IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P26

This data sheet last evaluated: May 2012; last change in preferred values: May 2012

cis-HC(O)CH=CHC(O)H + hυ $\rightarrow$ products
$trans$-HC(O)CH=CHC(O)H + hυ $\rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°_{298}$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
HCOCH=CHCHO$\rightarrow$ $trans/cis$	HCOCH=CHCHO $cis/trans$ (1)		
$\rightarrow$	HCOCH=CH + HCO (2)		~290
$\rightarrow$	HCOCH=CHCO + H (3)		
$\rightarrow$	2HCO + C$_2$H$_2$ (4)		~351
$\rightarrow$	CH$_3$COCH=CH$_2$ + CO (5)		<346
$\rightarrow$	3H-furan-2-one (6)		<346

Absorption cross-section data

Wavelength range/nm	Reference	Comments
193, 248, 308, 351	Tang and Zhu, 2005	(a)
220 - 460	Hufford et al , 1952	(b)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5$)

Measurement	Wavelength range/nm	Reference	Comments
absolute quantum yields			
$\phi((HCO))= 0.55 \pm 0.07$	193	Tang and Zhu, 2005	(c)
$\phi((HCO)) = 0.12 \pm 0.07$	248		
relative quantum yields (φ %)			
$\varphi(1) = {\sim}45$ (cis-trans & trans-cis)	320 - 480	Bierbach et al., 1994	(d)
$\varphi(1) = \leq 30$ (cis-trans & trans-cis)	254		
$\varphi(2)= \geq 1.1$	193	Tang and Zhu, 2005	(e)
$\varphi(2)= \geq 3.7$	248		
$\varphi(2)= \geq 15$	308		
$\varphi(2)= \geq 23$	351		

$\varphi(6) = 0$	193
$\varphi(6) = \geq 2.8$	248
$\varphi(6) = \geq 1.2$	308
$\varphi(6) = \geq 1.1$	351

Comments

(a) Cross section data at 193 and 248 nm were determined by monitoring transmitted laser photolysis fluence as a function of butenendial pressure in the cell. The absolute cross-sections thus obtained were $(6.88 \pm 0.39) \times 10^{-18}$ and $(3.62 \pm 0.69) \times 10^{-19}$ cm^2 at 193 and 248 nm, respectively. The cited (1σ) error bars give estimated precision of the determination of the cross sections. At 308 and 351 nm upper limits of $< 6 \times 10^{-21}$ cm^2 were given.

(b) UV absorption spectrum of purified butene-2-dial (crystalline fumaric dialdehyde) dissolved in iso-octane was reported. The sample was mainly the *trans-* isomer. The spectrum showed two absorption bands, one peaked at 225 nm ($\varepsilon = 17\ 000$ cm^{-1}) and the other peaked at 354 nm ($\varepsilon = 70$ cm^{-1}).

(c) Quantum yield of HCO production determined from CRDS measurement of HCO concentration at 613.80 nm., using an absorption cross section of $\sim 2.0 \times 10^{-18}$ cm^2/molecule at this wavelength. The system was calibrated at 248 nm relative to formaldehyde photolysis at this wavelength, for which the recommended $\phi((HCO)) = 0.29$; at 193 nm HCO produced by the Cl + HCHO reaction was used for calibration, with Cl produced by CCl_4 photolysis at this wavelength. Estimated overall uncertainty in was 52% at 193 nm and 60% at 248 nm.

(c) Photo-oxidation studies in 1080 L quartz glass chamber surrounded by actinic fluorescent or low pressure mercury lamps. Total pressure 1000 mbar synthetic air and 296 ± 2 K. Loss of butenendial (*cis-* & *trans-* isomers) and formation of products, was measured from time-dependence of FTIR absorption. The main products formed included maleic anhydride, HCHO, CH3OH and CH3OOH, with minor amounts of 3H-furan-2-one.

(d) Relative yields based on measurements, using FTIR, of end products (3H-furan-2-one and acrolein) of laser photolysis of butenendial in a closed cell at 193, 248, 308 and 351 nm. The two products are assumed to result directly from channels (2) and (6). CO was observed at all wavelengths but could not be asigned to a specific channel due to complex secondary chemistry. Acetylene was also observed but only at 193 nm. If the *trans/cis* isomerisation yields of Bierbach et al. are included, the total photolysis yield of butenendial is probably close to unity.

Preferred Values

Absorption cross-sections at 294 K

λ/nm	$10^{20}\ \sigma$/cm^2	λ/nm	$10^{20}\ \sigma$/cm^2

λ	σ	λ	σ
193	688	310	1.40
200	732	320	1.92
210	758	330	2.29
220	841	340	2.38
225	966	350	2.06
230	933	360	1.57
235	395	370	1.34
240	149	380	1.07
248	36.2	390	0.73
250	17.3	400	0.45
260	0.80	410	0.26
265	0.22	420	0.13
270	0.07	430	0.05
272	0.04	440	0.03
280	0.27	450	0.02
290	0.54	460	0.01
300	1.00		

Quantum Yields

λ/nm	350-460	193	248	308	351
ϕ_1	0.45		<0.4		
ϕ_2	0	0.55± 0.29	0.12±0.07	0	0
ϕ_6		0	0.028	0.012	0.012

Comments on Preferred Values

There appear to be no measurements of the gas-phase UV/visible absorption spectrum of butene-2-dial but the absorption spectrum recorded by Hufford et al. (1952) in iso-octane solution resembles the gas phase spectrum of the related compound: 4-oxo-pentene-2-dial. The relative absorption coefficients extracted from Fig 1 of this work were scaled to the absolute gas phase cross-section σ(248 nm) determined by Tang and Zhu (2005) to provide the recommended values of σ over the range 193 - 460 nm.

The only direct determination of primary quantum yields are those for HCO production reported by Tang and Zhu (2005). These results show that channel (2) only occurs at λ <308 nm and is a major channel at 193 nm. The relative yields of the photolysis co-products by Tang and Zhu (2005) are only lower limits as secondary photolysis of these products occurs. Nevertheless it appears that channel (2) is not the only source of acrolein as it is observed at λ > 308 nm. 3H-furan-2-one was a minor product compared with acrolein. The *cis/trans* isomerisation yields reported by Bierbach et al (1994) are consistent with these results for channels (2) and (6), which are tentativly recommended. The major products observed from the photo-oxidation in synthetic air, reported by Bierbach et al., can be rationalised from secondary reactions of the primary photofragments.

References

Bierbach, A., Barnes, Ian, Becker, K.H., and Wiesen, Evelyn, *Environ.Sci.Technol.*, 1994, 28, 715 - 729.

Tang. Y. and Zhu, L., Chem Phys. Lett., , 2005, 409, 151 - 156.

Hufford, D.L., Tarbell, D.S., Koszalka, T.R., *J. Am. Chem. Soc.*, 1952, 74 3014 - 3018.

Figure 1: Absorption Spectrum of butene-2-dial