

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PF10

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This datasheet last evaluated: June 2015; last change in preferred values: June 2010.

### $n\text{-C}_6\text{F}_{13}\text{CH}_2\text{CHO} + h\nu \rightarrow \text{products}$

#### Primary photochemical transitions

| Reaction  | $\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$ | $\lambda_{\text{threshold}}/\text{nm}$ |
|---|--|--|
| $n\text{-C}_6\text{F}_{13}\text{CH}_2\text{CHO} + h\nu \rightarrow n\text{-C}_6\text{F}_{13}\text{CH}_2 + \text{HCO}$ | (1)  |  |
| $\rightarrow n\text{-C}_6\text{F}_{13}\text{CH}_2\text{CO} + \text{H}$  | (2)  |  |
| $\rightarrow n\text{-C}_6\text{F}_{13}\text{CH}_3 + \text{CO}$  | (3)  |  |

#### Absorption cross-section data

| Wavelength range/nm | References              | Comments |
|---------------------|-------------------------|----------|
| 230-400             | Chiappero et al. (2006) | (a)      |
| 230-350             | Solignac et al. (2007)  | (b)      |

#### Quantum yield data

| Measurement                           | Wavelength/nm | References              | Comments |
|---------------------------------------|---------------|-------------------------|----------|
| $\Phi_{\text{Total}} = 0.55 \pm 0.09$ | 254           | Chiappero et al. (2006) | (c)      |

#### Comments

- The UV absorption spectrum was recorded using a single sample of 1.5 mbar of  $n\text{-C}_6\text{F}_{13}\text{CH}_2\text{CHO}$  in a 10 cm quartz cell using a diode array spectrometer at 297 K. The reported UV spectrum of  $n\text{-C}_6\text{F}_{13}\text{CH}_2\text{CHO}$  shows a broad band centered at 295 nm and extending out to approximately 350 nm. Values of  $\sigma$  were given at 1 nm intervals.
- Absolute absorption cross-sections were measured with a resolution of 0.1 nm using a diode array spectrometer for 0.6–2.0 Torr (0.8–2.7 mbar) samples of  $n\text{-C}_6\text{F}_{13}\text{CH}_2\text{CHO}$  in a 100 cm cell at 298 K. The UV spectrum of  $n\text{-C}_6\text{F}_{13}\text{CH}_2\text{CHO}$  shows a broad band centered at 285 nm and extending out to approximately 350 nm. Values of  $\sigma$  were given at 1 nm intervals.
- Photolysis quantum yield measured using perfluoroacetic anhydride as a chemical actinometer. Mixtures of  $n\text{-C}_6\text{F}_{13}\text{CH}_2\text{CHO}$  and NO (added as radical scavenger) were irradiated using a low

pressure Hg lamp and the rate of loss of  $n\text{-C}_6\text{F}_{13}\text{CH}_2\text{CHO}$  was compared to that of perfluoroacetic anhydride in similar experiments.

### Preferred Values

#### Absorption cross-sections of $n\text{-C}_6\text{F}_{13}\text{CH}_2\text{CHO}$ at 298 K

| $\lambda/\text{nm}$ | $10^{20} \sigma/\text{cm}^2$ | $\lambda/\text{nm}$ | $10^{20} \sigma/\text{cm}^2$ |
|---------------------|------------------------------|---------------------|------------------------------|
| 230                 | 1.27                         | 290                 | 5.20                         |
| 235                 | 1.25                         | 295                 | 4.79                         |
| 240                 | 1.59                         | 300                 | 4.66                         |
| 245                 | 1.97                         | 305                 | 3.90                         |
| 250                 | 2.43                         | 310                 | 3.78                         |
| 255                 | 2.57                         | 315                 | 2.67                         |
| 260                 | 3.12                         | 320                 | 2.37                         |
| 265                 | 3.80                         | 325                 | 1.79                         |
| 270                 | 4.39                         | 330                 | 1.03                         |
| 275                 | 5.01                         | 335                 | 0.75                         |
| 280                 | 5.27                         | 340                 | 0.30                         |
| 285                 | 5.30                         | 345                 | 0.18                         |
|                     |                              | 350                 | 0.00                         |

#### Quantum Yields of $n\text{-C}_6\text{F}_{13}\text{CH}_2\text{CHO}$

$$\Phi_{\text{Total}} = 0.55 \text{ at } 254 \text{ nm}$$

#### Reliability

$$\Delta\Phi_{\text{Total}} = \pm 0.10 \text{ at } 254 \text{ nm}$$

#### Comments on Preferred Values

The absorption spectrum reported by Chiappero et al. (2006) is based upon the measured absorption by one sample using a 10 cm pathlength and is considered less reliable than that measured by Solignac et al. (2007) using a range of sample partial pressures in a 100 cm absorption cell. The absorption spectrum from Solignac et al. (2007) is recommended.

Chiappero et al. (2006) assumed a wavelength independent photolysis quantum yield of 0.01 for  $n\text{-C}_6\text{F}_{13}\text{CH}_2\text{CHO}$  (based on an assumption that the quantum yield depends inversely on the molecular size of the fluorinated aldehyde and that the quantum yield for photolysis of  $n\text{-C}_6\text{F}_{13}\text{CH}_2\text{CHO}$  is approximately one quarter less than that for  $\text{CF}_3\text{CH}_2\text{CHO}$  measured 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 8 days at 11 km altitude and 20 days at 0 km. Measurements of the photolysis quantum yield at atmospherically relevant wavelengths are needed to better understand the role of photolysis in the atmospheric chemistry of this molecule.

#### References

Chiappero M. S., Malanca, F. E., Argüello, G. A., Wooldridge, S. T., Hurley, M. D., Ball, J. C., Wallington, T. J., Waterland, R. L., Buck, R. C.: *J. Phys. Chem. A*, 110, 11944, 2006.

