IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P23

This data sheet last evaluated: June 2011; last change in preferred values: June 2011.

$CH_3C(O)C(O)CH_3 + h\upsilon \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°_{298}$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3C(O)C(O)CH_3 \rightarrow CH_3C(O) + CH_3C(O)$ (1)		390
$\rightarrow CH_3C(O) + CH_3 + CO$ (2)		338
$\rightarrow 2CH_3 + 2CO$ (3)		300

Absorption cross-section data

Wavelength range/nm	Reference	Comments
208-476	McMillan, 1966	(a)
230-470	Plum *et al*., 1983	(b)
206-493	Horowitz *et al*., 2001	(c)
184.9	Rajakumar *et al*., 2008	(d)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi = 0.16$	290-390	Plum *et al*., 1983	(e)
$\phi(CH_3CO) = 0.76$(61 Torr) = 0.79(101 Torr) = 0.79(207 Torr) = 0.86(302 Torr) = 0.92(419 Torr) = 0.90(509 Torr) = 0.96(643 Torr)	248	Rajakumar *et al*., 2008	(f)

Comments

(a) Conventional spectrophotometric study of biacetyl absorption spectrum.

(b) Conventional spectrophotometric study (Cary 17-D) using biacetyl pressures of ~4 mbar to 17 mbar. Data taken from Spectral Atlas: (http://www.atmosphere.mpg.de/enid/2295) which gives absorption cross sections read at 1- and 2-nm intervals from Fig. 1 of Plum et al (1983).

(c) Absorption measurements as a function of biacetyl pressure using a diode array spectrometer. Biacetyl pressure range of 0.5–10 Torr in which no deviations from Beer–Lambert law were observed. Cross sections averaged over 1 nm intervals are listed. Reported accuracy of the biacetyl data in this work was ±4% or not less than $\pm 1 \times 10^{-21}$ $cm^2 molecule^{-1}$, whichever was the larger.

(d) UV absorption measurements were made using a Hg pen-ray lamp light source at 184.9 combined with narrow bandpass filters and a photodiode detector. The cross section determined for this wavelength was 1.46×10^{-18} $cm^2 molecule^{-1}$. The concentration of biacetyl was determined by UV absorption at 248 nm, using the cross section of Horowitz et al. (2001).

(e) Rate of photolysis of biacetyl in air mixtures at atmospheric pressure measured in an environmental chamber. The quantum yield for the photodissociation of biacetyl was obtained by comparison of the measured rate of removal of glyoxal with the rate of photolysis of NO_2 under similar experimental conditions.

(f) Quantum yields determined from CH_3CO production measured in its visible absorption band (490 - 660 nm) by CRDS following photolysis of biacetyl at 248 nm in a crossed beam pulsed laser photolysis cell. CH_3CO yields were determined relative to amounts from reference reaction: HO + CH_3CHO, with HO produced by co-photolysis of H_2O_2. Cited data for $\phi(CH_3CO)$ were for N_2 bath gas; a rather weaker pressure dependence was found for He.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
206	10.30	303	1.46	400	5.12
207	9.86	304	1.38	401	5.19
208	9.14	305	1.32	402	5.26
209	7.97	306	1.27	403	5.38
210	6.74	307	1.21	404	5.54
211	5.82	308	1.10	405	5.75
212	5.18	309	0.95	406	6.00
213	4.70	310	0.82	407	6.26
214	4.29	311	0.71	408	6.47
215	3.90	312	0.62	409	6.59
216	3.55	313	0.54	410	6.69
217	3.21	314	0.48	411	6.82
218	2.90	315	0.44	412	6.97
219	2.58	316	0.41	413	7.11
220	2.26	317	0.38	414	7.31
221	1.96	318	0.36	415	7.47
222	1.70	319	0.34	416	7.57
223	1.50	320	0.33	417	7.62
224	1.35	321	0.33	418	7.51
225	1.27	322	0.32	419	7.39
226	1.23	323	0.30	420	7.37
227	1.24	324	0.26	421	7.32

228	1.28	325	0.23	422	7.25
229	1.34	326	0.21	423	7.24
230	1.41	327	0.20	424	7.13
231	1.47	328	0.19	425	6.98
232	1.53	329	0.19	426	6.81
233	1.59	330	0.20	427	6.57
234	1.68	331	0.20	428	6.43
235	1.80	332	0.21	429	6.34
236	1.92	333	0.20	430	6.31
237	2.09	334	0.22	431	6.40
238	2.15	335	0.23	432	6.63
239	2.21	336	0.25	433	6.78
240	2.29	337	0.26	434	6.78
241	2.39	338	0.28	435	6.72
242	2.54	339	0.30	436	6.56
243	2.69	340	0.30	437	6.40
244	2.80	341	0.32	438	6.42
245	2.89	342	0.35	439	6.28
246	2.94	343	0.37	440	6.51
247	2.99	344	0.39	441	6.67
248	3.05	345	0.41	442	6.99
249	3.15	346	0.44	443	7.23
250	3.31	347	0.47	444	6.85
251	3.48	348	0.50	445	6.49
252	3.60	349	0.53	446	5.90
253	3.68	350	0.57	447	5.43
254	3.73	351	0.61	448	5.01
255	3.75	352	0.65	449	4.33
256	3.78	353	0.68	450	4.06
257	3.84	354	0.73	451	3.44
258	3.94	355	0.77	452	3.20
259	4.09	356	0.82	453	2.65
260	4.27	357	0.86	454	2.16
261	4.41	358	0.92	455	1.72
262	4.46	359	0.97	456	1.39
263	4.49	360	1.02	457	1.14
264	4.49	361	1.08	458	0.85
265	4.48	362	1.19	459	0.73
266	4.49	363	1.26	460	0.55
267	4.54	364	1.33	461	0.45
268	4.63	365	1.41	462	0.36
269	4.81	366	1.49	463	0.28
270	4.95	367	1.57	464	0.22
271	5.00	368	1.66	465	0.18
272	4.98	369	1.76	466	0.14
273	4.92	370	1.85	467	0.12
274	4.85	371	1.94	468	0.10
275	4.76	372	2.02	469	0.08
276	4.70	373	2.10	470	0.07
277	4.68	374	2.17	471	0.06
278	4.67	375	2.25	472	0.05
279	4.68	376	2.33	473	0.04
280	4.71	377	2.41	474	0.04

281	4.73	378	2.50	475	0.03
282	4.65	379	2.58	476	0.03
283	4.50	380	2.68	477	0.03
284	4.32	381	2.79	478	0.02
285	4.14	382	2.92	479	0.02
286	3.94	383	3.07	480	0.02
287	3.77	384	3.22	481	0.02
288	3.62	385	3.39	482	0.02
289	3.50	386	3.53	483	0.02
290	3.38	387	3.67	484	0.02
291	3.28	388	3.82	485	0.02
292	3.20	389	4.00	486	0.01
293	3.11	390	4.17	487	0.01
294	2.96	391	4.34	488	0.02
295	2.73	392	4.47	489	0.02
296	2.50	393	4.56	490	0.02
297	2.29	394	4.62	491	0.02
298	2.10	395	4.67	492	0.02
299	1.93	396	4.73	493	0.02
300	1.77	397	4.82		
301	1.64	398	4.92		
302	1.54	399	5.02		

Quantum Yields

At 248 nm: $\phi_1 + \phi_2 = 0.76$ for $p < 80$ mbar;
$\phi_1 = 2$; $\phi_2 = 0$ for $p = \infty$;

290 – 380 nm: $\phi_1 + \phi_2 + \phi_2 = 0.16$ (average for atmospheric photolysis at surface).

Comments on Preferred Values

Biacetyl exhibits two distinct absorption regions relevant for atmospheric photolysis. The first region consists of a broad band between 340 – 480 nm, superimposed by three distinct peaks at 417.2, 433.0 and 442.8. The second region shows a broad band with some structure with a maximum absorption near 272 nm. The preferred values for the absorption cross-sections are based on those determined by Horowitz *et al*. (2001), which, are in satisfactory agreement with the earlier data of Plum *et al*. (1983) and McMillan et al, 1966 (e.g. σ_{max} = 4.65 x 10^{-20} $cm^2 molecule^{-1}$ at 270 nm for the second band). The values given above are averaged over 1 nm and are taken from the compilation in http://www.atmosphere.mpg.de/enid/, which also contains data at other resolution. The overall accuracy for both bands is estimated at ±5%. The single wavelength determination of Rajakumar *et al*. (2008) at 184.9 nm is consistent with a third strong absorption band below 200 nm indicated by the data of Horowitz, (2001).

The recommended quantum yields for $\phi_1 + \phi_2$ are based on the data of Rajakumar *et al.* (2008), which are the only wavelength-resolved quantum yield data that have appeared. The observed pressure dependence of $\phi(CH_3CO)$ is due to dissociation of initially formed excited CH_3CO^* and is reproduced reasonably well, over the range of pressures covered in this study, by a Stern–Volmer relationship for the quenching of CH_3CO^*. This analysis using an assumed high pressure limiting yield of $\phi^\infty(CH_3CO) = 2$, gave a zero pressure quantum yield of $\phi^o(CH_3CO) = 0.76 \pm 0.05$. The authors estimate the overall uncertainty in experimental values

of $\phi(CH_3CO)$ from biacetyl photolysis at 248 nm to be 15% at the 2σ (95% confidence) level. For calculation of atmospheric photolysis rate of biacetyl in the lower troposphere, the average values reported by Plum et al (1983) can be used.

References

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