IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ_OH_70

This datasheet last evaluated: November 2019; last change in preferred values: June 2019

$HO(aq) + CH_2CHCHO \rightarrow HOCH_2CH_2CHO + HOCHCHCHO$ (30%)
$+ (HOCH_2CHCHO)_2$ (70%)

(product distribution taken from Lilie and Henglein (1970))

Rate coefficient data

k/ L mol^{-1} s^{-1}	T/K	pH	I/ mol L^{-1}	Reference	Technique/ Comments
Relative Rate Coefficients					
7.0×10^9	294	-	-	Lilie and Henglein, 1970	PR / UV-Vis (a)

$\Delta G_R°$ (aq): Aqueous phase thermochemical data not available. As well, gas phase thermochemical data $H_R°$ (g) are not available.

Comments

(a) HO radicals were generated by irradiation of N_2O saturated solutions; $c(N_2O) = 2.5 \times 10^{-2}$ M, concentration of the carbonyl compounds was given as "some 10^{-4} molar", concentration of the compound radicals was calculated to be around 10^{-5} M; Lilie and Henglein determined the rate coefficient to be 4.2×10^9 M^{-1}s^{-1}, referring to the reference reaction HO + SCN$^-$ with k(HO + SCN$^-$) = 6.6×10^9 M^{-1} s^{-1}; the selected reference rate coefficient $k = 1.10 \times 10^{10}$ M^{-1}s^{-1} was used for recalculation; analysis was performed within a buffered pH range from 5 to 9; Lilie and Henglein determined, that 30% of the nonhydrated compound radical disproportioned to yield the enol and β-alcohol while the rest forms a dimer from radical recombination; as no exact temperature is given, T = 294 K is assumed for room temperature.

Preferred Values

Parameter	Value	*T*/K
k / L mol^{-1} s^{-1}	7.0×10^9	294
Reliability		
$\Delta \log k$	±0.15	294

Comments on Preferred Values

The only available determination of the rate constant has been performed by Lilie and Henglein (1970). That value has been recalculated, using the newly recommended value for the reference reaction. The error of this determination is estimated as ±33% or $\Delta \log k = 0.15$. It should be noted that this rate coefficient refers to room temperature, which we estimate as T = 294 K.

References

Lilie, J. and Henglein, A.: Ber. Bunsen-Ges. Phys. Chem., 74(4), 388-393, 1970.