

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PCI30

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### $\text{C(O)Cl}_2 + h\nu \rightarrow \text{products}$

#### Primary photochemical processes

Reaction		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{C(O)Cl}_2 + h\nu$	$\rightarrow \text{ClCO} + \text{Cl}$ (1)	320	374
	$\rightarrow \text{CO} + 2 \text{Cl}$ (2)	352	340
	$\rightarrow \text{CCl}_2 + \text{O}({}^3\text{P})$ (3)	699	171

#### Preferred Values

##### Absorption cross-sections for $\text{C(O)Cl}_2$ at 298 K

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$
184.4	234	211.6	13.3
186.0	186	213.9	12.6
187.8	146	216.2	12.3
189.6	116	218.6	12.2
191.4	90.3	221.0	12.2
193.2	71.5	223.5	12.4
195.1	52.4	226.0	12.7
197.0	39.9	228.6	13.1
199.0	31.2	231.2	13.4
201.0	25.2	233.9	13.6
203.0	20.9	236.7	13.1
205.1	17.9	239.5	12.5
207.3	15.8	242.4	11.6
209.4	14.3		

##### Quantum yield for $\text{C(O)Cl}_2$ at 298 K

$\Phi(1) = 1.0$  for  $\lambda > 184 \text{ nm}$ .

##### Comments on Preferred Values

The preferred values of the absorption cross sections are those reported by Gillotay et al. (1993). The spectrum is a continuum; the values listed are averaged over  $500 \text{ cm}^{-1}$  intervals. The results of Gillotay et al. (1993) are in good agreement with the earlier results of Chou et al. (1977). Gillotay et al.

(1993) reported values over the wavelength range 170-310 nm and the temperature range 210-295 K. The temperature effect is only significant at longer wavelengths ( $\lambda > 250$  nm). The observations of Wijnen (1961), Heicklen (1965) and earlier investigators (Calvert and Pitts, 1966) show that process (1) is the primary photolysis pathway. In the atmosphere, the overall photolysis proceeds by process (2) [i.e., ClCO decomposes to yield a second Cl atom] and the quantum yield for Cl atom formation will be 2.0.

### References

- Calvert, J. G. and Pitts, Jr., J. N.: Photochemistry, page 231, John Wiley and Sons, Inc., New York, 1966.
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- Heicklen, J.: J. Am. Chem. Soc., 87, 445, 1965.
- Wijnen, W. H.: J. Am. Chem. Soc., 83, 3014, 1961.