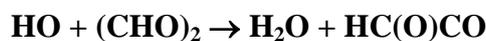


Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC16

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 hardcopy without explicit written permission. This data sheet last evaluated 29th May 2008 (with revision of the preferred values).



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$6.6 \times 10^{-18} T^2 \exp[(820 \pm 30)/T]$	209-391	Feierabend et al., 2008	PLP-LIF (a)
$(9.15 \pm 0.8) \times 10^{-12}$	296		
<i>Relative Rate Coefficients</i>			
$(1.06 \pm 0.04) \times 10^{-11}$	298 ± 2	Plum et al., 1983	RR (b)

Comments

- (a) Glyoxal-He mixtures were prepared and stored in Pyrex bulbs, and the glyoxal concentrations in the flow stream from these bulbs was measured by UV absorption at 254 nm prior to being mixed with other gas streams and entering the reaction cell, and also by FTIR spectroscopy either before or after the reaction cell. These measurements indicated that any wall losses of glyoxal during passage through the reaction cell were <5%. Over the temperature range 209-296 K, the measured rate coefficients were well fit by the Arrhenius expression $k = 2.8 \times 10^{-12} \exp[(340 \pm 50)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Rate coefficients were also measured for DO + (CHO)₂ at 293 K, 298 K, 349 K and 390 K, resulting in $k = 3.7 \times 10^{-12} \exp[(285 \pm 40)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (b) HO radicals were generated by the photolysis of CH₃ONO in air, and the concentrations of glyoxal and cyclohexane (the reference compound) were measured by differential optical absorption spectroscopy and GC, respectively. The measured rate coefficient ratio of $k(\text{HO} + \text{glyoxal})/k(\text{HO} + \text{cyclohexane}) = 1.52 \pm 0.05$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 6.97 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 2003).

Preferred Values

$k = 3.1 \times 10^{-12} \exp(340/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200-300 K.
 $k = 9.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

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

Comments on Preferred Values

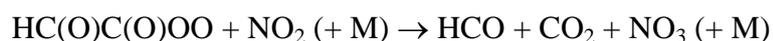
The room temperature rate coefficients from the absolute rate study of Feierabend et al. (2008) and the relative rate study of Plum et al. (1983) are in good agreement. The temperature dependence of Feierabend et al. (2008) is accepted (using their 209-296 K Arrhenius expression). The preferred 298 K rate coefficient is the average of the room temperature rate coefficients of Plum et al. (1983) and Feierabend et al. (2008), and the A-factor is adjusted to fit the preferred 298 K rate coefficient. The room temperature rate coefficient and temperature dependence are similar to those for other aldehydes

(IUPAC, 2008). The reaction is assumed to proceed via overall H-atom abstraction to yield H₂O + HC(O)CO. Niki et al. (1985) and Orlando and Tyndall (2001) have shown, from product studies of the Cl atom- and HO radical-initiated reactions of glyoxal using FTIR spectroscopy, that the HC(O)CO radical reacts by the pathways.



Niki et al. (1985) determined that at 298 K and 933 mbar (700 Torr) total pressure, $k_b \sim k_c$ and $k_a/k_b = 3.5 \times 10^{18} \text{ molecule cm}^{-3}$. More recently, Orlando and Tyndall (2001) measured the rate coefficient ratio k_c/k_b to be $k_c/k_b = 1.0 \pm 0.2$, independent of temperature over the range 224-317 K at 933 mbar (700 Torr) total pressure, in good agreement with the earlier measurement of Niki et al. (1985). Assuming an temperature-independent rate coefficient of $k_b (= k_c) = 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, Orlando and Tyndall (2001) also derived a rate coefficient at 933 mbar pressure for the HC(O)CO decomposition of $k_a = 1.4 \times 10^{12} \exp[-(3160 \pm 500)/T] \text{ s}^{-1}$. This results in a rate coefficient ratio k_a/k_b at 298 K a factor of 2 higher than that derived by Niki et al. (1985).

In the presence of NO₂, Orlando and Tyndall (2001) observed no evidence for the formation of the PAN-type compound HC(O)C(O)OONO₂, even at 224 K. Based on the observed formation of CO, CO₂, HO₂NO₂ and N₂O₅, Orlando and Tyndall (2001) postulated that HC(O)C(O)OO radicals react with NO₂ as follows,



with subsequent reactions of HCO with O₂ to form HO₂ + CO, of HO₂ with NO₂ to form HO₂NO₂, and of NO₃ with NO₂ to form N₂O₅, thereby leading to the observed products.

References

- Atkinson, R.: Atmos. Chem. Phys. 3, 2233, 2003.
Feierabend, K. J., Zhu, L., Talukdar, R. K. and Burkholder, J. B.: J. Phys. Chem. A 112, 73, 2008.
IUPAC,: <http://iupac.pole-ether.fr>, 2013.
Niki, H., Maker, P. D., Savage, C. M., and Breitenbach, L. P.: Int. J. Chem. Kinet. 17, 547, 1985.
Orlando, J. J. and Tyndall, G. S.: Int. J. Chem. Kinet. 33, 149, 2001.
Plum, C. N. Sanhueza, E., Atkinson, R., Carter, W. P. L., and Pitts Jr., J. N.: Environ. Sci. Technol. 17, 479, 1983.

