(ref 27), and assuming that trapping characteristics will not change (Generating assuming that trapping orthateristics will not orthogonal significantly as the pressure is raised, the condensation reaction yielding $H(OH_2)_2^+$, reaction 3, in gaseous water with a measured termolecular rate of 4.2×10^{-27} cm⁸ molecules⁻² s⁻¹ at 305 K (ref 3) should be observable at total pressures in excess of 5.6 $\times 10^{-5}$ torr in the ICR.

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O(³P) Atom Formation in γ - and 184.9-nm-Irradiated Aqueous Perchlorate Solutions[†]

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 $O(^{3}P)$ atom formation was studied in γ -irradiated and 184.9-nm-photolyzed aqueous perchlorate solutions by measuring the ethylene resulting from the $O({}^{3}P)$ reaction with cyclopentene (CP). The linearity of $G(O({}^{3}P))$ with perchlorate concentration in the range 0.1-4 M gives evidence of a "direct-action effect", and its relative independence of CP concentration shows that $O(^{3}P)$ is quite unreactive with the perchlorate ion. The rate-constant ratio, $k(O(^{3}P)+ClO_{4})/k(O(^{3}P)+CP)$, was studied by competition experiments carried out by photolysis of ClO⁻ at 366 nm; it is $<5.4 \times 10^{-5}$. Quantum yield measurements, carried out on 1.0 and 2 M solutions, reveal that the photolysis produces $O(^{3}P)$ with a quantum yield of unity. $\phi(O_{2}) = 0.53$. The γ -ray-induced formation of $O(^{3}P)$ is attributed to direct excitation of ClO_{4}^{-} by energy-rich secondary electrons, e_{s}^{-} , in competition with energy-loss processes in water and sodium ions. Excitations of perchlorate ion to a state forming O(³P) atoms proceeds with a direct-effect yield, $G_{de}(O(^{3}P))$, of 0.28, only a small fraction of $G_{de}(-ClO_{4}^{-})$, which is 5.1. Some experiments with added Na₂SO₄ are also reported.

Introduction

The perchlorate ion decomposes in aqueous solution by a "direct effect" mechanism.¹⁻⁸ In neutral solutions, the ion is unreactive with e_{aq} , H, and OH, the free radical species formed by the radiolytic decomposition of water. It has been shown that the breakdown yield in liquid and frozen solutions of perchloric acid is proportional to the electron fraction of the ClO_4^- . $G(-ClO_4^-) = 5.1 \pm 0.3$ $ClO_4^-/100$ eV directly absorbed by the $ClO_4^{-,7}$ Chlorate and chloride ions are products formed in yields directly proportional to perchlorate concentration. Thus, they may be considered primary reaction products. Other products reported are ClO_2 , ClO^- , ClO_2^- , H_2O_2 , H_2 , and O_2 . But these species are chemically reactive with one or more of the water radiolysis radicals, H, OH, and e_{aq}, so their yields are complex functions of the dose and the dose rate.

The "direct-action" effect is considered to involve both ionization and excitation of \mbox{ClO}_4^- in the primary processes

$$ClO_4^- \xrightarrow{\gamma - lays} ClO_4 + e^-, (ClO_4^-)*$$

A/- FO 1/0

Rapid decomposition of ClO_4 and (ClO_4^-) * then produces ClO_3^- , ClO_2 , $O(^3P)$ and O_2 .

$$(\text{ClO}_4^-)^* \rightarrow \text{ClO}_3^- + \text{O}(^3\text{P})$$
$$\text{ClO}_4 \rightarrow \text{ClO}_2 + \text{O}_2$$

[†]Work performed under the auspices of the Office of Basic Energy Sciences of the U.S. Department of Energy.

O(³P) is a known product of the radiolysis of water and of aqueous ClO_4^- solutions.⁹ In the present work, we use cyclopentene (CP) as a probe for determining the yields of $O(^{3}P)$ as a function of ClO_{4}^{-} concentration in neutral solutions. Our results indicate that O(³P) results from a direct-action mechanism, quite possibly from $(ClO_4)^*$. If excitation is the only mechanism for $O(^{3}P)$ formation, then our studies provide a means of measuring the relative importance of excitation processes in the γ -ray-induced decomposition of ClO₄⁻. Preliminary results are also reported on the photochemical decomposition of ClO_4^- into $O(^{3}P)$ atoms at 184.9 nm, and the effect of sulfate ion on $O(^{3}P)$ formation in photolyzed and γ -irradiated solutions.

Experimental Section

Our γ -irradiation technique using 50-mL syringes as the irradiation cell have been described.9 We used reagent grade $NaClO_4$ (G. F. Smith) after recrystallization as the monohydrate. Details of CP purification, solubilization, and spectrophotometric analysis at 185 nm have also been reported.¹⁰ The measurement of the rate constant ratio, $k(O(^{3}P)+ClO_{4})/k(O(^{3}P)+CP)$, was carried out by photolysis at 366 nm with ClO^{-} as the source of $O(^{3}P)$ atoms. The ClO₄-CP solutions were irradiated with a Rayonet photochemical reactor lamp (RPR-3500 A). Immediately after photolysis in 20-mL syringes, the samples were treated with 1.0 mL of 5% phenol and diluted to 50 mL. The dissolved ethylene from 10-mL samples of this solution was extracted on a Van Slyke apparatus and then

TABLE I: Effect of Perchlorate Concentration on Ethylene Formation in γ -Irradiated Cyclopentene Solutions

| | | | - | | | |
|---|-------------------------------------|-------------|-------|-------------------|----------------------------|----------------------------|
| [ClO ₄ ⁻], M | [C ₅ H ₈], M | $G(C_2H_4)$ | K | $G(C_2H_4)_{cor}$ | $G(C_2H_4)_{\text{ClO}_4}$ | $(G(C_2H_4)_{ClO_4})^{-1}$ |
| 0.00 | 0.00073 | 0.00153 | 1.000 | 0.00153 | 0.000 | |
| 0.1 | 0.00073 | 0.00229 | 0,993 | 0.00231 | 0.00078 | 1282 |
| 0.125 | 0.00073 | 0.00247 | 0.991 | 0.00249 | 0.00096 | 1042 |
| 0.167 | 0.00073 | 0.00279 | 0.988 | 0.00282 | 0.00129 | 775 |
| 0.25 | 0.00073 | 0.00355 | 0.983 | 0.00361 | 0.00208 | 481 |
| 0.50 | 0.00073 | 0.00482 | 0.966 | 0.00499 | 0.00346 | 289 |
| 1.0 | 0.00073 | 0.00752 | 0.934 | 0.00805 | 0.00652 | 153 |
| 0.00 | 0.0045 | 0.00196 | 1.000 | 0.00196 | 0.0000 | |
| 0.1 | 0.0045 | 0.00279 | 0.999 | 0.00279 | 0.00083 | 1205 |
| 0.125 | 0.0045 | 0.00312 | 0.999 | 0.00312 | 0.00116 | 860 |
| 0.167 | 0.0045 | 0.00340 | 0.998 | 0.00341 | 0.00145 | 691 |
| 0.25 | 0.0045 | 0.00410 | 0.997 | 0.00411 | 0.00215 | 465 |
| 0.50 | 0.0045 | 0.00556 | 0.994 | 0.00559 | 0.00363 | 275 |
| 1.00 | 0.0045 | 0.00899 | 0.988 | 0.00910 | 0.00714 | 140 |
| 0.00 | 0.00085 | 0.00139 | 1.000 | 0.00139 | 0.0000 | |
| 1.00 | 0.00085 | 0.00749 | 0.940 | 0.00797 | 0.00658 | 152 |
| 2.00 | 0.00085 | 0.0122 | 0.873 | 0.01397 | 0.0126 | 79 |
| 3.00 | 0.00085 | 0.0170 | 0.834 | 0.0204 | 0.0190 | 52.6 |
| 4.00 | 0.00085 | 0.0199 | 0.797 | 0.0250 | 0.0236 | 42.4 |
| | | | | | | |

TABLE II: Photolysis of Cyclopentene-Sodium Perchlorate Solutions at 184.9 nm

| no. | $[C_{s}H_{s}], mM$ | [NaClO ₄], M | $[C_{2}H_{4}],$ $\mu M/min$ | $[O_2],$ $\mu M/min$ | $\phi(C_2H_4)$ | $\phi(O({}^{3}P))$ | $\phi(O_2)$ | |
|-----|--------------------|--------------------------|--------------------------------|-------------------------|----------------|--------------------|-------------|--|
| 1 | 0.100 | 1.0 | 2.44 | 0.24 | 0.24 | 0.96 | 0.023 | |
| 2 | 0.100 | 1.0 | 2.50 | | 0.24 | 0.96 | | |
| 3 | 0.100 | 2.0 | 2.93 | 1.41 | 0.24 | 0.95 | 0.11 | |
| 4 | 0.100 | $\overline{2.0}$ | 3.25 | | 0.26 | 1.04 | | |
| 5 | | 0.50 | | 5.20 | | | 0.56 | |
| 6 | | 1.0 | | 5,51 | | | 0.47 | |
| 7 | | 1.0 | | 6.33 | | | 0.54 | |
| 8 | | 2.0 | | 7.40 | | | 0.55 | |
| 9 | | 2.0 | | 7.33 | | | 0.55 | |

measured on a gas chromatograph.⁹ Results for a 0.80 mM CP solution were

| [ClO ₄ -], M | 10^{11} [C ₂ H ₄], mol/min |
|--------------------------|---|
| 0.00 | 14.42 |
| 0.20 | 13.56 |
| 0.60 | 13.50 |
| 1.50 | 12.70 |

We calculate a maximum ratio $k(O({}^{3}P)+ClO_{4}^{-})/k(O({}^{3}P)+CP)$ of 5.4 × 10⁻⁵ from these data. In terms of the ratio $k(O({}^{3}P)+ClO_{4}^{-})/k(O({}^{3}P)+O_{2})$ this value becomes 2.1 × 10⁻⁵ since $O({}^{3}P)$ atoms react 2.6 times faster with CP than with O_{2} . Our value compares with a published value of 1.6 × 10⁻².¹¹ We are unable to explain this large discrepancy.

Photochemical experiments were carried out at 184.9 nm by using a low-pressure mercury vapor lamp containing 5 mm of argon.¹² The output of this lamp provided an average input into a 13.6 mL, 2 cm diameter, 2 cm deep silica cell of 16.04×10^{-6} einstein/min. Complete absorption of light in the stirred solutions in the cell was always achieved. The 0.005 M methanol actinometer, calibrated at 184.9 nm by Barrett and Baxendale,¹² was employed to determine the lamp output. A yield of 0.60 molecule of H₂ per quantum of light was used in our calculations. γ -Irradiated LiF served as the optical filter to remove the 253.7-nm line.¹³ The extinction coefficients employed in the measurement of quantum yields were

| molecule | extinction | ref |
|--------------------|--|--------------|
| H,O | 1.45 cm ⁻¹ | present work |
| C.H. | 7580 M ⁻¹ cm ⁻¹ | 10 |
| ClO ⁷ - | $3.985 \text{ M}^{-1} \text{ cm}^{-1}$ | present work |
| SO4 ²⁻ | 193 M ⁻¹ cm ⁻¹ | 13 |
| CH ₃ OH | $12.7 \text{ M}^{-1} \text{ cm}^{-1}$ | 12 |

The γ -ray energy absorbed was determined with the Fricke dosimeter ($G(Fe^{3+}) = 15.6$), and corrections to dose were made according to the relative densities of the solu-

tions. The energy absorbed by a given molecule or ion was calculated from its electron fraction in the solution.

Results

In order to evaluate the contributions of excitation phenomena to the "direct effect" in the radiolysis of aqueous perchlorate solutions, we used photolytic data to supplement the γ -ray studies. The γ -ray results appear in Table I. The yields show an initial rise in $G(C_2H_4)$ up to 0.1 M ClO₄⁻ and then a nearly linear increase with concentration up to 4 M ClO₄⁻, the limit of our present studies (see Figure 1).

From Figure 1, it is clear that C_2H_4 arises from at least two sources, namely, O(³P) atoms from water and O(³P) atoms from the radiolysis of ClO₄⁻. And since more C_2H_4 is produced from 4.52×10^{-3} M CP than from 0.77×10^{-3} M CP, it is likely that some C_2H_4 forms by a direct action on CP. $(G(O(^3P)) = 4G(C_2H_4).)^{10}$

 $O(^{3}P)$ atoms also result from the 184.9-nm photolysis of ClO_{4}^{-} . This reaction appears to be particularly efficient at this wavelength since $\phi(C_{2}H_{4}) = 0.25$ giving $\phi(O(^{3}P)) = 1.00$. Oxygen is the resultant permanent gaseous product and in the absence of CP forms with a quantum yield of 0.53 (see Table II). Thus, the recombination reaction of $O(^{3}P)$ atoms is dominant, and the excess O_{2} above $\phi(O_{2}) = 0.50$ may be explained by reaction of the $O(^{3}P)$ with ClO_{4}^{-} . In view of the near unity value of $\phi(O(^{3}P))$, we consider the 10% excess outside of experimental error. In the presence of CP, O_{2} yields are drastically lowered as expected in view of its high reactivity with the radicals of CP.

Discussion

Effect of ClO_4^- Concentration on $O({}^{3}P)$ Formation by γ -Rays. The $O({}^{3}P)$ atoms are far less reactive with ClO_4^- than with BrO_3^- . The nearly linear form of the $G(C_2H_4)$ vs. $[ClO_4^-]$ curve contrasts sharply with similar curves with



Figure 1. Effect of perchlorate ion concentration on $G(C_2H_4)$ in γ -irradiated cyclopentene solutions: (\bullet) 0.00073 M C_5H_8 ; (Δ) 0.0045 M C_5H_8 ; (O) 0.00085 M C_5H_8 .

BrO₃⁻¹⁴ The relative rate-constant ratio, $k(O({}^{3}P)+ClO_{4}^{-})/k(O({}^{3}P)+CP)$ is 5.4 × 10⁻⁵ and compares with k- $(O({}^{3}P)+BrO_{3}^{-})/k(O({}^{3}P)+CP)$ of 0.0058, which is 100-fold hig3AJO Thus, the (ClO_{4}^{-}) system is an excellent one for studying O({}^{3}P) formation at high salt concentrations.

We agree with the conclusions of the investigators cited above that the decomposition of ClO_4^- is a direct effect. The primary products result solely from direct ionization or excitation of ClO_4^- by secondary electrons. We analyze our results in terms of the following mechanism:

$$(H_2O)(ClO_4^-)(Na^+) \xrightarrow[\gamma-rays]{k_0} e_s^- + products$$

$$e_s^- + H_2O$$
, Na⁺ $\xrightarrow{k_1}$ $(e_s^-)'$ + products (1)

$$\mathbf{e_s}^- + \operatorname{ClO_4}^- \xrightarrow{\mathbf{k_2}} \operatorname{O}({}^{3}\mathrm{P}) + \operatorname{ClO_3}^- + (\mathbf{e_s}^-)'$$
(2)

$$C_5H_8 + O(^{3}P) \xrightarrow{k_3} C_2H_4 + C_3H_4O$$
(3)

$$\operatorname{ClO}_4^- + \operatorname{O}({}^3\mathrm{P}) \xrightarrow{R_4} \operatorname{ClO}_3^- + \operatorname{O}_2$$
 (4)

In this mechanism we assume that γ -rays produce secondary electrons in the solution in amounts proportional to the electron fraction of the components. Steady-state analysis of the above mechanism yields eq I, expressing $G(C_2H_4) =$

$$\frac{1}{1 + k_4(\text{ClO}_4^-)/k_3(\text{CP})} \frac{G(\text{e}_{\text{s}}^-)}{1 + k_1(\text{H}_2\text{O})/k_2(\text{ClO}_4^-)}$$
(I)

 $G(C_2H_4)$ as a function of ClO_4^- concentration, where $G(e_s^-)$ is the yield of secondary electrons involved in reactions 2 and 3; $[1 + k_4(ClO_4^-)/k_3(CP)]^{-1}$ corrects $G(C_2H_4)$ for loss of $O(^3P)$ to ClO_4^- . Our value for k_4/k_3 is 5.4×10^{-5} (see Experimental Section). The yields adjusted for loss to ClO_4^- appear in column 5 of Table I. A small yield of C_2H_4 occurs in ClO_4^- -free solutions. This yield originates in part from the $O(^3P)$ generated in pure water and possibly also from direct excitation of CP by e_s^- . At the present time we are unable to separate these two effects. Therefore, in order to compute the yield due to the ClO_4^- alone, we substract the yield at zero ClO_4^- concentration from the corrected C_2H_4 yields in the ClO_4^- solutions and designate it $G(C_2H_4)_{ClO_4^-}$. The simplified equation thus becomes

$$\frac{G(e_{s}^{-})}{G(C_{2}H_{4})_{ClO_{4}^{-}}} = 1 + \frac{k_{1}(H_{2}O)}{k_{2}(ClO_{4}^{-})}$$
(II)



Figure 2. Relative moderating effect of water and perchlorate ion on the transfer of energy from e_s^- in 0.1–1.0 M NaClO₄ solutions (test of eq II): (•) 0.0045 mol dm⁻³ C₅H₈; (O) 0.00073 mol dm⁻³ C₅H₈.



Figure 3. Relative moderating effect of water and perchlorate ion on the transfer of energy from e_s^- in 1.0–4.0 M NaClO₄ solutions (test of eq II).

We evaluate the rate-constant ratio by plotting (G- $(C_2H_4)_{CO_4})^{-1}$ vs. $[ClO_4^{-}]^{-1}$. The results are shown in Figures 2 and 3. Figure 2 shows the plot for the concentration range 0.1-1.0 M ClO₄⁻; Figure 3 shows the plot for 1.0-4.0 M ClO_4 . There is a slight divergence between the data for the two CP concentrations. From these data we calculate a rate-constant ratio k_1/k_2 of 2.17 \pm 0.04 for the lower range of ClO_4^- concentrations and 2.7 for the 1–4 M range. But since $G(O(^{3}P)) = 4G(C_{2}H_{4})$,⁹ these ratios must be lowered by a factor of 4, giving k_1/k_2 values of 0.54 and 0.68, respectively, for the two concentration ranges. Thus, the ClO_4^- is only about 2 times more effective than water in accepting excitation energy from e_s . This contrasts with the BrO_3 where the corresponding k_1/k_2 ratio is 0.13, indicating an eightfold greater effectiveness of BrO3-. Thus, the BrO_3^- is fourfold more effective than ClO_4^- in accepting excitation energy.

TABLE III: Effect of Sulfate Concentration on $O(^{3}P)$ Formation in Aqueous C₅H₈-Na₂SO₄-NaClO₄ Solutions Irradiated by γ -Rays and 184.9-nm Light

| | | | 184.9-nm light ^a | | |
|---|---|--|---------------------------------|---|--|
| [Na ₂ - SO ₄], M | [Na- ClO ₄], M | γ -rays ^a $G(C_2H_4)^b$ | C₂H₄ rel yield | rel absorbn by ClO ₄ - | |
| $\begin{array}{c} 0.00 \\ 1.00 \\ 1.80 \\ 0.00 \\ 0.10 \\ 0.20 \\ 0.50 \end{array}$ | $\begin{array}{c} 0.00\\ 0.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ \end{array}$ | $\begin{array}{c} 0.00153\\ 0.00153\\ 0.00150\\ 0.0075\\ 0.0075\\ 0.0075\\ 0.0074\\ 0.0055\end{array}$ | 1.00 0.173 0.083 0.032 | 1.00 0.24 0.14 0.06 | |

^a All solutions contain 0.1 mM C_5H_8 . ^b $G(O(^{3}P)) =$ $4G(C, H_4).$

Photolysis of ClO_4^- Solutions at 184.9 nm. Excitation of ClO_4^- by 184.9-nm light produces $O(^{3}P)$ with a quantum yield of unity (see Table II). Because of the low molar extinction coefficient of ClO₄⁻ at 184.9 nm, 1 and 2 M solutions were used to minimize free-radical interferences from the dissociation products of water. $\phi(O(^{3}P))$ equal to 1.0 is deduced from $\phi(C_2H_4)$ since only 25% of the O(³P) atoms produce C_2H_4 . The quantum yield for O_2 formation averages slightly greater than one half (0.53). This result shows that most of the $O(^{3}P)$ atoms recombine and only a small fraction react with ClO₄⁻ in 1.0 and 2.0 M solutions. Thus we have quite simply

$$\text{ClO}_4^- + h\nu \rightarrow [\text{ClO}_4^-]^*$$

$$(\text{ClO}_4^-)^* \to \text{ClO}_3^- + O(^3\text{P}) \tag{5}$$

$$O(^{3}P) + O(^{3}P) \rightarrow O_{2}$$
(6)

Note in Table II that the $\phi(O_2)$ of 0.53 was measured in CP-free solutions. In the presence of CP, radical scavenging of O2 and CP reaction with O(3P) drastically lowers $\phi(O_2)$.

Effect of SO_4^{2-} on the Radiolysis and Photolysis of ClO_4^{-} Solutions. In liquid water a significant fraction of es energy in the range below 20 eV results in excitation of water.¹⁵ Furthermore, since the energy-loss process is that "optically allowed", excited states "form in proportion to the ratio of absorption coefficients at a particular frequency to that frequency".¹⁶ Therefore, optically absorbing ions are expected to compete with water for es energy. According to this concept, one expects direct excitation processes in γ -irradiation to be moderated by the addition of suitable inert ions or molecules with high molar extinction coefficients in the region of water and ClO₄⁻ absorption. We have studied the effect of Na₂SO₄ on the photochemical and radiation yields of C₂H₄ in ClO₄--CP solutions in order to test this hypothesis.

The sulfate ion is quite suitable for these studies. Neither photolysis nor radiolysis of SO42- produces O(3P) atoms. Our results are given in Table III. Note that in the absence of ClO_4 , γ -ray radiolysis of 1.0 and 1.8 M Na_2SO_4 solutions has no effect on $O(^{3}P)$ production from the water. In the presence of ClO_4^- , solutions of 0.1 and $0.2 \text{ M Na}_2\text{SO}_4$ have no effect, but there appears to be a substantial loss of C_2H_4 in 0.5 M Na_2SO_4 .

As expected, because of its high extinction coefficient at 184.9 nm relative to that of ClO_4^- , SO_4^{2-} has a pronounced effect on photochemical O(³P) formation in 1 M ClO_4^- solutions. $\epsilon_{ClO_4^-}^{184.9} = 3.98; \epsilon_{SO_4^-}^{184.9} = 193$. (See Table III.)

The relative yield of C_2H_4 diminishes roughly as the relative absorption of the ClO_4 in the solutions. At 0.1 M Na_2SO_4 , the yield is reduced to 0.17 of that in the SO_4^{2-} -free solution. This result contrasts quite sharply with the lack of an SO_4^{2-} effect at this concentration in the γ -irradiated solutions. However, since there was about a 25% reduction of $G(C_2H_4)$ in the 0.5 M SO₄²⁻-1.0 M ClO₄⁻ solution, there is some indication that "inner" filtration moderates the direct excitation effect in the ClO_4^- . More work at higher SO_4^{2-} concentrations needs to be carried out

Mechanism of the "Direct Effect". Early investigators described the "direct effect" for the decomposition of ClO₄in terms of ionization and excitation processes.^{2,3,6} The suggested reactions are given in eq 7 and 8. The complex

$$ClO_4^- + e_s^- \rightarrow ClO_4 + 2e_s^- \tag{7}$$

$$ClO_4^- + e_s^- \rightarrow (ClO_4^-)^* + e_s^- \tag{8}$$

reactions occurring in the decomposition of ClO₄ radicals are unknown, but it is probably the major source of ClO_{3} , Cl⁻, and O_2 . Our results reveal that reaction 5 is but a small fraction of ionization reaction 7. Our estimation of G_{de} - $(O(^{3}P))$ is only 0.28 atoms/100 eV energy absorbed by the ClO_4^- . And since $O(^{3}P)$ atoms disappear by recombination, their contribution to $G(O_2)$ is about 0.15, only 3.2% of $G_{de}(O_2)$ ^{2,3} Therefore, ClO_4 does not dissociate into ClO_3 + $O(^{3}P)$ but probably into O_{2} directly (ClO₂ is an observed product at concentrations above 6 M).⁷

The perchlorate ion may be excited to higher states dissociating to products other than O(³P), but we conclude that the state produced by light of 6.7 eV energy is of relatively minor importance in contributing to the γ -rayinduced decomposition of ClO₄-. Our photochemical study demonstrates that reaction 5 proceeds with a quantum yield of 1.0. Since $G_{de}(O(^{3}P))$ involves only 0.28/5.1 =5.5% of the ClO_4^- decomposed, the $(ClO_4^-)^*$ formed via reaction 8 is not one of the principal decomposition reactions of ClO₄⁻.

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