The Radiolysis of Concentrated Neutral Sodium Perchlorate Aqueous Solutions

by J. Konstantatos and D. Katakis

Nuclear Research Center Democritos, Aghia Paraskevi Attikis, Athens, Greece (Received November 7, 1966)

The products of decomposition of ClO_4^- in the γ radiolysis of neutral concentrated aqueous solutions of NaClO₄ are mainly ClO_3^- , ClO_2^- , and possibly some Cl⁻. A small amount of ClO₂ was also detected, which decreases further by a postirradiation reaction. The ClO_3^- and ClO_2^- yields were found to be proportional to the NaClO₄ molar concentration up to 8 *M*. Bromide ion decreases the chlorate and increases the chlorite yields. The formation of H₂O₂ in air-saturated solutions is also influenced by the NaClO₄ concentration, the (H₂O₂) vs. dose curves resembling, however, those obtained in pure neutral water.

Introduction

The so-called direct action of radiation on the perchlorate ion in acid solutions has been studied by a number of investigators¹⁻³ and some of the general features of the mechanism were revealed. In the present paper, these studies are extended to neutral solutions of ClO_4^{-} . The advantage of the perchlorate system in studying the direct effect of radiation over other systems such as formic acid,⁴ sulfuric acid,⁵ hydrogen peroxide,⁶ nitrate,⁷ etc., is that it seems to be unreactive toward the water free radicals¹ at least in the bulk of the solution and free of confusing chain reactions. In addition, high concentrations can be attained throughout the pH range, and the form of the anion species present (ClO₄-) remains unchanged, which is not the case in most of the other compounds studied.

In the present work attention is paid to the effect of varying concentrations of Br^- which is used as a scavenger. The reactions of Br^- with the radiolysis products of water in dilute solutions are well known⁸⁻¹⁰ and may be used to draw conclusions about the processes in the radiolysis of water containing large amounts of perchlorate ion.

Experimental Section

Dosimetry and Solutions. The irradiations were made with a Co⁶⁰ source. The rate of energy absorption, ca. 4×10^{19} ev/l. min, was determined with the Fricke dosimeter and corrected on the basis of the electron density of each concentrated NaClO₄ solution.

All reagents were of analytical grade. The $NaClO_4$ solutions were prepared from the appropriate $HClO_4$

solutions by neutralization with sodium hydroxide. Solutions prepared from recrystallized analytical grade NaClO₄ were found to contain an impurity which reacted with Fe^{2+} . Such an impurity was not found in solutions prepared by neutralization of HClO₄.

Analytical Methods. Chloride was determined by potentiometric titration with $AgNO_3$ using a silver electrode and a calomel electrode with a chloride-free bridge. The determination was done in the absence of Fe²⁺ and Fe³⁺ which interfere with the analysis. The iodide method,¹¹ with ammonium molybdate as a catalyst, sodium hydrogen phthalate as buffer, and NaI instead of KI to avoid precipitation of KClO₄, could not be used unmodified for the analysis of H₂O₂ at pH 4.5–4.8 in irradiated concentrated NaClO₄ solutions. A product is formed during the radiolysis of such solutions, reacting slowly at this pH with the iodide reagent (Figure 1), whereas H₂O₂ reacts instantly (Figures 1 and 2). At pH 7 the reaction of this product with the iodide reagent becomes negligible, whereas

- (1) D. Katakis and A. O. Allen, J. Phys. Chem., 68, 3107 (1964).
- (2) M. Cottin, J. Chim. Phys., 53, 903 (1956).
- (3) B. Milling, G. Stein, and J. Weiss, Nature, 170, 710 (1952).
- (4) D. Smithies and E. J. Hart, J. Am. Chem. Soc., 82, 4775 (1960).
- (5) J. W. Boyle, Radiation Res., 17, 427 (1962).

- (7) H. A. Mahlman, J. Chem. Phys., 35, 936 (1961); 32, 601 (1960).
- (8) T. J. Sworski, J. Am. Chem. Soc., 76, 4687 (1954).
- (9) A. O. Allen and R. A. Holroyd, *ibid.*, 77, 5852 (1955).
- (10) A. Rafi and H. C. Sutton, Trans. Faraday Soc., 61, 877 (1965).
- (11) C. J. Hochanadel, J. Phys. Chem., 56, 587 (1952).

⁽⁶⁾ D. J. Currie and F. S. Dainton, *Trans. Faraday Soc.*, 61, 1156 (1965); A. R. Anderson and E. J. Hart, *J. Phys. Chem.*, 65, 804 (1961).



Figure 1. Iodide analysis of a 2.5 *M* NaClO₄, 10 m*M* NaBr air-saturated, pH 5.5 solution, irradiated at a dose of *ca*. $5 \times 10^{21} \text{ ev/l.}$; \bigcirc and \bigcirc , pH 4.8 with and without catalyst, respectively; \bigcirc and \bigcirc , pH 7 with and without catalyst, respectively.

the reaction with H_2O_2 (Figure 2) in the presence of the ammonium molybdate catalyst also slows down, but much less, tending to completion within *ca.* 10 min. In the absence of the catalyst the reaction of H_2O_2 becomes slower even at pH 4.8 or 1.5.

The values at pH 4.8 in the presence of catalyst (Figure 1) were found to be ca. 10% lower when the analysis was performed 24 hr after the end of irradiation.

The product of decomposition of the perchlorate ion, which has the behavior described above, is identified as the chlorite ion. Chlorate is excluded because, under the condition of the analysis, it does not react with the iodide reagent. Cl₂ and ClO₂ are also excluded as major products, since the results are practically not affected when the irradiated solutions are degassed before the analysis. ClO₂ in particular has a high extinction coefficient, 1300, at 350 m μ .¹² The absorption of the irradiated solutions at this wavelength corresponded, immediately after irradiation, to no more than 1-2 μM ClO₂. Three hours after irradiation even this small absorption disappears. Finally ClO⁻ is also excluded because the irradiated solutions did not give any reaction with iodide (without catalyst) at pH 9 where hypochlorite has been reported¹³ to react. The presence of H_2O_2 in most of the samples is an additional reason for ruling out ClO-, which reacts fast with it.¹⁴ BrO⁻ and BrO₂⁻ are also ruled out because they are too reactive to persist in



Figure 2. Iodide analysis of H_2O_2 : O, 33 $\mu M H_2O_2$ solution at pH 7, with catalyst added; ---, the value obtained instantly at pH 4.8; \bullet , 1.2 mM H_2O_2 solution at pH 1.5 without catalyst.

the irradiated solution and BrO_3^- because it is not expected to react with iodide in neutral solution. Only trace amounts of bromine were found in the radiolysis of up to 10 mM aqueous bromide solutions saturated with air.¹⁰

On the basis of these observations the analysis was done as follows.

(a) Chlorite was determined at pH 1.5 where it reacts fast with iodide. At this pH, without catalyst, the reaction of H_2O_2 with I^- is slow (Figure 2), amounting to a small correction in the determination of chlorite. The extinction coefficient of iodine at 350 m μ under these conditions is about 2% higher than with the usual iodide reagent.

(b) Determination of the sum of ClO_2^- and H_2O_2 is done at pH 4.5 with the iodide reagent containing catalyst. The reaction is complete within 45 min. Peroxide is calculated by subtracting the ClO_2^- determined as described in (a). Oxidation of I⁻ by air was taken into account in the blank, both for pH 1.5 and 4.8.

(c) The sum of ClO_3^- , ClO_2^- , and H_2O_2 is measured by heating with a Fe²⁺ solution 1 mM in Fe²⁺, 1 M in

⁽¹²⁾ W. Buser and H. Hanish, Helv. Chim. Acta, 35, 2547 (1952).

⁽¹³⁾ L. A. Prince, Anal. Chem., 36, 613 (1964).

⁽¹⁴⁾ R. E. Connick, J. Am. Chem. Soc., 69, 1509 (1947); B. Makower and W. C. Bray, *ibid.*, 55, 4765 (1933).

 $\rm HClO_4$, containing $\rm Cd^{2+}$ as a catalyst, and spectrophotometric determination of the Fe³⁺ formed, at 240 mµ. From this sum, by subtraction, one calculates chlorate. The presence of excess Fe²⁺ eliminates the possibility of interference by the reactions between the possible intermediate chlorine compounds $\rm HClO_2$, $\rm HClO$, and $\rm ClO_2^{-15}$ and the reaction¹⁴

$$HClO + H_2O_2 \longrightarrow H_2O + O_2 + H^+ + Cl^-$$

which are reported to be fast. Besides, except for the reaction of HClO with H_2O_2 , the other reactions are not expected to alter the stoichiometry of the over-all oxidation of the ferrous ion.

Results

The only oxygen compounds of chlorine found in appreciable quantities in the radiation-induced decomposition of ClO_4^- in neutral concentrated aqueous solutions are ClO₃⁻ and ClO₂⁻. Chloride was found to be formed in small amounts. In a solution 6 M in NaClO₄, with no Br⁻ added, $G(Cl^-)$ was less than 0.2. The corresponding chloride yield in acid solutions is at least 2-3 times larger. From the absorption at 350 $m\mu$, ClO₂ seems to be present in a low $(1-2 \mu M)$ steadystate concentration and probably plays an important role during irradiation. Its disappearance after irradiation and perhaps partly during the irradiation also may be due to reaction with H₂O₂. This postirradiation effect is too small in magnitude to affect appreciably the analysis of the other products. Larger amounts of ClO_2 were found in 8 M NaClO₄ solutions.^{2,16} In acid solutions we found no evidence for the formation of either ClO_2^- or ClO_2 .

The yields of ClO_3^- and ClO_2^- at 2 and 6 *M* NaClO₄ and varying concentrations of bromide are summarized in Table I. The ClO_3^- concentration is linear with dose up to 10^{22} ev/l. in all ClO_4^- concentrations studied. The ClO_2^- lines usually had an intercept suggesting high initial *G* values. After this initial period the yields of ClO_2^- seemed to be linear with dose, although the low concentrations do not permit a definite statement to be made.

The ClO_3^- lines had no intercept. Air and oxygen do not seem to have an effect on the yields of ClO_3^- , ClO_2^- , and Cl^- larger than experimental error. No decomposition of chlorate was detected in an irradiated air-saturated neutral 0.1 mM KClO₃ solution, in agreement with the observations of Bugaenko.¹⁷ Addition to this solution of 1 mM NaBr did not induce any decomposition of KClO₃ under irradiation.

Bromide ion affects both the chlorate and chlorite formed in neutral concentrated $NaClO_4$ solutions. With increasing Br⁻ concentration there is a decrease

Bromide (pH	5.8-6.0)*		
$(NaClO_4), M$	(Br ⁻), mM	G(ClO3-)	G(ClO ₂ -)
2	50	0.41	0.05 ± 0.02
2	10	0.41	0.05 ± 0.02
2	1	0.43	0.05 ± 0.02
2	0.3	0.48	0.05 ± 0.02

Table I: Chlorate and Chlorite Yields in Concentrated

NaClO₄ Solutions at Various Concentrations of

2 1 0.45 0.05	± 0.02			
2 0.3 0.48 0.05	± 0.02			
2 0.01 0.52 0.05	± 0.02			
2 0 0.58 0.05 :	± 0.02			
6 10 1.18 0	. 26			
6 1 1.24 0 .	. 22			
6 0 1.60 0	. 16			
^a No change in pH was recorded after irradiation.				

of $G(\text{ClO}_3^-)$, both in aerated and deaerated solutions. The corresponding increase in $G(\text{ClO}_2^-)$ is more clearly illustrated in the results at 6 M NaClO₄; at 2 MNaClO₄ the G values of ClO_2^- are too low to permit accurate comparisons. The decrease in $G(\text{ClO}_3^-)$ is somewhat larger than the increase in $G(\text{ClO}_2^-)$. The $G(\text{ClO}_2^-)$ over $G(\text{ClO}_3^-)$ ratio seems to be higher at the higher NaClO₄ concentrations. It is interesting to note that in acid solutions Cl⁻ and Br⁻ were found to protect rather than to decrease the observed chlorate yields.

In deaerated solutions hydrogen peroxide is formed in small nonreproducible amounts, as in the case of pure water¹⁸ and of scavenger-free HClO₄ solutions.¹ The hydrogen peroxide at various concentrations of NaClO₄ and Br⁻ as a function of dose in aerated solutions is given in Figure 3. Contrary to ClO_3 , the peroxide concentration is not linear with dose. The amount of the peroxide formed is generally higher at lower bromide concentrations. Increase in the NaClO₄ concentration causes also a decrease in the peroxide formed. The H_2O_2 concentration vs. dose curves at a given bromide concentration bend over faster in the presence of NaClO₄ than in pure water, this being more pronounced at the high NaClO₄ concentrations. At 6 M NaClO₄ and 10 mM NaBr, peroxide is already suppressed to negligible amounts. However, this suppression does not seem to be extended to the initial yields. At 6 M NaClO₄ the initial yield appears much

⁽¹⁵⁾ R. C. Thompson and G. Gordon, Inorg. Chem., 5, 557, 562 (1966).

⁽¹⁶⁾ L. T. Bugaenko, Bull. Univ. Moscow, Chem. Ser., No. 3, 21 (1961).

⁽¹⁷⁾ L. T. Bugaenko, Russ. J. Phys. Chem., 38, 2899 (1964).

⁽¹⁸⁾ H. Fricke, E. J. Hart, and H. P. Smith, J. Chem. Phys., 6, 229 (1938).



Figure 3. Hydrogen peroxide formation in air-saturated NaClO₄ solutions at pH 5.8-6.0. Dose rate 4×10^{19} ev/l. min; solutions 2 *M* in NaClO₄: O, 10 mM; •, 1 mM; 0, 0.01 mM; and 0, 0 mM NaBr added; \Box , 4 *M* NaClO₄, NaBr 10 mM; \triangle , 6 *M* NaClO₄, 10 mM NaBr; \triangle , 6 *M* NaClO₄, 1 mM NaBr.

smaller than at 2 M NaClO₄, but this may be partly due to the fast bending of the curves. The initial H₂O₂ production in 2 M NaClO₄ solutions is faster than that reported^{8,9} for water. Allen and Holroyd⁹ have shown that impurities in water cause high initial peroxide yields by removing OH radicals from the system. The possibility that such impurities are introduced in our solutions with the sodium perchlorate cannot be disregarded, although this is probably not the only reason for the high initial yields.

The peroxide concentration vs. dose curve obtained with an air-saturated neutral solution containing 1 mM KClO₃ and 1 mM NaBr was essentially identical with the one obtained without KClO₃. This observation is consistent with the absence of a radiation-induced decomposition of KClO₃ in neutral solutions.

Figure 4 gives $G(ClO_3^{-})$ and the final $G(ClO_2^{-})$ as a function of the NaClO₄ concentration in solutions containing 10 mM NaBr. Up to the concentration studied (8 M NaClO₄) the plot is linear. Deviation from linearity in acid solutions was observed at concentrations as low as 3 M in HClO₄. The values for $G(ClO_3^{-})$ in scavenger-free solutions reported here generally agree with the values of Cottin,² although they are considerably lower than those of the Russian investigators.

An air-saturated 2 M NaClO₄ solution, carefully freed from carbonate and at pH 7.5, gave within experimental error the same ClO₃⁻ and ClO₂⁻ yields as those reported in Table I. Carbonate, therefore,



Figure 4. Chlorate and chlorite yields in NaClO₄ solutions 10 mM NaBr: O, ClO₂⁻; \bullet , ClO₂⁻.

or the small difference of pH have no influence on these yields.

Discussion

The proportionality of $G(ClO_3^{-})$ and of the final $G(ClO_2^{-})$ to the NaClO₄ concentration suggests direct effect.¹⁻³ Furthermore, the fact that ClO₃- has rates of formation independent of dose indicates that the ClO₃- yields do not depend on competition with H₂O₂ for the free radicals in the bulk of the solution. The involvement of ClO_2^{-} in competition kinetics cannot be excluded because of the intercept in the concentration vs. dose lines observed, although this intercept may be due to impurities, as in the case of H_2O_2 . The lack of reproducibility in the values of the intercept favors this interpretation. A small contribution to the chlorate due to reactions of ClO₂⁻ could hardly be detected. The formation and the reactions that ClO₃- undergo have ended when this compound or its precursor diffuses out of the spur. Additional evidence that ClO_3^{-} does not react in the bulk of the solution is provided by the observation that in neutral solutions ClO_3^{-} is unaffected by radiation, both in the presence and absence of bromide.

Three different values were reported¹⁹ for the rate constant of the hydrated electron with ClO_3^- , covering a range of two orders of magnitude. The reason for this discrepancy is not known, but even the highest value, 3.5×10^8 l. mole⁻¹ sec⁻¹ ²⁰ is about $^{1}/_{50}$ as large as the corresponding rate constants of H₂O₂ and O₂

⁽¹⁹⁾ M. Anbar and P. Neta, Report of Israel Atomic Energy Commission, IA-1079, 1966.

⁽²⁰⁾ J. H. Baxendale, et al., Nature, 201, 468 (1964).

which are present in our system in concentrations comparable to or even higher than (ClO_3^{-}) . With the lowest value, 4×10^6 l. mole⁻¹ sec⁻¹,²¹ the reaction of e_{aq}^{-} with ClO_3^{-} is even more unfavorable. Moreover, the lack of an effect by KClO₃ in neutral solutions on the peroxide yield seems also to indicate negligible scavenging by this compound of OH radicals.

One of the arguments that can be advanced is that the reactions which the products of decomposition of ClO_4 or ClO_4 itself possibly undergo do not affect the qualitative features of the phenomenological kinetics of the $H_2O_2-O_2$ system, at least after a short initial period. Both in aerated and deaerated solutions the H_2O_2 formation has the same general characteristics as in neutral water. The effect of Br⁻ in particular in decreasing the H_2O_2 formed at a given dose, the nonlinearity of the H_2O_2 vs. dose plots, and the low, irreproducible H₂O₂ yields in deaerated solutions are all phenomena familiar from the radiolysis of dilute neutral water solutions. No attempt is made in this paper to make a complete analysis of the $H_2O_2-O_2$ system. It is only pointed out that the peroxide yields obtained (Figure 3) are consistent with the results obtained in concentrated perchloric acid solutions.¹ There it was found that not only the molecular hydrogen but also the hydrogen atom yield decrease with increasing ClO₄⁻ concentration, which led to the conclusion that ionization of ClO_4^- to ClO_4 and $e_{aq}^$ is relatively unimportant. More specifically, the decrease at higher NaClO₄ concentrations of the peroxide formed at a given dose can be considered as a consequence of a corresponding decrease in the difference, expressed in equivalents, between the G values of the reducing species (e.g., H, e_{aq}-, H₂O₂) and those of the oxidizing species (e.g., OH, oxygen atoms) and to reactions of H₂O₂ with the radiolysis products of ClO₄- $(e.g., with ClO_2).$

Reactions of HO₂ or further stepwise free-radical reduction of the radiolysis products of ClO_4^- are unlikely since such processes are expected to depend on whether oxygen is present or not in the system, contrary to our observations.

The observed decrease in $G(ClO_3^{-})$ and increase in final $G(ClO_2^{-})$ when Br^{-} is added to the concentrated NaClO₄ solutions may be due to one or more of the following reasons.

(a) Bromide facilitates the reformation of ClO_4^- from ClO_3^- or from precursors of ClO_3^- , or somehow inhibits the formation of ClO_3^- from ClO_4^- .

(b) It causes further reduction of ClO_3^- or its precursors.

(c) It inhibits the oxidation of lower oxidation states of chlorine to ClO_3^{-} .

The results of Table I and in particular at 2 M $NaClO_4$ show that the chlorate yield does not change when bromide concentration is increased beyond a certain limit (ca. 10 mM). This indicates that any process for the effect of bromide must be considered as taking place in the bulk of the solution rather than in the spur. Generally, of course, one expects Brto react with OH but the present experiments do not provide a means to distinguish between the resulting bromine atoms and the OH radicals in the spurs. The results, however, obtained with helium ions¹ showed that free radicals in the spur induce the decomposition of the excited perchlorate ion or inhibit the reformation of ClO_4 -. It was also suggested, based on the linearity of the G values of the decomposition products with the ClO_4 – concentration, that at least at moderate concentrations the reformation of ClO_4^- or dissipation of its excitation energy involves one species from perchlorate and one or none from H₂O rather than two species from perchlorate.

Part of the difference in the ClO_3^- yield in the presence of Br⁻ appears as ClO_2^- . The rest may be attributed to an over-all decrease in $G(-\text{ClO}_4^-)$ or a further reduction, eventually to Cl⁻. The fact that KClO₃ in neutral solutions does not decompose under irradiation and that KClO₃ does not affect the H₂O₂ yield indicates that if process (b) operates, it refers to the effect of Br⁻ on the precursors of ClO₃⁻ rather than on ClO₃⁻ itself.

On the basis of the above arguments the reactions

$$OH + ClO_2 \longrightarrow HClO_3$$
 (1)

$$2\text{ClO}_2 + \text{H}_2\text{O}_2 \longrightarrow 2\text{HClO}_2 + \text{O}_2 \qquad (2)$$

must be postulated as taking place in the bulk of the solution. The effect of Br^- on the perchlorate decomposition products in neutral solutions can be attributed mainly to suppression of reaction 1. The low concentration of ClO₂ suggests that reaction 1 is fast, in agreement with Bugaenko.¹⁷ From the results of Table I and Figure 3 one can estimate that the rate constant for reaction 1 is of the same order of magnitude as that for the reaction of OH with Br⁻.

Acknowledgment. This work was performed under the auspices of the Greek Atomic Energy Commission. The authors are grateful to Dr. A. O. Allen who, during his stay at the N.R.C. Democritos as an expert from the International Atomic Energy Agency, made valuable suggestions and constructive criticism of this work.

⁽²¹⁾ J. K. Thomas, S. Gordon, and E. J. Hart, J. Phys. Chem., 68, 1524 (1964).