Authors:

Jean-Christophe Loison (Univ. Bordeaux, France)

Stephen J. Klippenstein (Argonne National Laboratory, Argonne, USA)

Kevin M. Hickson (Univ. Bordeaux, France)

30 November 2014

$$\mathbf{O(^3P) + CH_2(^3\Sigma^-_g) \rightarrow H_2CO(^1A_1)} \qquad \Delta H^\circ_{298} = -\,820\ \text{kJ mol}^{-1}\ \text{(Baulch \textit{et al.}, 2005)}$$

$$\mathbf{\rightarrow H_2(^1\Sigma^+_g) + CO(^1\Sigma^+_g)} \qquad \mathbf{(1)} \qquad \Delta H^\circ_{298} = -\,751\ \text{kJ mol}^{-1}\ \text{(Baulch \textit{et al.}, 2005)}$$

$$\mathbf{\rightarrow H(^2S) + H(^2S) + CO(^1\Sigma^+_g)} \qquad \mathbf{(2)} \qquad \Delta H^\circ_{298} = -\,315\ \text{kJ mol}^{-1}\ \text{(Baulch \textit{et al.}, 2005)}$$

$$\mathbf{\rightarrow H(^2S) + HCO(^2A')} \qquad \mathbf{(3)} \qquad \Delta H^\circ_{298} = -\,489\ \text{kJ mol}^{-1}\ \text{(Baulch \textit{et al.}, 2005)}$$

Rate Coefficient Data *k*

k / cm^3 molecule^{-1} s^{-1}	*T* / K	Reference	Comments
Rate Coefficient Measurements			
1.3×10^{-10}	390-600	(Vinckier & Debruyn 1979)	
8.4×10^{-11}	298	(Homann & Schweinfurth 1981)	
1.4×10^{-10}	296	(Bohland *et al.* 1984)	
$k_1 = 1.0 \times 10^{-10}$	1500-2500	(Frank *et al.* 1987)	
$k_2 = 2.0 \times 10^{-10}$	1500-2500	(Frank et al. 1987)	
Reviews and Evaluations			
$3.4 \times 10^{-10} \times \exp(-270/T)$	300 – 3000	(Baulch *et al.* 2005) (p. 839)	
Preferred value			
$k_1 = 4.0 \times 10^{-11}$	10-300	$F_0 = 1.6$, $g = 3$	
$k_2 = 1.0 \times 10^{-10}$	10-300	$F_0 = 1.4$, $g = 3$	
$k_3 = 2.0 \times 10^{-12}$	10-300	$F_0 = 3.0$, $g = 3$	

k comprised between $k(T)/F$ and $k(T) \times F$, *g* defined by $F(T) = F_0 \times \exp(g \times |1/T - 1/300|)$

Comments

The reactants correlate with singlet, triplet and quintet states. S. Klippenstein performed preliminary CASPT2 scans of the interaction between rigid fragments and found no barrier on both the singlet and triplet electronic surfaces in agreement with expectations for such radical-radical reactions as well as with the high experimental rate constant at room temperature. The rate constant from (Bohland *et al.* 1984) is a direct kinetic study and is likely reliable. The weak temperature dependency adopted by (Baulch et al. 2005) was designed to fit the (Bohland *et al.* 1984) room temperature value and the high temperature values from (Frank *et al.* 1987). This expression may give realistic values above 300 K, but certainly does not at low temperature. Considering the absence of barrier found by S. Klippenstein, we recommend the use of a constant value between 10 and 300 K close to the (Bohland *et al.* 1984) value. The first step of the reaction is the formation of singlet and triplet H_2CO. Dissociation of the singlet H_2CO

produced can be roughly deduced from H_2CO photodissociation (Zhang *et al.* 2004, Lee & Lewis 1980), which is supposed to arise from the ground electronic state after internal conversion (so involving only singlet surfaces). The primary competition is between formation of HCO + H and CO + H_2, the HCO + H formation being favored at high energy. For the O + CH_2 reaction there is so much energy in the HCO product that most of it will dissociate (Song *et al.* 2013, Neyer *et al.* 1992, Peters *et al.* 2013, Wang *et al.* 1973). It is difficult to estimate the amount of HCO produced with less than 70 kJ/mol (barrier for HCO dissociation). Moreover the dissociation of energized HCO has been found to be non-statistical (Neyer et al. 1992). The amount of non dissociating HCO is likely quite low but even if only 5% of HCO is stabilized k_3 is as high as 5×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. For the H_2 + CO channel, there is also so much energy that some of the H_2 can also dissociate. Then H + H + CO will be the prominent product. As in interstellar chemistry the branching ratio between H + H and H_2 of the O + CH_2 reaction is not important (H/H_2 ratio is fully driven by H_2 formation on grain) we use the high temperature k_1/k_2 ratio deduced from (Frank et al. 1987) even at low temperature. One critical point is the rate constant for the H + HCO channel which should only account for few percent of the total rate. This reaction could therefore be a minor source of HCO radical under interstellar conditions.

References

D.L. Baulch D.L., Bowman C.T., Cobos C.J., Cox R.A., Just T., Kerr J.A., Pilling M.J., Stocker D., et al., 2005, J. Phys. Chem. Ref. Data*,* 34**,** 757

Bohland T., Temps F., Wagner H.G., 1984, Ber. Bunsenges. Phys. Chem. *,* 88**,** 1222

Frank P., Bhaskaran K.A., Just T., 1987, 21st Symp. Int. Combustion**,** 885

Homann K.H., Schweinfurth H., 1981, Ber. Bunsen-Ges. Phys. Chem*,* 85**,** 569

Lee K.C., Lewis R.S., 1980, Adv. Photochem.*,* 12**,** 1

Neyer D.W., Kable S.H., Loison J.C., Houston P.L., Burak I., Goldfield E.M., 1992, J. Chem. Phys.*,* 97**,** 9036

Peters P.S., Duflot D., Wiesenfeld L., Toubin C., 2013, The Journal of Chemical Physics*,* 139**,** 164310

Song L., van der Avoird A., Groenenboom G.C., 2013, J. Phys. Chem. A*,* 117**,** 7571

Vinckier C., Debruyn W., 1979, J. Phys. Chem.*,* 83**,** 2057

Wang H.Y., Eyre J.A., Dorfman L.M., 1973, J. phys. Chem.*,* 59**,** 5199

Zhang X., Zou S., Harding L.B., Bowman J.M., 2004, J. Phys. Chem. A*,* 108**,** 8980