IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PCl33

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$CCl_3CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
$CCl_3CHO + h\nu$	$\rightarrow CCl_3 + HCO$ (1)		
	$\rightarrow CCl_3CO + H$ (2)		
	$\rightarrow CHCl_3 + CO$ (3)		
	$\rightarrow CCl_2CHO + Cl$ (4)		

Absorption cross-section data

Wavelength range/nm	References	Comments
200-340	Rattigan et al., 1993	(a)
200-370	Rattigan et al., 1998	(b)
200-345	Talukdar et al., 2001	(c)

Quantum yield data

Measurement	Wavelength/nm	References	Comments
$\Phi[H] = 0.04 \pm 0.005$	193	Talukdar et al., 2001	(d)
$\Phi[O(^3P)] < 0.02$	248		
$\Phi[H] < 0.01$	248		
$\Phi[O(^3P)] < 0.01$	308		
$\Phi[H] < 0.002$	308		
$\Phi[Cl] = 1.3 \pm 0.3$	308		
$\Phi[-CCl_3CHO] = 1.00 \pm 0.05$	290-400	Wenger et al., 2004	(e)

Comments

(a) Absolute absorption cross-sections were measured using a dual-beam diode array spectrometer over the temperature range 240-300 K. The UV spectrum of trichloroacetaldehyde shows a broad band, centered at 290 nm and extending out to 360 nm. Values of σ were given at 5 nm intervals at 296 K and 243 K. A second absorption band appears at <230 nm.

(b) Absolute absorption cross-sections were measured using a dual-beam diode array spectrometer over the temperature range 243-298 K. Values of σ were given at 5 nm intervals at 298 K together with the values of B in the expression $\ln \sigma(T) = \ln \sigma(298\ \text{K}) + B(T\text{-}298)$.

(c) Absolute absorption cross-sections were measured using a diode array spectrometer over the temperature range 240-360 K. Values of σ were listed at 298 K at 2 nm intervals, together with the values of B in the expression $\ln \sigma(T) = \ln \sigma(298\ \text{K}) + B(T\text{-}298)$.

(d) Determined from pulsed laser photolysis of CCl_3CHO with detection of H, $O(^3P)$ and Cl atoms by resonance fluorescence. Experiments were carried out at 298 ± 2 K, and the H, $O(^3P)$ and Cl atom signals were placed on an absolute basis by use of photolysis of HBr (193 nm) or CH_3SH (248 and 308 nm) as reference compounds for H atom formation, photolysis of O_3 in the presence of N_2 at 248 and 308 nm as a reference compound for production of $O(^3P)$ atoms, and photolysis of Cl_2 at 308 nm as a reference compound for production of Cl atoms. Because Cl atoms react with CCl_3CHO, their yield was obtained by extrapolation to zero time. Cl atom formation was shown to be a primary process. Photolysis of CCl_3CHO at 248 nm in the presence of O_2 led to the formation of CO and $C(O)Cl_2$, with no formation of $CHCl_3$ (thereby ruling out the occurrence of channel (3) at 248 nm).

(e) Determined from the photolysis of CCl_3CHO in the ~200 m^3 volume EUPHORE chamber under natural sunlight conditions at 298 ± 5 K. Cyclohexane was added to scavenge Cl atoms and SF_6 was added to monitor dilution and loss through leakage. CCl_3CHO was monitored by FTIR spectroscopy and GC. The formation yield of Cl atoms was obtained from the amounts of cyclohexane consumed during the photolyses. The measured decay rates of CCl_3CHO, corrected for dilution, were compared to the calculated decay rates for a photodissociation quantum yield of 1.00.

Preferred Values

Absorption cross-sections of CCl_3CHO at 298 K and their temperature dependence

Wavelength/nm	10^{20} σ (298 K)/cm^2	10^4 B/K^{-1} [a)]
200	186.9	22.0
202	152.5	23.9
204	121.8	27.2
206	95.7	30.6
208	73.8	34.1
210	56.3	37.5
212	42.6	40.9
214	31.8	44.0
216	23.8	47.2
218	17.7	50.2
220	13.1	52.9
222	9.75	55.6
224	7.24	57.6
226	5.39	59.0
228	4.06	60.4
230	3.07	60.5
232	2.39	59.5
234	1.90	55.9
236	1.62	49.2
238	1.43	41.6
240	1.39	33.0
242	1.41	24.0
244	1.53	16.4

246	1.66	10.4
248	1.91	6.50
250	2.18	3.73
252	2.54	1.50
254	2.92	0.324
256	3.36	-0.569
258	3.84	-0.877
260	4.35	-1.23
262	4.90	-1.65
264	5.48	-1.62
266	6.07	-1.50
268	6.68	-1.41
270	7.28	-1.22
272	7.88	-1.07
274	8.46	-0.931
276	8.99	-0.584
278	9.49	-0.412
280	9.94	-0.481
282	10.3	-0.235
284	10.6	0.242
286	10.8	0.475
288	10.9	0.750
290	10.9	1.09
292	10.8	1.51
294	10.6	1.96
296	10.3	2.38
298	9.92	2.71
300	9.25	3.07
302	8.77	3.60
304	8.17	4.37
306	7.50	5.25
308	6.86	6.10
310	6.18	6.91
312	5.58	7.90
314	4.98	9.30
316	4.33	11.2
318	3.68	13.2
320	3.09	15.1
322	2.51	16.7
324	2.09	18.5
326	1.76	21.1
328	1.43	25.0
330	1.12	30.3
332	0.849	36.6
334	0.590	43.3
336	0.373	49.8
338	0.261	55.6
340	0.188	60.2
342	0.136	65.0
344	0.100	69.0

[a)] $\ln \sigma(T) = \ln \sigma(298\ \mathrm{K}) + B(T\text{-}298)$

Quantum yields of CCl_3CHO

$\Phi(4) = 1.0$ over the wavelength range 290-400 nm.

Comments on Preferred Values

The preferred values for the cross-sections are those reported by Talukdar et al. (2001), which are in excellent agreement with the earlier data of Rattigan et al. (1998) except at 230-250 nm where the Rattigan et al (1998) cross-sections are somewhat lower. The preferred quantum yield is based on the studies of Talukdar et al. (2001) at 308 nm and of Wenger et al. (2004) using natural sunlight photolysis over the wavelength region 290-400 nm. Wenger et al. (2004) observed the formation of $C(O)Cl_2$, CO and Cl atoms from the photolysis of CCl_3CHO at 290-400 nm, with molar yields of 0.83 ± 0.04, 1.01 ± 0.05 and 1.18 ± 0.06, respectively, which when combined with the data of Talukdar et al. (2001) indicates that the dominant primary process at λ >290 nm is to form Cl + CCl_2CHO [channel (4)].

References

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