

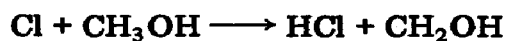
MEASUREMENTS OF THE UV ABSORPTION CROSS-SECTIONS FOR HO₂ AND CH₃O₂ IN THE GAS PHASE

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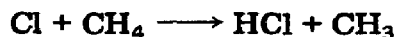
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Summary

Relative values of the gas phase absorption cross-sections σ for hydroperoxy (HO₂) and methylperoxy (CH₃O₂) radicals were determined at 298 K over the wavelength λ ranges 210 - 250 nm and 210 - 280 nm respectively. These determinations were based on measurements of the initial optical density (OD)⁰ of each radical *vs.* wavelength immediately following its flash photolytic generation. Chlorine atoms produced by the photolysis ($\lambda \geq 300$ nm) of Cl₂ were stoichiometrically converted into the desired peroxy radical via the reaction sequences



or



Cross-section ratios for the two radicals, determined in separate experiments at several wavelengths, agreed well with those calculated using data from the complete (OD)⁰ *vs.* λ sets and were used to establish the relative intensities of the absorption spectral curves for the two radicals. These spectral data were converted to absolute cross-sections using measurements of the fractional photodissociation of Cl₂ per flash in conjunction with measurements of the initial methylperoxy radical OD as a function of Cl₂ concentration. The results are compared with existing data in the literature for both relative and absolute absorption cross-sections and the effect of these new values on the existing kinetics data base for both radicals is discussed.

1. Introduction

Hydroperoxy (HO₂) and methylperoxy (CH₃O₂) radicals both play major roles in atmospheric and combustion chemistry. This importance has

spawned interest in the development and use of analytical techniques for the sensitive detection and quantitative measurement of each species. For many radical reactions, experiments can be designed so that pseudo-first-order conditions with respect to the radical decay are satisfied. In such cases absolute radical concentrations are not generally needed and an analytical methodology for relative concentrations suffices. However, for the peroxy radicals, the list of reactions of atmospheric interest includes self-disproportionation, cross-disproportionation and interactions with a host of other radical transients. In these cases, the reaction classification can be described under the best of conditions as second order, and more commonly as a mixture of first and second order. Under such circumstances, uncertainties in the measurement of the required absolute radical concentrations result in increased uncertainties in the derived kinetics parameters.

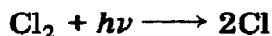
Following the discovery of moderately strong absorption bands for HO_2 and CH_3O_2 in the 200 - 300 nm region, a significant part of the gas phase kinetics data base for both species has been acquired utilizing UV absorption spectroscopy. For HO_2 , there is fairly good agreement among several studies [1 - 4] on the shape of the absorption spectrum over the range 200 - 250 nm. These same studies show excellent agreement in the reported absolute magnitudes of cross-section σ at wavelengths λ greater than 220 nm with a slightly broader range of values reported for $\lambda \leq 220$ nm. This agreement might be fortuitous, however, since the values from two of the studies [1, 3] require re-evaluation. In these two studies, the cross sections were derived from fits of kinetics data for HO_2 radical disproportionation obtained by modulation spectroscopy and the rate constants k calculated from these analyses differ significantly from currently accepted values [5]. For this reason, recommended values for the absolute HO_2 absorption cross-section were calculated [5] by averaging the σ vs. λ curves from all three studies to yield the average shape of the absorption spectrum which was then normalized to the direct absolute calibration by Sander *et al.* [6] at 227.5 nm.

For CH_3O_2 , many more measurements of the UV absorption spectrum exist, but the published absorption coefficients differ by more than a factor of two. For example, the values determined by Parkes and coworkers [7] from fits of molecular modulation data are systematically greater than those calculated from the more direct calibrations of Hochanadel *et al.* [8] and Kan *et al.* [9]. This discrepancy as well as a broad range of higher values extracted from the molecular modulation k/σ determinations of Cox and Tyndall [10] have generally been dismissed as being due to the less direct nature of the molecular modulation measurements. However, in a study nearly identical with that of ref. 9, Adachi *et al.* [11] report absorption coefficients in good agreement with the higher range of numbers. Finally, using a direct calibration procedure, Sander and Watson [12] report a value for σ at 250 nm which is slightly lower than the values from Kan *et al.* [9] and Hochanadel *et al.* [8] and considerably lower than a recent indirect determination by Pilling and Smith [13] from successive fits to kinetic data.

We recently have been investigating peroxy radical reactions of atmospheric importance utilizing flash photolysis kinetic absorption spectroscopy. In the analysis of our data on HO₂ self-disproportionation [14] and its combination with NO₂ [15] we utilized the National Aeronautic and Space Administration (NASA) Data Panel recommendation [5] for σ_{HO_2} which, as mentioned, is scaled to ref. 6. For consistency we decided to scale the body of $\sigma_{\text{CH}_3\text{O}_2}$ vs. λ data to the analogous ref. 12 for use in reducing data from our current study of HO₂ plus CH₃O₂ gas phase cross-disproportionation. During the course of the experiments, however, we encountered some rather surprising results. At every monitoring wavelength, the initial optical density due to CH₃O₂ absorption was substantially greater than that expected from the corresponding initial HO₂ optical density (OD)_{HO₂}⁰, and the calculated absorption cross-section ratios for the two radicals. In the absence of any reasonable explanation for these observations, we decided to redetermine both σ_{HO_2} and $\sigma_{\text{CH}_3\text{O}_2}$ directly in our apparatus. In this paper we report the results of our measurements of the relative UV absorption cross-sections for the two radicals and their absolute calibration at 298 K.

2. Experimental details

The flash photolysis UV absorption apparatus used in this study has been described in detail in earlier publications [14, 15]. With the cell thermostatted at 298 K, radical formation was initiated by the flash photolysis ($\lambda \geq 300$ nm) of Cl₂



In the presence of CH₃OH or CH₄, O₂ and N₂, the desired peroxy radical was produced via the reaction sequence



or



In the presence of only an inert diluent (N₂ or argon) the change in Cl₂ optical density at 330 nm immediately after the flash provided a calibration of the initial chlorine atom concentration [Cl]⁰. In the radical formation experiments, concentrations of the reagents were chosen to ensure that peroxy radical production was complete on a time scale 10 - 50 μs . The ranges of concentrations were as follows: Cl₂, (5.4 - 52.0) $\times 10^{15}$ molecules cm⁻³; CH₃OH, (1.0 - 4.0) $\times 10^{15}$ molecules cm⁻³; CH₄, (0.6 - 1.0) $\times 10^{18}$ molecules cm⁻³; O₂, (0.4 - 1.6) $\times 10^{18}$ molecules cm⁻³. In these experiments, the N₂ concentration was that required to bring the total pressure in the cell

to 100 Torr. The reagents had the following purities: CH₄, 99.99%; Cl₂, 99.96% (used after redistillation); CH₃OH, spectral grade (used after vacuum drying and redistillation); O₂, 99.99%; N₂, 99.999%; argon, 99.999%. Photolysis mixtures were prepared by combining calibrated flows of the gases in a mixing chamber immediately upstream of the reaction cell. The total flow rate through the cell was chosen to permit complete sample replacement every four to five flashes, corresponding to a residence time of about 30 s.

The initial radical optical densities (OD)⁰ were determined from light transmission *vs.* time (*i.e.* radical decay) curves recorded with a 50 μs time resolution. These measurements were made at spectral resolutions of 1.3 and 2.6 nm using a 75 W xenon arc lamp and a multipass optical configuration through the reaction cell (four passes, 225 cm path length). The linearity of the detection system was checked at several wavelengths using neutral density filters calibrated for the UV region. Individual experimental curves were signal averages of 20 - 200 flashes (50 was typical) depending on the radical concentration. Because of the low radical concentrations and the 50 μs acquisition channel width, the calculation of (OD)⁰ required only minor second-order kinetics extrapolation of the digitized transmission *vs.* time curves to the time of the flash to account for radical decay via self-reaction. The ranges of reagent concentrations given above, coupled with a flash energy of 400 J, resulted in [Cl]⁰ ≈ (0.2 - 1.9) × 10¹⁴ molecules cm⁻³. This variation was used to investigate the efficiency of conversion of chlorine atoms into the peroxy radicals and to provide a direct calibration of the absorption cross-sections. Most of the data in the relative cross-section experiments were taken with an initial radical concentration of 0.7 × 10¹⁴ molecules cm⁻³ as described below.

The shape of the absorption curve for each radical was determined from multiple sets of (OD)⁰ *vs.* λ measurements. These were obtained from radical decay profiles recorded typically at 5 nm increments under conditions of constant reagent flows. Experimental reproducibility was checked by sweeping both up and down in wavelength during the course of 1 day and by performing replicate experiments for each radical on subsequent days. Precise values of the ratio σ_{HO₂}/σ_{CH₃O₂} at several wavelengths were determined from measurements of (OD)⁰ for the two radicals as measured in alternate HO₂ and CH₃O₂ experiments. For these experiments, one of the flow controllers was switched between CH₃OH and CH₄ while the Cl₂ flow, O₂ flow and total pressure were kept constant. This procedure was repeated until several transmission curves for each radical were obtained at the wavelength, the (OD)⁰ values extrapolated and the ratios calculated. Ratios were derived from data taken on several days employing different monochromator resolutions and a fourfold range in [Cl₂]. The ratios were then used to "fine-tune" the vertical positioning of the two radical spectral curves. Finally, the spectral curves were converted into σ *vs.* λ profiles by determining the fractional dissociation δ of Cl₂ per flash. On the assumption that each chlorine atom is stoichiometrically converted into a peroxy radical, the initial optical density (according to the Beer-Lambert absorption law) for each radical is given by

$$(\text{OD})_x^0 = 2\delta[\text{Cl}_2]\sigma_x l \quad (\text{Ia})$$

where l is the analysis pathlength and σ_x is the absorption cross-section for the radical species x at the wavelength of measurement. As mentioned earlier, the Cl_2 photolysis calibration was performed by measuring the change in Cl_2 light absorption at 330 nm on flash photolysis. These measurements were made using $\text{Cl}_2\text{-N}_2$ and $\text{Cl}_2\text{-Ar}$ mixtures and an analysis time scale much shorter than the chlorine atom recombination lifetime. If I^0 is the transmitted analysis light intensity in the absence of Cl_2 , I' the pre-flash intensity in the presence of Cl_2 and I'' the post-flash intensity in the presence of Cl_2 , the following equations can be written:

$$\ln\left(\frac{I'}{I^0}\right) = -[\text{Cl}_2]\sigma_{\text{Cl}_2} l = -(\text{OD})_{\text{Cl}_2} \quad (\text{II})$$

$$\ln\left(\frac{I''}{I^0}\right) = -(1 - \delta)[\text{Cl}_2]\sigma_{\text{Cl}_2} l \quad (\text{III})$$

where σ_{Cl_2} and $(\text{OD})_{\text{Cl}_2}$ are respectively the Cl_2 absorption cross-section [5] and the Cl_2 optical density at 330 nm. Equations (II) and (III) can be combined to give

$$\ln\left(\frac{I''}{I'}\right) = \delta(\text{OD})_{\text{Cl}_2} \quad (\text{IV})$$

and δ can be determined from the slope of a plot of $\ln(I''/I')$ vs. $(\text{OD})_{\text{Cl}_2}$. Over the range of $[\text{Cl}_2]$ typically used in these experiments, the differences between I' and I'' were of the order of a few tenths of a per cent. Thus a statistically meaningful determination of this ratio involved using the 50-flash summation of 512 (50 μs width) channels of digitized signal taken before and after the flash. With $[\text{Cl}_2]$ calculated from 330 nm optical density measurements, eqn. (Ia) can be rewritten as

$$(\text{OD})_x^0 = 2\delta(\text{OD})_{\text{Cl}_2} \frac{\sigma_x}{\sigma_{\text{Cl}_2}} \quad (\text{Ib})$$

Thus the radical absorption cross-section at a given wavelength can be calculated from the slope of a plot of the initial radical optical density at that wavelength vs. the optical density of Cl_2 at 330 nm. It should be noted that this determination does not require a path length calibration but depends only on the measurement of δ and a knowledge of $\sigma_{\text{Cl}_2}(330 \text{ nm})$.

The remaining consideration in this analysis is the validity of the assumption of the stoichiometric conversion of the chlorine atoms into the peroxy radicals. This was examined in detail by computer simulation of mechanisms which included the peroxy radical formation reactions, their self-disproportionation, plus any possible secondary reactions. As secondary reactions we considered additional chlorine atom loss processes as well as reactions which depleted the hydroxymethyl or methyl radicals without accompanying peroxy radical formation. In the HO_2 system, these included



Analogous reactions for the CH_3O_2 system were



In cases where measured rate constants did not exist, worst case scenarios (*i.e.* collisional rate constants) were used in the simulation. Since, in both systems, these interfering reactions were in competition with reactions (1) or (3) and (2) or (4), their relative effects were dictated by the concentrations of CH_3OH (or CH_4) and O_2 . Experimentally, we observed that increases in CH_3OH (or CH_4) over the ranges cited earlier had very little effect in increasing the peroxy radical production. In fact, at the upper end of these ranges in concentration, the initial radical optical density was invariant with $[\text{CH}_3\text{OH}]$ or $[\text{CH}_4]$. These observations were confirmed by the modeling calculations which showed that (for the concentrations of CH_3OH , CH_4 and O_2 used in most of the experiments) the efficiency of the chlorine atom to peroxy radical conversion was better than 95% when $[\text{Cl}]^0$ was 1×10^{14} molecules cm^{-3} or less. These predictions are more complicated when the reactions of CH_3 or CH_2OH with Cl_2 are added to the above two mechanisms:



The net effect of these two reactions at low $[\text{Cl}]^0$ is to delay the peak formation of the peroxy radical with little reduction in the conversion efficiency. However, at $[\text{Cl}]^0 \geq 1 \times 10^{14}$ molecules cm^{-3} this recycling of chlorine atoms increases the efficiency of reactions (5) - (12) and, depending on the value of k_{13} or k_{14} , can result in efficiencies below 85%. These results dictated the concentration range for the analysis of the calibration data as will be discussed in Section 3.

3. Results

Examples of the light transmission *vs.* time profiles for both HO_2 and CH_3O_2 , from which the $(\text{OD})^0$ values are calculated, are shown in Fig. 1 and Fig. 2 respectively. For fixed concentration conditions, values of $(\text{OD})^0$ at

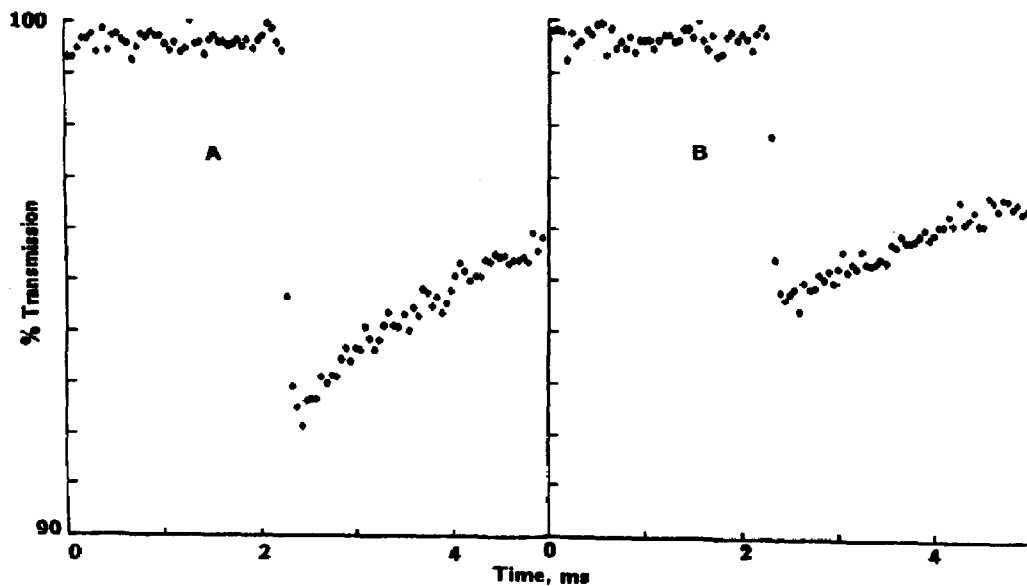


Fig. 1. HO_2 transmission curves at (a) 225 nm recorded with a 2.6 nm resolution (signal average of 50 flashes with a 50 μs per channel time resolution; $[\text{HO}_2]^0 \approx 1.2 \times 10^{14}$ molecules cm^{-3}) and (b) 220 nm recorded with a 2.6 nm resolution (signal average of 75 flashes with a 50 μs per channel time resolution; $[\text{HO}_2]^0 \approx 6.5 \times 10^{13}$ molecules cm^{-3}).

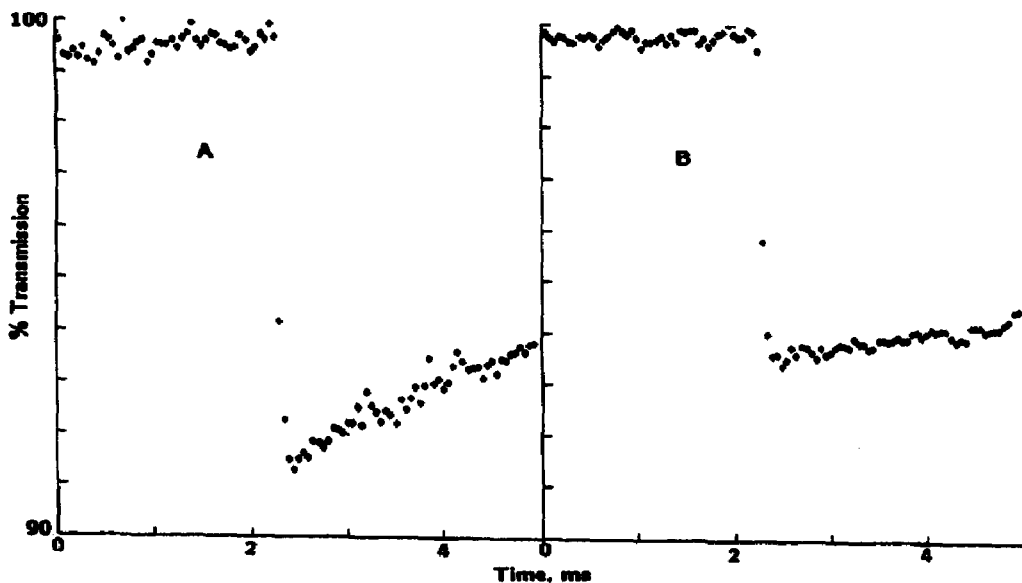


Fig. 2. CH_3O_2 transmission curves at (a) 225 nm recorded with a 2.6 nm resolution (signal average of 60 flashes with a 50 μs per channel time resolution; $[\text{CH}_3\text{O}_2]^0 \approx 1.1 \times 10^{14}$ molecules cm^{-3}) and (b) 240 nm recorded with a 2.6 nm resolution (signal average of 30 flashes with a 50 μs per channel time resolution; $[\text{CH}_3\text{O}_2]^0 \approx 7.5 \times 10^{13}$ molecules cm^{-3}).

any wavelength were generally reproducible to better than 5%, thereby allowing for precise determination of the shape of the absorption spectra of both radicals. Measurements of $(OD)_{HO_2}^0 / (OD)_{CH_3O_2}^0$ at 215 nm, 225 nm and 230 nm, taken in alternate experiments as described earlier, were also reproducible to better than 5% and yielded values for $\sigma_{HO_2} / \sigma_{CH_3O_2}$ at these wavelengths of 1.23, 0.86 and 0.64 respectively. The agreement between these alternate set values and ratios calculated from the spectral curve data was better than 10% and the set values were used to scale the two complete spectral data sets to one another. At 230 nm, the ratio experiments were performed over a range of $[Cl]^0$ from 1×10^{14} to 2×10^{14} molecules cm^{-3} without any significant difference in the results. Since our modeling calculations indicated that stoichiometric peroxy radical production could not be guaranteed at these higher concentrations, we suspect that the extent of secondary reaction interference was similar in both radical systems for this limited range in $[Cl]^0$. This is not surprising since the concentrations of CH_3OH and CH_4 chosen for these experiments were such that first-order removal of chlorine atoms via reactions (1) and (3) were identical. The 215 and 230 nm ratio experiments were conducted with $[Cl]^0 = 7 \times 10^{13}$ molecules cm^{-3} . Excellent reproducibility was obtained for 215 nm ratios determined at monochromator spectral resolutions of 1.3 and 2.6 nm as well as with a 20 nm (full width at half-maximum) bandpass interference filter used together with a 5.2 nm instrument bandpass. The last of these configurations was used to check for any stray light interference in our measurements.

The determination of the fractional dissociation δ of Cl_2 per flash was made for $0 \leq [Cl_2] \leq 5 \times 10^{16}$ molecules cm^{-3} and the data are plotted according to eqn. (IV) in Fig. 3. The N_2 diluent and argon diluent data points are each an average of three or four separate measurements. As can be seen, they are in excellent agreement and can be represented by a linear equation going through the origin as predicted by eqn. (IV) for optically thin conditions in Cl_2 relative to the photoflash. A linear least-squares fit of the data (indicated by the line drawn) yields a value for δ of $(1.94 \pm 0.11) \times 10^{-3}$ where the uncertainty is two standard deviations. The abscissa values for this plot were determined from actual optical density measurements at 330 nm for the various Cl_2 flows.

Over this same range in $[Cl_2]$, measurements of $(OD)_{CH_3O_2}^0$ at 225 nm were recorded. These methylperoxy optical densities (each an average of several determinations) are plotted against $(OD)_{Cl_2}$ in Fig. 4. Excellent linearity is seen for the data obtained at Cl_2 optical densities of 1.5 or less, corresponding to $[Cl]^0 \leq 1 \times 10^{14}$ molecules cm^{-3} . At higher chlorine atom concentrations, the slope appears to decrease such that the observed radical concentration is 10% - 15% lower than expected from stoichiometric conversion (as predicted by the modeling calculations). A fit of the lower concentration data to eqn. (Ib) using a linear least-squares analysis yields a slope, $2\delta \{ \sigma_{CH_3O_2}^0(225 \text{ nm}) / \sigma_{Cl_2}(330 \text{ nm}) \}$, of $(5.15 \pm 0.24) \times 10^{-2}$ where the uncertainty is again two standard deviations. The range of Cl_2 concentration over which we limited this analysis was determined from two statistical considerations.

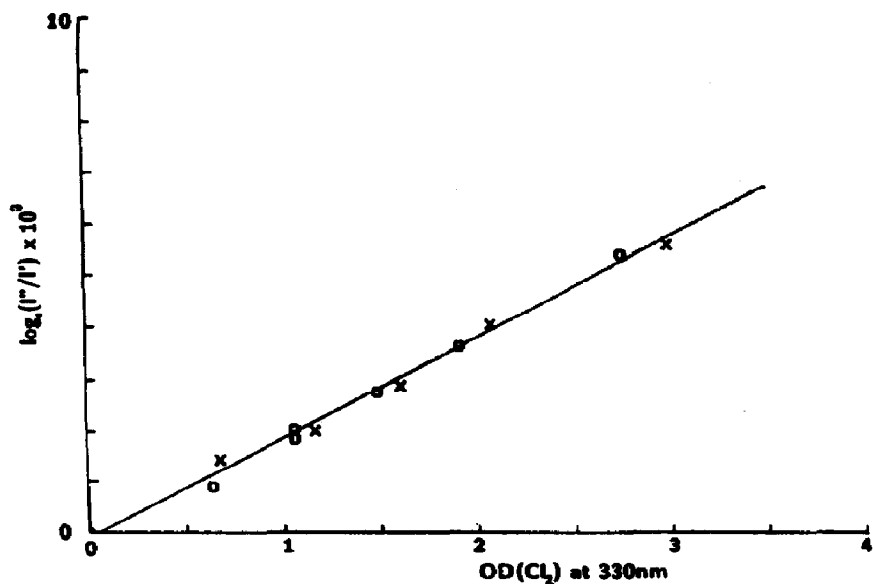


Fig. 3. Plot of $\ln(I''/I')$ vs. the optical density of Cl_2 (measured at 330 nm): \circ , N_2 diluent data; \times , argon diluent data. The slope is the fractional photodissociation of Cl_2 ($\delta = (1.94 \pm 0.11) \times 10^{-3}$).

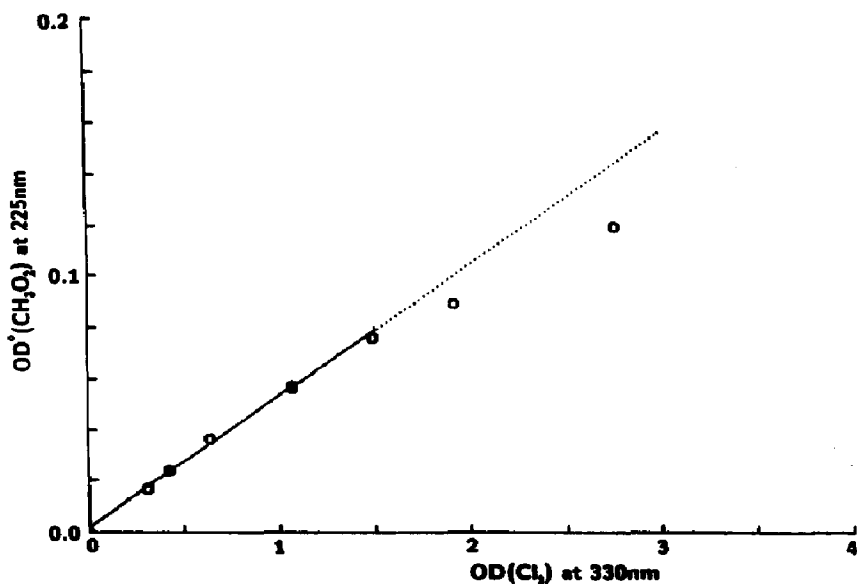


Fig. 4. Plot of the initial optical density of CH_3O_2 (measured at 225 nm) vs. the optical density of Cl_2 (measured at 330 nm). The slope, $(5.15 \pm 0.24) \times 10^{-2}$, equals $2\delta(\sigma_{CH_3O_2}/\sigma_{HO_2})$.

These were (1) the observation of any statistically significant change in slope on the inclusion of an additional (higher concentration) data point and (2) the corresponding change (if any) in the intercept to a value statistically greater than zero on the inclusion of the same data point. Using the value for

δ determined earlier and the recommended evaluation [5] for σ_{Cl_2} (330 nm), we calculate $\sigma_{\text{CH}_3\text{O}_2}$ (225 nm) = $3.39 \times 10^{-18} \text{ cm}^2$. From a propagation of error analysis, the purely statistical (95% confidence) error band on this absorption cross-section is given by $\pm 25 \times 10^{-20} \text{ cm}^2$. On the basis of an assessment of possible sources of systematic error (*e.g.* uncertainty in the value of σ_{Cl_2} (330 nm), reproducible errors in flow settings etc.) in these calibration measurements we assign a maximum additional 5% uncertainty resulting in our final recommendation of

$$\sigma_{\text{CH}_3\text{O}_2} (225 \text{ nm}) = (339 \pm 42) \times 10^{-20} \text{ cm}^2$$

This cross-section was next used to assign absolute ordinate values to the normalized absorption spectra of the two radicals. The calibrated cross-section data for HO_2 and CH_3O_2 are plotted *vs.* wavelength in Fig. 5. The

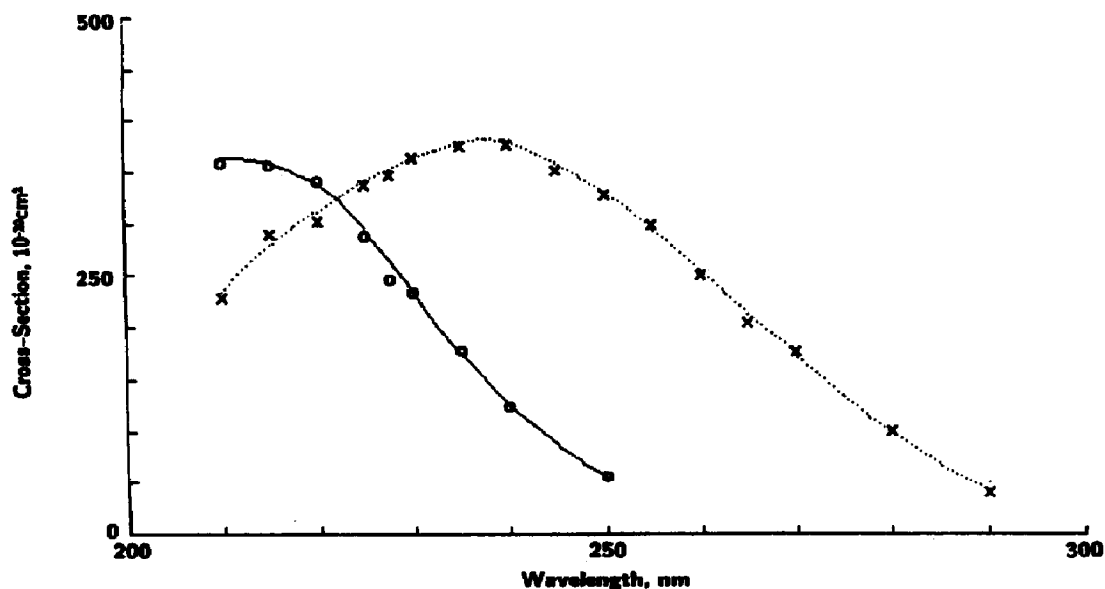


Fig. 5. Calibrated cross-section data for HO_2 (○) and CH_3O_2 (×) as a function of wavelength. The lines drawn through the experimental points are a smooth representation of the absorption spectra.

lines drawn through the data points are a smooth curve interpretation of the experimental data and represent our best assessment of the actual radical absorption cross-sections. The measured and smooth-curve values are both given in Table 1. The coupling of an error propagation analysis from the calibration with the uncertainties in the absorption spectra measurements results in a recommended 15% error band on these tabulated absorption cross-sections.

TABLE 1
UV absorption cross-sections for HO₂ and CH₃O₂

Wavelength (nm)	Absorption cross-sections σ ($\times 10^{-20}$ cm ²) for HO ₂ and CH ₃ O ₂			
	HO ₂ <i>measured</i>	HO ₂ <i>smoothed</i>	CH ₃ O ₂ <i>measured</i>	CH ₃ O ₂ <i>smoothed</i>
210	359	365	230	235
215	358	360	292	280
220	342	340	304	315
225	290	295	339	340
227.5	248	265	349	355
230	235	235	366	365
235	178	175	377	380
240	124	125	378	380
245	—	85	354	360
250	56	55	329	330
255	—	—	301	295
260	—	—	252	255
265	—	—	207	215
270	—	—	178	175
275	—	—	—	135
280	—	—	101	100
285	—	—	—	65
290	—	—	41	40

4. Discussion

At 227.5 nm, our σ_{HO_2} of $(265 \pm 40) \times 10^{-20}$ cm² compares quite favorably with the value of $(300 \pm 40) \times 10^{-20}$ cm² measured by Sander *et al.* [6]. At wavelengths longer than 225 nm, our tabulation for σ_{HO_2} is in good agreement with present recommendations [5] based on this latter calibration. Below 225 nm, however, our measurements range from 15% - 25% lower than the NASA evaluation. We believe that the evaluation at these shorter wavelengths needs to be reconsidered since it appears that the recomputation may have favored ref. 1 alone rather than using an average calculated from refs. 1 - 4. In this regard, it is instructive to compare the present HO₂ results directly with those from the earlier investigations. Of the three, only in refs. 2 and 3 are directly calibrated measurements of the absorption coefficients *vs.* wavelength presented. These calibrated values agree very well with those of the present work (the maximum difference is only 10% at 210 nm). By contrast, in ref. 1, the absorption spectrum was normalized by fits of the in-phase *P* and in-quadrature *Q* components of kinetics data taken by molecular modulation spectroscopy at 210 nm and the rate constant for HO₂ self-disproportionation derived from this same analysis is 75% higher than recommended at present. Since the rate constant is proportional to the

product PQ while the cross-section is proportional to $(PQ)^{1/2}$, a significant overestimation of the 210 nm absorption cross-section may exist. In the molecular modulation studies of ref. 4, the wavelength dependence of P was normalized to a 220 nm cross-section value computed in a manner similar to that used in ref. 1. Although the agreement between ref. 4 and the present study is excellent for all but the 210 and 215 nm points, this might be fortuitous since the kinetics parameters derived from the same P and Q measurements used in the σ calibration are again inconsistent with present recommendations. For example, no pressure dependence in the computed rate constants for HO_2 self-disproportionation was observed between 25 and 760 Torr in ref. 4 whereas a 50% increase is predicted by several recent studies [5, 14, 16]. We conclude, therefore, that the present work along with refs. 2, 3 and 6 constitute the most reliable data base on which to make recommendations of the gas phase UV absorption cross-section for HO_2 .

Comparisons with the CH_3O_2 absorption cross-sections reported in the literature are not as easily resolved. First, our $\sigma_{\text{CH}_3\text{O}_2}$ value of $330 \times 10^{-20} \text{ cm}^2$ at 250 nm is considerably larger than the calibration by Sander and Watson [12] of $245 \times 10^{-20} \text{ cm}^2$ conducted in experiments nearly identical with those of the present work. As mentioned in Section 1, the discrepancy between our observed optical densities and those calculated using the cross-section value from ref. 12 provided the motivation for the present measurements. The reasons for the difference in σ values are not readily apparent. Barring scattered light problems which could result in erroneously low radical OD measurements, only an incorrect $[\text{Cl}_2]$ or path length calibration could introduce errors into the "calibration slope" calculations of the earlier study. In the present work, the path length is not needed since the abscissa values in both Fig. 3 and Fig. 4 are the actual measured Cl_2 optical densities.

The CH_3O_2 absorption spectra reported by Hochanadel *et al.* [8] and Kan *et al.* [9] were recorded in flash photolytic systems using azomethane as the CH_3 source. The absolute cross-section values from these two studies both lie systematically lower than those reported here although the differences are within the combined uncertainties of the measurements. In ref. 8 the calibration was performed by equating the decrease in azomethane concentration (measured spectroscopically) with the production of two CH_3 radicals. Thus, any additional loss processes for azomethane (*i.e.* by chemical reaction) would result in an overestimation of $[\text{CH}_3]^0$ and a low value for σ . In ref. 9 the CH_3 radical yield was assumed to be twice the N_2 yield (produced via azomethane photolysis). It seems to be unlikely that this calibration measurement could overestimate the initial radical concentration since secondary reactions are unlikely to strip azomethane down to N_2 . However, the calibration (performed as a function of azomethane concentration) utilized very high initial radical concentrations in the range $(1 - 4) \times 10^{14} \text{ molecules cm}^{-3}$. As discussed earlier, the potential for the lack of stoichiometric production of the peroxy radical is greatest at these higher concentrations. Thus we can easily reconcile a slight underestimation of the absorption cross-sections in the experiments described in refs. 8 and 9.

A far more significant disparity exists between our results and the measurements by Adachi *et al.* [11] whose study was nearly identical with that of ref. 9 with the exception that the calibration and optical density measurements were performed at only one concentration of azomethane. These researchers report the highest set of cross-section values in the literature, differing from ours by an average factor of 1.5 over the complete wavelength range and by a larger factor from the other direct calibration studies. There do not appear to be any obvious errors in the experiments by Adachi and coworkers who report a cross-section for CH_3 at 216.4 nm in this same paper which is in good agreement with other workers (including ref. 8). However, our optical density measurements for the Cl_2 calibration runs would have to be in error by 50% or the chlorine atom to peroxy radical conversion stoichiometry would have to be 0.65 to resolve the differences. Such errors would have translated uniformly to the σ_{HO_2} values as well (independent of wavelength) which, as stated, agree very well with other direct measurements. The cross-sections in ref. 9 are totally inconsistent with the ratios of the optical densities for HO_2 and CH_3O_2 observed in our experiments.

Finally, while the present work was being completed, the results of a nearly identical (relative cross-section) set of experiments were presented [17] to the scientific community. The shape of the absorption spectra and relative cross-section values from that investigation agree within 10% with all the present results except σ_{HO_2} at 210 nm for which the agreement is within 20%. This favorable comparison, together with the earlier cited agreement on the absolute HO_2 absorption cross-sections, lends added support for the values of $\sigma_{\text{CH}_3\text{O}_2}$ reported here.

The effect of the present results on the existing kinetics data base for HO_2 and CH_3O_2 radicals merits consideration at this point. With respect to HO_2 , only at $\lambda < 225$ nm is there more than a 10% difference between the present measurements and the NASA recommendation. (As mentioned earlier, this short wavelength difference nearly disappears with a more critical re-evaluation.) In kinetic spectroscopic applications, most calculations of the absolute HO_2 radical concentration have utilized the NASA cross-section values at $\lambda \geq 225$ nm or the values reported in ref. 8. Thus, even for the self-disproportionation reaction whose rate constant depends linearly on the measured concentration, little correction is required. The situation is more volatile for the methylperoxy radical kinetics data base. As we have previously discussed, published values for $\sigma_{\text{CH}_3\text{O}_2}$ vary over a factor of 2 and much of the cited agreement on the self-disproportionation rate constant is fortuitous. This occurs because measurements of k/σ from these same studies show a 65% spread which is not systematic with respect to the absolute cross-sections reported. Rate constant recommendations for this reaction have been based on the average of the k/σ values scaled to an absorption cross-section from ref. 8 or ref. 12. Use of our new measurements for σ would require corrections to k of 15% or 35% respectively. In view of the unsatisfactory agreement among the rate constant values we are remeasuring the rate constant for CH_3O_2 self-disproportionation in conjunction with our current investigation of the reaction between HO_2 and CH_3O_2 .

In conclusion, we believe that the gas phase absorption cross-sections reported in this paper have been determined under controlled and well-understood reaction conditions. Since the chemistries associated with the two radical production mechanisms are nearly identical, we believe that the precision of the measurements of the relative σ values for HO_2 and CH_3O_2 is a very reasonable reflection of the accuracy of these ratios. Given the alternating sequencing of the ratio measurements, it is difficult to imagine any unforeseen systematic error which could occur in either the HO_2 or the CH_3O_2 experiments alone and thus not be cancelled out when the ratio is computed. With respect to the absolute calibration measurements, we did not use flow rate computations for the determination of the Cl_2 concentration but rather measured the actual chlorine optical density under the calibration conditions. Checks on stoichiometric peroxy radical production were made both experimentally and via computer modeling. For comparative purposes, it would be better if future absorption cross-section measurements were conducted on radical pairs as in the present study. By doing so, problems in chemistry or in scaling of the spectra are more easily detected.

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