# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PBr11

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## $CF_3Br$ (Halon-1301) + hν → products

### Primary photochemical processes

| Reaction | $\Delta H°$/kJ mol$^{-1}$ | $\lambda_{threshold}$/nm |
|---|---|---|
| $CF_3Br + h\nu \rightarrow CF_3 + Br$ | 296 | 404 |

### Absorption cross-section data

| Wavelength range/nm | Reference | Comments |
|---|---|---|
| 168-280 | Gillotay and Simon, 1989[1] | (a) |
| 190-285 | Burkholder *et al.*, 1991[2] | (b) |
| 190-320 | Orkin and Kasimovskaya, 1995[3] | (c) |

### Quantum yield data

| Measurement | Wavelength/nm | Reference | Comments |
|---|---|---|---|
| 1.12 ± 0.16 | 193 | Talukdar, Vaghjiani, and Ravishankara, 1992[4] | (d) |
| 0.92 ± 0.15 | 222 | | |

### Comments

(a) Spectra were obtained using a thermostatted absorption cell with a single pass optical path of 2 m coupled to a monochromator capable of a maximum resolution of 0.015 nm. Pressures of $CF_3Br$ used covered the range 0.8 – 950 mbar. Spectra were recorded at 295 K, 270 K, 250 K, 230 K, and 210 K. The data were fitted to a polynomial expression giving the cross sections as a function of temperature and pressure.

(b) Spectra were obtained using thermostatted absorption cells with single pass optical paths of 98.1 cm and 150 cm, coupled to spectrographs having resolutions in the range 0.4-0.5 nm. Spectra were recorded at 296 K, 270 K, 250 K, 230 K, and 210 K. The data were fitted to a polynomial expression giving the cross sections as a function of temperature and pressure.

(c) Spectra were obtained using a cell thermostatted at 295 K with a single path optical length of 14.0 cm and coupled to a double beam spectrophotometric system. Sample pressures in the range 0.013–1 bar were used.

(d) Pulsed laser photolysis of $CF_3Br$-$N_2$ mixtures and detection of $Br(^2P_{3/2})$ by resonance fluorescence. A small amount of $H_2$ was added to ensure rapid quenching of the $Br(^2P_{1/2})$ also produced. The $Br(^2P_{3/2})$ measurements were calibrated by $CH_3Br$ photolysis at the same wavelength for which a quantum yield of unity was assumed.

## Preferred Values

**Absorption cross-sections of $CF_3Br$ at 295 K and 210 K.**

| λ/nm | $10^{20}$ σ/cm$^2$ | | λ/nm | $10^{20}$ σ/cm$^2$ | |
|---|---|---|---|---|---|
| | 295 K | 210 K | | 295 K | 210 K |
| 190 | 6.50 | 7.11 | 230 | 2.98 | 2.24 |
| 192 | 7.49 | 8.27 | 232 | 2.35 | 1.67 |
| 194 | 8.49 | 9.43 | 234 | 1.83 | 1.21 |
| 196 | 9.48 | 10.6 | 236 | 1.40 | 0.863 |
| 198 | 10.4 | 11.7 | 238 | 1.06 | 0.607 |
| 200 | 11.2 | 12.6 | 240 | 0.789 | 0.420 |
| 202 | 11.8 | 13.2 | 242 | 0.574 | 0.287 |
| 204 | 12.2 | 13.6 | 244 | 0.418 | 0.193 |
| 206 | 12.4 | 13.8 | 246 | 0.301 | 0.129 |
| 208 | 12.3 | 13.6 | 248 | 0.216 | 0.0848 |
| 210 | 12.0 | 12.9 | 250 | 0.153 | 0.0562 |
| 212 | 11.3 | 12.1 | 252 | 0.107 | 0.0371 |
| 214 | 10.6 | 11.1 | 254 | 0.0751 | 0.0241 |
| 216 | 9.69 | 9.86 | 256 | 0.0524 | 0.0163 |
| 218 | 8.65 | 8.54 | 258 | 0.0364 | 0.0110 |
| 220 | 7.58 | 7.25 | 260 | 0.0252 | 0.0074 |
| 222 | 6.52 | 5.97 | 262 | 0.0176 | |
| 224 | 5.50 | 4.84 | 264 | 0.0121 | |
| 226 | 4.56 | 3.86 | 266 | 0.0086 | |
| 228 | 3.73 | 2.96 | 268 | 0.0061 | |

## Quantum Yields

Φ = 1.0 over the range 200-270 nm.

*Comments on Preferred Values*

The preferred values of the absorption cross-sections at 295 K are the mean of the values obtained in the studies of Gillotay and Simon,[1] Burkholder *et al.*,[2] and Orkin and Kasimovskaya.[3] Molina *et al.*[5] have also reported values at 5 nm intervals. The agreement among these four studies,[1-3,5] over the wavelength range of the preferred values, is excellent. The temperature dependence of the of the cross sections down to 210 K has been studied by Gillotay and Simon[1] and by Burkholder *et al.*[2] and in both cases polynomial expressions were derived giving the cross sections as a function of temperature and wavelength. There are significant differences between the two studies.[1,2] Thus at λ > 220 nm both studies reported a

decrease in absorption as the temperature was lowered, but near the absorption peak ( ~ 205 nm) Burkholder *et al.*[2] found the cross-sections to be independent of temperature, while Gillotay and Simon[1] found the absorption to increase with decreasing temperature, with a 20% increase at the lowest temperature studied. Furthermore, at 210 K there is good agreement on the values of $\sigma$ at longer wavelengths (~280 nm), but the discrepancy between the two studies[1,2] increases steadily in going to shorter wavelengths with the values of Gillotay and Simon[1] being ~30% larger than those of Burkholder *et al.*[2] at 190 nm. Provisionally, the preferred values at 210 K are taken as the mean of the values of Gillotay and Simon[1] and of Burkholder *et al.*[2]

The preferred quantum yields are based on the study of Talukdar *et al.*[4] in which it was shown that photolysis occurs with unit quantum efficiency by rupture of the C-Br bond to give $CF_3$ + Br. $CF_3Br$ has no apparent tropospheric chemistry loss mechanism[2] and is estimated to have a tropospheric lifetime against direct solar photoexcitation of greater than 1000 years.[5]

## References


1. D. Gillotay and P. C. Simon, J. Atmos. Chem. **8**, 41 (1989).
2. J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjiani, and A. R. Ravishankara, J. Geophys. Res. **96**, 5025 (1991).
3. V. L. Orkin and E. E. Kasimovskaya, J. Atmos. Chem. **21**, 1 (1995).
4. R. K. Talukdar, G. L. Vaghjiani, and A. R. Ravishankara, J. Chem. Phys. **96**, 8194 (1992).
5. L. T. Molina, M. J. Molina, and F. S. Rowland, J. Phys. Chem. **86**¸ 2672 (1982).