# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PF2



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This datasheet last evaluated: June 2015; last change in preferred values: July 2004.

## $C(O)F_2 + h\nu \rightarrow$ products

### Primary photochemical transitions

| Reaction | | | $\Delta H°/kJ \cdot mol^{-1}$ | $\lambda_{threshold}/nm$ |
|---|---|---|---|---|
| $C(O)F_2 + h\nu$ | $\rightarrow FCO + F$ | (1) | 562 | 213 |
| | $\rightarrow CO + 2F$ | (2) | 683 | 175 |
| | $\rightarrow CF_2 + O(^3P)$ | (3) | 700 | 171 |

### Quantum yield data

| Measurement | Wavelength/nm | Reference | Comments |
|---|---|---|---|
| $\Phi_1 = 0.94 \pm 0.06$ | 193 | Nölle et al., 1992, 1999 | (a) |
| $\Phi_1 = 0.58 \pm 0.05$ | 210 | Nölle et al., 1999 | (b) |
| $\Phi_1 = 0.57 \pm 0.05$ | 210 | | (b,c) |
| $\Phi_1 = 0.07 \pm 0.03$ | 220 | | (b) |
| $\Phi_1 = 0.11 \pm 0.02$ | 220 | | (b,c) |

*Comments*

(a) Laser photolysis at 296-298 K with initial $C(O)F_2$ pressures of 10-30 mbar. Because of the high concentrations of FCO radicals in the laser photolysis experiments, formation of $C(O)F_2$ was assumed to occur via the reaction FCO + FCO $\rightarrow$ $C(O)F_2$ + CO as observed in analogous experiments with C(O)FCl (Nölle et al., 1999). Therefore, the cited quantum yield is the measured value ($0.47 \pm 0.03$) corrected for reformation of $C(O)F_2$ from the FCO radical self-reaction.

(b) Photolysis at 298 K using a medium pressure mercury lamp-monochromator combination, with initial $C(O)F_2$ pressures of 2.1-6.3 mbar. Because of the low concentrations of FCO radicals in these experiments, reformation of $C(O)F_2$ from the reaction FCO + FCO $\rightarrow$ $C(O)F_2$ + CO was not anticipated to be significant, as confirmed by observations in analogous experiments with C(O)FCl (Nölle et al., 1999). Therefore, the cited quantum yield is the measured value.

(c) With added $N_2$ diluent gas at pressures of 600-1000 mbar.

## Preferred Values

### Absorption cross-sections for $C(O)F_2$ at 298 K

| λ/nm | $10^{20}$ σ/cm$^2$ | λ/nm | $10^{20}$ σ/cm$^2$ |
|---|---|---|---|
| 186.0 | 5.5 | 205.1 | 0.74 |
| 187.8 | 4.8 | 207.3 | 0.52 |
| 189.6 | 4.2 | 209.4 | 0.40 |
| 191.4 | 3.7 | 211.6 | 0.28 |
| 193.2 | 3.1 | 213.9 | 0.20 |
| 195.1 | 2.6 | 216.2 | 0.12 |
| 197.0 | 2.1 | 218.6 | 0.081 |
| 199.0 | 1.6 | 221.0 | 0.049 |
| 201.0 | 1.3 | 223.5 | 0.035 |
| 203.0 | 0.95 | 226.0 | 0.024 |
| | | 228.6 | 0.018 |

### Quantum yields for $C(O)F_2$ at 298 K

$\Phi_1 = 0.94$ at 193 nm
$\Phi_1 = 0.57$ at 210 nm
$\Phi_1 = 0.09$ at 220 nm

*Comments on Preferred Values*

The preferred values of the absorption cross sections are those reported by Molina and Molina (1982) over the wavelength range 184-199 nm and by Nölle et al. (1992) at longer wavelengths. The results of these two studies are in excellent agreement over the range 200-208 nm; from 208-225 nm the results of Molina and Molina (1982) are 15-25% smaller than those of Nölle et al. (1992). The spectrum shows considerable structure; the values listed are averages over 500 cm$^{-1}$ intervals. Nölle et al. (1992, 1999) photolyzed $C(O)F_2$ at three wavelengths in the range 193-220 nm. The overall quantum yield for loss of $C(O)F_2$, which must be through channel (1), decreases monotonically with increasing wavelength. In the absence of confirmatory data, the quantum yields measured by Nölle et al. (1992, 1999) are recommended.

## References


Molina, L. T. and Molina, M. J.: Results presented at the 182nd American Chemical Society National Meeting, New York, August 1982.

Nölle, A., Heydtmann, H., Meller, R., Schneider, W. and Moortgat, G. K.: Geophys. Res. Lett., 19, 281, 1992.

Nölle, A., Krumscheid, C. and Heydtmann, H.: Chem. Phys. Lett., 299, 561, 1999.