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# Generation of Chlorine Dioxide from $ClO_2^-$ by Pulse Radiolysis

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The yield of $ClO_2^{\cdot}$ in irradiated aqueous solutions of $NaClO_2$ has been determined by pulse and steady-state radiolyses. The yield was found to be dependent on $ClO_2^-$ concentration but independent of pH. The solvated electron was found to react with $ClO_2^-$ with a rate constant $(2.5 \pm 0.5) \times 10^9$ $s^{-1}$ $mol^{-1}$ $dm^3$ to yield $ClO^-$. In its reaction with $ClO_2^-$ the $OH^{\cdot}$ radical was found to produce two species; $ClO_2^{\cdot}$ and an $OH^{\cdot}$ adduct. At sufficiently high $ClO_2^-$ concentrations the adduct reacts with $ClO_2^-$ producing further $ClO_2^{\cdot}$.

Chlorine dioxide, a well-known bleaching agent in the pulp industry, is a stable radical in acidic aqueous solutions. At high pH values it is readily consumed, but the rate of its hydrolytic reaction is slow enough to allow conventional kinetic studies, *e.g.* by stop-flow methods. In contrast to this, the oxidative reactions of $ClO_2^{\cdot}$ with organic matter as well as with hydrogen peroxide are extremely rapid and do not readily lend themselves to kinetic investigation. In particular, $ClO_2^{\cdot}$ is a powerful electrophilic agent with a high affinity towards anions. Consequently, kinetic studies of such reactions presuppose *in situ* generation of $ClO_2^{\cdot}$ in solutions where the other reactants are already present. Pulse radiolysis is admirably suited for this task and the present work deals with the yield and mechanism of $ClO_2^{\cdot}$ production in irradiated $ClO_2^-$ solutions. In addition the reactivity of the $ClO_2^{\cdot}$ thus produced towards $H_2O_2$ and $O_2^{\cdot -}$ will be investigated. In this respect our work can be envisaged as an extension of the studies by Buxton *et al.*[1]

## EXPERIMENTAL

### APPARATUS

The microtron accelerator,[2] computerized detection systems[3] and conductometric equipment[4] are described elsewhere. The radiation dose was monitored with a secondary emission chamber previously calibrated with an aerated aqueous $10^{-2}$ mol $dm^{-3}$ KSCN solution taking

$$G\varepsilon[(SCN)_2^{\cdot -}] = 2.14 \times 10^4 \text{ at } 500 \text{ nm.}^5$$

In the conductometric experiments dose calibration was accomplished by use of an Ar-purged $CCl_4$-saturated aqueous solution using

$$Ge_{aq}^- + GH^{\cdot} = 3.1 \text{ and } \lambda(HCl) = 425\ \Omega^{-1}\ cm^{-1} \text{ equiv.}^6$$

$\gamma$-irradiation was carried out in an AECL220 $^{60}Co$ $\gamma$-cell with a dose rate of 420 krad $h^{-1}$.

The stopped-flow apparatus used was of Gibbson–Durrum type with a mixing time of *ca.* 2 ms. Cuvettes with 10 and 20 mm optical path lengths were used in the pulse radiolysis and stopped-flow experiments, respectively.

## MATERIALS

Sodium chlorite [Alpha technical quality, $\varepsilon(ClO_2^-, 262\ nm) = 122$, $\varepsilon(ClO_2^-, 292\ nm) = 78$] was triply recrystallized. In the third recrystallization step rhombic single crystals of $NaClO_2 \cdot nH_2O$ were obtained. These crystals were heated and carefully dried *in vacuo* until a constant optical density at 262 nm for a given weight of dissolved sample was obtained. For the final sample $\varepsilon(ClO_2^-, 262\ nm) = 149$ and $\varepsilon(ClO_2^-, 292\ nm) = 92$ were obtained. The main 'impurities' in commercial chlorite were found to be $Ca(OH)_2$ and $H_2O$. Throughout this work triply recrystallized $NaClO_2$ was used. However, control experiments at various concentrations showed that the behaviour of the commercial product is indistinguishable from that of the purified sample.

$Na_2B_4O_7 \cdot 10H_2O$, $Na_2HPO_4 \cdot 2H_2O$, $H_2O_2$ (all P. A. Merck), NaOH (P. A. EKA), NaOCl (Kebo–Grave, technical quality), Ar (Aga, $O_2 < 5$ ppm) and $N_2O$ (Aga, $O_2 < 2\%$) were all used as received. Reduction of the $O_2$ content in the $N_2O$ was deemed unnecessary as no change in the pulse-radiolytic yield of $ClO_2^{\cdot}$ in $10^{-4}$ mol dm$^{-3}$ $ClO_2^-$ solutions was observed when the $O_2$-concentration in $N_2O$ was increased to 10%.

Chlorine dioxide solutions were prepared as follows: Concentrated sulphuric acid was added dropwise to a 3–4 mol dm$^{-3}$ sodium chlorite solution purged with a steady stream of argon. The outgoing gas-stream was successively passed through a 15 cm solid sodium chlorite column and a gas-washing bottle before finally being absorbed in triply distilled water. The pH of the final solution was around 4. The solution obtained in this way remained stable for at least 5 h in the dark.

## UNITS

The $G$ value is defined as the number of molecular events per 100 eV absorbed energy. The concentration ($c$ in mol dm$^{-3}$) in water is related to the $G$ value and the dose (in krad) through the following equation

$$c = \frac{GD}{9.65 \times 10^5}.$$

The optical density is defined as

$$\log_{10} \frac{I_0}{I} = \varepsilon c l$$

where the extinction coefficients ($\varepsilon$) used throughout this work have the units cm$^{-1}$ mol$^{-1}$ dm$^{-3}$.

## ANALYSIS

The $ClO_2^{\cdot}$ concentration was measured spectrophotometrically. The extinction coefficient at 360 nm was evaluated iodometrically and found to be in excellent agreement with the reported value of 1250.[7] Hypochlorite in the absence of chlorine dioxide and chlorite was determined spectrophotometrically at 292 nm ($\varepsilon = 420$).[1] This $\varepsilon$-value was also confirmed by iodometry. In irradiated alkaline solutions of sodium chlorite (0.1 mol dm$^{-3}$) where both $ClO_2^{\cdot}$ and $ClO^-$ were present, $ClO^-$ was quantitatively converted into $ClO_2^{\cdot}$ by acidifying (pH $\approx$ 5) the solution. Under these conditions HOCl is converted to $ClO_2^{\cdot}$ according to the reaction

$$HOCl + 2ClO_2^- + H^+ \rightarrow 2ClO_2^{\cdot} + Cl^- + H_2O.$$

By addition of small amounts of hypochlorite to chlorite solutions this reaction was found to proceed quantitatively as long as $ClO_2^-$ was in large excess, the total concentration of $ClO_2^-$ exceeded $10^{-2}$ mol dm$^{-3}$ and $3 < pH < 7.5$. To our knowledge this is a novel method of analysing small amounts of hypochlorite in the presence of chlorite.

The hypochlorite concentration was determined from the difference in $ClO_2^{\cdot}$ absorption at 360 nm between acidified and alkaline samples. A gas chromatograph equipped with an argon detector and a 3 m × $\frac{1}{8}$in. column filled with molecular sieve 13 X was used for gas analysis.

## RESULTS

### PULSE RADIOLYSIS

When a dilute aqueous solution is irradiated with ionizing radiation ($\gamma$-rays, fast electrons *etc.*) the short-lived radicals $OH^{\cdot}$, $e^-_{aq}$, and $H^{\cdot}$ are formed in well-defined yields. In the presence of $N_2O$ or $H_2O_2$, $e^-_{aq}$ (at high pH also $H^{\cdot}$) is converted into $OH^{\cdot}$.[8] Oxygen reacts rapidly with $e^-_{aq}$ and $H^{\cdot}$. It is therefore necessary to remove $O_2$ from the solution by purging with an inert gas (*e.g.* Ar) prior to irradiation.

When dilute ($10^{-4}$ mol dm$^{-3}$) $ClO_2^-$ solutions are irradiated with short electron pulses the magnitude and relative change of the transient signals are not linearly proportional to the delivered dose as long as the latter exceeds *ca.* 3 krad per pulse. Therefore throughout this work care was taken to limit the dose to the linear regime.

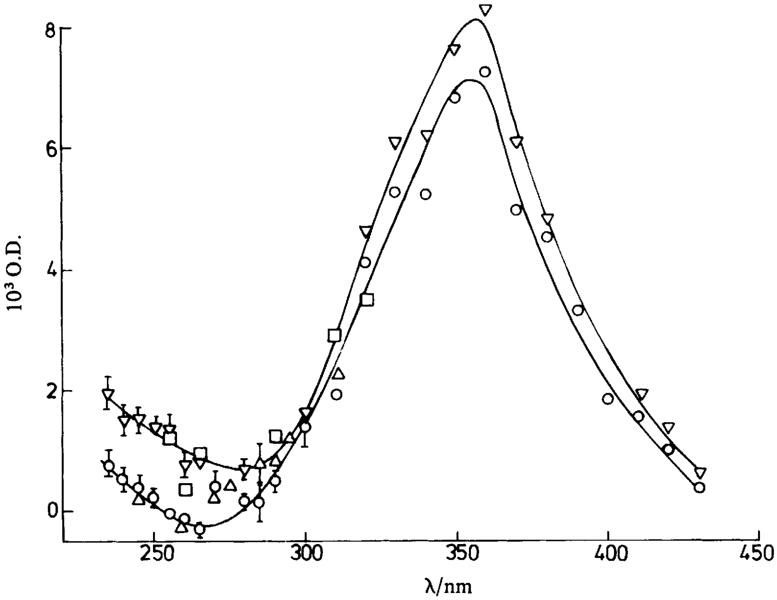


FIG. 1.—Transient spectra obtained on pulsed irradiation of $10^{-4}$ mol dm$^{-3}$ aqueous $N_2O$-saturated $ClO_2^-$ solutions at pH 9.3. Dose 2.4 krad. ▽, $N_2O$-saturated, maximum signal 8 $\mu$s after the electron pulse; ○, $N_2O$-saturated, stationary signal 200 $\mu$s after the electron pulse; □,△, the corresponding values around 290 nm when the solution is purged with Ar.

In fig. 1 the transient absorptions obtained on pulsed radiolysis of a $10^{-4}$ mol dm$^{-3}$ $NaClO_2$ solution purged with $N_2O$ are presented. These spectra are constructed from 10–20 superpositioned kinetic traces at each wavelength. Over the entire spectral region the dynamics of the transient absorption consists of a severeal $\mu$s long build-up to an absorption maximum followed by a *ca.* 100 $\mu$s decay to a long lived (> 10 ms) absorbance. In view of the spectral shape and long time stability we assign the absorbance around 360 nm to the $ClO_2^{\cdot}$ molecule. Below 260 nm a weak but significant absorbance is observed which eventually disappears completely. The low optical densities over the entire spectrum defy a quantitative kinetic evaluation. Nevertheless, it appears that the first half-life of the short wavelength transient is similar to that of the transient decay at 360 nm.

In argon-saturated $10^{-4}$ mol dm$^{-3}$ $ClO_2^-$ solutions one obtains an almost identical transient absorption, with the following two differences. (1) The 360 nm absorption band is less intense. (2) A weak and stable absorption appears at *ca.* 290 nm. When t-butanol is added in a thousandfold excess over $ClO_2^-$ to the Ar-saturated solution no transient is observed above 260 nm with the exception of a stable absorbance with maximum around 290 nm. As shown by Buxton *et al.*[1] $e_{aq}^-$ reacts with $ClO_2^-$ to yield $ClO^-$ as a final product which absorbs at 292 nm ($\varepsilon = 420$). In none of these experiments could any appreciable transient absorbance be detected at *ca.* 290 nm where $ClO^{\cdot}$ absorbs strongly.[1]

When the concentration of $ClO_2^-$ exceeds *ca.* $10^{-3}$ mol dm$^{-3}$ the absorbance at 360 nm appears immediately after the electron pulse and remains stable over tens of milliseconds.

## YIELDS

The pulse-radiolytic yield of $ClO_2^{\cdot}$ obtained from the optical density at 360 nm plotted against [$ClO_2^-$] is depicted in fig. 2. The data points in the figure were taken from straight-line fits of the optical density plotted against dose per pulse in the dose range 0.3-2 krad. The measurements made at pH 9.3 and pH 6.3 gave identical results. In a $10^{-1}$ mol dm$^{-3}$ $ClO_2^-$ solution the optical density at 360 nm was found to be proportional to the delivered dose per pulse at least up to 25 krad and also independent of pH in the range 3.1-12.5. From this absorbance $G(ClO_2^{\cdot}) = 6.8 \pm 0.3$ was calculated. In argon-saturated solutions containing $(1\text{-}5) \times 10^{-3}$ mol dm$^{-3}$ $ClO_2^-$ and 1 mol dm$^{-3}$ t-butanol at pH 9.3 the yield $G(ClO^-) = 2.5 \pm 0.4$ was obtained from the optical measurements at 292 nm after correction for the concommitant bleaching of $ClO_2^-$.

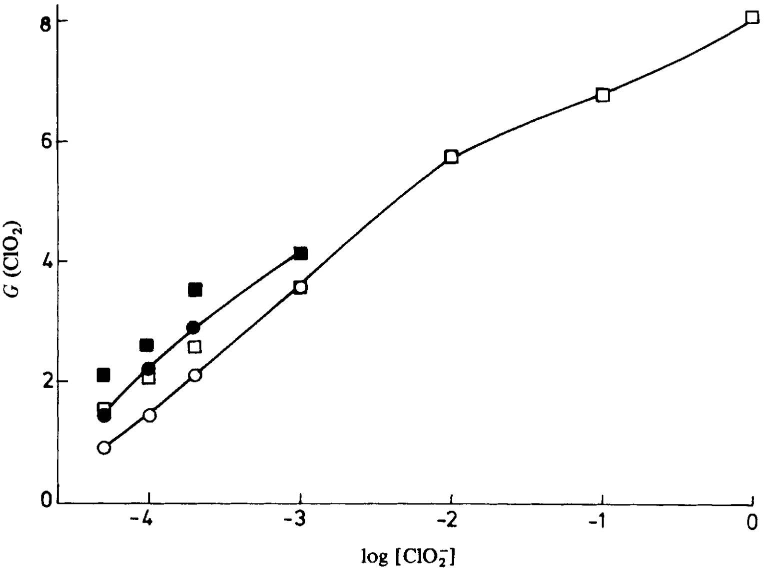


FIG. 2.—Yield of $ClO_2^{\cdot}$ as a function of $ClO_2^-$. □, Ar-saturated initial yield; ○, Ar-saturated final yield; ■, $N_2O$-saturated initial yield; ●, $N_2O$-saturated final yield.

In addition to the optical measurements pulse radiolysis was also combined with conductometric detection. In the pH range 8.4-10.4 solutions containing $2 \times 10^{-4}$ and

TABLE 1.—PULSE RADIOLYTIC $G(OH^-)$ VALUES AS MEASURED BY CONDUCTOMETRY

| pH | $ClO_2^-$ | purging gas | $(G\lambda)_{in}$[a] | $(G\lambda)_\infty$ | $G_{in}(OH^-)$[a] | $G_\infty(OH^-)$ |
|---|---|---|---|---|---|---|
| 8.4 | $2\times10^{-4}$ | Ar | 372 | 251 | 2.8 | 1.9 |
| 8.4 | $2\times10^{-4}$ | $N_2O$ | 447 | 371 | 3.4 | 2.8 |
| 10.3 | $2\times10^{-4}$ | Ar | 299 | 276 | 2.3 | 2.1 |
| 10.3 | $2\times10^{-4}$ | $N_2O$ | 395 | 364 | 3.0 | 2.8 |
| 8.6 | $10^{-3}$ | Ar | 452 | 425 | 3.4 | 3.2 |
| 8.6 | $10^{-3}$ | $N_2O$ | 609 | 570 | 4.6 | 4.3 |
| 10.4 | $10^{-3}$ | Ar | 519 | 476 | 3.9 | 3.6 |
| 10.4 | $10^{-3}$ | Ar | 453 | 406 | 3.4 | 3.1 |
| 10.4 | $10^{-3}$ | $N_2O$ | 538 | 507 | 4.1 | 3.8 |
| 10.4 | $10^{-3}$ | $N_2O$ | 610 | 571 | 4.6 | 4.3 |
| 10.4[b] | $10^{-3}$[b] | Ar[b] | 74[b] | $25\pm15$[b] | | |

[a] The measurements were made at the same time after the end of the electron pulse as were the corresponding absorbance measurements presented in fig. 2 ($6 < t/\mu s < 10$). [b] 1 mol dm$^{-3}$ t-BuOH.

$10^{-3}$ mol dm$^{-3}$ $ClO_2^-$ ($N_2O$ or Ar saturated) were studied. In all these measurements we observed an instantaneous ($t < 0.5$ μs) increase in the conductivity of the irradiated sample followed by a slight decay resulting in a constant signal level after *ca.* 100 μs. Thus the dynamics of the transient conductivity signal closely resembles that of the 360 nm absorbance. Some representative yields are presented in table 1. In order to calculate $G(OH^-)$ we used the following equivalent conductances $\lambda(OH^-) = 180\ \Omega^{-1}\ cm^{-1}$ equiv. and $\lambda(ClO_2^-) = 48\ \Omega^{-1}\ cm^{-1}$ equiv.[6] The change in conductivity in the presence of t-BuOH shows that an ion with a slightly higher equivalent conductance than $ClO_2^-$ is formed. This is in keeping with the formation of $ClO^-$ from $ClO_2^-$.

## RATE CONSTANTS

Table 2 summarizes the rate constants determined in this work. For comparison available literature values are compiled. In Ar-saturated $10^{-4}$ mol dm$^{-3}$ $ClO_2^-$ solutions at pH 10 the decay rate of $e_{aq}^-$ measured at 690 or 560 nm displays a drastic dose dependence without noticeable deviation from first-order kinetics. The measured rate constant increases with increasing dose and this is paralleled by an increasing

TABLE 2.—RATE CONSTANTS

| reaction | $k/s^{-1}\ mol^{-1}\ dm^3$ | literature value[a] |
|---|---|---|
| $e^-(aq)+ClO_2^-$ | $(2.5\pm0.5)\times10^9$ | $4.5\times10^{10}$ |
| $OH^\cdot+ClO_2^-$ | $(7\pm1)\times10^9$ | $6.3\times10^9$ |
| $O^{\cdot-}+ClO_2^-$ | $(2.0\pm0.5)\times10^8$ | $1.9\times10^8$ |
| $ClO_2^\cdot+HO_2^-$ | $(8\pm0.5)10^4$ | |
| $ClO_2^\cdot+H_2O_2$ | $<4$ | |
| $ClO_2^\cdot+O_2^{\cdot-}$ | $(3.3\pm0.2)\times10^9$ | |
| | $[OCl^-]_{tot}+[H_2O_2]_{tot}\approx2\times10^3$ | |

[a] All literature values were taken from ref. (1).

difference between initial and final $ClO_2^{\cdot}$ values as observed at 360 nm. By utilizing a dose of *ca.* 600 krads per pulse and by varying the $ClO_2^-$ concentration between $2.5 \times 10^{-5}$ and $4.0 \times 10^{-4}$ mol dm$^{-3}$ we obtained a set of pseudo-first-order rate constants as a function of $[ClO_2^-]$. From the slope of the measured rate constants plotted against $[ClO_2^-]$ the rate constant $k(ClO_2^- + e_{aq}^-)$ was calculated. It is only in the light of the above observations that the strong discrepancy between the present and previously published values (see table 2) can be understood.

The build-up of the 360 nm absorbance in solutions at pH 10 or pH 14 (1 mol dm$^{-3}$ NaOH) containing varying $ClO_2^-$ concentrations afforded the rate constants for $OH^{\cdot}$ and $O^{\cdot -}$, respectively.

Previously the rate constant for the reaction

$$OH^{\cdot} + HO_2^- \rightarrow O_2^{\cdot -} + H_2O$$

has been determined to be $6.7 \times 10^9$ s$^{-1}$ dm$^3$ mol$^{-1}$.[9] This value is almost identical to $k(ClO_2^- + OH^{\cdot}) = (7 \pm 1) \times 10^9$ s$^{-1}$ dm$^3$ mol$^{-1}$. Moreover, the corresponding rate constants for $O^{\cdot -}$ are about an order of magnitude lower. Therefore at pH > p$K_a$ ($H_2O_2$) the $OH^{\cdot}$ radical produces roughly equal amounts of $O_2^{\cdot -}$ and $ClO_2^{\cdot}$ in equimolar $ClO_2^- + H_2O_2$ solutions. At pH 12 using $10^{-2}$ mol dm$^{-3}$ $ClO_2^-$ and $1.3 \times 10^{-2}$ mol dm$^{-3}$ $H_2O_2$ the decay of the 360 nm absorbance strictly followed second-order kinetics and yielded the rate constant for the reaction between superoxide and $ClO_2^{\cdot}$.

The rate constant between $ClO^-$ and $H_2O_2$ was determined in a Gibbson–Durrum stopped-flow apparatus by measuring the decay of the 292 nm absorption (due to $ClO^-$) upon mixing $ClO^-$ with an excess of $H_2O_2$. The rate constant was found to be almost independent of pH in the interval pH 8-10.

Finally the rate constant between $HO_2^-$ and $ClO_2^{\cdot}$ was determined pulse-radiolytically by monitoring the decay of the 360 nm absorbance at varying $H_2O_2$ concentration and pH (between 7 and 13) and calculating $[HO_2^-]$ from the formula

$$[HO_2^-] = [H_2O_2]_{tot} \frac{10^{-11.65}}{10^{-pH} + 10^{-11.65}}$$

where 11.65 is the p$K_a$ of $H_2O_2$. These determinations are presented in fig. 3. At pH < 7 the measured rate constant seems to reach an independent pH value from which an upper limit for the rate constant $k(ClO_2^{\cdot} + H_2O_2)$ was estimated.

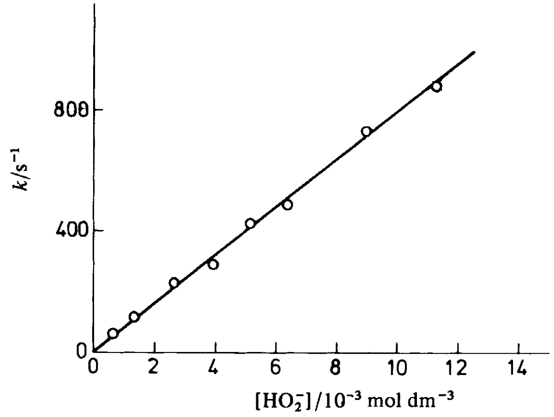


FIG. 3.—Pseudo-first-order rate constants for the decay of $ClO_2^{\cdot}$ plotted against $HO_2^-$ concentration measured at 360 nm.

### $\gamma$-RADIOLYSIS

The yields of $ClO_2^{\cdot}$ at two different $ClO_2^-$ concentrations as obtained by $\gamma$-radiolysis are given in table 3. The formation of hypochlorite is concommitant with the generation of $ClO_2^{\cdot}$ in accordance with ref. (1). The pulse-radiolytically determined value $G(ClO^-) = 2.5 \pm 0.4$ for $(1\text{-}5) \times 10^{-3}$ mol dm$^{-3}$ $ClO_2^-$ solutions compares well with $G(ClO^-) = 2.5 \pm 0.6$ found in $10^{-2}$ mol dm$^{-3}$ $ClO_2^-$ solutions in $\gamma$-radiolysis. Actually, the $\gamma$-radiolytic value of $G(ClO^-)$ is probably higher due to the initial formation of $H_2O_2$. From the rate constants in table 2 it is seen that at pH $\approx$ 10

Table 3.—$\gamma$-Radiolytic yields

| $ClO_2^-$ /mol dm$^{-3}$ | dose /krad | pH | $G(ClO_2^{\cdot})$ | $G^*$ $(ClO_2^{\cdot})^a$ | $G^{**}$ $(ClO^-)^b$ |
|---|---|---|---|---|---|
| $10^{-2}$ | 6.6 | 4.44 | — | 10.05 | — |
| $10^{-2}$ | 13.2 | 4.44 | — | 10.36 | $2.5 \pm 0.6$ |
| $10^{-2}$ | 6.6 | 9.64 | 5.65 | — | — |
| $10^{-2}$ | 13.2 | 9.64 | 4.90 | — | — |
| | | | mean = $5.3 \pm 0.5$ | | |
| $10^{-1}$ | 4.6 | 10.04 | 6.46 | 13.2 | 3.4 |
| $10^{-1}$ | 4.6 | 7.09 | — | 12.2 | 2.8 |
| $10^{-1}$ | 6.6 | 10.04$^c$ | 5.5 | 11.3 | 2.9 |
| | | | mean = $6.0 \pm 0.5$ | | mean = $3.0 \pm 0.3$ |

[a] $G^*$ $(ClO_2^{\cdot})$ is the yield of $ClO_2$ when one HOCl reacts with two $ClO_2^-$ to form two $ClO_2$ molecules. [b] $G^{**}$ $(ClO^-) = \frac{1}{2}[G^*(ClO_2) - G(ClO_2)]$. [c] After analysis of the $ClO_2$ formed at pH 10.04 the sample was acidified to pH 5.3 and $ClO_2$ was redetermined. In this sample $G(O_2)$ was determined to $0.9 \pm 0.05$.

$$\frac{k'[ClO_2][H_2O_2]}{k''[ClO_2][H_2O_2]} \approx 1.$$

Consequently

$$G(ClO^-)_{\text{obs}} \simeq G(ClO^-)_{\text{meas}} + \tfrac{1}{2}G(O_2)$$

and

$$G(ClO_2^{\cdot})_{\text{obs}} \approx G(ClO_2^{\cdot})_{\text{meas}} + G(O_2).$$

Therefore $G(ClO^-)$ at pH 10 should be $2.9 \pm 0.6$ and $G(ClO_2^{\cdot}) = 6.2 \pm 0.7$ in $10^{-2}$ mol dm$^{-3}$ $ClO_2^-$ solutions. Similarly in $10^{-1}$ mol dm$^{-3}$ $ClO_2^-$ solutions the real values should be $G(ClO^-) = 3.4 \pm 0.5$ and $G(ClO_2^{\cdot}) = 6.9 \pm 1$. Within the limits of accuracy a satisfactory agreement is thus found between the $\gamma$-radiolytic and pulse radiolytic $ClO^-$ and $ClO_2^{\cdot}$ yields.

## DISCUSSION

### REACTION BETWEEN $e_{aq}^-$ AND $ClO_2^-$

At concentrations below $5 \times 10^{-3}$ mol dm$^{-3}$ $ClO_2^-$ the pulse-radiolytic value of $G(ClO_2^{\cdot})$ in argon-saturated solutions is lower than in $N_2O$ saturated solutions. This difference reflects the higher efficiency of $N_2O$ compared with $ClO_2^-$ in capturing $e_{aq}^-$

in these solutions. Allowing for this effect it is concluded that once $e^-_{aq}$ reacts with $ClO_2^-$ the following stoichiometry holds:

$$e^-_{aq}+2ClO_2^-+H_2O \rightarrow ClO_2^{\bullet}+ClO^-+2OH^-.$$

The findings in the presence of t-BuOH also clearly show that $e^-_{aq}$ produces $ClO^-$ from $ClO_2^-$. Moreover, $G(ClO_2^{\bullet})$ in Ar-saturated solutions is not more than 0.6 $G$ units lower than that obtained in $N_2O$-saturated solutions. Therefore $ClO_2^{\bullet}$ must also be produced by the hydrated electron. This can proceed in either of two ways:

$$\left.\begin{aligned} e^-_{aq}+ClO_2^- &\rightarrow ClO^-+O^{\bullet -} \\ O^{\bullet -}+H_2O &\rightarrow OH^{\bullet}+OH^- \\ OH^{\bullet}+ClO_2^- &\rightarrow ClO_2^{\bullet}+OH^- \end{aligned}\right\} \qquad (1)$$

$$\left.\begin{aligned} e^-_{aq}+ClO_2^- &\rightarrow ClO_2^{\bullet\, 2-} \\ ClO_2^{\bullet\, 2-}+ClO_2^-+H_2O &\rightarrow ClO_2^{\bullet}+ClO^-+2OH^-. \end{aligned}\right\} \qquad (2)$$

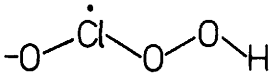
Mechanism (1) appears less probable in the light of the findings of ref. (1), where the equivalent reaction

$$ClO^-+OH^{\bullet}(O^{\bullet -}) \rightarrow ClO^{\bullet}+OH^-(O^{2-})$$

was reported to take place. No intermediate $ClO_2^{\bullet\, 2-}$ could be detected, showing that if it exists it must react further with a rate constant close to that of the initial $e^-_{aq}$ addition to $ClO_2^-$.

### REACTION OF $OH^{\bullet}$ WITH $ClO_2^-$

In an $N_2O$-saturated $10^{-3}$ mol dm$^{-3}$ $ClO_2^-$ solution all free $OH^{\bullet}$ radicals initially produced react with $ClO_2^-$. Therefore one would expect $G(ClO_2^{\bullet}) = 6.1$. This is, however, not the case. Indeed *ca.* 1.8 $G$ units are missing. This is confirmed independently by optical and conductometric measurements. The initial $G(ClO_2^{\bullet})$ and $G(OH^-)$ values are equal and *ca.* $4.3 \pm 0.4$. Based on this observation we conclude that $OH^{\bullet}$ produces two radicals; $ClO_2^{\bullet}$ and $X^{\bullet}$. Radical $X^{\bullet}$ with a $G$ value *ca.* 1.8 has an observable if weak absorption below 260 nm. The $X^{\bullet}$ radical is stable but is eventually consumed by $ClO_2^{\bullet}$ and self-recombination. At sufficiently high $ClO_2^-$ concentrations ($[ClO_2^-] > 10^{-3}$ mol dm$^{-3}$) it reacts further with $ClO_2^-$ to yield more $ClO_2^{\bullet}$ in a secondary reaction. This is manifested in the increasing yield of $ClO_2^{\bullet}$ with increasing $ClO_2^-$ concentration in the $10^{-3}$-$10^{-2}$ mol dm$^{-3}$ region to reach $G(ClO_2^{\bullet}) \approx 6$. The quantitative agreement between $G(ClO_2^{\bullet})$ and $G(OH^-)$ clearly indicates the formation of an adduct between $ClO_2^-$ and $OH^{\bullet}$. From the fact that $X^{\bullet}$ has a high p$K_a$ value it can be argued that the adduct is probably a peroxide with the following structure.



The existence of the intermediate $X^{\bullet}$ is further manifested in its reaction with luminol.[10]

### CHLORITE AS AN EFFICIENT SOURCE OF $ClO_2$

The primary aim of this work was to investigate quantitatively the feasibility of *in situ* generation of $ClO_2^{\bullet}$. As the results testify electron irradiation is an excellent method for this purpose. Thus this system should prove of much value to the chemist concerned with the reactivity of $ClO_2^{\bullet}$ towards various oxidizable compounds. There are two drawbacks to this method:

(1) The transient presence of a reactive intermediate ($X^{\bullet}$) which is liable to react with the substrate investigated. Since $X^{\bullet}$ has a high reactivity towards $ClO_2^-$ itself a sufficient excess (100 fold) of $ClO_2^-$ over the substrate investigated will eliminate this unwanted side reaction.

(2) A simultaneous generation of hypochlorite occurs. The acid form of HOCl is comparable with $ClO_2^{\bullet}$ in its reactivity towards many substances while the dissociated form $ClO^-$ is relatively inert. Therefore, we conclude that this method of generating $ClO_2^{\bullet}$ is generally useful at pH > 8.5.

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