IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P22

This data sheet updated: 17th February 2005.

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pinonaldehyde[a] + hυ → products

Absorption cross-section data

Wavelength range/nm	Reference	Comment
275-345	Hallquist et al., 1997	(b)

Quantum Yield Data

Measurement	Wavelength/nm	Reference	Comment
ϕ(effective) = 0.14 ± 0.03	sunlight	RADICAL, 2002	(c)
ϕ(effective) ≈ 0.4	sunlight	Jaoui and Kamens, 2003	(d)

Comments

(a) (3-acetyl-2,2-dimethyl-cyclobutyl)-acetaldehyde.

(b) The UV spectrum was determined from long path (39.1 m) absorption measurements in a 0.48 m^3 chamber. Measurements were made over the wavelength range 275-345 nm, at a resolution of 0.6 nm, using diode array spectroscopy. Cross sections were reported as averages over 5 nm intervals. Measurements were made at (300 ± 1) K and low pressure (< 0.1 mbar), and calibrated through measurement of the pressure change on admission of pinonaldehyde to the reaction vessel. A procedure was adopted which took account of an observed gradual wall loss of pinonaldehyde. Pinonaldehyde was synthesized from the ozonolysis of α–pinene. Its stated purity was 95%, based on GC-MS and NMR analyses.

(c) Natural sunlight photolysis of pinonaldehyde-cyclohexane-air mixtures in a 180 m^3 outdoor chamber (the European Photoreactor, EUPHORE). The photolysis rate of pinonaldehyde was determined from its measured decay (HPLC), following correction for its removal by wall loss and dilution (which accounted for ca. 60% of its removal). Cyclohexane was included in the reaction mixtures as an HO scavenger. An effective (i.e. assumed wavelength-independent) photodissociation quantum yield was determined from the observed photolysis rate relative to a theoretical rate, which was calculated using the absorption cross sections of Hallquist et al. (1997), the measured actinic flux and the assumption of a unity quantum yield.

(d) Natural sunlight photolysis of pinonaldehyde-air and pinonaldehyde-cyclohexane-air mixtures in a 190 m^3 outdoor chamber, with GC-MS detection. The system was characterized by simulation using a detailed chemical mechanism, which also included pinonaldehyde removal by wall loss and dilution (which accounted for ca. 70-80% of its removal). An effective (i.e. assumed wavelength-independent) photodissociation quantum yield was derived from the simulations, based on light absorption described by the cross sections of Hallquist et al. (1997) and the measured actinic flux. More than nine products were identified or tentatively identified and quantified using GC-MS.

Preferred Values

Absorption cross-sections for pinonaldehyde at 300 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
277.5	12.19	312.5	6.84
282.5	12.96	317.5	4.90
287.5	13.48	322.5	3.07
292.5	12.94	327.5	1.72
297.5	12.17	332.5	0.72
302.5	10.62	337.5	0.29
307.5	8.94	342.5	0.08

Quantum Yields

No recommendation.

Comments on Preferred Values

The preferred absorption cross sections are from the study of Hallquist et al. (1997), which are the only reported values. The measurements appear to be reliable, although corrections were required to allow for wall removal of pinonaldehyde. As pointed out by Hallquist et al. (1997), the cross sections are consistent with additive contributions from the aldehyde and ketone groups in pinonaldehyde, based on cross sections reported for simple aldehydes and ketones. Confirmatory studies are required.

The studies of RADICAL (2002) and Jaoui and Kamens (2003) are indicative of removal of pinonaldehyde through photolysis, with effective quantum yields which are substantially below unity at wavelengths > 290 nm. Large corrections for pinonaldehyde wall loss and dilution were required in both studies, such that no firm quantum yield recommendation is made. Jaoui and Kamens (2003) identified a series of products which provided evidence for photolysis via both molecular and radical-forming channels. Further studies of the quantum yield and photolysis product channels are required.

References

Hallquist, M., Wängberg, I. and Ljungström, E.: Environ. Sci. Technol., 31, 3166, 1997.

Jaoui, M. and Kamens, R. M.: Atmos. Environ., 37, 1835, 2003.

RADICAL: 'Evaluation of radical sources in atmospheric chemistry through chamber and laboratory studies', Final report on the EU project 'RADICAL', Co-ordinator, Dr. G. K. Moortgat. Report EUR 20254 EN., 2002.