If the positive and negative ion react, the calculation for that ion pair is terminated, and calculations on a new ion pair are initiated. If a charged species reacts with one of the solute molecules, the program treats the resultant ion pair identically, except that the diffusion rate and mobility for the new product species are used and the time increment is changed appropriately.

The process of moving the charged species and checking for reaction continues until (1) the charged pair is neutralized and the event is terminated; or (2) a maximum time is reached which corresponds to the experimental time window (t_{max} = 5 ns for these experiments). If one of the reactive species undergoes a displacement moving it outside the large box, the charged pair is moved so that the negative ion is at the center of the large box and the same separation distance is maintained. This rarely occurs under our conditions.

For 0.05 M solution of scavenger, 1000 ion pairs were sufficient to obtain good statistics, while, for a concentration of 0.001 M scavenger, 8000 ion pairs are studied. Because we are observing the neutralization of a scavenger ion, at lower concentrations of scavenger more ion pairs must be studied to improve the statistics. A run for 8000 steps takes approximately 25 h on a DEC Microvax II (approximately equivalent to a VAX 11-780).

Table VI contains the parameters that were used for the calculations. Note that the results are only very weakly dependent on the reaction radius as long as the reaction radius is considerably smaller than r_c.

The Primary Process ClO_3^- (+$h\nu$) → ClO^- + O_2 in the Photolysis of Aqueous ClO_3^- Solutions

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The quantum yield, Φ_1, in the primary process $ClO_3^-(+h\nu) \rightarrow ClO^- + O_2$ (1) and the sum of the quantum yields $\Phi_2 + \Phi_3$ in the primary processes ClO_3^- $(+h\nu) \rightarrow ClO_2 + O^-$ (2) and $ClO_3^- \rightarrow ClO_2^- + O(^3P)$ (3) were measured in the steady-state photolysis of aqueous ClO_3^- solutions at 214 and 229 nm. The ratio of the yields of ClO^- and ClO_3^- in the reactions $ClO_2 \rightarrow ClO^- + O_2$ and $ClO_2 + O^- \rightarrow ClO_3^-$ (4) was determined by γ-radiolysis of aqueous solutions of ClO_2 at varying pH. The finding that the ratio between the yields of ClO^- and ClO_3^- in reactions 4 equals the ratio between Φ_1 and the quantum yield, $\Phi_0 = 1 - \Phi_1 - \Phi_2 - \Phi_3$, for ClO_3^- returning to the ground state is taken as evidence that process 1 results from a cage-back reaction. This result combined with recent studies of the radiolysis of $KClO_3$ crystals suggest that the primary processes in the photolysis of aqueous ClO_3^- originate in a common process by which O^- is expelled from ClO_3^- upon photoexcitation. The expelled O^- may escape the solvent cage containing ClO_2 (process 2), or react in a cage-back reaction (process 0 and 1). During the expulsion of O^- the photoproducts may convert to ClO_2^- and $O(^3P)$ (process 3).

Introduction

Formation of O_2 by a primary photochemical process has been observed in the photolysis of aqueous solutions of ClO_3^-,[1,2] MnO_4^-,[3-5] BrO_3^-,[1,6] and BrO_4^-.[7] It has been discussed whether the formation of O_2 takes place before or after equilibrium between the excited oxoanion and the solvent is attained. Early experiments have shown that O_2 formed by photolysis of aqueous MnO_4^- originates solely[3] from MnO_4^- and that O_2 is formed also by photolysis of MnO_4^- in an 2-propanol glass at 90 K.[4] These observations were taken as evidence for formation of O_2 in one step either from a vibrationally excited permanganate ion in the electronic ground state[3] or directly from an electronically excited state.[4] Recent observations suggest, however, that the excited state of permanganate from which O_2 is formed is in thermal equilibrium with the solvent. Thus it was found that the formation of oxygen can be suppressed by addition of certain reducing agents (such as acetone) that do not react with O_2 or MnO_4^- in the dark.[6] The observations even suggest that O_2 is formed via a long-lived intermediate thought to be a peroxide of Mn(V).[6]

Studies of the photochemistry of aqueous BrO_3^- similarly suggest that O_2 is formed from a state in thermal equilibrium with the solvent. Thus the observation that addition of allyl alcohol suppresses the formation of O_2[8] led to the suggestion that O_2 is formed by a cage-back reaction between $O(^3P)$ and BrO_2^-.[6] However, a more recent investigation has shown that $O(^3P)$ reacts relatively slowly with oxoanions! Therefore, it appears more likely that the cage-back reaction leading to formation of O_2 involves BrO_2 and O^-, the main products in the photolysis of aqueous BrO_3^-, rather than BrO_2^- and $O(^3P)$.

In the present work we have studied the primary process

$$ClO_3^- \xrightarrow{h\nu} ClO^- + O_2 \qquad (1)$$

with the object of testing the hypothesis that process 1 results from a cage-back reaction between ClO_2 and O^-.

According to the hypothesis, those of the excited ClO_3^- ions that have relaxed to a state with an energy smaller than required for a separation into ClO_2 and O^- (process 2) or into ClO_2^- and $O(^3P)$ (process 3) should pass through the transition state for the

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$$ClO_3^- \xrightarrow{h\nu} ClO_2 + O^- \qquad (2)$$

$$ClO_3^- \xrightarrow{h\nu} ClO_2^- + O(^3P) \qquad (3)$$

thermal reaction between ClO_2 and O^-. This means that the ratio between the yields of ClO^- and ClO_3^- in the reaction between ClO_2 and O^- should equal the ratio between the quantum yield of process 1 and the quantum yield for ClO_3^- returning to its ground state after the excitation.

The reactions between O^- and ClO_2 were studied by γ-radiolysis of aqueous solutions of ClO_2 at varying pH. Quantum yields for formation of ClO_2 and ClO^- were measured by steady-state photolysis at 214 and 229 nm of air-saturated aqueous solutions of ClO_3^- containing ClO_2^- in small concentrations.

By comparing the results of the present study with those of recent studies of the radiolysis of $KClO_3$ crystals, we are led to propose a mechanism for the photolysis of aqueous chlorate.

Experimental Section

All aqueous solutions were prepared with triply distilled water. Uranyl oxalate and aqueous stock solutions of chlorine dioxide containing 0.1–0.3 mol dm^{-3} chlorine dioxide were prepared as described[9,10] and stored in the dark, the chlorine dioxide solutions at 0 °C. All chemicals were Merck p.a. or Suprapur except sodium chlorite which was Matheson, Coleman and Bell analytical grade. Gases were ultra-high-purity grade.

In all experiments the temperature was ambient, 21 ± 1 °C.

The light sources for irradiation at 214 and 229 nm were respectively a Phillips 93106 E Zn lamp and a Phillips 93107 E Cd lamp fitted with Acton Research filter 210N and 230 N. The photochemical cell was a 2 cm long cylindrical optical cell made from Suprasil and fitted with a magnetic stirrer. The light was collimated by two quartz lenses. The illumination was uniform over the entire volume (5.95 cm^3) of the empty cell. The solutions were stirred during irradiation. The light intensities at 214 and 229 nm, as measured with a 5×10^{-4} mol dm^{-3} uranyl oxalate actinometer,[9,11] were $(3.40 \pm 0.20) \times 10^{-7}$ and $(1.67 \pm 0.08) \times 10^{-7}$ einstein dm^{-3} s^{-1}, respectively. The quantum yields for the decomposition of uranyl oxalate were taken to be 0.46 ± 0.02 and 0.54 ± 0.02, respectively.[9,11] The light absorption in the photochemical experiments was 87.5% at 229 nm and >99% at 214 nm.

The photochemical experiments included the following operations: The initial optical density of the solution contained in the reaction cell was measured at 358.5 nm, then the solution was irradiated for varying lengths of time (1.25–10 min) and the optical density was again measured at 358.5 nm. The concentration of ClO_2 was determined by using an extinction coefficient of 1250 dm^3 mol^{-1} cm^{-1} at 358.5 nm.[10] The solution was then transferred to a 25-mL measuring flask, sodium bicarbonate and potassium iodide were added in the prescribed amount,[12] and the quantity $[ClO^-] + 0.5[ClO_2]$ was determined from measurements of the optical density of I_3^- at 351 nm against a blank prepared from a unirradiated solution.

The γ-radiolysis of aqueous ClO_2 was carried out with a ^{60}Co γ source. Doses were measured with the Fricke dosimeter (G(Fe(III)) = 15.6, ϵ(Fe(III)) = 2187).[13] The O_2 produced by irradiation of He-saturated ClO_2 solutions was measured by gas chromatography.[14] The reaction vessel was a 50-mL syringe. The dose rate in these experiments was 1.05 Gy s^{-1}.

In other experiments in which yields of ClO^-, ClO_2^-, and ClO_3^- were determined, the reaction vessel was a round-bottom Pyrex flask with fused-in inlet and outlet for adding and withdrawing solutions and for bubbling through with gases. In these experiments the dose rate was 0.65 Gy s^{-1}.

TABLE I: *G* Values for O_2, ClO^-, ClO_2^-, and ClO_3^- by γ-Radiolysis of Aqueous ClO_2 Solutions

pH	$[ClO_2]/10^{-3}$ mol dm^{-3}	gas	$G(O_2)$	$G(ClO^-)^b$	$G(ClO_2^-)^b$	$G(ClO_3^-)^b$
7	1.3	Ar, He	1.18	1.15	4.76	2.38
7	0.6	N_2O		2.03	2.48	3.87
7	0.7	N_2O		2.06	2.37	3.83
7	0.8	N_2O		2.07	2.52	3.82
7	1.1	N_2O		2.12	2.35	3.94
11.0^a	1.1	N_2O		2.00		3.88
11.3^a	1.1	N_2O		1.89		3.92
11.7^a	1.1	N_2O		1.78		3.96
12.0^a	1.3	He	1.80			
12.0^a	0.3	N_2O		1.60	2.11	4.06
12.0^a	0.6	N_2O		1.55	2.16	
12.0^a	1.2	N_2O		1.63	2.37	
12.26^a	0.4	N_2O		1.40	2.06	4.64
12.70^a	0.3	N_2O		1.33	1.5	4.90

^{a}pH ≡ 14 + log [OH$^-$]. ^{b}pH adjusted to ~10 immediately after irradiation (see Experimental Section).

Yields of ClO^-, ClO_2^-, and ClO_3^- were determined as described,[12] after ClO_2 had been removed by bubbling through with N_2.

Preliminary experiments showed that the reactions[10,15,16]

$$HClO + 2ClO_2^- + H^+ \rightarrow 2ClO_2 + Cl^- + H_2O \qquad (4)$$

$$HClO + ClO_2^- \rightarrow ClO_3^- + Cl^- + H^+ \qquad (5)$$

$$2ClO_2 + HClO + H_2O \rightarrow 2ClO_3^- + Cl^- + 3H^+ \qquad (6)$$

interfered in neutral and acid solutions. Consequently, pH was adjusted to approximately 10 immediately after irradiation.

The yields were corrected for ClO_2^- and ClO_3^- formed by disproportionation of ClO_2

$$2ClO_2 + 2OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O \qquad (7)$$

by subtracting $[ClO_2^-]$ and $[ClO_3^-]$ found in a unirradiated but otherwise identically treated ClO_2 solution. In neutral and weakly alkaline solution the corrections were small. In strongly alkaline solution, however, the corrections due to reaction 7 could be as large as 25%. However, strict adherence to the following procedure gave reproducible results: A measured volume of ClO_2 stock solution was added to a known volume (100 mL) of N_2O-saturated H_2O. The reaction flask was shaken for 2 min. A measured volume of aqueous NaOH was added immediately before the start of the irradiation. After irradiation, the pH of the solution was adjusted to 9.5–10.5 by adding sulfuric acid. The additions of ClO_2 stock solution and of NaOH and H_2SO_4 (0.1–2.5 cm^3) were performed with calibrated Hamilton syringes. The time between addition of NaOH and H_2SO_4 (3–3.5 min) was monitored. After the addition of H_2SO_4, the solution was transferred to a bubbling flask and purged of ClO_2 by bubbling through with N_2 for 40 min and then analyzed for ClO^-, ClO_2^-, and ClO_3^-. To obtain the corrections for ClO_2^- and ClO_3^- formed in reaction 7, the experiment was repeated without irradiation.

Results

γ-Radiolysis of Aqueous ClO_2 Solutions. The ratio between the yields of ClO^- and ClO_3^- in the reaction of ClO_2 with O^- was determined by γ-radiolysis of aqueous ClO_2 solutions. The products were found to be O_2, ClO^-, ClO_2^-, and ClO_3^-. G values (yields per 100 eV absorbed) of the products determined in Ar, He, and N_2O-saturated ClO_2 solutions at varying pH are shown in Table I. The G values shown in Table I are in general larger (by 10–15%) than may be inferred from the G values of the primary formed species.[17] Note that $G_{ClO^-} + G_{ClO_3^-}$ decreases somewhat (4–5%) in the pH range 7 < pH < 12.

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The primary radiolytic processes relevant to the present investigation are

$$H_2O \rightsquigarrow e_{aq}^-;\quad OH/O^-;\quad H^\bullet;\quad H_2O_2$$

The corresponding G values are[17] 2.65, 2.75, 0.65, and 0.70.

In solutions saturated with N_2O at 1 atm ($[N_2O] = 2.6 \times 10^{-2}$ mol dm^{-3}) e_{aq}^- is converted into OH/O^- by

$$e_{aq}^- + N_2O \rightarrow O^- + N_2 \qquad (8)$$

$$OH = H^+ + O^- \qquad pK_a = 11.9^{17} \qquad (9)$$

ClO_2^- is produced by

$$ClO_2 + e_{aq}^- \rightarrow ClO_2^- \qquad (10)$$

$$ClO_2 + H^\bullet \rightarrow ClO_2^- + H^+ \qquad (11)$$

Since $G_{ClO_2^-}$ was determined in solutions that were made alkaline after the irradiation but before the removal of ClO_2 (see Experimental Section), ClO_2^- was also produced by

$$2ClO_2 + H_2O_2(HO_2^-) \xrightarrow{OH^-} 2ClO_2^- + 2H_2O + O_2 \qquad (12)$$

Reaction 10 is not expected to be completely quenched in N_2O-saturated solutions. By taking $k_{10} \sim 2 \times 10^{10}$ dm^3 mol^{-1} s^{-1}, we find that at $[ClO_2] = 10^{-3}$ mol dm^{-3} about 5% of e_{aq}^- reacts with ClO_2.

The reactions with OH and O^- are

$$ClO_2 + OH \rightarrow HClO + O_2 \qquad (13)$$

$$ClO_2 + OH \rightarrow ClO_3^- + H^+ \qquad (14)$$

$$ClO_2 + O^- \rightarrow ClO^- + O_2 \qquad (15)$$

$$ClO_2 + O^- \rightarrow ClO_3^- \qquad (16)$$

The ratio between the yields of ClO^- and ClO_3^- in the reaction between O^- and ClO_2 equals k_{15}/k_{16}.

The relative rate constants $R_{13} = k_{13}/(k_{13} + k_{14})$ and $R_{15} = k_{15}/(k_{15} + k_{16})$, where $k_{13} + k_{14} = (4.0 \pm 0.4) \times 10^9$ dm^3 mol^{-1} s^{-1} [18] and $k_{15} + k_{16} = (2.7 \pm 0.4) \times 10^9$ dm^3 mol^{-1} s^{-1},[18] were determined in the following way: Since the rate constant for attaining equilibrium between OH and O^- (reaction 8)[19] is about 30 times larger than $(k_{13} + k_{14})[ClO_2]$ at $[ClO_2] \sim 10^{-3}$ mol dm^{-3}, we assume that equilibrium between OH and O^- is maintained during the reaction of O^- and OH with ClO_2. Denoting the fraction of OH + O^- that reacts as OH by Y_{OH}, i.e., $Y_{OH} = (k_{13} + k_{14})X_{OH}/((k_{13} + k_{14})X_{OH} + (k_{15} + k_{16})X_{O^-})$, where $X_{OH} = 1 - X_{O^-} = [OH]/([OH] + [O^-])$, we find

$$G(ClO^-)/(G(ClO^-) + G(ClO_3^-)) = R_{13}Y_{OH} + R_{15}(1 - Y_{OH}) \qquad (17)$$

Figure 1 shows a plot of $G(ClO^-)/(G(ClO^-) + G(ClO_3^-))$ against Y_{OH}. By a least-squares treatment of the data we find $R_{13} = 0.350 \pm 0.010$ and $R_{15} = 0.180 \pm 0.008$. By including the error in $k_{13} + k_{14}$ and $k_{15} + k_{16}$, we estimate the error limits in R_{15} to be ± 0.03. From the value of R_{15} we find $k_{15}/k_{16} = 0.22 \pm 0.03$. Further we find $k_{13} = 1.4 \times 10^9$ dm^3 mol^{-1} s^{-1}, $k_{14} = 2.6 \times 10^9$ dm^3 mol^{-1} s^{-1}, $k_{15} = 4.9 \times 10^8$ dm^3 mol^{-1} s^{-1}, and $k_{16} = 2.2 \times 10^9$ dm^3 mol^{-1} s^{-1}. Note that in previous reports it has tacitly been assumed that only reactions 14 and 16 occur.[2,18]

Steady-State Photolysis of Aqueous ClO_3^- Solutions. The ratio between the quantum yield of process 1, Φ_1 (formation of ClO^- and O_2), and the quantum yield for ClO_3^- returning to the ground state after excitation, Φ_0 was determined by steady-state photolysis.

Steady-state photolysis studies of aqueous solutions of ClO_3^- are complicated by reactions among the primary photoproducts OH, ClO_2, O, ClO_2^-, and ClO^-. In order to suppress the effect of all secondary reactions except

$$OH + ClO_2^- \rightarrow ClO_2 + OH^-, \qquad k_{18} = 6.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\,{}^{19} \qquad (18)$$

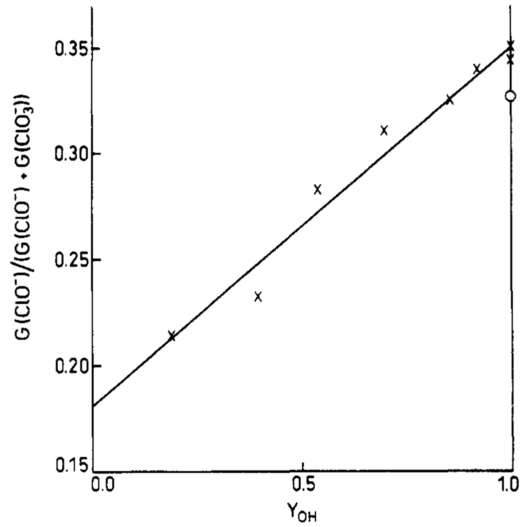

Figure 1. $G(ClO^-)/(G(ClO^-) + G(ClO_3^-))$ plotted against Y_{OH} (see text); (×) solutions saturated with N_2O at 1 atm; (○) saturated with Ar at 1 atm.

the photochemical measurements were made with ClO_3^- solutions saturated with air and containing HCO_3^- and ClO_2^- in concentrations large enough to intercept nearly all OH radicals but so low that more than 90% of the exciting light was absorbed by ClO_3^-. Absorption of light by ClO_2^- is assumed to have only a small effect on the results since the photochemical reactions of ClO_2^- are[1]

$$ClO_2^- \xrightarrow{h\nu} ClO + O^- \qquad (19)$$

$$ClO + ClO_2^- \rightarrow ClO^- + ClO_2 \qquad (20)$$

followed by reactions 9 and 18. Furthermore, we assume that oxygen atoms in air-saturated solutions formed by process 3 are converted into ClO_2 by[1,21,22]

$$O + O_2 \rightarrow O_3 \qquad (21)$$

$$O_3 + ClO_2^- \rightarrow O_3^- + ClO_2 \qquad (22)$$

$$O_3^- \rightarrow O^- + O_2 \qquad (23)$$

followed by reactions 9 and 18. In order to suppress reactions 4–6 the solutions were made slightly alkaline (pH 8.0–8.5) by adding sodium bicarbonate in concentrations varying from 3×10^{-4} to 10^{-3} mol dm^{-3}. Because of reactions 24 and 25[19,21] the

$$HCO_3^- + OH \rightarrow CO_3^- + H_2O \qquad (24)$$

$$CO_3^- + ClO_2^- \rightarrow CO_3^{2-} + ClO_2 \qquad (25)$$

presence of HCO_3^- is expected to have no effect on the measured quantum yield of ClO_2.

We denote the quantum yields of the processes 2 and 3 by Φ_2 and Φ_3, respectively, and the measured quantum yields of ClO^- and ClO_2 by $\Phi(ClO^-)$ and $\Phi(ClO_2)$. Provided that all OH radicals react in reaction 18 we have

$$\Phi(ClO^-) = \Phi_1; \quad \Phi(ClO_2) = 2\Phi_2 + 2\Phi_3 \qquad (26)$$

However, Table II shows that $\Phi(ClO_2)$ decreases with increasing time of irradiation and more so at low ClO_2^- concentrations. Since the percentage of light absorbed by ClO_2 and ClO^- at the end of the irradiation in no case exceeds 0.2%, we assume that the observed effect is due to reactions 13 and 14 only. Accordingly,

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TABLE II: Quantum Yields $\Phi(ClO^-)$ and $\Phi(ClO_2)$ for Formation of ClO^- and ClO_2 by Photolysis of Aqueous ClO_3^- Solutions Containing ClO_2^- and HCO_3^-

λ^a/nm	t/min	$[ClO_3^-]$/mol dm^{-3}	$[ClO_2^-]/10^{-4}$ mol dm^{-3}	$[HCO_3^-]/10^{-3}$ mol dm^{-3}	% light abs. by ClO_2^-	$\Phi(ClO^-)$	$\Phi(ClO_2)$	$\Phi_1{}^c$	$\Phi_2 + \Phi_3{}^d$
229	10.0	1.0	4.0	1.0	10	0.14	0.54	0.14	0.27
214	2.5	0.1	1.0	0.3	5	0.161	0.500	0.154	0.268
214	5.0	0.1	1.0	0.3	5	0.149	0.459	0.138	0.263
214	1.25	0.4	1.0	0.3	1.3	0.158	0.554	0.154	0.289
214	2.5	0.4	1.0	0.3	1.3	0.162	0.507	0.155	0.273
214	5.0	0.4	1.0	0.3	1.3	0.154	0.465	0.142	0.265
214	2.5	0.4	2.0	1.0	2.5	0.140	0.551	0.136	0.287
214	5.0	0.4	2.0	1.0	2.5	0.150	0.493	0.143	0.266
214	1.25	0.4	4.0	1.0	5	0.144	0.560	0.143	0.283
214	2.5	0.4	4.0	1.0	5	0.147	0.565	0.145	0.290
214	5.0	0.4	4.0	1.0	5	0.145	0.520	0.141	0.276
214	5.0	0.4	0	0.3	0	0.17	0		

[a] Wavelength of photolyzing light. [b] Length of time of irradiation. [c] For $t = 0$, $\Phi_2 + \Phi_3 = {}^1/_2\Phi(ClO_2)$ and $\Phi_1 = \Phi(ClO^-)$ (see text). [d] $\Phi_3/\Phi_2 = 0.1$ at $\lambda = 193$ nm.[1]

we may calculate Φ_1 and $\Phi_2 + \Phi_3$ in the following way. The rate equations for ClO_2 and ClO^- are

$$d[ClO_2]/dt = (\Phi_2 + \Phi_3)I + k_{18}[OH][ClO_2^-] - (k_{13} + k_{14})[OH][ClO_2] \quad (27)$$

$$d[ClO^-]/dt = \Phi_1 I + k_{13}[ClO_2][OH] \quad (28)$$

where I is the light intensity and t the time. Assuming steady-state conditions for OH radicals, i.e.

$$d[OH]/dt = 0 = (\Phi_2 + \Phi_3)I - k_{18}[OH][ClO_2^-] - (k_{13} + k_{14})[OH][ClO_2] \quad (29)$$

we find by integration of eq 27 and 28

$$[ClO_2](1 + 0.5(k_{13} + k_{14})[ClO_2]/(k_{18}[ClO_2^-])) = 2(\Phi_2 + \Phi_3)It \quad (30)$$

where $(k_{13} + k_{14})/k_{18} = 0.61$ and

$$[ClO^-] - 0.25k_{13}[ClO_2]^2/(k_{18}[ClO_2^-]) = \Phi_1 It \quad (31)$$

where $k_{13}/k_{18} = 0.21$. Φ_1 and $\Phi_2 + \Phi_3$ are shown in Table II. Previously was reported $\Phi_3/\Phi_2 = 0.1$ at $\lambda = 193$ nm.[1]

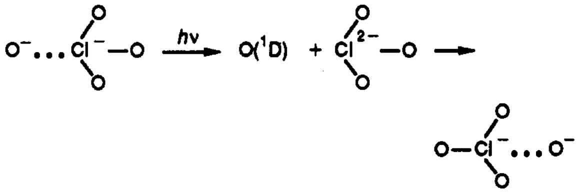
Note that Φ_1 and $\Phi_2 + \Phi_3$ varies only slightly with time of irradiation and with $[ClO_2^-]$ for $[ClO_2^-] > 10^{-4}$. The average values for Φ_1 and $\Phi_2 + \Phi_3$ are 0.145 ± 0.007 and 0.276 ± 0.011, respectively. Including the error in the determination of the light intensity (see Experimental Section) we estimate the error limits in Φ_1 and $\Phi_2 + \Phi_3$ to be ±0.012 and ±0.02, respectively. Since the sum of all quantum yields equals unity, $\Phi_0 = 1 - \Phi_1 - \Phi_2 - \Phi_3$, and we find $\Phi_1/\Phi_0 = 0.250 \pm 0.016$.

Discussion

The ratio between the yields of ClO^- and ClO_3^- in the reaction between O^- and ClO_2 equals k_{15}/k_{16}. The fact that k_{15}/k_{16} (0.22 ± 0.03) equals Φ_1/Φ_0 (0.250 ± 0.016) within the experimental error suggests that the ClO_3^- ions that after excitation have not decomposed according to processes 2 and 3 pass through the transition state for the reaction between ClO_2 and O^-. Thus our findings are in accordance with the hypothesis that O_2 formation by process 1 can be described as resulting from a cage-back reaction between ClO_2 and O^-, a reaction having a rate which probably is at least 3 orders of magnitude greater than the rate of the OH/O^- equilibration.

Since the relaxation processes in solvent water that result from a displacement of charges such as that taking place in the present case are very fast ($\sim 10^{-13}$ s)[23] any transients that remain stable for a few vibrations will attain thermal equilibrium with the solvent before reacting further. Thus process 1 can be very fast. However, with reference to the suggested formation of a Mn(V) peroxide in the photolysis of MnO_4^{-}[5] and to the formation of peroxonitrite observed in the photolysis of NO_3^{-}[24] it is not unlikely that process 1 in the photolysis of ClO_3^- similarly involves a breakdown of peroxochlorite to hypochlorite and molecular oxygen in a relatively slow step. ($t_{1/2} \sim 10^{-7}$ s as found in the photolysis of MnO_4^{-}[5]).

A picture of processes 2 and 3 emerges by comparing the results of the present studies with studies of the radiolysis of $KClO_3$ and $KClO_4$ crystals.[25] ESR studies have shown that self-trapping of radiation-induced electrons leads to structures containing the units ClO_2^-,O^- (in $KClO_3$)[26] and ClO_3^-,O^- (in $KClO_4$)[27] rather than to doubly negative anions with geometries resembling those of ClO_3^- and ClO_4^-, respectively. Thus the unit of ClO_2^-,O^- may be taken to represent the electron adduct of ClO_3^-. Moreover, a study of a set of photochemical conversions of ClO_3^-,O^- in $KClO_4$[28] involving charge transfer from O^- to ClO_3^-



(32)

indicates that expulsion of O^- from ClO_3^{2-} in the last step of process 32 begins immediately upon transfer of the electron to ClO_3^-. According to Walsh's rule,[29] ClO_3^- excited by light of a wavelength within the first absorption band in the optical spectrum of ClO_3^- should have the same symmetry as the electron adduct of ClO_3^-. We therefore suggest that the excited state of ClO_3^- is repulsive and that O^- upon the photoexcitation of ClO_3^- is expelled immediately. The expelled O^- may then escape the solvent cage containing ClO_2 and become solvated (process 2) or react with ClO_2 in cage-back reaction (process 1). Since the affinity of gaseous ClO_2 is greater than that of O[30,31] and the dark reaction corresponding to process 2 is less endergonic than that corresponding to process 3[18,32] a formation of a chlorite ion and an oxygen atom can take place prior to the solvation of O^- as observed (process 3).

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