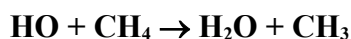


# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO<sub>x</sub>\_VOCl

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hard copy without explicit written permission.

This data sheet updated: 4<sup>th</sup> June 2013 (with no revision of the preferred values).



$$\Delta H^\circ = -57.8 \text{ kJ}\cdot\text{mol}^{-1}$$

## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(4.3 \pm 0.9) \times 10^{-12}$	$1234 \pm 15$	Bott and Cohen, 1989	SH-RA
$1.59 \times 10^{-20} T^{2.84} \exp(-978/T)$	223-420	Vaghjiani and Ravishankara, 1991	PLP-LIF
$6.35 \times 10^{-15}$	298		
$4.0 \times 10^{-12} \exp[-(1944 \pm 114)/T]$	278-378	Finlayson-Pitts et al., 1992	DF-RF
$5.87 \times 10^{-15}$	298		
$9.65 \times 10^{-20} T^{2.58} \exp(-1082/T)$	293-800	Dunlop and Tully, 1993	PLP-LIF (a)
$(5.62 \pm 0.43) \times 10^{-15}$	293		
$2.56 \times 10^{-12} \exp[-(1765 \pm 146)/T]$	233-343	Mellouki et al., 1994	PLP-LIF
$(6.34 \pm 0.88) \times 10^{-15}$	298		
$1.85 \times 10^{-20} T^{2.82} \exp[-(987 \pm 6)/T]$	195-296	Gierczak et al., 1997	PLP-LIF/ FP-LIF (b)
$(6.40 \pm 0.38) \times 10^{-15}$	298		
$5.65 \times 10^{-21} T^{3.01} \exp[-(959 \pm 36)/T]$	295-668	Bonard et al., 2002	PLP-LIF
$(6.23 \pm 0.20) \times 10^{-15}$	295		
$(6.2 \pm 0.2) \times 10^{-15}$	296	Amedro et al., 2012	PLP-LIF/FAGE (c)

## Comments

- (a) The temperature-dependent expression cited is that for the rate coefficients of Dunlop and Tully (1993) ( $T = 293\text{-}800$  K) combined with those of Vaghjiani and Ravishankara (1991) ( $T = 223\text{-}420$  K) and as such covers the temperature range 223-800 K.
- (b) The temperature-dependent expression cited is that for the rate coefficients of Gierczak et al. (1997) ( $T = 195\text{-}296$  K) combined with those of Vaghjiani and Ravishankara (1991) ( $T = 223\text{-}420$  K) obtained using a similar technique, and therefore covers the temperature range 195-420 K.
- (c) FAGE setup permitting measurement of OH and HO<sub>2</sub> in a flow system at 1 bar, with detection limit of approx.  $1 \times 10^6$  molecules  $\text{cm}^{-3}$ . Experiment configured for on-line (OLC) and 90degree (NDC) extraction of photolysate. Different fitting processes were tested to extract the pseudo first-order rate constants from the chemical decays. Cited values obtained in OLC configuration which had less statistical error.

## Preferred Values

$k = 6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.85 \times 10^{-12} \exp(-1690/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200-300 K.

### Reliability

$\Delta \log k = \pm 0.06$  at 298 K

$\Delta(E/R) = \pm 100 \text{ K}$ .

### Comments on Preferred Values

The absolute rate coefficients of Vaghjiani and Ravishankara (1991), Finlayson-Pitts et al. (1992), Dunlop and Tully (1993), Mellouki et al. (1994), Gierczak et al. (1997) and Bonard et al. (2002) are in good agreement. However, over the temperature range ~250-420 K these rate coefficients of Vaghjiani and Ravishankara (1991), Finlayson-Pitts et al. (1992), Dunlop and Tully (1993), Mellouki et al. (1994), Gierczak et al. (1997) and Bonard et al. (2002) are ~20% lower than most of the previously reported absolute rate coefficients (Atkinson, 1994).

The preferred values are derived from the absolute rate coefficient data of Vaghjiani and Ravishankara (1991) and Gierczak et al. (1997), both conducted over significant and overlapping temperature ranges. The temperature-dependent expression obtained by Gierczak *et al.* (1997) from a fit of their data and those of Vaghjiani and Ravishankara (1991) to the three-parameter equation  $k = CT^n \exp(-D/T)$  is accepted, of  $k = 1.85 \times 10^{-20} T^{2.82} \exp(-987/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 195-420 K (Gierczak et al., 1997). The preferred Arrhenius expression,  $k = A \exp(-B/T)$ , is centered at 250 K and is derived from the three-parameter equation with  $A = C e^n T^n$  and  $B = D + nT$ . The recommended three-parameter expression leads to calculated rate coefficients at 800 K and 1234 K which are within 12% and 3%, respectively of the values measured by Dunlop and Tully (1993) at 800 K and Bott and Cohen (1989) at 1234 K, and agrees to within 8% with the rate coefficients measured by Bonard et al. (2002) over the temperature range 295-668 K.

## References

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- Bott and Cohen (1989)
- Vaghjiani and Ravishankara (1991)
- ▲ Finlayson-Pitts et al. (1992)
- ▼ Dunlop and Tully (1993)
- ◆ Mellouki et al. (1994)
- ◆ Gierczak et al. (1997)
- Recommendation

