k_{1c}/k_1 is assumed to be 50%, which provides the best fit of the atomic oxygen concentrations. However, the determination of k_2 is not very sensitive to this assumption. It can be seen in Figure 7 that the reaction $Cl + O_3$ is approximately 99% complete after 4 ms. A correction of ozone consumption via the reaction $O_2(^{1}\Sigma_g^{+})$

+ $O_3 \rightarrow O$ + 2 O_2 ranging 1-10% has been made in the determination of k_2 . The effect of the disproportional reaction ClO + ClO on ClO concentrations is negligible.

Registry No. Atomic oxygen, 17778-80-2; chlorine oxide, 14989-30-1.

O(³P) Atom Formation by the Photolysis of Hydrogen Peroxide in Alkaline Aqueous Solutions¹

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The quantum yield of O(³P) atom scavengeable by cyclopentene, $\Phi_0(O(^{3}P))$, in the photolysis of H₂O₂ and HO₂⁻ with 248-nm light was determined over the pH range 3-12.9. $\Phi_0(O(^3P))$ from H₂O₂, determined at pH 3, is $(2.6 \pm 0.6) \times 10^{-4}$. At pH 8.7-12.9, $\Phi_0(O(^{3}P))$ from HO₂⁻ is essentially constant, within experimental error, at 0.08 ± 0.015. All of the observations on the effects of pH and the concentrations of cyclopentene, H_2O_2 , and HO_2^- are consistent with the formation of $O(^{3}P)$ and OH⁻ in a primary photochemical event, with 0.08 O(³P) per photon absorbed by HO₂⁻ escaping the cage and undergoing homogeneous reactions with cyclopentene, OH^- , HO_2^- , and H_2O_2 . The rate constants derived relative to reaction with cyclopentene are $k_{\text{OH}^-} = 0.040 \pm 0.007$, $k_{\text{HO}_2^-} = 0.5 \pm 0.2$, and $k_{\text{H}_2\text{O}_2} = 0.15 \pm 0.03$.

Introduction

A suitable mechanism to explain $O(^{3}P)$ atom formation in γ -ray irradiated alkaline solutions has not been published. In a recent paper,² we conclude that the participation of subexcitation electron activation of OH⁻ fails to account for O(³P) atom formation nor can it be attributed to excitation of the OH⁻ by a "direct" action of energy-rich secondary electrons. Looking for a reasonable mechanism, we decided to test the hypothesis that the "spur" reaction forming "molecular" H_2O_2 might yield $O(^{3}P)$ in a side reaction. According to "spur" theory, OH radicals form in clusters and the H_2O_2 observed results from their pairwise recombination. In alkaline solutions, because of the ionization of OH, O⁻ forms. Two possible reactions are

$$OH + O^- \rightarrow HO_2^- \tag{1}$$

$$OH + O^- \rightarrow OH^- + O(^3P)$$
 (2)

Reaction 1 produces molecular peroxide; reaction 2 supplies O(³P) atoms.

The photolysis of H_2O_2 at 253.7 nm is reported to have a primary quantum yield for H₂O₂ dissociation of 0.5 independent of pH.^{3,4} The dissociation has been discussed in terms of reactions 3 and 4.4.5 The possibility of a primary photolysis step in which

$$HO_{2}^{-} + h\nu \rightarrow OH + O^{-}$$
(3)

$$HO_2^- + h\nu \rightarrow OH^- + O(^3P) \tag{4}$$

 e_{aq} is produced from HO₂ was ruled out by Behar and Czapski⁶ on the basis that no initial absorbance due to O₂⁻ was observed in the flash photolysis of HO_2^- in the presence of O_2 , and their work supported the occurrence of reaction 3.

In photolysis, the primary dissociation products are located in a cage, much smaller than a radiation "spur", but by a diffusive secondary encounter as in reaction 2 could provide a mechanism equivalent to primary process 4. In solutions enriched in ¹⁸O, the yields of the scrambled and enriched products can be accounted for by the assumption of O-atom formation.⁷ Furthermore, O₃ has been a reported^{6,8,9} as a product of the flash photolysis of aerated, aqueous HO₂. It is possible that reaction 5 contributes to ozone formation, although this has not been shown.

$$O + O_2 \rightarrow O_3 \tag{5}$$

Experimental Section

Except for a description of our photolytic technique, the preparation of solutions, extraction of C_2H_4 from the solutions, and its analysis by chromatography have already been described.¹⁰⁻¹¹ Owing to the inherent instability of alkaline peroxide solutions, especially with cyclopentene present, care was taken to inject the H_2O_2 into the alkaline solutions just prior to photolysis. Optical density measurements were also carried out within a few minutes of the time of photolysis. (The optical density was used to determine the fraction of the incident light absorbed by H_2O_2 and HO_2^{-} .) A standard pulse radiolysis syringe-type arrangement was used for all irradiations and the transfer of solutions. The cell, 5 cm in length and 2 cm in diameter, was irradiated (on its 2 cm end) by 20-ns flashes of 248-nm light provided by a KrF excimer laser (Lambda Physik, EMG 102) delivering a maximum intensity of 100-200 mJ per pulse. This laser generated a rectangular beam, about 1×4 cm at the position of the sample. Multiple pulses at a rate of a few pulses/second irradiated magnetically stirred solutions. The dose rate was varied from 0.5 to 8 μ M einsteins/pulse. A 0.01% aqueous pyridine solution served as the actinometer. We used a calibration factor of 2.34×10^{-4} einsteins/OD unit measured at 365.5 nm in 1.0-cm optical cell.¹²

Results and Discussion

The possibility of formation of e_{aq}^- and HO_2 in a primary photolysis step was examined by flash photolysis of 1 mM HO_2^-

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Figure 1. $\Phi(O(^{3}P))^{-1}$ vs. [cyclopentene]⁻¹ at the pH's indicated. (a) All samples were buffered with 5 mM Na₂B₄O₇. The equilibrium concentrations of H₂O₂ and HO₂⁻ were as follows: at pH 8.72, 1.48 and 2.21 × 10⁻³ mM; at pH 9.19, 1.49 and 6.59 × 10⁻³ mM; at pH 9.72, 1.48, and 2.23 × 10⁻² mM. (b) The sample at pH 10.22 was buffered with 5 mM Na₂B₄O₇. The equilibrium concentrations of H₂O₂ and HO₂⁻ were as follows: at pH 10.22, nd HO₂⁻ were as follows: at pH 10.22, nd HO₂⁻ were as follows: at pH 10.22, 1.48 and 0.2057 mM; at pH 11.27, 0.424 and 0.208 mM; at pH 11.53, 0.328 and 0.304 mM. (c) The equilibrium concentrations of H₂O₂ and HO₂⁻ were as follows: at pH 11.27, 0.424 and 0.208 mM; at pH 11.53, 0.328 and 0.304 mM. (c) The equilibrium concentrations of H₂O₂ and HO₂⁻ were as follows: at pH 11.54, 0.78 and 0.71 mM; at pH 11.78, 0.58 and 0.89 mM; at pH 12.07, 0.31 and 1.04 mM. (d) $\Phi(O(^{3}P))^{-1}$ vs. [cyclopentene]⁻¹ at pH 11.82 over an "extended" range of cyclopentene concentration. The equilibrium concentrations of H₂O₂ and HO₂⁻ were 0.041 and 0.994 mM.

(at pH 11.5) under conditions where about 10% absorption was excepted, on the basis of the absorption observed (22%) when 1 mM I⁻ was flash photolyzed, assuming the quantum yield of e_{aq}^{-} is the same in both cases. (The quantum yield in the case of I⁻ is 0.2. for 253.7-nm light.¹³) We found no absorption at all (<0.5%) and conclude that e_{aq}^{-} is not produced. This conclusion agrees with that of Behar and Czapski.⁶

The quantum yield for O(³P) from H_2O_2 was determined to be (2.6 ± 0.6) × 10⁻⁴ at pH 3, $[H_2O_2] = 1$ mM, and was essentially the same at 1 and 2 mM cyclopentene. The results in basic solution are consistent with the reasonable assumption that light absorbed by H_2O_2 gives this quantum yield independent of pH.

No effects of light intensity on the quantum yields of $O({}^{3}P)$ from H_2O_2 or HO_2^{-} were observed when the light intensity was decreased by a factor of ten.

The quantum yields, $\Phi(O(^{3}P))$, plotted in Figure 1, were calculated on the basis of the light absorbed by HO_{2}^{-} . The yield of ethylene per reaction of $O(^{3}P)$ with cyclopentene is 0.25, so

the ethylene quantum yields were multiplied by 4 to get the $\Phi(O(^{3}P))$ values.¹¹ To determine the fraction of the light absorbed by HO_{2}^{-} , we used a value of 11.60 for the pK of the equilibrium

$$\mathrm{H}_{2}\mathrm{O}_{2} \rightleftharpoons \mathrm{H}^{+} + \mathrm{HO}_{2}^{-} \tag{6}$$

This value is near the most recent "handbook" value¹⁴ of 11.62 and is at the lower end of values quoted in the literature, ^{5,14-16} i.e., 11.6–11.85; we favor use of the value of 11.60 because of the fact that this minimizes a tendency of the derived $\Phi_0(O(^3P))$ values (Figure 2) to increase with decreasing pH in the range 10–8.7. The effect of ionic strength on this equilibrium was taken into account by the equation⁵

$$pK = pH - \log \left([HO_2^{-}] / [H_2O_2] \right) + \frac{0.5\mu^{1/2}}{1 + \mu^{1/2}}$$
(I)

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Figure 2. The limiting quantum yields for $O({}^{3}P)$ from photolysis of HO_{2}^{-1} with 248 nm light, $\Phi_{0}(O({}^{3}P))$, derived from the results shown in Figure 1, as a function of pH. A correction has been made for $O({}^{3}P)$ coming from $H_{2}O_{2}$ photolysis; the correction amounts to 11% at the lowest pH and becomes negligible at pH 9.72.

where μ is the ionic strength. Samples at pH <10.25 were buffered with 5 mM Na₂B₄O₇.

The fraction of light absorbed by HO_2^- was calculated on the basis of $[HO_2^-]/[H_2O]$ from eq I and the absorption coefficients (at 248 nm) $\epsilon_{HO_2^-} = 268$ and $\epsilon_{H_2O_2} = 30.7 \text{ M}^{-1} \text{ cm}^{-1}$. At the highest pH's, essentially all of the light is absorbed by HO_2^- , while at pH 8.72, only 1.28% is absorbed by HO_2^- .

The results are shown in Figure 1 as $1/\Phi(O(^{3}P))$ vs. 1/[cy-clopentene], and were analyzed in terms of the mechanism

$$O + CP \rightarrow all \text{ products, including } C_2H_4$$
 (7)

$$O + OH^- \rightarrow HO_2^- \tag{8}$$

$$O + H_2O_2 \rightarrow OH + HO_2 \tag{9}$$

$$O + HO_2^- \rightarrow OH + O_2^- \tag{10}$$

where CP represents cyclopentene.

This results in

$$\frac{1}{\Phi(O(^{3}P))} = \frac{1}{\Phi_{0}(O(^{3}P))} + \frac{1}{\frac{1}{[CP]}} \frac{1}{\Phi_{0}(O(^{3}P))} \left\{ \frac{k_{8}[OH^{-}]}{k_{7}} + \frac{k_{9}[H_{2}O_{2}]}{k_{7}} + \frac{k_{10}[HO_{2}^{-}]}{k_{7}} \right\} (II)$$

Several sets of values of k_8/k_7 , k_9/k_7 , and k_{10}/k_7 were tried. For a set of rate constant ratios, the best value of $\Phi_0(O(^3P))$ was determined (iteratively) for each data set to obtain a reasonable fit of eq II with the experimental points. The straight lines in Figure 1 are calculated on the basis of $k_8/k_7 = 0.040 (\pm 0.007)$, $k_9/k_7 = 0.15 (\pm 0.03)$, $k_{10}/k_7 = 0.5 (\pm 0.2)$, and the $\Phi_0(O(^3P))$ values, which are plotted vs. pH in Figure 2. The error limits on the rate constant ratios were estimated qualitatively from the effects of changes on the fit with experiment data. The rate constant ratio k_8/k_7 is the same as was derived from BrO₃⁻ photolysis.¹¹ The small value of this ratio may be due to the spin forbidden nature of reaction 8. The $\Phi_0(O(^3P))$ values in Figure 2 have been corrected for $O(^{3}P)$ from $H_{2}O_{2}$, as noted in the figure legend.

The value of $\Phi_0(O({}^{3}P))$ from HO_2^{-} photolysis is independent of pH, over the range 8.7–12.9, within experimental error. There is no evidence to indicate that $OH + O^{-}$ produced in a primary event reacts to produce $O({}^{3}P) + OH^{-}$ (although $OH + O^{-}$ must be an important channel of the photolysis in order to explain the value^{3,4} of 0.5 for the primary quantum yield for dissociation). That is, at high pH, the fast reaction $OH^{-} + OH \rightarrow O^{-} + H_2O$ might be expected to reduce the yield of $O({}^{3}P)$ if a cage reaction of $OH + O^{-}$ were producing $O({}^{3}P)$. The results obtained are entirely consistent with a homogeneous competition kinetics scheme based on reactions 7–10 and the assumption that $O + OH^{-}$ is produced in the primary photolysis event. Furthermore, over the range of cyclopentene concentration which could be used,¹⁷ there is no evidence that $\Phi_0(O({}^{3}P))$ is increased due to interference with cage recombination at high [CP].

Previous results^{2,3} on HO₂⁻ and H₂O₂ photolysis at 253.7 nm indicate a primary quantum yield of 0.5 for dissociation of HO₂⁻ or H₂O₂. Isotopic studies⁷ in the case of H₂O₂ indicate a minimum quantum yield of 0.15 for H₂O₂ \rightarrow O + H₂O. On the basis of our measured quantum yield of O(³P) from H₂O₂, most of the O must be formed in the ¹D excited state, which is energetically allowed, and react with H₂O to give 2 OH. Perhaps the small yield of O(³P) which we measure from H₂O₂ represents a small fraction of the O(¹D) which are deactivated to O(³P). In the case of HO₂⁻, our results require more than two orders of magnitude enhancement of the O(³P) yield compared with the case of H₂O₂.

In the radiolysis of water, an increase in $G(O({}^{3}P))$ in the pH range 11.5-12 followed by an even more rapid decrease in the pH range 12.5-13 has been observed.¹¹ Because the increase takes place in the same pH range that $OH^{-} + OH \rightarrow O^{-} + H_{2}O$ begins to convert OH to its basic form, O⁻, a reasonable explanation of the experimental observations is that O⁻ and OH can react (reaction 2) in the spurs to yield $O({}^{3}P)$. A subsequent decrease of $G(O({}^{3}P))$ at higher pH is expected when all of the OH is converted to O⁻; furthermore, at pH ~13, most of the $O({}^{3}P)$ would react with OH⁻ rather than with cyclopentene at millimolar concentration.

In the photolysis of HO_2^- , if $O({}^3P)$ and OH^- were the only primary products, the only possible effect of pH would be a decrease in $\Phi_0(O({}^3P))$ at high pH due to reaction of OH^- with O. On the other hand, for O^- and OH formed as primary photolysis products, there is no mechanism whereby an increase in pH can cause an increase in reaction 2. However, by analogy with the results in radiolysis, a decrease in $\Phi_0(O({}^3P))$ at pH 12–13 might be expected if $O({}^3P)$ results, in the photolysis, from reaction 2. The fact that such a decrease is not observed argues against reaction 2 as a source of $O({}^3P)$ in the photolysis. We must conclude then that the reaction proposed to explain the radiolysis results is unimportant in the photolysis, perhaps because of substantial differences in "spur" kinetics and cage kinetics.

Registry No. H_2O_2 , 7722-84-1; HO_2^- , 14691-59-9; $O(^3P)$, 17778-80-2; OH^- , 14280-30-9; CP, 142-29-0; C_2H_4 , 74-85-1.

⁽¹⁷⁾ We have searched for an O-atom trapping reagent which might be employed over a wider concentration range than is possible with CP. The most promising is the sodium salt of 1-cyclopentene-1-carboxylic acid which, like CP, captures O atoms and forms ethylene but with smaller yield (0.15 vs. 0.25 ethylene formed per O atom consumed).