IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PF7

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n-C_3F_7CHO + hν → products

Primary photochemical transitions

Reaction		$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
n-C_3F_7CHO + hν → *n*-C_3F_7 + HCO	(1)		
→ *n*-C_3F_7CO + H	(2)		
→ *n*-C_3F_7H + CO	(3)		

Absorption cross-section data

Wavelength range/nm	References	Comments
265-334	Borkowski and Ausloss (1962)	(a)
185-500	Hashikawa et al. (2004)	(b)
230-400	Chiappero et al. (2006)	(c)
230-390	Solignac et al. (2007)	(d)

Quantum yield data

Measurement	Wavelength/nm	References	Comments
$\Phi_1 = 0.31 \pm 0.07$	254	Chiappero et al. (2006)	(e)
$\Phi_3 = 0.32 \pm 0.07$	254	Chiappero et al. (2006)	(e)
$\Phi_{Total} = 0.023 \pm 0.012$	290-400	Solignac et al. (2007)	(f)

Comments

(a) The absolute absorption cross-section at 319 nm was measured using a UV spectrometer.

(b) Absolute absorption cross-sections were measured using a diode array spectrometer at 298 K. The UV spectrum of *n*-C_3F_7CHO shows a broad band, centered at 310 nm and extending out to approximately 360 nm. Values of σ were given at 1 nm intervals.

(c) Absolute absorption cross-sections were measured using a diode array spectrometer at 248-297 K. The UV spectrum of *n*-C_3F_7CHO shows a broad band, centered at 310 nm and extending out to approximately 360 nm. Values of σ were given at 1 nm intervals. There was no discernable effect of temperature on the UV spectrum.

(d) Absolute absorption cross-sections were measured with a resolution of 0.1 nm using a diode array spectrometer for 1.4–8.0 Torr (1.9-10.7 mbar) samples of *n*-C_3F_7CHO at 298 K. The UV spectrum of *n*-C_3F_7CHO shows a broad band, centered at 310 nm and extending out to approximately 360 nm. Values of σ were given at 1 nm intervals.

(e) Photolysis quantum yield measured using perfluoroacetic anhydride as a chemical actinometer. Mixtures of 0.5-5.5 mbar of *n*-C_3F_7CHO and 20-70 mbar of NO (added as radical scavenger) were irradiated using a low pressure Hg lamp and the rate of loss of *n*-C_3F_7CHO was compared to that of perfluoroacetic anhydride in similar experiments. The formation of *n*-C_3F_7NO and *n*-C_3F_7H were measured by IR spectroscopy and used to derive quantum yields for processes (1) and (3).

(f) Photolysis of *n*-C_3F_7CHO in one atmosphere of pure dry air in the presence of an OH radical tracer (di-*n*-butyl ether) in the ~200 m^3 EUPHORE chamber facility under natural sunlight conditions. The measured rate of photolysis of *n*-C_3F_7CHO was $(1.3 \pm 0.6) \times 10^{-5}$ s^{-1}. When compared to the maximum photolysis rate calculated using unit quantum yield for photodissociation across the atmospheric range of absorption of *n*-C_3F_7CHO a quantum yield of 0.023 ± 0.012 was derived.

Preferred Values

Absorption cross-sections of *n*-C_3F_7CHO at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
200	0.34	305	7.97
205	0.12	310	8.29
210	0.21	315	7.77
215	0.16	320	7.83
220	0.11	325	6.40
225	0.14	330	5.32
230	0.09	335	4.74
235	0.10	340	2.91
240	0.15	345	1.98
245	0.24	350	1.52
250	0.41	355	0.65
255	0.68	360	0.13
260	1.03	365	0.04
265	1.54	370	0.00
270	2.18		
275	2.97		
280	3.87		
285	4.87		
290	5.83		
295	6.79		
300	7.45		

Quantum Yields of *n*-C_3F_7CHO

$\Phi_1 = 0.31$ at 254 nm

$\Phi_3 = 0.32$ at 254 nm

Reliability

$\Delta\Phi_1 = \pm 0.10$

$\Delta\Phi_3 = \pm 0.10$

Comments on Preferred Values

There is good agreement between the absorption cross sections measured by Borkowski and Ausloss, (1962), Hashikawa et al. (2004), Chiappero et al. (2006), and Solignac et al. (2007). Taking an average of the results from Hashikawa et al. (2004), Chiappero et al. (2006), and Solignac et al. (2007) gives the recommended values. The quantum yield measurements at 254 nm reported by Chiappero et al. (2006) and at 290-400 nm are recommended.

Chiappero et al. (2006) assumed a wavelength independent photolysis quantum yield of 0.11 for *n*-C_3F_7CHO (based upon a linear interpolation of the measured quantum yields for CF_3CHO and C_4F_9CHO) at 308 nm and estimated the photolysis lifetimes in the summer and winter solstices and the fall and spring equinoxes. Chiappero et al. (2006) averaged the lifetimes to give annual averages of approximately 0.75 days at 11 km altitude and 2 days at 0 km. Use of the recommended quantum yield of 0.023 in place of the value of 0.11 used by Chiappero et al. (2006) will increase the photolytic lifetimes by approximately a factor of 5. In either case, photolysis is the dominant atmospheric fate of *n*-C_3F_7CHO.

References

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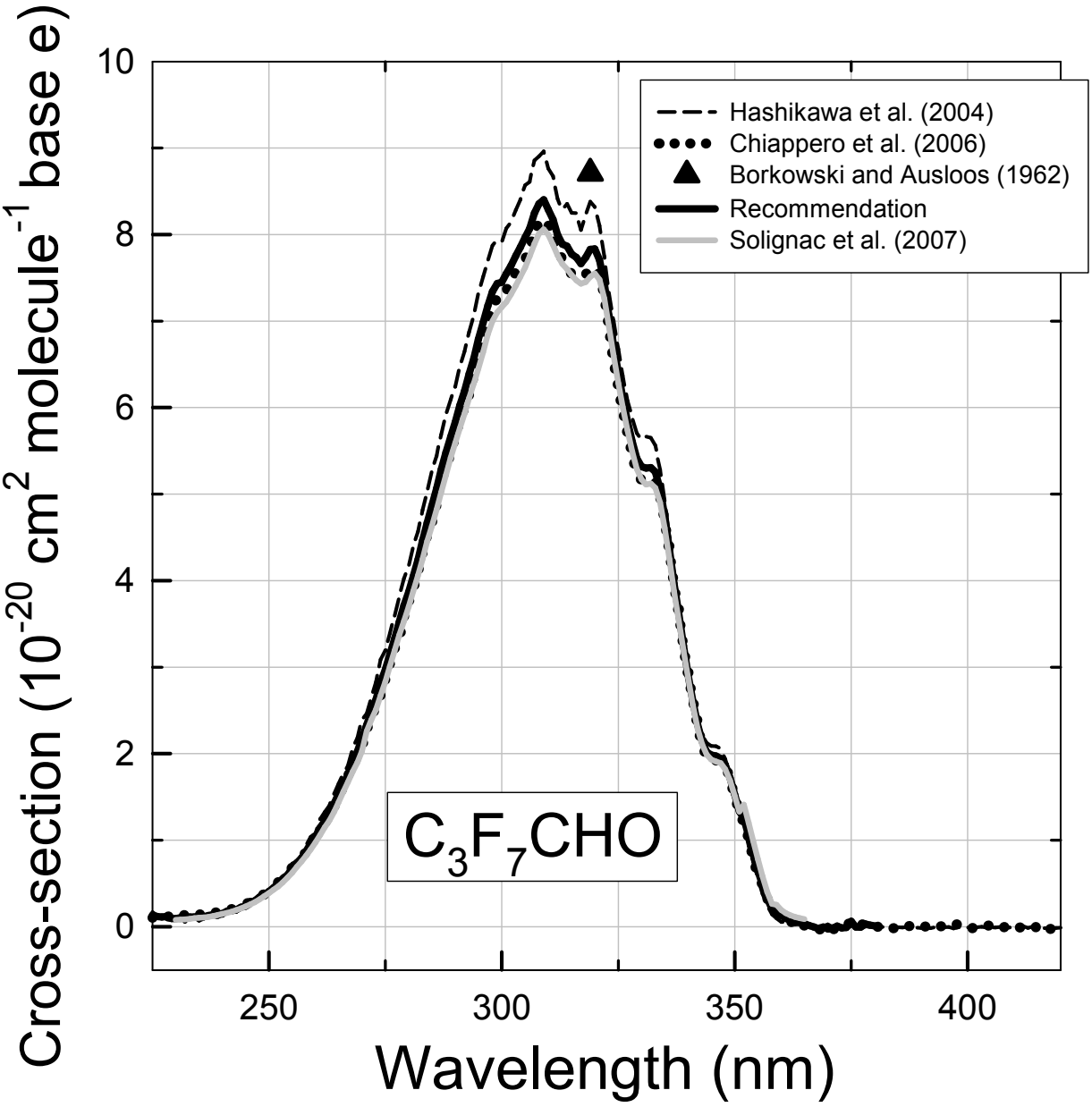
Cross-section (10^{-20} cm^2 $molecule^{-1}$ base e)
Wavelength (nm)
C_3F_7CHO
Hashikawa et al. (2004)
Chiappero et al. (2006)
Borkowski and Ausloos (1962)
Recommendation
Solignac et al. (2007)
0
2
4
6
8
10
250
300
350
400