

COMPUTED AND EXPERIMENTAL PRODUCT CONCENTRATIONS IN THE RADIOLYSIS OF WATER*

A. W. BOYD† and M. B. CARVER‡

Atomic Energy of Canada Limited Research Co., Chalk River Nuclear Laboratories, Chalk River,
Ontario, Canada K0J 1J0

and

R. S. DIXON§

Atomic Energy of Canada Limited Research Co., Whiteshell Nuclear Research Establishment,
Pinawa, Manitoba, Canada R0E 1L0

(Received 13 February 1979; accepted 19 April 1979)

Abstract—A recently developed computer program has been used to obtain product concentrations and their dependence on individual rate constants in the irradiation of water. Comparison with experimental values yields a value for the rate constant for the reaction of O_3^- and H_2 and shows that improved rate constant ratios can be obtained from steady-state measurements in neutral and acid oxygenated solutions. These comparisons also show the need for further studies of the radiolysis of alkaline solutions.

INTRODUCTION

THE MODELLING of the behaviour of transients in pulse radiolysis experiments has been done for several years using computer programs such as that written by Schmidt.⁽¹⁾ These programs are not, in general, satisfactory for the calculation of steady-state concentrations in continuous irradiations at low dose rates in a system such as water. However, two versatile programs^(2,3) have been developed and applied to studies of the effect of water radiolysis on zircaloy corrosion in reactor systems.^(4,5)

Recently a program capable of calculating concentrations of transients and stable products in water under these conditions has been developed in our laboratories.⁽⁶⁾ The program is fast and user-oriented, and can be applied over wide ranges of dose rates and times. Using this program we have computed steady-state concentrations and their dependence on each of the rate constants in pure water and solutions containing added H_2 , H_2O_2 or O_2 at various pHs. These computed values have been compared with the experimental data in the literature.⁽⁷⁻¹³⁾

Improvements in the accuracy of the rate constants which can be obtained from these comparisons are discussed. A value of the rate constant for reaction of O_3^- with H_2 has been derived from our calculations and the data of Kabakchi, Shubin and Dolin.⁽¹¹⁾

THE COMPUTER PROGRAM

The program package MACKSIM, for mass action kinetics simulation, was developed at Chalk River Nuclear Laboratories (CRNL) specifically to utilize the latest proven developments in numerical integration techniques for solution of kinetics problems.

The variety of time constants inherent in most sets of kinetic equations has long been recognized as a deterrent to their integration by traditional means, as numerical stability requirements dictate that the integration step be limited by the smallest time constant. The backward differencing method proposed by Curtis and Hirschfelder⁽¹⁴⁾ for such stiff differential equation systems effectively relaxed this constraint, and the algorithm published by Gear⁽¹⁵⁾ combining this technique with a practical error controlled step size and order selection has come into widespread use in a variety of scientific disciplines.

A considerably improved version of this al-

*AECL No. 6612.

†Physical Chemistry Branch.

‡Mathematics and Computations Branch.

§Research Chemistry Branch.

gorithm incorporating the sparse matrix routines of Curtis *et al.*⁽¹⁶⁾ has been developed at CRNL and has been vigorously tested and used for some time in the general simulation package FORSIM.⁽¹⁷⁾

The MACKSIM package combines this integration algorithm with a simple flexible user interface which permits a straightforward definition of the chemical reaction equations, their associated rate constants, initial conditions, radiolytic yields, dose rate profile and other necessary data.

The program is written in ANSI standard Fortran and is readily portable between computers. MACKSIM has been tested against benchmark kinetic problems such as the 10 reaction cesium flare problem reported by Edelson⁽¹⁸⁾ and the 80

reaction photochemical smog model of Farrow and Edelson.⁽¹⁹⁾ In each case the accepted results were obtained in very short computing times precisely within the requested relative error tolerance. One can, therefore, accept with confidence results returned from MACKSIM for the radiolysis of water and other applications. As an additional check, MACKSIM also automatically monitors charge balance during the integration and has an option to compute stoichiometric balance. A user's manual is available.⁽²⁰⁾

COMPARISONS

The reactions and yields used in our calculations are listed in Table I. As shown, the majority of the reaction rate constants are taken from the com-

TABLE I. REACTIONS AND YIELDS USED FOR CALCULATION OF PRODUCT CONCENTRATIONS IN WATER RADIOLYSIS

Reaction No.		Rate Constant L·mol ⁻¹ ·s ⁻¹	Reference
1	OH + H ₂ → H + H ₂ O	3.6 × 10 ⁷	(24) and (27)
2	OH + H ₂ O ₂ → HO ₂ + H ₂ O	3.3 × 10 ⁷	(24)
3	OH + O ₂ ⁻ → O ₂ + OH ⁻	9.0 × 10 ⁹	(24)
4	H + O ₂ → HO ₂	1.8 × 10 ¹⁰	(23)
5	H + O ₂ ⁻ → HO ₂ ⁻	2.0 × 10 ¹⁰	assumed
6	e ⁻ + O ₂ → O ₂ ⁻	1.9 × 10 ¹⁰	(21)
7	e ⁻ + H ₂ O ₂ → OH + OH ⁻	1.2 × 10 ¹⁰	(21)
8	e ⁻ + O ₂ ⁻ $\xrightarrow{H_2O}$ HO ₂ ⁻ + OH ⁻	1.3 × 10 ¹⁰	(21)
9	e ⁻ + H ⁺ → H	2.2 × 10 ¹⁰	(21)
10	e ⁻ + H ₂ O → H + OH ⁻	2.0 × 10 ¹	(21)
11	e ⁻ + HO ₂ ⁻ → O ⁻ + OH ⁻	3.5 × 10 ⁹	(21)
12	OH + HO ₂ → H ₂ O + O ₂	1.2 × 10 ¹⁰	(24)
13	OH + OH → H ₂ O ₂	5.5 × 10 ⁹	(24)
14	H + HO ₂ → H ₂ O ₂	2.0 × 10 ¹⁰	(23)
15	H + H ₂ O ₂ → H ₂ O + OH	9.0 × 10 ⁷	(23)
16	H + OH ⁻ → e ⁻ + H ₂ O	2.1 × 10 ⁷	(23)
17	HO ₂ + O ₂ ⁻ → O ₂ + HO ₂ ⁻	8.9 × 10 ⁷	(28)
18	HO ₂ + HO ₂ → H ₂ O ₂ + O ₂	2.0 × 10 ⁶	(24)
19	H ⁺ + O ₂ ⁻ → HO ₂	4.5 × 10 ¹⁰	assumed
20	HO ₂ → H ⁺ + O ₂ ⁻	8.0 × 10 ⁵	to give pK=4.75 with k ₁₉
21	H ⁺ + HO ₂ ⁻ → H ₂ O ₂	2.0 × 10 ¹⁰	assumed
22	H ₂ O ₂ → H ⁺ + HO ₂ ⁻	3.56 × 10 ⁻²	to give pK=11.8 with k ₂₁

TABLE 1 (Contd)

Reaction No.		Rate Constant L·mol ⁻¹ ·s ⁻¹	Reference									
23	OH + OH ⁻ → H ₂ O + O ⁻	1.2 × 10 ¹⁰	(29)									
24	O ⁻ + H ₂ O → OH + OH ⁻	1.7 × 10 ⁶	(29)									
25	H ⁺ + OH ⁻ → H ₂ O	1.43 × 10 ¹¹	(30)									
26	H ₂ O → H ⁺ + OH ⁻	2.6 × 10 ⁻⁵	(30)									
27	H + OH → H ₂ O	2.0 × 10 ¹⁰	(13) and ref. therein									
28	H + H → H ₂	1.0 × 10 ¹⁰	"									
29	e ⁻ + H $\xrightarrow{\text{H}_2\text{O}}$ H ₂ + OH ⁻	2.5 × 10 ¹⁰	"									
30	e ⁻ + e ⁻ $\xrightarrow{2\text{H}_2\text{O}}$ H ₂ + OH ⁻ + OH ⁻	5.0 × 10 ⁹	"									
31	e ⁻ + OH → OH ⁻	3.0 × 10 ¹⁰	"									
32	O ⁻ + O ₂ → O ₃ ⁻	3.0 × 10 ⁹	(24)									
33	O ⁻ + H ₂ → H + OH ⁻	8.0 × 10 ⁷	(24)									
34	O ⁻ + H ₂ O ₂ → H ₂ O + O ₂ ⁻	2.0 × 10 ⁸	(24)									
35	OH + HO ₂ ⁻ → HO ₂ + OH ⁻	5.0 × 10 ⁹	(24)									
36	HO ₂ ⁻ + O ⁻ → OH ⁻ + O ₂ ⁻	8.0 × 10 ⁸	(24)									
37	O ₃ ⁻ + H ₂ O ₂ → O ₂ ⁻ + O ₂ + H ₂ O	1.6 × 10 ⁶	(24)									
38	O ₃ ⁻ + HO ₂ ⁻ → O ₂ ⁻ + O ₂ + OH ⁻	8.9 × 10 ⁵	(24)									
39	O ₃ ⁻ → O ₂ + O ⁻	3.0 × 10 ² (a)	pH 13 (31)									
40	O ₃ ⁻ + H ₂ → O ₂ + H + OH ⁻	2.5 × 10 ⁵	fitted to (11) see text									
41	O ₂ ⁻ → products	6.0 × 10 ⁻² (a)	pH 13 (31)									
<u>Primary Yield</u>												
G(molecules/100 eV)	(b)	e ⁻ 2.7	H ⁺ 2.8	H 0.55	H ₂ 0.45	OH ⁻ 0.1	OH 2.75	HO ₂ ⁻ -	HO ₂ -	H ₂ O ₂ 0.7	O ₂ ⁻ -	O ₂ -

(a) First order rate constants

(b) From (25) and (26)

pilations of Anbar, Bambeneck, Farhatiz and Ross.⁽²¹⁻²⁴⁾ The list is not exhaustive; reactions that would be negligible under any of the experimental conditions in Refs. 7-13 have been excluded. Reactions (19)-(26) give the dissociation equilibria of HO₂, H₂O₂, OH and H₂O. Reactions (27)-(31) should be important only at the high dose rates used in pulse radiolysis and reactions (32)-(41) should be negligible below pH 10. Reactions (1)-(18) then, in addition to the equilibrium reactions, should be sufficient to determine the behaviour of water at low dose rates below pH 10.

Pure water

The most suitable experimental data for com-

parison with computed values appear to be those of Schwarz⁽¹⁰⁾ which were obtained at relatively high dose rates thus reducing the effect of impurities.

The complete set of reactions in Table 1 was first used to obtain H₂, H₂O₂ and O₂ steady-state concentrations at the dose rates used by Schwarz.⁽¹⁰⁾ The effect of removing reactions was then determined and as expected the elimination of reactions (11), (16), (18) and (30)-(41) changed the steady-state concentrations only slightly (less than 0.5%). The removal of each of reactions (28) and (29) reduces the concentrations by 1-2% at the highest dose rate, i.e. 8.1 × 10²² eV·L⁻¹·s⁻¹. For each of the remaining reactions the effect of

changing each rate constant by 10% was calculated. Those reactions where the resulting steady-state concentrations of H_2 , H_2O_2 or O_2 changed by more than 1% are listed in order of importance in Table 2.

The calculated steady-state concentrations using reactions (1)–(10), (12)–(15) and (17) and the equilibrium reactions are compared with the experimental values in Fig. 1. The difference between the calculated and experimental values is within the uncertainties in the rate constants but the H_2 concentration depends on too many rate constants to be of much use in determining their values.

As a further check on our computations the yields of H_2 and H_2O_2 for the high dose rate irradiations in Refs. 8 and 9 were calculated. The values agreed with those previously calculated using the program of Schmidt.⁽¹⁾ The determination of rate constants using the experimental yields at these dose rates has been discussed.^(12,13)

Water with added H_2 , H_2O_2 , O_2

In two early papers^(7,8) Hochanadel reported a number of elegant measurements of steady-state concentrations in water with the addition of H_2 , H_2O_2 and O_2 . In the first paper⁽⁷⁾ water initially containing H_2 and H_2O_2 was irradiated and the concentrations of all three products were measured until they reached constant values. In this case only reactions (1)–(8), (12)–(15) in addition to the equi-

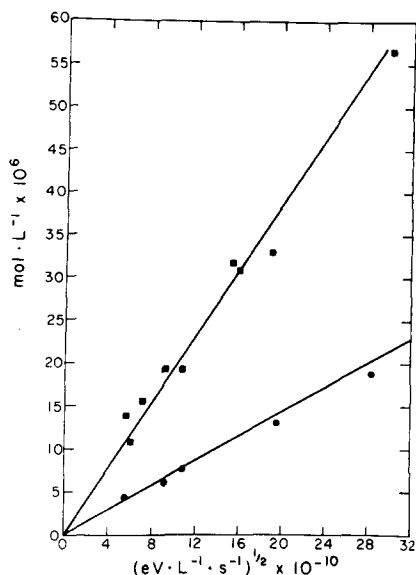


FIG. 1. Computed and Experimental Steady State Concentrations in the Irradiation of Pure Water: ■, Experimental values⁽¹⁰⁾ for $(H_2O_2)_{ss} + (O_2)_{ss}$; ●, Experimental value⁽¹⁰⁾ for $(H_2O_2)_{ss}$; —, Computed values.

rium reactions were found to be necessary. A comparison of the computed and the experimental values is shown in Fig. 2. The lack of sensitivity of the steady-state concentrations to changes in the rate constants is shown by the data in Table 3.

TABLE 2. EFFECT OF INCREASING RATE CONSTANTS BY 10% ON STEADY-STATE CONCENTRATIONS OF H_2 IN PURE WATER AT $8.2 \times 10^{22} \text{ eV} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$

No.	Reaction	Change in H_2 st.st Conc. %
1	$OH + H_2 \rightarrow H_2O + H$	-22
2	$OH + H_2O_2 \rightarrow H_2O + HO_2$	+10
3	$OH + O_2^- \rightarrow OH^- + O_2$	+ 9
6	$e^- + O_2 \rightarrow O_2^-$	+ 7.5
13	$OH + OH \rightarrow H_2O_2$	+ 4.3
4	$H + O_2 \rightarrow HO_2$	+ 4.2
5	$H + O_2^- \rightarrow HO_2^-$	- 3.9
7	$e^- + H_2O_2 \rightarrow OH + OH^-$	- 3.1

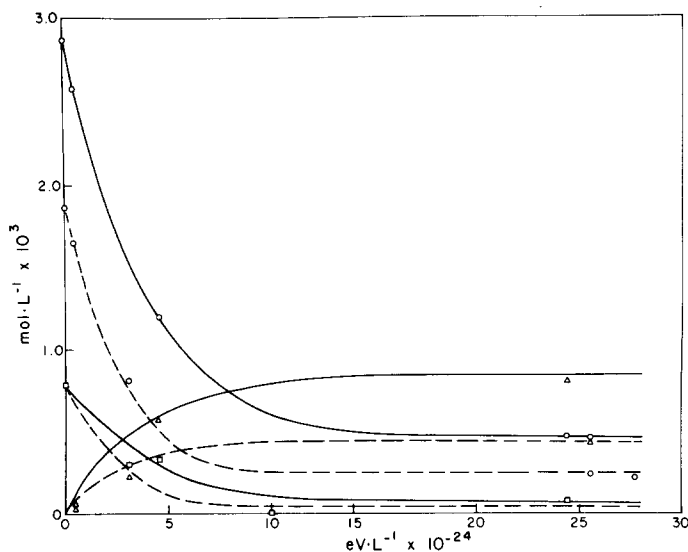


FIG. 2. Computed and Experimental Concentrations of H_2 , H_2O_2 and O_2 in the Irradiation of Water with H_2 and H_2O_2 added initially. Dose rate $4.17 \times 10^{18} \text{ eV} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$. Experimental Values:⁽⁷⁾ \square , H_2 ; \circ , H_2O_2 ; \triangle , O_2 . Computed Values; —, Initial H_2O_2 $2.86 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, initial H_2 $7.83 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$; ---, Initial H_2O_2 $1.86 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, initial H_2 $7.83 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$.

TABLE 3. EFFECT OF INCREASING RATE CONSTANTS BY 10% ON STEADY-STATE CONCENTRATIONS IN WATER IRRADIATED AT $4.17 \times 10^{18} \text{ eV} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ INITIALLY CONTAINING $2.86 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1} \text{ H}_2\text{O}_2$ AND $7.83 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \text{ H}_2$

No.	Reaction	% Change in st.st Conc.		
		H_2	H_2O_2	O_2
1	$\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$	- 9	< 1	< 1
2	$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$	+ 9	< 1	< 1
6	$\text{e}^- + \text{O}_2 \rightarrow \text{O}_2^-$	+ 7	+ 8	- 2
7	$\text{e}^- + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}^-$	- 6	- 7	+ 2
3	$\text{OH} + \text{O}_2^- + \text{OH}^- + \text{O}_2$	+ 2	< 1	< 1

In his second paper⁽⁸⁾ Hohanadel measured the concentrations of H_2O_2 at constant concentrations of H_2 and O_2 . With just O_2 added, only reactions (1)–(4), (7) and (12) and the equilibrium reactions are necessary, and the steady-state H_2O_2 concentration is almost directly proportional to the O_2 concentration and the ratio k_6/k_7 . The H_2O_2 concentration is insensitive to changes in the rate constants of the other reactions because practically all the H atoms react with O_2 and, in the absence of H_2 , most of the OH radicals react with

O_2^- . From the ratios of O_2 and H_2O_2 concentrations given by Hohanadel⁽⁸⁾ our computed ratio of k_6 to k_7 is 1.6 ± 0.16 as against Hohanadel's estimate of 1.35 ± 0.15 . However it should be noted that different G-values for the primary species were used in these calculations.

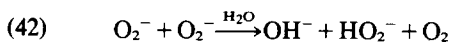
With both H_2 and O_2 added we find that all but reactions (1)–(8), (14), (15) and (17) (and the equilibrium reactions) can be eliminated without changing the steady-state concentration of H_2O_2 . The dependence of this concentration on changes

in rate constants is given in Table 4. The comparison between the calculated values and the experimental values of Hochanadel is shown in Fig. 3. The difference between these two sets of values for $\sim 5 \times 10^{-4}$ mol·L⁻¹ of H₂ and O₂ is probably outside the limits of uncertainty of the rate constants. For example, if we keep k_6/k_7 constant, we must change k_1 or k_2 by $\sim 30\%$ to reduce the H₂O₂ concentration by 15%. Either change would give steady-state hydrogen concentrations in pure water which are outside the limits of the values of Schwarz.⁽¹⁰⁾

In one of the earliest papers to show the existence of two reducing species in the radiolysis of water Barr and Allen⁽⁹⁾ measured the time dependence of the H₂O₂ concentration in water containing excess H₂ and various amounts of O₂. As shown in Fig. 4 the agreement between the computed values (using the equilibrium reactions and

(1)–(10), (12), (14), (15) and (17)) and their experimental data is reasonable.

The disappearance of O₂⁻ was previously believed (see for example the references in Ref. (24)) to proceed by reaction (42)



with a rate constant $k_{42} = 1.7 \times 10^7$ L·mol⁻¹·s⁻¹. Recently Bielski and Allen^(28,32) showed that k_{42} is extremely small (< 0.3 L·mol⁻¹·s⁻¹) and that O₂⁻ disappears by reaction with HO₂, reaction (17). If we substitute reaction (42) for reaction (17) (with $k_{42} = 1.7 \times 10^7$ L·mol⁻¹·s⁻¹) the calculated time to attain the maximum H₂O₂ concentration is reduced by as much as 20%. This is therefore consistent with the work of Bielski and Allen.^(28,32)

As Barr and Allen pointed out the maximum H₂O₂ concentration is largely governed by the

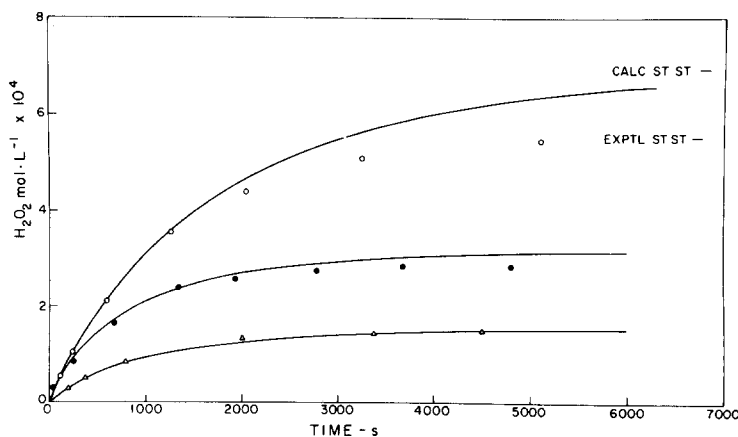


FIG. 3. Experimental and Computed Concentrations of H₂O₂ in the Irradiation of Water with Constant Concentrations of O₂ and H₂. Dose rate 9.22×10^{18} eV·L⁻¹·s⁻¹. Experimental values:⁽⁶⁾ Δ , O₂ 4.52×10^{-4} mol·L⁻¹; H₂, 0; \bullet , O₂ 7.6×10^{-5} mol·L⁻¹; H₂ 7.37×10^{-4} mol·L⁻¹; \circ , O₂ 5.48×10^{-4} mol·L⁻¹; H₂ 4.92×10^{-4} mol·L⁻¹; —, Computed Values.

TABLE 4. EFFECT OF INCREASING RATE CONSTANTS BY 10% ON STEADY-STATE CONCENTRATION OF H₂O₂ IN WATER IRRADIATED AT 9.22×10^{18} eV·L⁻¹·s⁻¹ WITH (H₂) = 4.42×10^{-4} mol·L⁻¹ AND (O₂) = 5.48×10^{-4} mol·L⁻¹

No.	Reaction	% Change in st.st H ₂ O ₂ Conc.
6	$e^- + \text{O}_2 \rightarrow \text{O}_2^-$	+ 6
7	$e^- + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}^-$	- 5
1	$\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$	+ 5
2	$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$	- 4

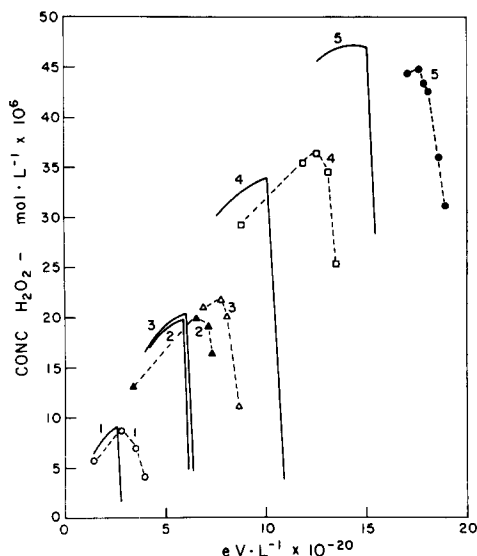


FIG. 4. Experimental and Computed Concentrations of H_2O_2 in the Irradiation of Water with H_2 and O_2 added initially. Dose rate $4.17 \times 10^{18} \text{ eV} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$. Experimental values⁽⁹⁾ initial H_2 $7 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$; \circ , Initial O_2 $1.13 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$; \blacktriangle , Initial O_2 $2.50 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$; \triangle , Initial O_2 $2.58 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$; \square , Initial O_2 $4.35 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$; \bullet , Initial O_2 $6.14 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$; —, Computed Values.

primary yields of H_2O_2 , OH and e^- and the ratio k_6/k_7 . However, it is relatively insensitive to changes in the latter, e.g. a 10% change in either rate constant produces less than a 2% change in the calculated value of $[\text{H}_2\text{O}_2]_{\text{max}}$.

The above measurements⁽⁷⁻¹⁰⁾ were all made in neutral water. Kabakchi, Shubin and Dolin⁽¹¹⁾ measured steady state concentrations of H_2 , H_2O_2 and O_2 in water initially containing O_2 at two dose rates over the pH range 0–13. Their results are compared with our computed values in Fig. 5. In neutral solutions (pH 5–8) the dependence of the steady-state concentrations on the rate constants is similar to that previously discussed for the experiments of Hochanadel with added H_2 and O_2 .⁽⁸⁾ As the sensitivity to these rate constants is small the differences between the computed values and some of the experimental values of Kabakchi *et al.*⁽¹¹⁾ cannot be resolved by reasonable changes in the rate constants. In the pH range 0–2 we find that the computed steady state concentrations for the conditions of Kabakchi *et al.*⁽¹¹⁾ depend only on reactions (1), (2), (4), (9), (12), (14), (15) and (18) in addition to the equilibrium reactions (out of all the reactions in Table 1). The computed H_2 steady-state concentration is sensitive only to the ratio k_2/k_1 and the disagreement with the results of Kabakchi *et al.* again appears to be outside the

uncertainties in the rate constants. It is possible, however, that we have omitted reactions and species that are important at low pH. Note that although H_2O_2^+ has a $\text{pK} = 1.2$ ^(33,34) its reactions appear to be similar to those of HO_2 and should not change our computed values significantly.

In basic solutions our knowledge of the species and reactions in irradiated water is limited. Reactions (32)–(41) are important in these solutions but other species or reactions may be significant. The stabilities of O_2^- and O_3^- have been measured over the pH range 11–14⁽³¹⁾ although the mechanisms of their disappearance are not well established. The only reaction for which a rate constant has not been reported is that of $\text{O}_3^- + \text{H}_2$ (k_{40}). However, by comparing computed and experimental steady-state concentrations at high pH, a value can be assigned to k_{40} . The accuracy of this is limited by the uncertainties in the other rate constants.

The measurements reported by Kabakchi *et al.*⁽¹¹⁾ in basic solution are at pH 11, 12 and 13. At each of these pHs we have calculated the steady-state concentrations and their dependence on the rate constants, assuming a range of values for k_{40} . At pH 13 a value of $k_{40} = 2.5 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, together with the values listed in Table 1 for the remaining rate constants, gives a computed value in agreement with the measured steady-state concentration of H_2 .⁽¹¹⁾ The uncertainties in the rate constants k_{39} and k_{41} given by Czapski and Dorfman⁽³¹⁾ lead to an uncertainty of $\pm 20\%$ in this computed value of k_{40} . Using this value of $2.5 \times$

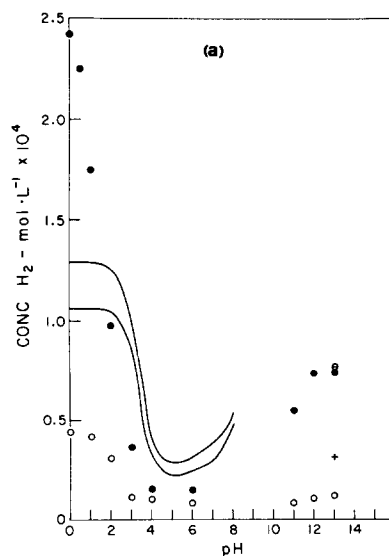


FIG. 5(a).

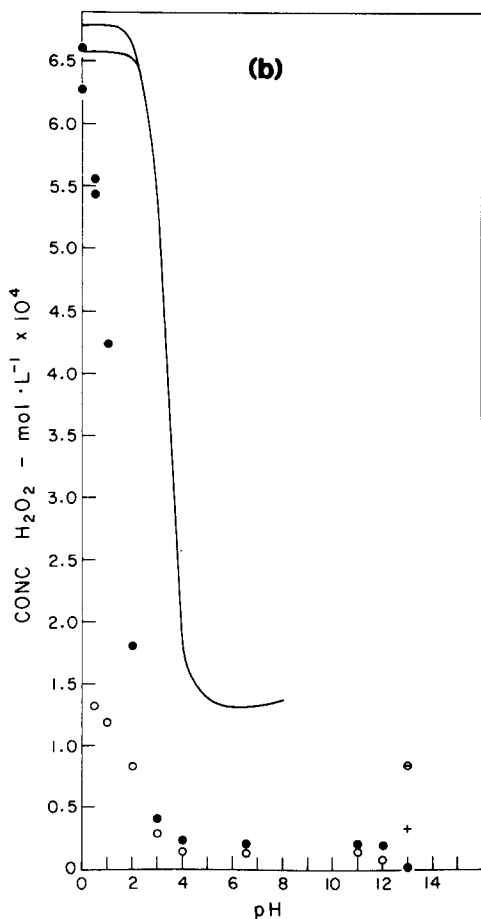


FIG. 5(b).

$10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ and the values of k_{39} and k_{41} from Czapski and Dorfman⁽³¹⁾ the computed steady-state concentration at pH 11 is $2.8 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ which is some 5 times greater than the measured value.⁽¹¹⁾ Since the sensitivity of O_2^- to impurities is well documented^(28,32,35) a possible explanation of the disagreement at pH 11 is that the O_2^- in the experiments of Kabakchi *et al.*⁽¹¹⁾ disappears more rapidly than predicted from the measured value of k_{41} .⁽³¹⁾ For example a tenfold increase in k_{41} reduces the computed steady-state H_2 concentration at pH 11 to $8.5 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$. However, if the effective value of k_{41} at pH 11 is higher than the measured value⁽³¹⁾ then so may be the effective value at pH 13. To obtain agreement between the computed and measured H_2 steady-state concentration at pH 13 with $k_{41} = 0.6 \text{ s}^{-1}$ requires that k_{40} be decreased to $5.0 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. (Increasing k_{41} another factor of ten would reduce k_{40} to $5.0 \times 10^3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$). Although there is some evidence that the impurities affecting O_2^- disap-

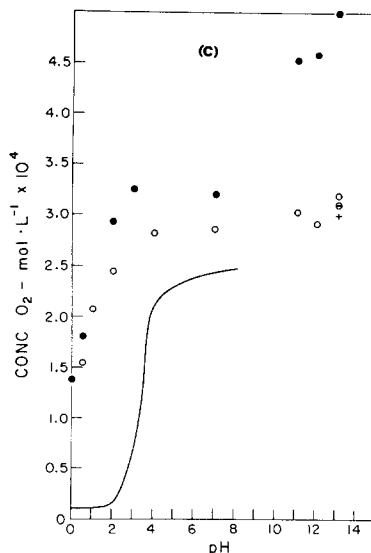


FIG. 5(c).

PEARANCE may be precipitated at pH 13⁽³⁵⁾ the uncertainty in the value of k_{40} must be increased. A reasonable estimate would appear to be $k_{40} = 1.5 \pm 1.0 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$.

CONCLUSIONS

1. Comparisons between computed and experimental values of steady state concentrations show that the radiolysis of pure water and neutral solutions can be modelled satisfactorily using reactions (1)–(31) and published G -values and rate constants. By measuring the dependence of the computed steady-state concentrations on each rate constant, the importance of each reaction can be determined under a given set of experimental conditions.

2. More accurate measurements of the steady-state concentrations in neutral and acidic solutions containing added oxygen or oxygen and hydrogen will reduce the uncertainties in the values of k_6/k_7 and k_2/k_1 .

3. A rate constant of $1.5 \pm 1.0 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for the reaction of O_3^- with H_2 is consistent with steady-state measurements at pH 13. This should

be verified by pulse radiolysis. Further steady-state measurements in alkaline oxygenated solutions are necessary for a complete understanding of these systems.

Acknowledgements—We would like to dedicate this paper to Michel Magat, in honour of his many contributions to physical chemistry and particularly to radiation chemistry. In addition we would like to thank Eva Rosinger whose early work⁽³⁶⁾ on the use of the program FORSIM (the forerunner of MACKSIM) to calculate product concentrations in irradiated water led to the developments reported here.

REFERENCES

1. K. H. SCHMIDT, A. E. C. *Research and Development Report*, ANL-7693, 1970.
2. A. R. CURTIS and E. M. CHANCE, *Report AERE-R 7345*, 1974.
3. E. M. CHANCE, A. R. CURTIS, I. P. JONES and C. R. KIRLAY, *Report AERE-R 8775*, 1977.
4. W. G. BURNS and P. B. MOORE, *Radiation Effects* 1976, **30**, 233.
5. W. G. BURNS and P. B. MOORE, *Proc. Int. Conf. on Water Chemistry of Nuclear Reactor Systems*. Bournemouth, England, 1977.
6. M. B. CARVER and A. W. BOYD, *Int. J. Chem. Kinet.* To be published.
7. C. J. HOCHANADEL, *J. phys. Chem.* 1952, **56**, 587.
8. C. J. HOCHANADEL, *Proc. Int. Conf., Peaceful Uses of Atomic Energy*, United Nations. 1955, **7**, 521.
9. N. F. BARR and A. O. ALLEN, *J. phys. Chem.* 1959, **63**, 928.
10. H. A. SCHWARZ, *J. phys. Chem.* 1962, **66**, 255.
11. S. A. KABAKCHI, V. N. SHUBIN and P. I. DOLIN, *High Energy Chemistry* 1967, **1**, 127.
12. C. WILLIS, A. W. BOYD, A. E. ROTHWELL and O. A. MILLER, *Int. J. Radiat. Phys. Chem.* 1969, **1**, 373.
13. A. W. BOYD, C. WILLIS and G. C. LALOR, *Can J. Chem.* 1971, **50**, 83.
14. C. F. CURTIS and J. O. HIRSCHFELDER, *Proc. Nat. Acad. Sci., U.S.A.* 1952, **38**, 235.
15. C. W. GEAR, *Comm. ACM* 1971, **14**, 176.
16. A. R. CURTIS, M. J. D. POWELL and J. K. REID, *J. Inst. Math. Appl.* 1974, **13**, 117.
17. M. B. CARVER, *AAICA* 1975, **3**, 195.
18. D. EDELSON, *J. Chem. Ed.* 1975, **52**, 642.
19. L. A. FARROW and D. EDELSON, *Int. J. Chem. Kinet.* 1974, **6**, 787.
20. M. B. CARVER and D. H. HANLEY, *Atomic Energy of Canada Limited Report*, AECL-6358, 1978.
21. M. ANBAR, M. BAMBENECK and A. B. ROSS, *Selected Specific Rates of Reactions of Transients from Water in Aqueous Solution—I. Hydrated Electron*. National Standards Reference Data Series—National Bureau of Standards, NSRDS-NBS 43, 1973.
22. A. B. ROSS, *Selected Specific Rates of Reactions of Transients from Water in Aqueous Solution*. National Standards Reference Data Series—National Bureau of Standards, NSRDS-NBS 43, Supplement, 1975.
23. M. ANBAR, FARHATAZIZ and A. B. ROSS, *Selected Specific Rates of Reactions of Transients from Water in Aqueous Solution—II. Hydrogen Atom*. National Standards Reference Data Series—National Bureau of Standards, NSRDS-NBS 51, 1975.
24. FARHATAZIZ and A. B. ROSS, *Selected Specific Rates of Reactions of Transients from Water in Aqueous Solution—III. Hydroxyl Radical and Perhydroxyl Radical and Their Radical Ions*. National Standards Reference Data Series—National Bureau of Standards, NSRDS-NBS 59, (1977).
25. A. O. ALLEN, *The Radiation Chemistry of Water and Aqueous Solutions*. Van Nostrand, New Jersey, 1961.
26. I. G. DRAGANIC and Z. D. DRAGANIC, *The Radiation Chemistry of Water*. Academic Press, New York, 1971.
27. K. H. SCHMIDT, *J. phys. Chem.* 1977, **81**, 1257.
28. B. H. J. BIELSKI and A. O. ALLEN, *J. phys. Chem.* 1977, **81**, 1048.
29. G. V. BUXTON, *Trans. Farad. Soc.* 1970, **66**, 1656.
30. K. H. SCHMIDT and S. M. ANDER, *J. phys. Chem.* 1969, **73**, 2846.
31. G. CZAPSKI and L. M. DORFMAN, *J. phys. Chem.* 1964, **68**, 1169.
32. G. H. J. BIELSKI, *Photochem. Photobiol.* 1978, **28**, 645.
33. B. H. J. BIELSKI and A. D. ALLEN, *Proc. 2nd Symp. Radiat. Chem. Tihany, Hungary*, 1966.
34. K. SEHESTED, O. L. RASMUSSEN and H. FRICKE, *J. phys. Chem.* **72**, 626 (1968).
35. D. BEHAR, G. CZAPSKI, J. RABANI, L. M. DORFMAN and H. A. SCHWARZ, *J. phys. Chem.* 1970, **74**, 3209.
36. E. L. J. ROSINGER and R. S. DIXON, *Atomic Energy of Canada Limited, Report AECL-5958*, 1977.