

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PBr2

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### HOBr + hv → products

#### Primary photochemical processes

Reaction		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
HOBr + hv → HO + Br	(1)	207	578
→ HBr + O( <sup>3</sup> P)	(2)	267	445
→ BrO + H	(3)	394	304

#### Absorption cross-section data

Wavelength range/nm	Reference	Comments
240-410	Orlando and Burkholder, 1995	(a)
234-400	Benter et al., 1995	(b)
240-390	Deters et al., 1996	(a)
235-430	Rattigan et al., 1996	(a)
260-545	Ingham et al., 1998 <sup>1</sup>	(c)

#### Quantum yield data

See Comments on Preferred Values

#### Comments

- HOBr was generated by allowing a gas phase mixture of Br<sub>2</sub>O with H<sub>2</sub>O to reach equilibrium. Corrections were necessary to account for the Br<sub>2</sub>O and Br<sub>2</sub> present in the mixture.
- HOBr generated in aqueous solution and flowed into an absorption cell.
- HOBr was generated by pulsed laser photolysis of flowing H<sub>2</sub>O<sub>2</sub>-Br<sub>2</sub> mixtures in an absorption cell through which the analysing beam could be passed twice to give an absorption path length of 2.6 m. Detection was achieved either by means of time-resolved photomultiplier measurements or by a diode array which could be gated from 0.06 ms to 5.06 ms. The spectral resolutions for the two techniques were 2 nm and 1.2 nm respectively.

## Preferred Values

### Absorption cross-sections of HOBr at 295 K.

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$
250	4.16	405	1.80
255	6.93	410	1.36
260	10.5	415	1.08
265	14.6	420	0.967
270	18.7	425	1.00
275	22.1	430	1.15
280	24.3	435	1.40
285	25.0	440	1.68
290	24.0	445	1.96
295	21.0	450	2.18
300	19.1	455	2.28
305	16.2	460	2.28
310	13.6	465	2.14
315	11.8	470	1.91
320	10.8	475	1.62
325	10.5	480	1.30
330	10.8	485	0.993
335	11.3	490	0.723
340	11.9	495	0.502
350	12.3	500	0.334
345	12.5	505	0.212
355	12.2	510	0.129
360	11.5	515	0.075
365	10.5	520	0.042
370	9.32	525	0.023
375	8.00	530	0.012
380	6.66	535	0.006
385	5.38	540	0.003
390	4.22	545	0.0001
395	3.24		
400	2.43		

#### *Comments on Preferred Values*

There remain significant uncertainties in the values of the absorption cross-sections despite a number of recent studies (Ingham et al., 1998; Orlando and Burkholder, 1995; Benter et al., 1995; Deters et al., 1996; Rattigan et al., 1996). However, the shape of the spectrum has been clarified. Orlando and Burkholder (1996), Deters et al. (1996) and Benter et al. (1995) observe two absorption bands between 200 and 400 nm with a rapid decline in the cross-sections beyond 400 nm. Rattigan et al. (1996) and Ingham et al. (1998) also observe these two bands but find another weak band with a maximum at  $\sim 460$  nm as predicted by theoretical calculations (Francisco et al., 1996; Minaev, 1999). Further evidence for the long wavelength band comes from a laser photolysis study of Barnes et al. (1994) who observed

OH production from HOBr photolysis over the range 400-600 nm. It now seems clear that the spectrum consists of three broad bands with maxima at  $\sim 284$  nm,  $\sim 351$  nm, and  $\sim 457$  nm.

At the maximum of the short wavelength band the measured values of the cross-sections differ by  $\sim 20\%$ , whilst in the 350 nm region the differences become as much as a factor of three. It is likely that this scatter, and the difficulty in detecting the long wavelength band, are largely due to the presence of impurities such as  $\text{Br}_2\text{O}$  and  $\text{Br}_2$ , which absorb strongly in the same spectral region as HOBr.

In most of the studies (Orlando and Burkholder, 1995; Deters et al., 1996; Rattigan et al., 1996) HOBr was generated by reaction of  $\text{Br}_2\text{O}$  with  $\text{H}_2\text{O}$ , leading to the production of equilibrium mixtures of  $\text{Br}_2\text{O}$ ,  $\text{H}_2\text{O}$ , and HOBr. Benter et al. (1995) achieved smaller  $[\text{Br}_2\text{O}]/[\text{HOBr}]$  ratios by generation and elution of HOBr from aqueous solution and Ingham et al.<sup>1</sup> attempted to circumvent the problems of impurities by in situ generation of the HOBr using pulsed laser photolysis of  $\text{H}_2\text{O}_2$ - $\text{Br}_2$  mixtures, calibrating the cross-sections relative to the better established cross-sections of  $\text{Br}_2$ . The study of Ingham et al. (1998) appears to have been the most successful in avoiding interference from impurities and their values are adopted as our preferred values. Their measurements<sup>1</sup> only went down to 260 nm but they fitted their results to an expression consisting of the sum of three Gaussian terms and the range of our preferred values have been extended slightly using calculated values from this expression. Experimental values reported for  $\lambda < 250$  nm are subject to large uncertainty and no recommendation is made.

OH quantum yields close to unity have been observed for photolysis of HOI and HOCl, and a similar value would be expected for HOBr. The only experimental study is that of Benter et al. (1995) who obtained a value of  $> 0.95$  at 363 nm but this value is dependent on the cross-sections used. Confirmation of unit quantum yield is desirable.

Calculations of the atmospheric lifetime of HOBr by Ingham et al. (1998) using their own cross-sections give values of  $\sim 5$  min in the lower stratosphere at a zenith angle of  $40^\circ$  and  $\sim 30$  min at the surface at high zenith angles.

## References

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