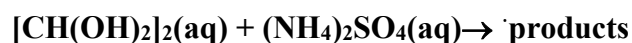


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ_TH1_GLYX_1

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This datasheet last evaluated: June 2017; last change in preferred values: May 2017



Rate coefficient data (*k*)

<i>k</i> /l mol ⁻¹ s ⁻¹	<i>T</i> /K	<i>pH</i>	<i>I</i> /mol l ⁻¹	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>					
$(2 \pm 1) \times 10^{-3}$	298	4.8-5.8	6.0-9.9	Nozière et al., 2009	UV-Vis (a)
0.13 ± 0.03	298	6.1-6.4	9.0-9.9	Nozière et al., 2009	UV-Vis (a)
$(5 \pm 1) \times 10^{-3}$	298	7.0-7.2	6.0-9.9	Nozière et al., 2009	UV-Vis (a)
2.61 ± 0.03	298	7.5-7.6	9.0	Nozière et al., 2009	UV-Vis (a)
7 ± 3	298	8.1	9.0	Nozière et al., 2009	UV-Vis (a)
$\leq 4.2 \times 10^{-6}$	295	4	9.3	Shapiro et al., 2009	UV-Vis (b)
5.4×10^{-7}	295	2.7-4.9	9.3	Schwier et al., 2010	UV-Vis (b)
5.6×10^{-9}	295	1.9	6	Yu et al., 2011	NMR (c)
$(4.4 \pm 0.3) \times 10^{-8}$	295	2.8	6	Yu et al., 2011	NMR (c)
$(4.1 \pm 0.3) \times 10^{-7}$	295	3.5	6-9.6	Yu et al., 2011	NMR (c)
$(1.1 \pm 0.2) \times 10^{-6}$	295	4	6	Yu et al., 2011	NMR (c)
$(2.0 \pm 0.4) \times 10^{-6}$	295	4.5	6	Yu et al., 2011	NMR (c)
7.0×10^{-5}	294	3.65	3.0	Sedehi et al., 2013	NMR (d)
3.7×10^{-4}	298	3.82	2.0	Sedehi et al., 2013	NMR (d)
1.1×10^{-4}	298	3.86	3.0	Sedehi et al., 2013	NMR (d)
7.3×10^{-3}	280	4.23	3.0	Sedehi et al., 2013	NMR (d)

Comments

- (a) The rate of this reaction was measured using UV-Vis following the formation of a product absorbing at 209 nm. Data listed are average values for each pH range from Figures 3 and 4. The reaction mixtures initially consisted of 0.5-1 M glyoxal and 2.0-3.3 M ammonium sulfate (AS). Products identified using high resolution mass spectrometry include acetal and hemiacetals and some N-substituted species.
- (b) The rate of this reaction was measured by following the appearance of a product peak at 277-280 nm using UV-Vis. The reaction mixtures initially consisted of 0-2.21 M glyoxal and 3.1 M AS in H₂O. Products identified using Aerosol Chemical Ionization Mass Spectrometry (Aerosol-CIMS) include acetal and hemiacetal species, imidazoles, and other N-containing adducts (Schwier et al., 2010).
- (c) The rate of this reaction was measured directly using NMR. The rate constants reported here were for the initial kinetics, based on the appearance of formic acid. Initial pH is given. The reaction mixture initially consisted of 1-1.5 M glyoxal and 2-3.2 M AS in D₂O. Products reported include imidazole, imidazole-2-carboxaldehyde, 1N-glyoxal substituted imidazole, and formic acid.

- (d) The rate of this reaction was measured directly using NMR. The rate constants reported here were derived based on the disappearance of glyoxal (except for the point taken at pH 3.65, which is based on the appearance of formic acid). The reaction mixture initially consisted of 0.33-0.5 M glyoxal and 0.67-1.00 M AS in D₂O. pH was monitored during the reaction and average pH is reported. Products reported were imidazoles and formic acid.

Preferred Values

Parameter	Value	T/K
$k / 1 \text{ mol}^{-1} \text{ s}^{-1}$	$10^{(1.2 \times \text{pH} - 9.8)}$	294-298
$\Delta \log k$	± 0.3	

Comments on Preferred Values

Recommendation is based on a curve fit to the data of Nozière et al. (2009), Schwier et al. (2010), Sedehi et al. (2013) and Yu et al. (2011). All data points are used from Nozière et al. (2009) and Yu et al. (2011), rather than the average values listed in the summary table. No clear dependence of the second order rate constant on ionic strength of the solution is apparent from the aggregate data, consistent with the observed first order dependence of the reaction rate on ammonium sulfate concentration (Shapiro et al. (2009), Schwier et al. (2010), Sedehi et al. (2013)). We note that glyoxal exhibits “salting-in” with ammonium sulfate in aqueous solutions (increasing glyoxal solubility with increasing ammonium sulfate concentration) (Yu et al., 2011, Waxman et al., 2015). Waxman et al. (2015) reported $K_s = -0.16 \text{ l mol}^{-1}$. The parameterization is valid for $1.9 \leq \text{pH} \leq 8.1$.

References

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