al., 1995	PLP-LIF (a)
(6.4 ± 0.6) x 10 ⁻¹¹	298		
(6.32 ± 0.27) x 10 ⁻¹¹	300	Baasandorj and Stevens, 2007	DF-LIF (b)
<i>Relative Rate Coefficients</i>			
(3.81 ± 0.80) x 10 ⁻¹¹	298 ± 2	Fantechi et al., 1998a	RR (c,d)
(4.27 ± 1.80) x 10 ⁻¹¹	298 ± 2	Fantechi et al., 1998a	RR (c,e)
(6.43 ± 0.54) x 10 ⁻¹¹	295 ± 1	Ferronato et al., 1998	RR (e,f)
(7.35 ± 0.78) x 10 ⁻¹¹	295 ± 1	Ferronato et al., 1998	RR (f,g)
(5.64 ± 0.13) x 10 ⁻¹¹	296 ± 2	Papagni et al., 2001	RR (h)
(6.45 ± 0.28) x 10 ⁻¹¹	298 ± 2	Imamura et al., 2004	RR (i,j)
(6.47 ± 0.32) x 10 ⁻¹¹	298 ± 2	Imamura et al., 2004	RR (e,i)
(5.6 ± 0.2) x 10 ⁻¹¹	298 ± 2	Carrasco et al., 2007	RR (d,i)

Comments

- (a) Rate coefficients for the reactions of HO, H¹⁸O and DO radicals with 2-methyl-3-buten-2-ol were measured, in the presence and absence of O₂ [up to 13.5 Torr (18 mbar) O₂ in the case of the HO radical reaction], over the temperature range 231-410 K. Above ~350 K the rate coefficients decreased with increasing temperature faster than predicted based on extrapolation of the lower temperature data. For the HO radical reaction, the rate coefficients in the presence of 2-13.5 Torr of O₂ were up to 15-20% higher than in the absence of O₂, while the measured rate coefficients for the DO radical reaction were invariant to the presence or absence of O₂. HO radicals were observed to be formed in the DO radical reaction, and the rate coefficients of the DO radical and H¹⁸O radical reactions were essentially identical to those for the HO radical reactions in the presence of O₂. These data indicated that the measured rate coefficients from the HO radical reaction in the absence of O₂ are low because of HO radical regeneration, whereas H¹⁸O and DO radical regeneration does not occur from reactions of H¹⁸O and DO radicals with 2-methyl-3-buten-2-ol (HO radicals being formed by elimination of the –OH group in the 2-methyl-3-buten-2-ol in the absence of O₂). The rate coefficient cited is derived (Rudich et al., 1995) from the rate coefficients measured for the HO and DO radical reactions in the presence of O₂ over the temperature range 230-300 K, and is expected to be applicable to atmospheric conditions.
- (b) Rate coefficients were measured over the temperature range 300-415 K at total pressures of helium diluent of 2-5 Torr (2.7-6.7 mbar), in the presence and absence of O₂. The room temperature rate coefficient measured in the presence of ~5-15% O₂ was ~15% higher than that measured in the absence of O₂ [as also observed by Rudich et al. (1995); see Comment (a)]. While the rate coefficient at 300 K was independent of total pressure over the range 2-5 Torr (2.7-6.7 mbar), at ≥335 K the measured rate coefficients in the presence of O₂ were

pressure dependent. These observations indicate that at temperatures ≥ 335 K and pressures < 5 Torr the reaction is in the fall-off regime. Hence only the 300 K pressure-independent rate coefficient is listed in the table. Rate coefficients were also measured for the reaction of DO radicals with 2-methyl-3-buten-2-ol over the same temperature range, with a 300 K rate coefficient of $(6.61 \pm 0.66) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

- (c) HO radicals were generated by the photolysis of H_2O_2 at 253.7 nm in air at 987 ± 7 mbar pressure. The concentrations of 2-methyl-3-buten-2-ol and isoprene (or propene) [the reference compounds] were measured during the experiments by FTIR spectroscopy. The measured rate coefficient ratios $k(\text{HO} + 2\text{-methyl-3-buten-2-ol})/k(\text{HO} + \text{isoprene})$ and $k(\text{HO} + 2\text{-methyl-3-buten-2-ol})/k(\text{HO} + \text{propene})$ are placed on an absolute basis by use of rate coefficients at 298 K and atmospheric pressure of $k(\text{HO} + \text{isoprene}) = 1.00 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003; IUPAC, current recommendation) and $k(\text{HO} + \text{propene}) = 2.63 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003).
- (d) Relative to $k(\text{HO} + \text{isoprene})$.
- (e) Relative to $k(\text{HO} + \text{propene})$.
- (f) HO radicals were generated by the photolysis (340-400 nm) of $^{13}\text{CH}_3\text{ONO-NO-(CH}_3)_2\text{C(OH)CH=CH}_2$ -propene (or ethene) [the reference compounds]-air mixtures at 933 mbar pressure. The concentrations of 2-methyl-3-buten-2-ol and propene (or ethene) were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(\text{HO} + 2\text{-methyl-3-buten-2-ol})/k(\text{HO} + \text{propene}) = 2.4 \pm 0.2$ and $k(\text{HO} + 2\text{-methyl-3-buten-2-ol})/k(\text{HO} + \text{ethene}) = 8.5 \pm 0.9$ are placed on an absolute basis by use of rate coefficients at 295 K and atmospheric pressure of air of $k(\text{HO} + \text{propene}) = 2.68 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{HO} + \text{ethene}) = 8.65 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003).
- (g) Relative to $k(\text{HO} + \text{ethene})$.
- (h) HO radicals were generated by the photolysis (at ≥ 300 nm) of $\text{CH}_3\text{ONO-NO-(CH}_3)_2\text{C(OH)CH=CH}_2$ -1,3,5-trimethylbenzene (the reference compound)-air mixtures at 987 mbar pressure. The concentrations of 2-methyl-3-buten-2-ol and 1,3,5-trimethylbenzene were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + 2\text{-methyl-3-buten-2-ol})/k(\text{HO} + 1,3,5\text{-trimethylbenzene}) = 0.995 \pm 0.022$ is placed on an absolute basis using a rate coefficient of $k(\text{HO} + 1,3,5\text{-trimethylbenzene}) = 5.67 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (Atkinson and Arey, 2003).
- (i) HO radicals were generated by the photolysis of $\text{CH}_3\text{ONO-NO-(CH}_3)_2\text{C(OH)CH=CH}_2$ -di-*n*-butyl ether, propene or isoprene (the reference compounds)-air mixtures at atmospheric pressure. The concentrations of 2-methyl-3-buten-2-ol and the reference compounds were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(\text{HO} + 2\text{-methyl-3-buten-2-ol})/k(\text{HO} + \text{di-}n\text{-butyl ether}) = 2.32 \pm 0.10$ (Imamura et al., 2004), $k(\text{HO} + 2\text{-methyl-3-buten-2-ol})/k(\text{HO} + \text{propene}) = 2.46 \pm 0.12$ (Imamura et al., 2004) and $k(\text{HO} + 2\text{-methyl-3-buten-2-ol})/k(\text{HO} + \text{isoprene}) = 0.56 \pm 0.02$ (Carrasco et al., 2007) are placed on an absolute basis by use of rate coefficients at 298 K and atmospheric pressure of air of $k(\text{HO} + \text{di-}n\text{-butyl ether}) = 2.78 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Mellouki et al., 1995), $k(\text{HO} + \text{propene}) = 2.63 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003), and $k(\text{HO} + \text{isoprene}) = 1.00 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003; IUPAC, current recommendation).
- (j) Relative to $k(\text{HO} + \text{di-}n\text{-butyl ether})$.

Preferred Values

$k = 8.1 \times 10^{-12} \exp(610/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230-300 K.

$k = 6.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

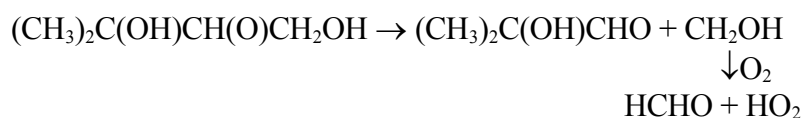
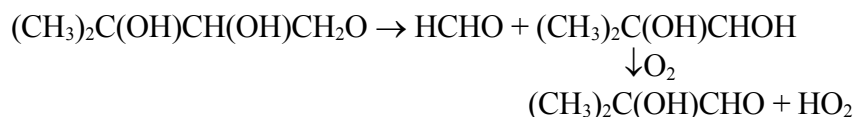
$\Delta \log (E/R) = \pm 200$ K.

Comments on Preferred Values

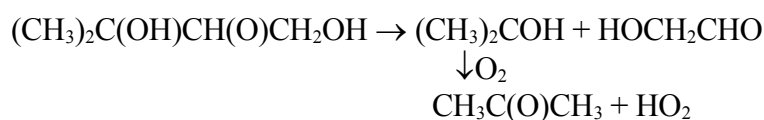
The room temperature rate coefficients of Rudich et al. (1995), Ferronato et al. (1998), Papagni et al. (2001), Imamura et al. (2004), Baasandorj and Stevens (2007) and Carrasco et al. (2007) are in reasonable agreement, although the rate coefficient of Ferronato et al. (1998) relative to ethene is somewhat higher than those of Rudich et al. (1995), Papagni et al. (2001), Imamura et al. (2004), Baasandorj and Stevens (2007) and Carrasco et al. (2007) and that of Ferronato et al. (1998) relative to propene. The two relative rate coefficients of Fantechi et al. (1998a) are significantly lower than the values measured by Rudich et al. (1995), Ferronato et al. (1998), Papagni et al. (2001), Imamura et al. (2004), Baasandorj and Stevens (2007) and Carrasco et al. (2007). The preferred 298 K rate coefficient is the average of the absolute and relative rate coefficients of Rudich et al. (1995), Ferronato et al. (1998), Papagni et al. (2001), Imamura et al. (2004) and Carrasco et al. (2007). The preferred temperature dependence is that reported by Rudich et al. (1995), and the pre-exponential factor is adjusted to fit the preferred 298 K rate coefficient.

The reaction proceeds almost totally by initial addition of HO to the C=C bond (Fantechi et al., 1998b; Ferronato et al., 1998; Alvarado et al., 1999; Spaulding et al., 2002; Reisen et al., 2003; Carrasco et al., 2007). In the presence of NO at atmospheric pressure of air the observed products are formaldehyde, acetone, glycolaldehyde, 2-hydroxy-2-methylpropanal [(CH₃)₂C(OH)CHO], and dihydroxynitrates [presumed to be (CH₃)₂C(OH)CH(OH)CH₂ONO₂ and (CH₃)₂C(OH)CH(ONO₂)CH₂OH] (Fantechi et al., 1998b; Ferronato et al., 1998; Alvarado et al., 1999; Spaulding et al., 2002; Reisen et al., 2003; Carrasco et al., 2007). Based on the product studies of Ferronato et al. (1998), Alvarado et al. (1999), Reisen et al. (2003) and Carrasco et al. (2007) carried out in the presence of NO, the product yields are: formaldehyde, 35 ± 4% (Ferronato et al., 1998), 29 ± 3% (Alvarado et al., 1999) and 33 ± 8% (Carrasco et al., 2007); acetone, 52 ± 5% (Ferronato et al., 1998), 58 ± 4% (Alvarado et al., 1999) and 67 ± 5% (Carrasco et al., 2007); glycolaldehyde, 50 ± 5% (Ferronato et al., 1998), 61 ± 9% (Alvarado et al., 1999) and 78 ± 20% (Carrasco et al., 2007); 2-hydroxy-2-methylpropanal, 31 ± 4% (Reisen et al., 2003) and 31 ± 11% (Carrasco et al., 2007) [note that Carrasco et al. (2007) had a standard of 2-hydroxy-2-methylpropanal available, in contrast to Riesen et al. (2003)]; and dihydroxynitrates, 5 ± 2% (Alvarado et al., 1999).

The reaction mechanism is discussed in detail in Alvarado et al. (1999) and Carrasco et al. (2007). Reactions of the (CH₃)₂C(OH)CH(OH)CH₂OO and (CH₃)₂C(OH)CH(OO)CH₂OH peroxy radicals (formed after addition of O₂ to the initially formed (CH₃)₂C(OH)CH(OH)CH₂ and (CH₃)₂C(OH)CHCH₂OH radicals) with NO lead to the formation of the dihydroxynitrates (CH₃)₂C(OH)CH(OH)CH₂ONO₂ and (CH₃)₂C(OH)CH(ONO₂)CH₂OH or NO₂ plus the dihydroxyalkoxy radicals (CH₃)₂C(OH)CH(OH)CH₂O and (CH₃)₂C(OH)CH(O)CH₂OH. At room temperature and atmospheric pressure of air these dihydroxyalkoxy radicals appear to dominantly decompose:



and/or



Hence, as observed, the yield of HCHO equals that of $(\text{CH}_3)_2\text{C}(\text{OH})\text{CHO}$ [$\sim 31\%$], and the yield of HOCH_2CHO equals that of $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ [$\sim 60\%$] (Ferronato et al., 1998; Alvarado et al., 1999; Reisen et al., 2003; Carrasco et al., 2007). Fantechi et al. (1998b) and Carrasco et al. (2007) have investigated the reaction in the absence of NO (see Carrasco et al., 2007, for details).

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