

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PCI2

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This data sheet updated: 20<sup>th</sup> July 2006.

### HOCl + hv → products

#### Primary photochemical processes

Reaction		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
HOCl + hv → HO + Cl	(1)	239	500
→ HCl + O( <sup>3</sup> P)	(2)	432	277

#### Preferred Values

##### Absorption cross-sections for HOCl at 298 K

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$
200	7.18	242	20.3	284	4.68
202	6.39	244	19.8	286	4.79
204	5.81	246	19.0	288	4.95
206	5.46	248	18.1	290	5.13
208	5.37	250	17.0	292	5.33
210	5.54	252	15.8	294	5.52
212	5.98	254	14.6	296	5.71
214	6.68	256	13.3	298	5.86
216	7.63	256	12.1	300	5.99
218	8.81	260	10.9	302	6.08
220	10.2	262	9.73	304	6.12
222	11.6	264	8.68	306	6.12
224	13.2	266	7.75	308	6.07
226	14.7	268	6.94	310	5.97
228	16.2	270	6.25	312	5.84
230	17.5	272	5.69	314	5.66
232	18.7	274	5.29	316	5.45
234	19.6	276	4.94	318	5.21
236	20.2	278	4.74	320	4.95
238	20.5	280	4.64	322	4.67
240	20.6	282	4.62	324	4.38

Continued:

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$
326	4.09	358	1.11	390	0.491
328	3.79	360	1.06	392	0.447
330	3.50	362	1.02	394	0.405
332	3.21	364	0.985	396	0.364
334	2.94	366	0.951	398	0.325
336	2.68	368	0.919	400	0.288
338	2.44	370	0.888	402	0.254
340	2.22	372	0.855	404	0.222
342	2.03	374	0.822	406	0.194
344	1.84	376	0.786	408	0.168
346	1.69	378	0.748	410	0.144
348	1.55	380	0.708	412	0.124
350	1.43	382	0.667	414	0.105
352	1.33	384	0.624	416	0.089
354	1.24	386	0.580	418	0.075
356	1.17	388	0.535	420	0.063

### Quantum yield for HOCl photolysis at 298 K

$\phi_1 = 1.0$  for  $\lambda > 200$  nm.

#### *Comments on Preferred Values*

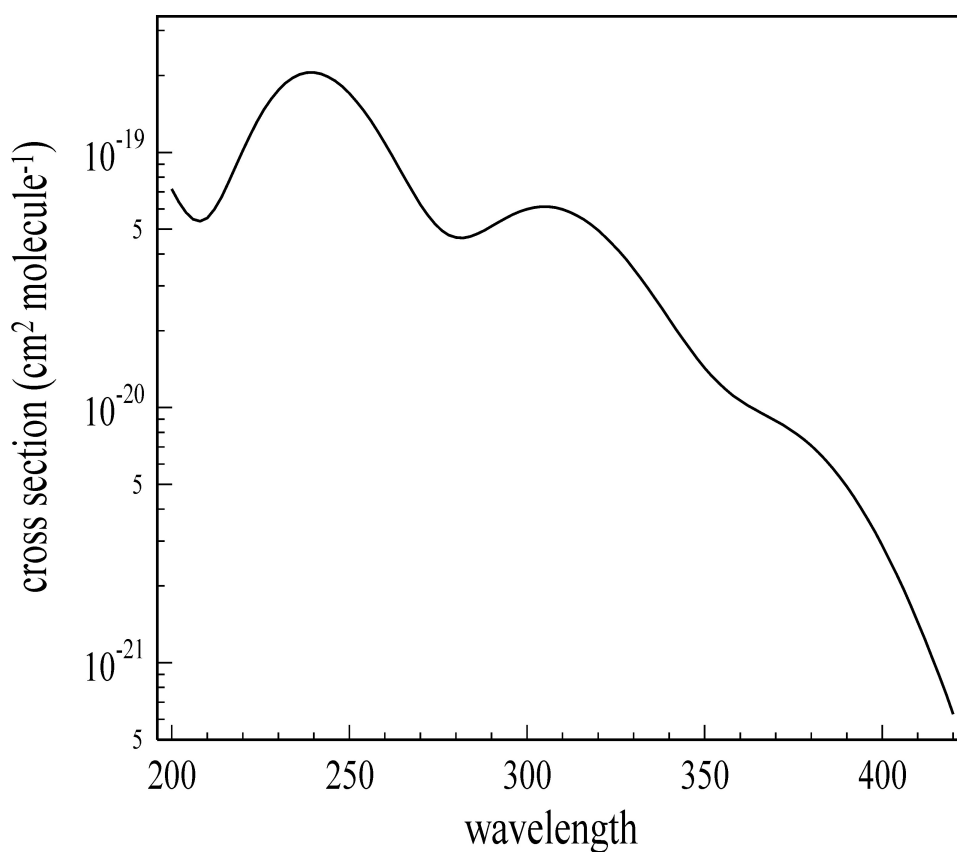
The preferred values of the absorption cross-sections at 298 K are the values calculated with the recent expression given by Barnes et al. (1998) based on their data from the laser induced fluorescence of HO and on the data of Burkholder (1993). In the Barnes et al. (1998) study a weak absorption centred at  $\approx 370$  nm that extends down to 500 nm is observed. The recommended values agree very well with the values reported by Knauth et al. (1979) and Jungkamp et al. (1995) at wavelengths between 250 and 350 nm. Earlier results (Molina and Molina, 1978; Spence et al., 1980; Mishalanie et al., 1986) were erroneous due to spectral interference from  $\text{Cl}_2\text{O}$  and  $\text{Cl}_2$ .

The preferred quantum yield values are based on the results of Molina et al. (1980), Butler and Phillips (1983), Vogt and Schindler (1992), and Schindler et al. (1987). An upper limit of  $\phi_2 < 0.02$  was determined by Butler and Phillips (1983) at 308 nm. Relative yields of  $\text{HO}(^2\Pi_{3/2}) / \text{HO}(^2\Pi_{1/2})$  were found to be 2.0 at 266 nm and 1.5 at 355 nm (Fujiwara and Ishiwata, 1998).

### References

- Barnes, R. J., Sinha, A., and Michelsen, H. A.: *J. Phys. Chem. A*, 102, 8855, 1998.  
Burkholder, J. B.: *J. Geophys. Res.* 98, 2963, 1993.  
Butler, P. J. D., and Phillips, L. F.: *J. Phys. Chem.* 87, 183, 1983.  
Fujiwara, H. and Ishiwata, T.: *J. Phys. Chem. A* 102, 3856, 1998.  
Jungkamp, T. P. W., Kirchner, U., Schmidt, M., and Schindler, R. N.: *J. Photochem. Photobiol. A* 91, 1-6, 1995.

Knauth, H. D., Alberti, H., and Clausen, H.: J. Phys. Chem. 83, 1604-1612, 1979.  
Mishalanie, E.A., Rutkowski, C. J., Hutte, R. S., and Birks, J. W.: J. Chem. Phys. 90, 5578-5584, 1986.  
Molina, L. T., and Molina, M. J.: J. Phys. Chem. 82, 2410-2414, 1978.  
Molina, M. J., Ishiwata, T. and Molina, L. T.: J. Phys. Chem. 84, 821, 1980.  
Schindler, R. N., Liesner, M., Schmidt, S., Kirchner, U., and Benter, Th.: J. Photochem. Photobiol. A: Chem. 107, 9-19, 1987.  
Spence, J. W., Edney, E. O., and Hanst, P. L.: J. Air Pollut. Control Assoc. 30, 50-52 1980.  
Vogt, R., and Schindler, R. N.: J. Photochem. Photobiol. A: Chem. 66, 133, 1992.



**HOCl absorption spectrum** (preferred values, see text for details)