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The UV absorption spectra of CH_2Br and CH_2BrO_2 and the reaction kinetics of CH_2BrO_2 with itself and with HO_2 at 298 K

Eric Villenave, Robert Lesclaux

Laboratoire de Photophysique et Photochimie Moléculaire, Université Bordeaux 1, URA 348 CNRS, 33405 Talence Cedex, France

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Abstract

The UV absorption spectra of the bromomethyl (CH_2Br) and bromomethylperoxy (CH_2BrO_2) radicals have been determined using the flash photolysis technique. CH_2Br exhibits the typical absorption band of halomethyl radicals, peaking near 230 nm, and CH_2BrO_2 exhibits the typical broad absorption of peroxy radicals, with a maximum at 240 nm. Rate coefficients were determined at 298 K for the self-reaction ($CH_2BrO_2BrO_2 + CH_2BrO_2 \rightarrow 2\ CH_2BrO + O_2$ (3), $k_3 = (1.05 \pm 0.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) and for the reaction with HO_2 ($CH_2BrO_2 + HO_2 \rightarrow$ products (5), $k_5 = (6.7 \pm 3.8) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}). As for fluorine and chlorine substitution, bromine substitution enhances the rate constant of the self-reaction, compared to that of the methylperoxy radical, whereas it does not significantly change the rate constant for the reaction with HO_2.

1. Introduction

The atmospheric oxidation processes of halogen-containing compounds have been extensively studied during the last few years, since such compounds can contribute to the transport of halogen species into the stratosphere. Most of the attention has been paid to chlorine compounds, which represent the most abundant emissions to the atmosphere. In contrast, very few studies of the oxidation processes of bromine-containing compounds have been reported so far, although it is well established that bromine depletes stratospheric ozone very efficiently and thus plays a significant role in stratospheric chemistry despite its low concentration [1,2].

Bromomethane (CH_3Br) is the principal source of atmospheric bromine. Its sources may be natural (oceans, volcanoes) or anthropogenic (e.g., fumigants, fire-fighting agents) [1–3]. Bromomethane is principally removed from the atmosphere by tropospheric oxidation initiated by OH attack,

$$CH_3Br + OH \rightarrow CH_2Br + H_2O, \tag{1}$$

with $k_1 = 3.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, corresponding to an atmospheric lifetime of about 1.7 years [4–6]. It has been shown recently that the principal oxidation product of CH_3Br in the absence of nitrogen oxides is formylbromide HC(O)Br [7,8], suggesting that the same reaction pathway occurs as in the oxidation of methane and chloromethane [9–11],

$$CH_2Br + O_2 + M \rightarrow CH_2BrO_2 + M, \tag{2}$$

$$CH_2BrO_2 + CH_2BrO_2 \rightarrow 2\ CH_2BrO + O_2, \tag{3a}$$

$$CH_2BrO_2 + CH_2BrO_2 \rightarrow CH_2BrOH + HC(O)Br + O_2, \tag{3b}$$

$$CH_2BrO + O_2 \rightarrow HC(O)Br + HO_2. \tag{4}$$

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The high yield of HC(O)Br and the absence of CH_2BrOH in the reaction products [7,8] suggest that reaction (3a) is the principal channel of reaction (3), as already observed for the equivalent reaction of CH_2ClO_2 [11]. The reaction of CH_2BrO_2 with HO_2,

$$CH_2BrO_2 + HO_2 \rightarrow \text{products}, \qquad (5)$$

must also be taken into account, both in the atmosphere (due to the abundance of HO_2 radicals), and in laboratory studies of reaction (3) (since channel (3a) results in the formation of HO_2 through reaction (4)).

Only one study of the UV spectrum of CH_2BrO_2 and of the kinetics of reaction (3), using pulse radiolysis, has been reported so far [8], whereas reaction (5) has never been investigated. The UV spectrum of CH_2BrO_2 was found to be very different from the usual spectrum of peroxy radicals and the kinetics of reaction (3) were found to be much faster than expected. We report a study of the kinetics of reactions (3) and (5), at room temperature. Experiments were performed by flash photolysis, using absorption spectrometry for real-time monitoring of radical concentrations. This method requires knowledge of the UV spectra of the radicals involved in the reaction system, with absolute values of absorption cross sections. For this purpose, the absolute UV spectrum of CH_2BrO_2 and also that of CH_2Br have been determined in this work, again at room temperature.

2. Experimental

All experiments were carried out using the flash photolysis apparatus described in detail elsewhere [12]. Briefly, it consisted of a 70 cm long pyrex cell and the flash was generated by discharging two capacitors through external argon flash lamps. Radical concentrations were monitored by time-resolved UV absorption spectrometry from 220 to 290 nm. The analysis beam from a deuterium lamp passed either once or twice through the cell and impinged onto a monochromator/photomultiplier unit. Individual experimental absorption curves were transferred to a digital oscilloscope and then passed to a microcomputer for averaging and further data analysis. Bromomethyl and bromomethylperoxy radicals were generated by flash photolysis of a slowly flowing $Cl_2/CH_3Br/N_2$ gas mixture, with or without added O_2, which was renewed between consecutive flashes:

$$Cl_2 + h\nu(\lambda > 280\ \text{nm}) \rightarrow 2\ Cl, \qquad (6)$$

$$Cl + CH_3Br \rightarrow HCl + CH_2Br, \qquad (7)$$

with $k_7 = 4.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} [8,13,14],

$$CH_2Br + O_2 + M \rightarrow CH_2BrO_2 + M. \qquad (2)$$

The concentration of molecular chlorine was maintained in the range $(1.5–4.5) \times 10^{16}$ molecule cm^{-3} and was measured by its absorption at 330 nm ($\sigma = 2.56 \times 10^{-19}$ cm^2 molecule^{-1} [15]). Methyl bromide and oxygen concentrations were chosen so that the sequence of conversion of chlorine atoms into radicals was very rapid (< 25 μs) on the time scale of the reactions studied and dominated over all other loss processes for Cl atoms. The methyl bromide concentration was measured by its absorption at 240 nm ($\sigma = 4.5 \times 10^{-20}$ cm^2 molecule^{-1} [15]) and varied over the range $(8.0–27.5) \times 10^{16}$ molecule cm^{-3}. Because of the concentrations of CH_3Br used and of its high UV absorption, experiments were not possible below 220 nm for determinations of UV spectra nor below 240 nm for kinetic measurements.

For the study of the reaction between CH_2BrO_2 and HO_2, hydroperoxy radicals were produced via the reaction of chlorine atoms with methanol,

$$Cl + CH_3OH \rightarrow HCl + CH_2OH, \qquad (8)$$

$$CH_2OH + O_2 \rightarrow HO_2 + CH_2O. \qquad (9)$$

CH_3OH was therefore added in sufficient concentration (about 1.3×10^{15} molecule cm^{-3}) to generate HO_2 and CH_2BrO_2 simultaneously and in comparable concentrations.

All experiments were performed at room temperature and 760 Torr and the initial radical concentrations were varied over the range $(3–7) \times 10^{13}$ molecule cm^{-3}.

Oxygen, nitrogen, synthetic air, methane (AGA Gaz Spéciaux, > 99.995%), chlorine (AGA Gaz Spéciaux, 5% in nitrogen, > 99.9%), methyl bromide (Aldrich, 99.95 + %), and methanol (Merck Spectroscopic grade, > 99.7%) were all used without further purification.

3. Results and discussion

3.1. UV absorption spectra of CH_2Br and CH_2BrO_2 radicals

The present kinetic study required an accurate determination of the ultraviolet absorption cross-sections for CH_2BrO_2. Thus, we have determined its absolute UV spectrum and we have taken the opportunity to also determine that of CH_2Br.

The UV spectra were obtained by extrapolating the transient signal back to the time origin to measure the initial absorbance precisely at each wavelength. This was necessary as the high intensity of scattered light from the flash rendered the first 200–300 μs of the trace unusable. Thus, initial radical concentrations were kept low enough ($\approx 4 \times 10^{13}$ molecule cm^{-3}) to prevent too fast a recombination of radicals during this dead time, so that extrapolation errors were minimized. Absorption cross sections were calibrated against the maximum of CH_3O_2, which is now well established at $\sigma = 4.58 \times 10^{-18}$ cm^2 $molecule^{-1}$ at 240 nm [9], by replacing CH_3Br with CH_4 before or after each determination of a spectrum, under the same experimental conditions.

The spectrum of CH_2Br was measured in the spectral range 220–280 nm, with a rather low signal to noise ratio due to the overlap with the CH_3Br absorption, and is shown in Fig. 1 with the corresponding absorption cross sections given in Table 1. In spite of the strong CH_3Br absorption below 240 nm, the maximum has been clearly characterized at around 230 nm ($\sigma = (8.76 \pm 1.31) \times 10^{-18}$ cm^2 $molecule^{-1}$). It is clear that the CH_2Br radical does not absorb at wavelengths longer than 260 nm, in disagreement with the spectrum reported by Nielsen et al. [8]. The spectrum we report here is very similar to that of CH_2Cl [16], as might be expected. The low signal to noise ratio did not allow reliable kinetic studies of the CH_2Br recombination to be performed. However, an estimation of the recombination rate constant can be made: $k(CH_2Br + CH_2Br) = (3.5 \pm 1.5) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K, 1 atm pressure nitrogen. This is close to the rate constant for recombination of CH_2Cl radicals of 2.8×10^{-11} cm^3 $molecule^{-1}$ s^{-1} [16].

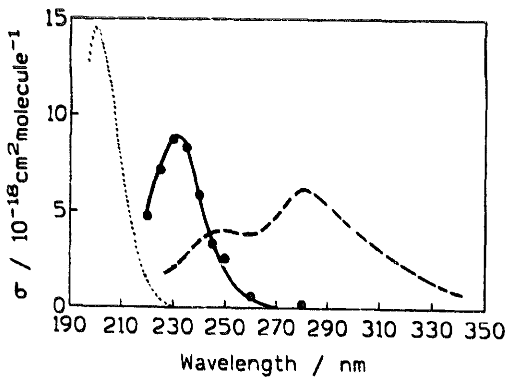

Fig. 1. UV spectrum of the CH_2Br radical: (———) this work; (- - -) Ref. [8]; the spectrum of CH_2Cl (· · · · · ·) is shown for comparison.

Table 1
Absolute UV absorption cross sections for CH_2Br, CH_2BrO_2 and HC(O)Br radicals at 298 K

Wavelength (nm)	σ (10^{-18} cm^2 $molecule^{-1}$)		
	CH_2Br	CH_2BrO_2	HC(O)Br [a]
220	4.76 ± 0.72	–	–
225	7.17 ± 1.08	–	–
230	8.76 ± 1.31	3.36 ± 0.27	–
235	8.32 ± 1.25	3.58 ± 0.28	–
240	5.87 ± 0.88	3.59 ± 0.11	0.19
250	2.56 ± 0.39	3.35 ± 0.10	0.22
260	0.61 ± 0.09	2.73 ± 0.13	0.32
270	–	2.17 ± 0.12	0.32
280	0.20 ± 0.03	1.38 ± 0.18	0.25
290	–	0.95 ± 0.15	0.15

[a] From Ref. [22].

The spectrum of CH_2BrO_2 was recorded at room temperature between 230 and 290 nm. It would have been interesting for us to monitor radical concentrations below 230 nm, to quantify the individual contribution of HO_2 to the absorption, but unfortunately this was not possible because of the strong absorption of CH_3Br at these wavelengths. The spectrum is presented in Fig. 2, and the corresponding cross sections are given in Table 1. The CH_2BrO_2 spectrum resembles those of most alkyl and halogen-substituted alkyl peroxy radicals [9,10] appearing as a broad band without any vibrational structure and with a maximum at 240 nm ($\sigma = (3.59 \pm 0.11) \times 10^{-18}$ cm^2 $molecule^{-1}$). The spectra of CH_3O_2 and CH_2ClO_2 are also given in Fig. 2 for comparison.

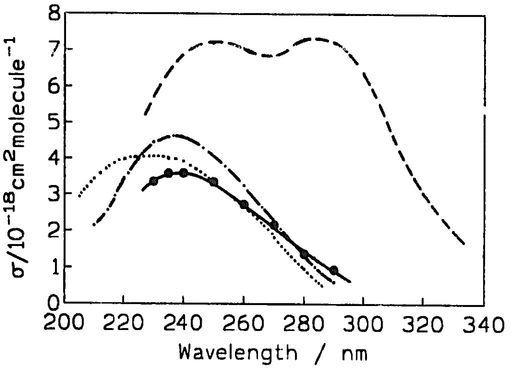

Fig. 2. UV spectrum of the CH_2BrO_2 radical: (———) this work; (– – –) Ref. [8]; the spectra of CH_2ClO_2 (· · · · · ·) and CH_3O_2 (· – · – ·) are shown for comparison.

Also included in the figure is the spectrum obtained by Nielsen et al. using the pulse radiolysis technique [8]. As with CH_2Br, their spectrum looks very different from the one obtained in this work, having two maxima (near 250 and 280 nm) and higher absorption cross sections (7.20 and 7.36 × 10^{-18} cm^2 molecule^{-1} at these wavelengths, respectively). Such differences are difficult to account for and cannot arise from simple systematic errors. They may rather be due to some secondary chemistry associated with the technique of pulse-radiolysis and, possibly, to the relative weakness of the C–Br bond.

3.2. The CH_2BrO_2 self-reaction

Kinetic measurements of k_3 were carried out principally at room temperature, at atmospheric pressure, and at monitoring wavelengths systematically varied from 240 to 280 nm. A typical decay trace is presented in Fig. 3. No systematic dependences of the results on O_2, CH_3Br or Cl_2 concentrations were found.

The usual mechanism for peroxy radical self-reactions suggests

$$CH_2BrO_2 + CH_2BrO_2 \rightarrow 2\ CH_2BrO + O_2, \qquad (3a)$$

$$CH_2BrO_2 + CH_2BrO_2 \rightarrow CH_2BrOH + HC(O)Br + O_2, \qquad (3b)$$

$$CH_2BrO + O_2 \rightarrow HC(O)Br + HO_2, \qquad (4)$$

$$CH_2BrO_2 + HO_2 \rightarrow CH_2BrOOH + O_2, \qquad (5a)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2. \qquad (10)$$

It has been established in the case of halogenated peroxy radicals, that other products are possible for reaction (5) [17–19], as discussed below.

This reaction mechanism is consistent with the end-product studies of the CH_3Br oxidation in the absence of NO [7,8], which showed that HC(O)Br is the only major product. Note that bromomethanol CH_2BrOH, produced in reaction channel (3b), has never been characterized as a reaction product. Consequently, we have considered that reaction (3a) is the dominant channel in reaction (3), even though no absolute yield has been reported for HC(O)Br. Therefore, we assume in the following that $\alpha = k_{3a}/k_3 = 1$. It should be emphasised that a similar high value was found for α in the case of CH_2ClO_2 ($\alpha = 1.0$) [11,20], $CHCl_2O_2$ ($\alpha > 0.95$) [11,20] and CH_2FO_2 ($\alpha > 0.77$) [21]. Therefore, high branching ratios seems to be the rule for the non-terminating channel (3a) in the case of halogen-substituted methylperoxy radicals. Thus, the above assumption that α is equal to 1 for reaction (3) is consistent with previous findings concerning halogenated radicals.

In those series of experiments where only CH_2BrO_2 was generated, HO_2 was formed as a secondary product of the self-reaction (3), according to the above mechanism in which reaction channel (3a) is the dominant channel of reaction (3). Thus, reaction (5) plays an important role in the overall reaction kinetics and k_3 had to be derived from simulations of the complete reaction mechanism. The value of k_5 was determined in parallel, as described

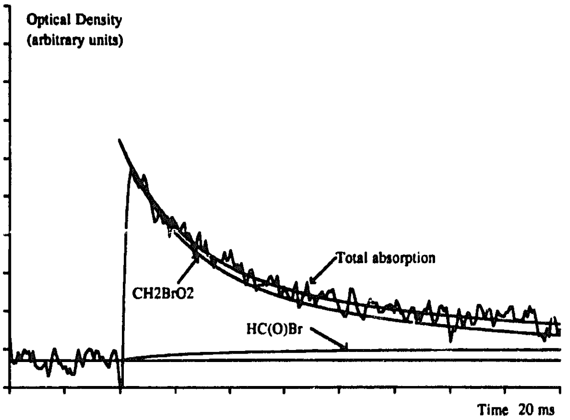

Fig. 3. Experimental decay trace and fit recorded at 260 nm for the self-reaction $CH_2BrO_2 + CH_2BrO_2$. The residual absorption (see text) can only be clearly seen at longer time scale.

below. In addition, the product absorptions were taken into account in the simulations. The spectrum of HC(O)Br used was that provided by Libuda and Zabel [22] and the corresponding absorption cross sections are given in Table 1. The contributions of the absorptions of CH_2BrOOH and H_2O_2 were quite small. It was assumed that the absorption cross sections of CH_2BrOOH were nearly the same as those of CH_3OOH.

It is assumed in the analysis that all bromomethoxy radicals, CH_2BrO, are converted into HO_2 according to reaction (4). Since a direct observation of HO_2 at shorter wavelengths (210–220 nm) was not possible, we have considered the possibility of Br-atom elimination from CH_2BrO at room temperature, as already observed in the case of other halogenated methoxy radicals such as $CHCl_2O$ [23,24], CCl_3O [25,26], $CHBr_2O$ and CBr_3O [27]. In such a case, BrO radicals are likely to be formed according to the following reactions:

$$CH_2BrO + M \rightarrow HCHO + Br + M, \qquad (11)$$

$$CH_2BrO_2 + Br \rightarrow CH_2BrO + BrO, \qquad (12)$$

as already observed in the case of the Br + CCl_3O_2 reaction [28].

Decay traces recorded at $\lambda = 313$ nm ($\sigma_{BrO} = 4.54 \times 10^{-18}$ cm^2 molecule^{-1} [15]) did not exhibit any specific absorption of BrO and therefore we conclude that CH_2BrO radicals are quantitatively converted into HO_2 by reaction (4). This behaviour is consistent with the results of the product study of Nielsen et al. [8] who did not report any formation of formaldehyde, thereby eliminating the possible occurrence of reaction (11). However, very recent results from the same group would contradict this conclusion, as evidences seem to have been obtained in favor of the occurrence of reaction (11) [29]. In addition, a possible decomposition of CH_2BrO into HBr and HCO, as recently observed in the case of CH_2ClO [11,19], cannot be discounted. If such a decomposition pathway occurred, it would necessarily be to a limited extent, since it does not produce HC(O)Br. In any case, it would not change our simulations of the above chemical mechanism, since it also results in the production of HO_2, via the fast reaction of HCO with O_2.

Experiments were performed at different wavelengths from 240 to 280 nm, and decay traces recorded over various time scales. The first and most significant part of the decay was easily simulated using the above mechanism. However, at longer time scales, a relatively small residual absorption was observed, which could not be completely accounted for by the individual absorptions of the products HC(O)Br, CH_2BrOOH and H_2O_2 (the residual absorption was about twice as high as the calculated one, with a maximum absorption occurring approximately between 240 and 260 nm).

The main absorbing product of the reacting system is HC(O)Br and its absorption spectrum has only been determined once [22]. Thus, we have performed an independent, approximate estimation of the spectrum and absorption cross sections, using our flash-photolysis setup. CH_2BrO_2 radicals were generated in the same conditions as above but in the presence of an excess NO (about 4×10^{14} molecule cm^{-3}) and 1 atm O_2. Under such conditions, CH_2BrO_2 radicals reacted quantitatively with NO and CH_2BrO reacted with O_2 to produce HO_2 and HC(O)Br. A chain reaction was initiated by OH radicals generated in the reaction of HO_2 with NO, but was rapidly quenched by the reaction of OH with NO and could therefore be easily accounted for in the simulation. Hence, HC(O)Br was produced in a clean and well-controlled reaction system, in which no other absorbing products were expected. Absorption cross sections of HC(O)Br were estimated at different wavelength from the residual absorption of experimental traces and found to be in reasonable good agreement (within 20%–30%) with those reported by Libuda and Zabel [22]. Thus, the uncertainties on HC(O)Br absorption cross sections are not sufficient to explain the presence of the residual absorption.

The spectrum and intensities of the residual absorption were not easily reproduced and tended to increase when HO_2 was generated along with CH_2BrO_2 in the study of reaction (5). We have therefore considered the possibility that this absorption is due to an unidentified product of reaction (5). By introducing into our simulations an adjustable cross section ($\sigma = (0.45 \pm 0.25) \times 10^{-18}$ cm^2 molecule^{-1} at 250 nm) to a product of reaction (5), it was actually possible to account correctly for the residual absorption. We have then decided to use this procedure to derive the values of k_3 reported below. It should be emphasized that, using this procedure, the values of k_3 were only increased by 20% compared to the value obtained by ignoring the residual absorption and introducing into the simulations the usual absorption cross sections of expected products given in Table 1.

Decay curves could be simulated correctly from 240 to 280 nm. The resulting weighted average values of the rate constant k_3 are reported in Table 2. It can be seen that the values are fairly constant from 250 to 280 nm whereas the value obtained at 240 nm is more than twice as high as others. We have no explanation for this particularity but we must consider that the absorption of CH_3Br at 240 nm begins to be quite significant, which may prevent an accurate analysis of the decay curve. In contrast, the absorption of CH_3Br has become low or negligible at other wavelengths, for which k_3 was constant within experimental uncertainties. Measurements at 240 nm were thus disregarded. The quoted errors are 1σ, representing only experimental scatter. There exists undoubtedly uncertainties on the reaction mechanism, even though a large part of the products have been identified by end-product analysis [7,8]. By combining the statistical errors and those due to the reaction mechanism, we estimate that a total uncertainty of nearly 40% should be assigned to k_3, giving

$$k_3 = (1.05 \pm 0.4) \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

at 298 K.

This value is more than a factor 30 smaller than the value of k_3 already reported in the literature [8]. It must be emphasised, however, that it is consistent with preceding rate constant determinations of halogen-substituted methylperoxy radicals, as discussed below.

3.3. The $CH_2BrO_2 + HO_2$ reaction

The rate constant k_5 was determined at room temperature and in one atmosphere of air. It has been verified that there was no effect of oxygen concentration on the value obtained. As explained before, CH_2BrO_2 and HO_2 were generated simultaneously and in comparable concentrations, such that the most important reaction in the analysis of decay traces was the cross-reaction (5). Due to the strong absorption of CH_3Br below 240 nm, where HO_2 exhibits its maximum absorption, we were unable to use the method adopted in our former studies of the $RO_2 + HO_2$ reactions [11,30] where pairs of traces, recorded at wavelengths specific to each radical, were analyzed simultaneously. Nevertheless, the kinetics of reaction (5) were investigated at several wavelengths between 250 and 280 nm and again, no significant variation of k_5 with wavelength could be observed.

Decay traces were analyzed using the same reaction mechanism as in the self-reaction study. As mentioned above, the residual absorption was larger than in the case of the study of reaction (5), where no HO_2 was generated at the initial stage of the reaction, and about three times as large as the calculated residual absorption obtained by simulation of the above mechanism. Therefore, as mentioned above, the absorbing species that is responsible for the residual absorption is likely to be a product of reaction (5). The possible reaction products are the following:

$$CH_2BrO_2 + HO_2 \rightarrow CH_2BrOOH + O_2, \qquad (5a)$$

$$CH_2BrO_2 + HO_2 \rightarrow HC(O)Br + H_2O + O_2, \qquad (5b)$$

$$CH_2BrO_2 + HO_2 \rightarrow CH_2O + HOBr + O_2. \qquad (5c)$$

The most strongly absorbing species in the above products are HC(O)Br and HOBr, assuming that the

Table 2
Average rate constants for reaction (3) and (5) obtained at different wavelengths

λ (nm)	k_3 (10^{-12} cm^3 molecule^{-1} s^{-1})	No. of determinations	k_5 (10^{-12} cm^3 molecule^{-1} s^{-1})	No. of determinations
240	2.45 ± 0.30	26	nd	–
250	1.04 ± 0.17	20	6.39 ± 0.70	4
260	0.99 ± 0.14	9	7.55 ± 0.91	4
270	1.05 ± 0.17	7	6.96 ± 0.34	3
280	1.16 ± 0.04	7	5.93 ± 0.45	2

CH_2BrOOH cross section is approximately equal to that of CH_3OOH. The absolute absorption spectrum of HOBr was determined recently by Orlando and Burkholder [31]. However, none of these products, whatever its yield, absorbs sufficiently to account for the residual absorption. A chain reaction might be induced by an alternative reaction channel forming OH radicals,

$$CH_2BrO_2 + HO_2 \rightarrow CH_2BrO + OH + O_2. \qquad (5d)$$

OH radicals would rapidly react with CH_3Br, thus maintaining a quasi-stationary concentration of CH_2BrO_2 and building-up additional amounts of products. However, simulations show that the chain is rapidly terminated by reaction (3) and cannot explain that the residual absorption is seen over several hundreds of milliseconds. We conclude that the residual absorption is either due to an unknown stable product, probably formed by reaction (5), or to secondary reactions involving products stuck to the walls. Note that higher absorption cross sections of CH_2BrOOH than expected cannot be set aside. Nevertheless, since the identified end-products are consistent with the above reaction mechanism, we have simulated the decay curves and determined k_5, by assigning an adjustable cross section to a product of reaction (5), as in the case of reaction (3), and with similar cross-section values. Note that in this case, the rate constant was about 40% to 50% higher than when determined by ignoring the residual absorption and by limiting the fit to the most significant part of the decay trace. In contrast to the case of the determination of k_3, this difference is significant here and introduces a large uncertainty into the determination of k_5, but at the same time shows that whatever the analysis method, the differences between the obtained values of k_5 remain acceptable to report a good evaluation of this rate constant.

The average of several determinations of rate constants at different wavelengths are given in Table 2. Again, the quoted errors are 1σ, representing only the experimental scatter. Combining these statistical errors with the uncertainties in the reaction mechanism, we estimate an overall uncertainty of about 60% for k_5. The resulting value is

$$k_5 = (6.7 \pm 3.8) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K.

Table 3
Rate constants for self-reactions and reactions with HO_2 of halogen-substituted peroxy radicals at 298 K. CH_3O_2 is included for comparison. Units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}

	$k(RO_2 + RO_2)$	$k(RO_2 + HO_2)$	Refs.
CH_3O_2	0.37	5.8	[9]
CH_2FO_2	4.0	> 2	[17,21]
CH_2ClO_2	3.7	5.2	[10]
$CHCl_2O_2$	3.9	5.8	[24]
CCl_3O_2	4.0	5.1	[24]
CH_2BrO_2	1.05	6.7	this work
CF_3CHFO_2	6.0	4.1	[32,33]
$CF_2ClCH_2O_2$	–	6.9	[33]

As far as we are aware, the present work represents the first determination of this rate constant and therefore no direct comparison with literature values is possible. However, the value is very similar to those of the corresponding reactions of methyl- and halogen-substituted methylperoxy radicals, as shown below.

4. Conclusion

UV spectra of both CH_2Br and CH_2BrO_2 radicals have been obtained in this work. The main uncertainties on these spectra arise from their overlap with the absorption of the CH_3Br precursor. This is particularly true for the CH_2Br spectrum which, consequently, has fairly large uncertainties on both the absolute cross sections and on the position of the maximum. Nevertheless, as was expected, both spectra are very similar to the corresponding spectra of CH_2Cl and CH_2ClO_2, in contrast to the preceding determination [8]. It should be noted that, from 250 to 280 nm, where CH_2BrO_2 was monitored for kinetic measurements, the cross-section values are the most accurate since there is no overlap with the CH_3Br absorption.

The uncertainties on k_3 and k_5 have been discussed above. It is of interest to compare their values to those of the corresponding reactions of other halogen-substituted peroxy radicals. Rate constant values for a few radicals are given in Table 3.

It is clear that fluorine and chlorine substitution enhances the rate constants of self-reactions, by about an order of magnitude for the methyl peroxy radical and even more for the ethyl peroxy radical ($k(C_2H_5O_2 + C_2H_5O_2) = 0.08 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} [9,10]). In contrast to alkyl peroxy radicals, all reactions of fluorine- and chlorine-substituted radicals have a similar rate constant, in the range $(2\text{–}4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Bromine substitution also apparently enhances the self-reaction rate constant in the case of the methyl peroxy radical, but to a lesser extent than for fluorine and chlorine substitution (about a factor three according to the present study). Nevertheless, this remains consistent with the observed enhancement induced by halogen substitution.

As far as the reactions with HO_2 are concerned, rate constants are remarkably constant for all reactions of halogen-substituted peroxy radicals that have been investigated so far, as seen in Table 3. This is also the case for the only reaction of a bromine-subsituted peroxy radical investigated so far and presented in this work, showing that the result is consistent with others, in spite of the difficulties encountered in measurements reported above. Thus, the result obtained in the present work confirms that halogen-substituted peroxy radicals (including bromine-substituted ones) all have a similar reactivity towards HO_2. However, large uncertainties still remain about the products of those reactions.

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