IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iBrOx12

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$HO + Br_2 \rightarrow HOBr + Br$

$\Delta H° \geq -12$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(4.2 \pm 0.7) \times 10^{-11}$	298 ± 2	Poulet et al., 1983	DF-LIF/EPR
$(5.28 \pm 0.63) \times 10^{-11}$	298 ± 3	Loewenstein and Anderson, 1984	DF-RF
$(2.8 \pm 1.2) \times 10^{-11}$	262-303	Boodaghians et al., 1987	DF-RF (a)
$(3.4 \pm 1.2) \times 10^{-11}$	293		
$1.98 \times 10^{-11} \exp[(238 \pm 70)/T]$	235-357	Gilles et al., 1999	PLP-LIF
$(4.80 \pm 0.70) \times 10^{-11}$	298		
$1.8 \times 10^{-11} \exp[(235 \pm 50)/T]$	230-360	Bedjanian et al., 1999	DF-MS
3.96×10^{-11}	298		
$4.31 \times 10^{-11} (T/298)^{-(0.66 \pm 0.03)}$	297-766	Bryukov et al., 2006	PLP-LIF (b)
$(4.30 \pm 0.17) \times 10^{-11}$	297		

Comments

(a) A least-squares fit of the measured rate coefficients results in $k = 5.8 \times 10^{-10} \exp[-(866 \pm 1107)/T]$ cm^3 molecule^{-1} s^{-1}, consistent with a temperature-independent rate coefficient over the small temperature range studied.

(b) A least-squares fit to the combined data of Gilles et al. (1999), Bedjanian et al. (1999) and Bryukov et al. (2006) results in $k = 4.31 \times 10^{-11} (T/298)^{-0.67}$ cm^3 molecule^{-1} s^{-1} over the temperature range 230-766 K (Bryukov et al., 2006).

Preferred Values

$k = 4.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.9 \times 10^{-11} \exp(240/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230-360 K.

Reliability

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

$\Delta(E/R) = \pm 150$ K.

Comments on Preferred Values

The rate coefficient is now well determined at room temperature, and the recommended value is the mean of those reported by Poulet et al. (1983), Loewenstein and Anderson (1984), Boodaghians et al. (1987), Gilles et al. (1999), Bedjanian et al. (1999) and Bryukov et al.

(2006). Boodaghians et al. (1987) found a near zero temperature dependence over the range 262-303 K while the more recent studies of Gilles et al. (1999), Bedjanian et al. (1999) and Bryukov et al. (2006) have obtained small negative temperature dependencies over the significantly wider temperature range of 230-766 K. Of the three most recent studies, those of Gilles et al. (1999) and Bedjanian et al. (1999) extended down to 230-235 K and the temperature dependence from these two studies is accepted. The pre-exponential factor, A, is adjusted to fit the preferred 298 K rate coefficient using this recommended temperature dependence.

Poulet et al. (1983), Loewenstein and Anderson (1984) and Bedjanian et al. (1999) determined that the products are Br + HOBr, with the alternative reaction pathway leading to HBr + BrO accounting for <1% of the overall reaction at 298 K (Loewenstein and Anderson, 1984).

References

Bedjanian, Y., Le Bras, G. and Poulet, G.: Int. J. Chem. Kinet. 31, 698, 1999.

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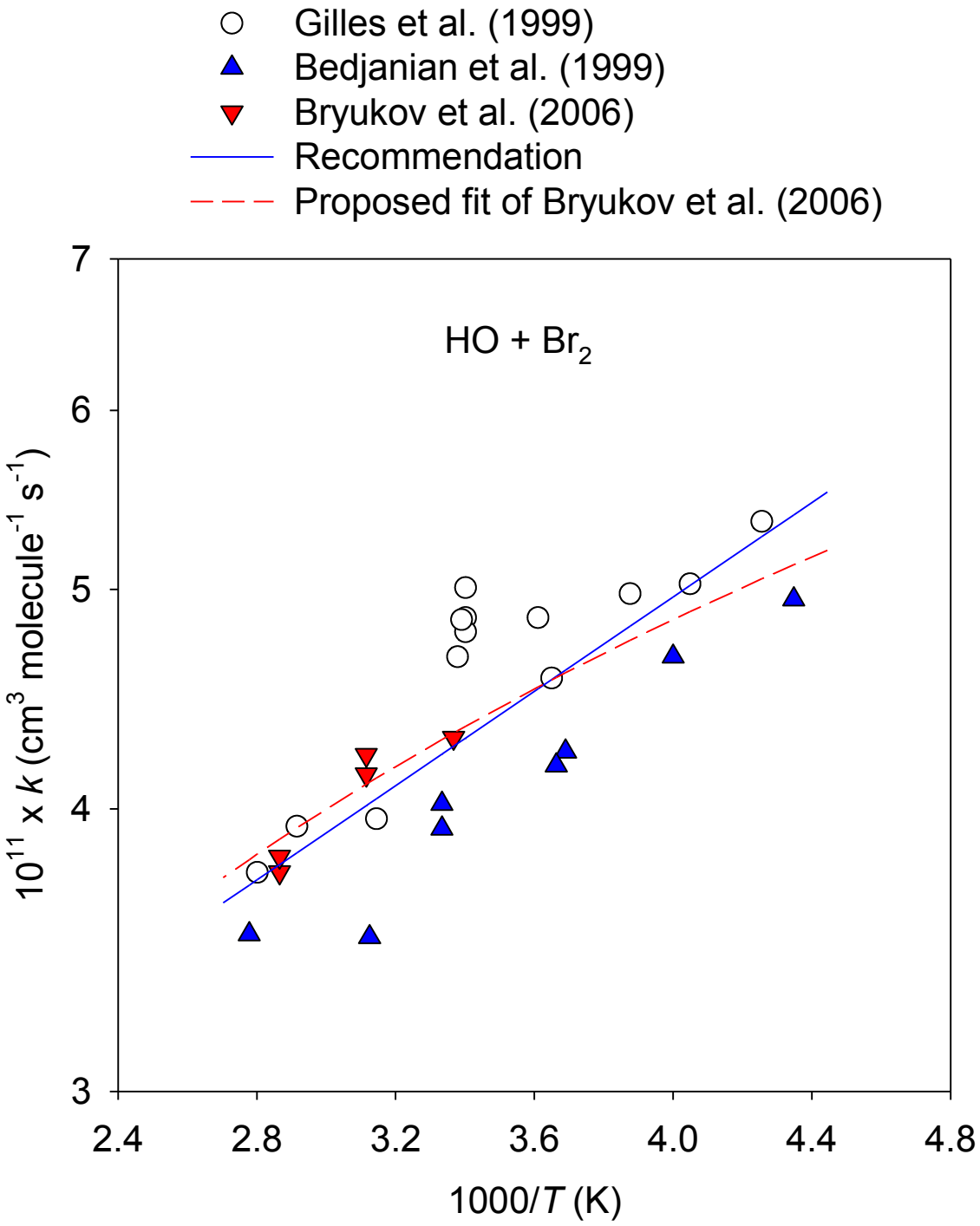
Bryukov, M. G., Dellinger, B. and Knyazev, V. R.: J. Phys. Chem. A 110, 9169, 2006.

Gilles, M. K., Burkholder, J. B. and Ravishankara, A. R.: Int. J. Chem. Kinet. 31, 417, 1999.

Loewenstein, L. M. and Anderson, J. G.: J. Phys. Chem. 88, 6277, 1984.

Poulet, G., Laverdet, G. and Le Bras, G.: Chem. Phys. Lett. 94, 129, 1983.


Gilles et al. (1999)
Bedjanian et al. (1999)
Bryukov et al. (2006)
Recommendation
Proposed fit of Bryukov et al. (2006)
HO + Br2
10^11 x k (cm^3 molecule^-1 s^-1)
1000/T (K)
7
6
5
4
3
2.4
2.8
3.2
3.6
4.0
4.4
4.8