The reaction III → IV is thus

$$\mathrm{III} + H_2O \xrightarrow{k_1} \mathrm{IV}$$

and does not involve OH^-. As the other reactant is water, it is sufficient to quote the pseudo first-order constant k_1'.

The observed kinetics can thus be explained by the following mechanism for the decomposition of 2-nitriminoimidazolidine in alkali solutions.

$$\mathrm{I} + OH^- \xrightarrow{\text{fast}} \mathrm{III}$$

$$\mathrm{III} + H_2O \xrightarrow{k_1} \mathrm{IV}$$

$$\mathrm{IV} + OH^- \xrightarrow{k_2} \text{2-imidazolidone}$$

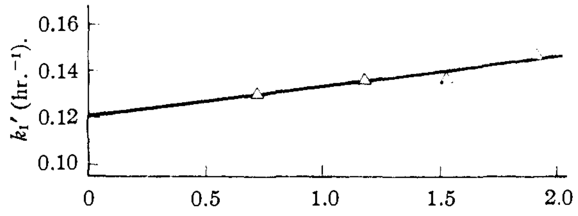

Fig. 6.—Salt effect on k_1'.

Acknowledgments.—The authors would like to thank Mr. G. Ensell, National Research Council, for construction of the absorption cell; Mr. W. G. Hatton of these Laboratories for the preparation of the reactants and Mr. D. Irwin for help with the experiments and calculations. Thanks are also due to Dr. E. Whalley and Dr. R. E. Robertson of the National Research Council for helpful discussions.

OTTAWA, CANADA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

The Radiation Chemistry of Nitrite Ion in Aqueous Solution(1)

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When deaerated solutions of KNO_2 at their natural *p*H are irradiated with γ- or X-rays, the main initial reaction is a formation of hydrogen and hydrogen peroxide. As peroxide builds up, a radiation-induced reaction between nitrite and peroxide sets in, which results in the formation of nitrate. This reaction is slower the higher the nitrite concentration. The kinetics of the nitrite–peroxide reaction were studied in detail by the irradiation of synthetic mixtures, and the results were satisfactorily explained by a free radical mechanism. The main feature of the mechanism is a competition between H_2O_2 and NO_2^- for reaction with H atoms generated in the water. The yield for H-atom formation is found to be 2.4 per 100 e.v. The initial yield of peroxide in the pure nitrite solutions is greater than the yield of hydrogen, and decreases with increasing nitrite concentration, at concentrations below 0.002 *M*. The effect of nitrite on the initial peroxide yield is qualitatively similar to the effect of bromide reported by Sworski. In nitrite solutions containing oxygen, an immediate nitrite oxidation occurs on irradiation, with a yield which increases with increasing ratio of the concentration of nitrite to that of oxygen.

The effect of X-rays on dilute aqueous solutions of KNO_2 has been briefly investigated by Fricke and Hart[2] and by Lefort.[3] A more extensive investigation was made in the hope that it might give some information as to the relative importance of the various modes of decomposition of water when subjected to ionizing radiations.

Experimental

Baker and Adamson reagent grade KNO_2 was recrystallized six times from water, thereby reducing the nitrate impurity to 0.6 mole %. This method of purification is difficult because the solubility of KNO_2 is high and has a small temperature coefficient. Reagent grade material gave the same results as the recrystallized KNO_2, and was used without further purification in later work. J. T. Baker C.P. 30% hydrogen peroxide was used without further purification. Distilled water was further purified as described by Johnson and Allen.[4] All other reagents were reagent grade and not further purified.

Three radiation sources were used. X-Rays were obtained by bombarding a gold target with 2 Mev. electrons from a Van de Graaff generator made by the High Voltage Engineering Corporation of Cambridge, Massachusetts. Two hollow cylindrical Co^{60} sources, of 120- and 1500-curie strength, supplied γ-rays. The dose rates[5] employed, in terms of μmole/l. min. of $FeSO_4$ oxidized in aerated 0.4 *M* H_2SO_4, were 42.5 for the X-rays, 12.0 and 143 for the γ-rays. During irradiation, the sample temperatures were close to 25° in all cases.

The deaerated samples were prepared by a procedure similar to that used by Johnson.[4] The cells used with the Van de Graaff generator were flat cylinders about 40 mm. in diameter and 20 mm. long, with the filling arm coming off one edge. The cells used with the cobalt source were tubes 10 mm. i.d. and 15 cm. long.

Nitrate was determined by the phenoldisulfonic acid method given by Snell.[6] Nitrite interferes with the analysis and was removed before evaporation and addition of the reagent solution by reaction with sulfamic acid. A 15-cc. portion of solution was taken; the final solution was made to 50 cc. and the optical density read on a Beckman model DU spectrophotometer. (One centimeter cells were used for all spectrophotometric work.) At 400 mμ, nitrate concn. (μ *M*) = 510 × O.D. This method did not give very satisfactory analyses, the probable error being of the order of 10%.

Hydrogen peroxide was determined by the method of J. A. Ghormley.[7,8] A standardization of the method (diluting the sample two to five) at 350 mμ gave: concn. (μ*M*) = 97.3 × O.D., which is in good agreement with the value given by Hochanadel.[8] Nitrite oxidizes iodide, and might be expected to interfere with the analysis. The reaction

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(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) H. Fricke and E. J. Hart, *J. Chem. Phys.*, **3**, 365 (1935).

(3) M. Lefort, Thesis, University of Paris, 1950.

(4) E. R. Johnson and A. O. Allen, THIS JOURNAL, **74**, 4147 (1952).

(5) In conformity with common usage in the field of radiation chemistry of aqueous solutions, the word "dose" is used in this paper to mean the total energy input, due to the irradiation, per unit volume of irradiated material. This usage is not strictly in accord with the more generally accepted meaning, which is the total energy input per unit mass of material (L. D. Marinelli, *Ann. Rev. Nuclear Sci.*, **3**, 249 (1953)).

(6) F. D. Snell, "Colorimetric Methods of Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1936, p. 269.

(7) A. O. Allen, C. J. Hochanadel, J. A. Ghormley and T. W. Davis, *J. Phys. Chem.*, **56**, 575 (1952).

(8) C. J. Hochanadel, *ibid.*, **56**, 587 (1952).

is slow, however, and when the analysis is completed in a few minutes, a reproducible blank is found proportional to the nitrite concentration and time after mixing (for short times) which is equal to 0.010 × (NO_2^-) optical density units per minute, where (NO_2^-) is in millimoles per liter. When peroxide is present in large amounts, a further dilution is necessary. The conversion factor from optical density to concentration is dependent on the concentration of reagent because of the dissociation of the triiodide ion, and when 2-cc. sample, 2.5 cc. of reagent is diluted to 50 cc., the relation is: concn. (μM) = 1020 × O.D.

Nitrite was determined by the method of Shin,[9] which is a diazotization of sulfanilamide followed by coupling of the diazonium salt with N-(1-naphthyl)-ethylenediamine dihydrochloride. One cc. of the sample was used and diluted to a final volume of 50 cc. The optical density was read at 540 mμ where: concn. (μM) = 944 × O.D. In some cases, greater sensitivity was gained by diluting to a smaller final volume. Neither hydrogen peroxide nor nitrate interfered with the analysis.

Millimolar ferrous sulfate in 0.4 M sulfuric acid was used as a dosimeter. The ferric ion produced was measured directly as the sulfate complex at 305 mμ. The molar extinction coefficient was 2190 at 23°. $G_{Fe^{+++}}$ was taken as 15.8, and the ratio of the γ-ray absorption coefficients of the dosimeter solution and the aqueous nitrite solutions was assumed to be 1.021.

Results

Deaerated Solutions.—All deaerated nitrite solutions were irradiated at their natural pH (presumably between 7 and 8).

Nitrate production in deaerated 10^{-3} M KNO_2 is given along with nitrite disappearance in 7 × 10^{-4} M KNO_2 in Fig. 1. Nitrate production is roughly equal to nitrite disappearance, but in fact appears to be somewhat greater. The apparent excess nitrate is undoubtedly due to errors in the nitrate determinations, of which incomplete removal of nitrite from the solution may be one of the most important. The nitrite determinations were reproducible to ±0.5%. In the remainder of the work, nitrite disappearance was determined and nitrate was assumed to be the product.

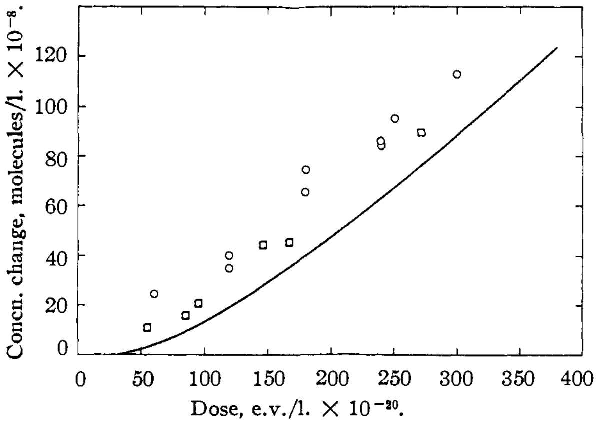

Fig. 1.—Oxidation of irradiated KNO_2 solutions: ○, nitrate formation in approximately 10^{-3} M KNO_2; □, nitrite disappearance in initially 7 × 10^{-4} M KNO_2. Curve drawn is calculated for 6 × 10^{-4} M KNO_2 (see text).

Figure 2 shows H_2O_2 production in deaerated solutions. The amount of H_2O_2 produced in a given time increases with increasing nitrite concentration, and the rate of production of H_2O_2 decreases with increasing total dose.

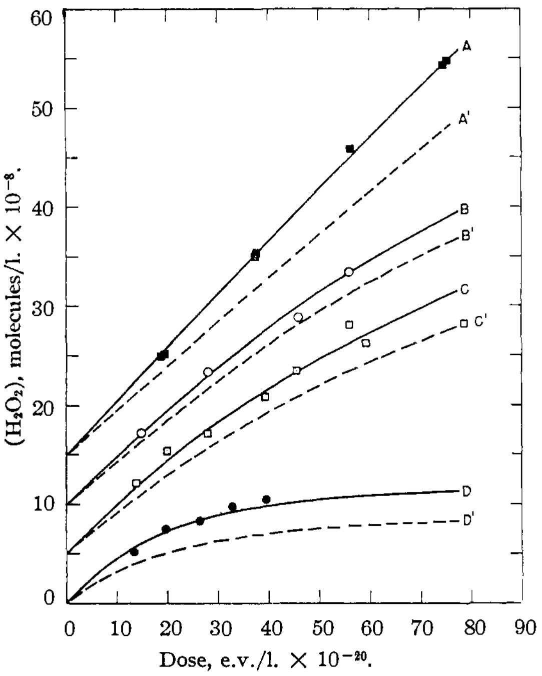

Fig. 2.—H_2O_2 production in irradiated KNO_2 solutions: ●, 10^{-4} M KNO_2; □, 5 × 10^{-4} M KNO_2; ○, 10^{-3} M KNO_2; ■, 5.9 × 10^{-3} M KNO_2. Ordinates for each concentration successively displaced 5 units. Curves A′, B′, C′, D′ calculated for E = 0; curves A, B, C, D calculated for values of E that give the best fit.

If N_2O_4 were produced in the reaction it would behave like H_2O_2 toward the iodide reagent used for analysis. A test for N_2O_4 was made by irradiating a 7 × 10^{-4} M KNO_2 sample for a dose of 2.7 × 10^{22} e.v./l. H_2O_2 was determined in this sample as 60 μM. Nitrogen gas was then bubbled through the sample for 20 minutes and, after correcting for evaporation loss, H_2O_2 was determined as 63 μM. Thus N_2O_4 is not a stable product.

Nitrite disappearance in 1 × 10^{-4} and 5 × 10^{-4} M KNO_2 is given in Fig. 3, and is seen to depend on nitrite concentration: the less nitrite present, the greater the disappearance. In Figs. 1 and 3, the nitrite disappearance is seen to accelerate as the total dose increases, indicating that nitrite oxidation is a secondary reaction. In Fig. 3, the sum of hydrogen peroxide formation and nitrite disappearance is given, and is seen to be approximately linear with dose and independent of initial concentration.

To obtain proper stoichiometry, we would expect that hydrogen gas should be formed in an amount equal to the sum of the peroxide formed and the nitrite oxidized. It was recently reported[10] that the yield of hydrogen formation on γ-irradiation of a number of aqueous solutions, including alkaline nitrite, is G_{H_2} = 0.45. The line in Fig. 3 is drawn with this slope, and corresponds fairly closely to the observed sum of peroxide formation and nitrite disappearance.

The present results indicate that the main initial reaction in nitrite solutions is a formation of

[9] M. B. Shin, *Ind. Eng. Chem., Anal. Ed.*, **13**, 33 (1941).

[10] H. A. Schwarz, J. P. Losee, Jr., and A. O. Allen, THIS JOURNAL, **76**, 4693 (1954).

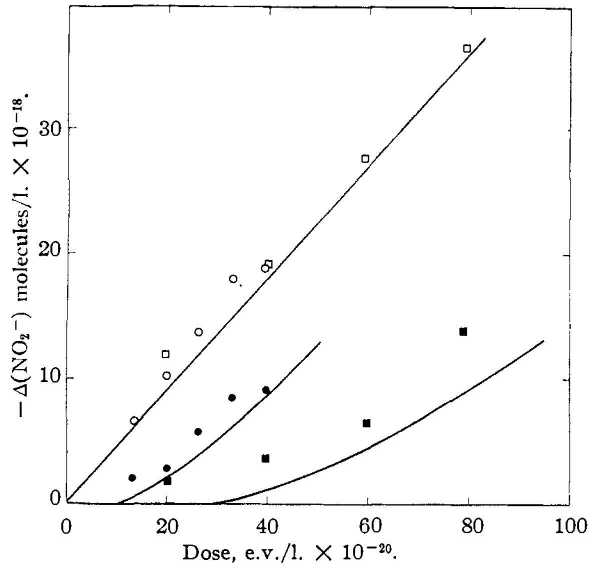

Fig. 3.—Nitrite disappearance in irradiated KNO_2 solutions: ■, 5 × 10^{-4} *M* KNO_2; ●, 10^{-4} *M* KNO_2. Open points represent sum of NO_2^- disappearance (from closed points) and hydrogen peroxide production for same solutions (shown in Fig. 2): □, (H_2O_2)-$\Delta(NO_2^-)$ in 5 × 10^{-4} *M* KNO_2; O, (H_2O_2)-$\Delta(NO_2^-)$ in 10^{-4} *M* KNO_2. All curves are calculated (see text).

H_2 and H_2O_2, with nitrate formation occurring later by a radiation-induced reaction between NO_2^- and H_2O_2. The rate of the nitrite–peroxide reaction increases as the H_2O_2 concentration builds up, but the reaction is slower the higher the nitrite concentration.

These results suggested a study of mixtures of nitrite and hydrogen peroxide. It was determined that in a solution 10^{-3} *M* in nitrite and 10^{-4} *M* in peroxide, no thermal reaction occurred in a period of 20 hours. Thus these mixtures could be conveniently worked with.

Solutions were prepared with various nitrite concentrations and with varying nitrite to peroxide ratios. Several samples of the same solution were irradiated for different periods such that up to 20 or 30% of the nitrite was oxidized. The nitrite and peroxide disappearances were linear with dose, within experimental error, so that values of the 100 e.v. yields for these disappearances, $-G_{NO_2^-}$ and $-G_{H_2O_2}$, were obtained, and are listed in Table I. In Fig. 4, the reciprocal of the nitrite disappearance yield, $-1/G_{NO_2^-}$, is plotted as a function of the average concentration ratio, $(NO_2^-)/(H_2O_2)$, present in the solutions during irradiation. A radiation-induced oxidation of NO_2^- by H_2O_2 occurs, the rate of oxidation increasing with decreasing $(NO_2^-)/(H_2O_2)$ ratio. Furthermore, $-1/G_{NO_2^-}$ is approximately linear with this ratio and depends mainly on the ratio, not on the individual concentrations, over the concentration range studied. A least mean square treatment of the data gives the following relation

$$-1/G_{NO_2^-} = (0.378 \pm 0.030) + (0.256 \pm 0.007)\,(NO_2^-)/(H_2O_2) \quad \text{(a)}$$

The given precision indices are the standard deviations.

TABLE I

YIELDS IN THE RADIATION INDUCED REACTION BETWEEN POTASSIUM NITRITE AND HYDROGEN PEROXIDE

Radiation source	Initial (NO_2^-), *M* × 10^4	Initial (H_2O_2), *M* × 10^4	Av. $\frac{(NO_2^-)}{(H_2O_2)}$	$-G_{NO_2^-}$	$-G_{H_2O_2}$
Co^{60}	5.83	0.665	7.44	0.430	0.034
VDG	5.16	0.902	5.75	.533	.102
Co^{60}	5.65	....	5.36	.598	...
Co^{60}	7.00	1.34	5.34	.596	...
Co^{60}	6.20	1.32	4.86	.618	...
Co^{60}	5.72	....	4.49	.636	...
Co^{60}	5.34	1.25	4.30	.633	.161
VDG	0.762	0.200	3.83	.582	.132
Co^{60}	5.80	1.80	3.36	.854	.412
Co^{60}	4.54	1.41	3.34	.814	.333
Co^{60}	5.68	2.37	2.53	1.03	.646
Co^{60}	2.48	....	2.03	1.10	...
VDG	5.34	2.71	1.99	1.23	.776
Co^{60}	2.48	....	1.82	1.18	...
Co^{60}	2.29	....	1.81	1.13	...
Co^{60}	5.56	3.60	1.55	1.21	.824
Co^{60}	1.70	....	1.20	1.36	...
VDG	2.74	2.94	0.90	1.50	1.15
VDG	0.895	0.110	0.78	1.50	1.28
VDG	8.03	10.03	0.78	1.53	1.37
Co^{60}	5.74	7.30	0.75	1.66	1.42
VDG	3.21	6.21	0.49	1.58	1.34

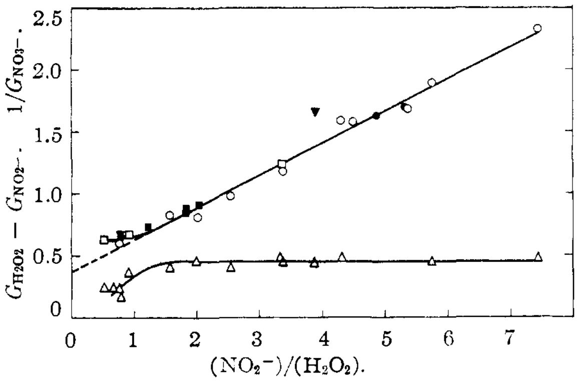

Fig. 4.—Radiation-induced reaction between KNO_2 and H_2O_2. Upper curve: reciprocal of the nitrite disappearance yield as a function of the average $(NO_2^-)/(H_2O_2)$ ratio; ordinate, e.v./molecule × 10^{-2}. Initial (NO_2^-) approximately: ▼, 0.8 × 10^{-4} *M*; ■, 2.0 × 10^{-4} *M*; □, 3.5 × 10^{-4} *M*; O, 5.5 × 10^{-4} *M*; ●, 7.5 × 10^{-4} *M*. Lower curve: △, difference between the NO_2^- disappearance yields and the H_2O_2 disappearance yields for all of the same solutions in which $\Delta_{H_2O_2}$ was determined; ordinate, molecules/100 e.v.

The differences between the NO_2^- and H_2O_2 disappearance yields are also shown in Fig. 4. (Here, the scale units represent the difference in yields, not in the reciprocal yields.) At the higher ratios, we have

$$G_{H_2O_2} - G_{NO_2^-} = 0.45 \pm 0.03 \quad \text{(b)}$$

If H_2 is produced at a constant rate throughout the reaction, stoichiometrically the yields should differ by this constant, provided the only other products are nitrate and water. The decrease of this difference at $(NO_2^-)/(H_2O_2)$ ratios below about 1.5 indicates that another reaction destroying peroxide is setting in. For this reason, experiments at ratios of less than 1.5 were not used in computing the equation for the nitrite disappearance line.

Solutions Containing Oxygen.—In KNO_2 solutions saturated with air or oxygen, the initial rate of H_2O_2 production is a function of both the NO_2^- concentration and the O_2 concentration (Fig. 5). At NO_2^- concentrations of the order of 3×10^{-4} *M* and lower, the peroxide production was a function of dose, and the initial stages of production were followed in order to get an initial slope. Air-saturated solutions were run with a KH_2PO_4–NaOH buffer (*p*H 7.2) and without a buffer (*p*H ~5 due to CO_2) with no noticeable difference in the results.

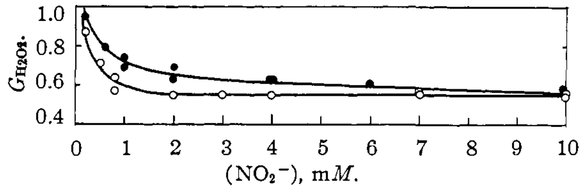

Fig. 5.—Initial H_2O_2 yields from γ-rays (smaller source) in oxygen-containing KNO_2 solutions as a function of concentration: ○, air-saturated; ●, oxygen-saturated.

The rate of production of H_2O_2 does not depend on the $(NO_2^-)/(O_2)$ ratio alone. While this type of dependence appears to hold satisfactorily at larger NO_2^- concentrations, the H_2O_2 production in oxygen-saturated solutions at low (NO_2^-) is not as large as would be expected on this basis from the results on air-saturated solutions.

Nitrite disappearance in KNO_2 solutions containing O_2 was linear with dose up to 25% reaction, the largest extent of disappearance studied. Yields for nitrite disappearance, given in Fig. 6, depend only on the concentration ratio $(NO_2^-)/(O_2)$ and are independent of the radiation intensity. The yields follow the law

$$-1/G_{NO_2^-} = (0.87 \pm 0.08) + (1.09 \pm 0.06)(O_2)/(NO_2^-) \quad (c)$$

shown as a curve in Fig. 6. The law is similar in form to equation (a) describing the NO_2^-–H_2O_2 reaction, but the dependence on (NO_2^-) is in the opposite sense.

Discussion

Deaerated Solutions.—When dilute aqueous solutions are irradiated, the water decomposes to yield the radicals H and OH, and molecules of H_2 and H_2O_2. Under some conditions, the amount of H_2O_2 found appears to exceed the amount of H_2, with a corresponding excess of H over OH. The stoichiometry of the situation may be expressed by three equations[11]

$$2H_2O = H_2 + H_2O_2 \quad (F)$$
$$2H_2O = H + H + H_2O_2 \quad (E)$$
$$H_2O = H + OH \quad (R)$$

The letters *F*, *E* and *R* will be used to indicate the yields of the corresponding reactions in molecules per 100 ev.

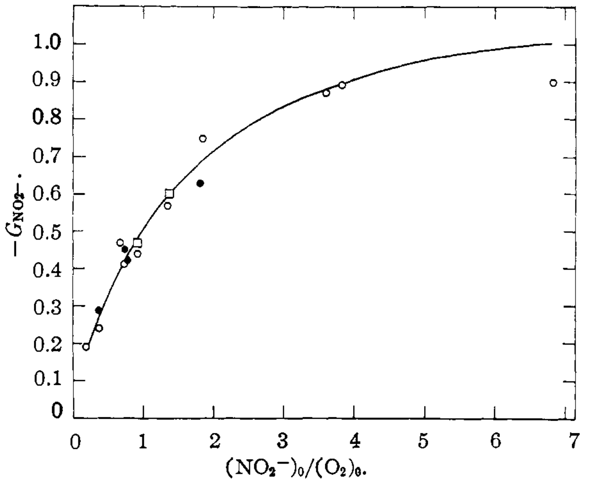

Fig. 6.—Initial NO_2^- disappearance yields from γ-rays in oxygen-containing KNO_2 solutions as a function of initial $(NO_2^-)/(O_2)$ ratio: ○ air-saturated solutions ((O_2) taken as 2.8×10^{-4} *M*) at a dose rate of 4.1×10^{19} e.v./l. min.; ●, oxygen-saturated solutions ((O_2) taken as 14×10^{-4} *M*) at a dose rate of 4.1×10^{19} e.v./l. min.; □, air-saturated solutions at a dose rate of 54×10^{19} e.v./l. min. Curve is calculated from equation (c).

The main initial net reaction in KNO_2 solutions produces H_2 and H_2O_2. The nitrite ion may reasonably be assumed to react with both H and OH, thus protecting H_2 and H_2O_2 from radical attack

$$OH + NO_2^- = NO_2 + OH^- \quad (1)$$
$$H + NO_2^- = NO + OH^- \quad (2)$$

When H_2O_2 is present in a concentration comparable to that of NO_2^-, a reaction occurs resulting in disappearance of H_2O_2 and oxidation of an equal amount of nitrite. The kinetics of this reaction (equation a) suggest that H_2O_2 and NO_2^- are competing for some intermediate. The most likely intermediate is the H atom, which can react with H_2O_2 to produce OH

$$H + H_2O_2 = OH + H_2O \quad (3)$$

The OH formed in (3) will react further according to (1). As long as (3) is relatively small, the NO_2 formed per unit time in (1) will be no greater than the NO from (2), and all the NO_2 will be consumed by the reaction

$$NO_2 + NO + H_2O = 2HNO_2 \quad (4)$$

which is known[12] to be very rapid, so that all the nitrite oxidized by OH is regenerated. If however a considerable fraction of the H reacts by (3), more NO_2 than NO is formed, and the excess should hydrolyze to form nitrate

$$2NO_2 + H_2O = HNO_2 + H^+ + NO_3^- \quad (5)$$

In deriving the reaction kinetics to be expected from such a mechanism, recourse is usually had to a "steady-state concentration" treatment, in which the intermediate radicals are assumed to be present throughout the solution in some uniform concentration, which does not change appreciably with time. This assumption is certainly not correct in radiation chemistry, where the radicals form in the tracks of ionizing particles, so that their distribution is not uniform. However, for any mechanism in which all rate-determining steps are first order

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(11) A. O. Allen, *Radiation Research*, **1**, 85 (1954).

(12) L. G. Wayne and D. M. Yost, *J. Chem. Phys.*, **18**, 767 (1950).

with respect to the intermediates (which is usually the case for non-chain reactions in solution), an equivalent treatment can be given without assuming uniform concentration of intermediates. We may demonstrate the procedure for the above mechanism.

All H atoms are assumed to disappear by (2) and (3). Considering any given H atom, the ratio of the probabilities that it should disappear by (2) or by (3), p_2/p_3, equals $k_2(NO_2^-)/k_3(H_2O_2)$, where the k's are bimolecular rate constants and the formulas in parentheses are the (uniform) solute concentrations. Since $p_2 + p_3 = 1$, we have $p_2 = k_2(NO_2^-)/[k_2(NO_2^-) + k_3(H_2O_2)]$. This must also represent the fraction of all H atoms which disappear by (2). Now the number of H atoms formed per liter per unit dose (unit dose = 100 e.v./l.) is $R + 2E$. Then if we represent by an italicized numeral the number of times the corresponding reaction occurs per liter per unit dose, we have

$$(\mathit{2}) = (R + 2E)\, k_2(NO_2^-)/[k_2(NO_2^-) + k_3(H_2O_2)]$$
$$(\mathit{3}) = (R + 2E)\, k_3(H_2O_2)/[k_2(NO_2^-) + k_3(H_2O_2)]$$

For OH, the number destroyed per unit dose per liter equals the number produced, or

$$(\mathit{1}) = R + (\mathit{3})$$

For NO_2

$$(\mathit{1}) = (\mathit{4}) + 2(\mathit{5})$$

For NO (at sufficiently high (H_2O_2))

$$(\mathit{2}) = (\mathit{4})$$

The number of nitrate molecules formed per liter per unit dose equals (*5*), and this also must equal the number of nitrite molecules disappearing, if NO is not accumulating. Hence

$$-d(NO_2^-)/d(\text{Dose}) = -G_{NO_2^-} = (\mathit{5})$$

Also

$$d(H_2O_2)/d(\text{Dose}) = G_{H_2O_2} = F + E - (\mathit{3})$$

Combining the above seven equations

$$G_{NO_2^-} = d(NO_2^-)/d(\text{Dose}) = E - \frac{R + 2E}{1 + (k_2(NO_2^-)/k_3(H_2O_2))} \qquad \text{(d)}$$

$$G_{H_2O_2} - G_{NO_2^-} = F \qquad \text{(e)}$$

The above treatment is mathematically equivalent to the usual "steady-state concentration" method, and differs only in that the number of intermediate radicals present is considered, rather than their concentrations. If reactions between radicals were rate-determining, the method could be used only after some assumption were made regarding the spatial distribution of the radicals as a function of time after their formation.

Comparing the predictions with the experimental results on H_2O_2–KNO_2 mixtures, we see that equation (e) agrees exactly with the experimental result (b). Equation (d) agrees with the experimental result (a) only if E is negligibly small. However, even if E were as large as 0.2, the resulting deviation from equation (a) would be within experimental error.

A more sensitive determination of E is provided by the experiments on the production of peroxide in nitrite solutions not initially containing peroxide. The yield of peroxide is always given by

$$G_{H_2O_2} = d(H_2O_2)/d(\text{Dose}) = F + E - \frac{R + 2E}{1 + (k_2(NO_2^-)/k_3(H_2O_2))} \qquad \text{(f)}$$

This equation may be integrated with the approximation that the nitrite concentration varies negligibly during an experiment, giving, under the condition $(H_2O_2) = 0$ when $(\text{Dose}) = 0$

$$(\text{Dose}) = -\frac{(R + 2E)(k_2/k_3)(NO_2^-)}{(R + E - F)^2} \ln\left[1 - \frac{(R + E - F)(H_2O_2)}{(F + E)(k_2/k_3)(NO_2^-)}\right] - \frac{(H_2O_2)}{R + E - F} \qquad \text{(g)}$$

If E were zero, then the constants 0.378 and 0.256 of equation (a) should equal $1/R$ and k_2/k_3R, respectively. The constants in (g) would then all be known. Peroxide-dose curves were constructed on this basis for different values of (NO_2^-), and are shown as dotted curves in Fig. 2. These curves lie well below the experimental values, showing that E has an appreciable value.

Values of E can be determined from the data on pure nitrite solutions, using (g), only if $R + 2E$ and k_2/k_3 are known. Values of $(R + 2E)$ and k_2/k_3 can be obtained from the data on nitrite–peroxide mixtures, using (d), only if E is known. To obtain values of all these constants, a method of successive approximations was used. Values of $(R + 2E)$ and k_2/k_3 were assumed, then the values of E for each (NO_2^-) were found which, when put into (g), gave the best fit to the experimental data of Fig. 2. Values of E for the different NO_2^- concentrations used in the KNO_2–H_2O_2 mixture experiments were then assigned by interpolation, and the data for the mixtures treated according to (d) by fitting $1/(-G_{NO_2^-} + E)$ as a linear function of $(NO_2^-)/(H_2O_2)$ by the method of least squares. The resulting new values of $R + 2E$ and k_2/k_3 were then used with the data on the pure nitrite solutions to obtain from (g) new values of E. After four repetitions, the results converged to yield the values shown in Fig. 7 as a function of (NO_2^-). The quantity plotted is $F + E$.

The value of E drops rapidly with increasing (NO_2^-) up to about 0.5 mM, but remains nearly constant between 0.5 and 6.0 mM. It was felt that the apparent rise from 0.5 to 6.0 mM was due to experimental error, and that the curve drawn in the figure represents a closer approximation to the true value of E than one drawn exactly through the points. To get the best values of $R + 2E$ and k_2/k_3 from the KNO_2–H_2O_2 mixture data, then, values of E for the different (NO_2^-) used were read from the curve of Fig. 7, and $1/(-G_{NO_2^-} + E)$ was again plotted against $(NO_2^-)/(H_2O_2)$. This plot is shown in Fig. 8. The fit of the points to a straight line is better than in Fig. 2, especially at the lowest nitrite concentration. The equation of the line is

$$1/(-G_{NO_2^-} + E) = 0.416 \pm 0.024 + (0.197 \pm 0.006)\,(H_2O_2)/(NO_2^-)$$

The good fit indicates that $R + 2E$, the H-atom yield, does not vary appreciably with (NO_2^-), although $F + E$, the H_2O_2 yield, does vary.

By comparison with (d), we find $R + 2E = 2.40 \pm 0.15$ and $k_2/k_3 = 0.47 \pm 0.03$. The precision indices quoted are "standard errors" based only on the scattering of the points about the line in Fig. 8.

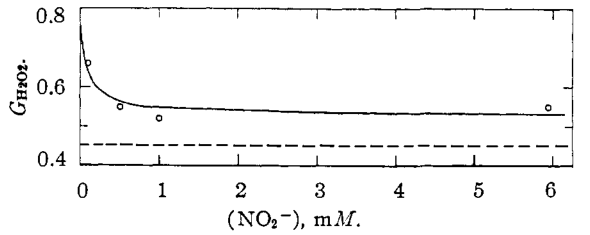

Fig. 7.—Initial H_2O_2 yield, $F + E$, as a function of KNO_2 concentration. The dotted line is the molecular yield of H_2.

The values are subject to an additional error because of the uncertainties in E, which affect the intercept and slope of the line. We estimate the probable error in $R + 2E$ as about 8%. Hochanadel's value[8] of 3.2 for the H_2O_2 yield in solutions of hydrogen and oxygen may be interpreted as $R + 2E + F$, giving $R + 2E$ as 2.75. The value is probably subject to an error of 0.3 and may be regarded as not in disagreement with the present result. Hart,[13] however, gives a value of 3.0 for $R + 2E$ from experiments on oxygenated solutions of formic acid, which appears to disagree with our value.

According to the mechanism, the initial excess of H_2O_2 over H_2 in pure deaerated KNO_2 solutions must lead to formation of an equivalent quantity of NO. As H_2O_2 builds up and becomes attacked by H atoms, the rate of increase of the NO concentration declines and becomes zero when the net rate of formation of H_2O_2 becomes equal to that of NO. As (H_2O_2) increases further, the rate of formation of NO_2 becomes larger than that of NO, and the NO concentration declines as a result of reaction (4). At high (H_2O_2), a low steady-state concentration of NO will be present, fixed by the relative rates of (4) and (5). The sum of peroxide formed and nitrite destroyed should equal $F \times$ (Dose) plus the NO present. The points in Fig. 3 representing this sum lie above the line, $0.45 \times$ (Dose), by somewhat less than 10^{18} molecules/l., on the average. The curves shown with the points representing nitrite disappearance in Figs. 1 and 3 were obtained by subtracting the calculated peroxide (Fig. 2) from $0.45 \times$ (Dose). They lie below the points by a similar amount. The corresponding quantity of NO would be very difficult to detect by analysis. The curves would lie much closer to the points if F were taken as 0.47 instead of 0.45.

The drop in $G_{H_2O_2} - G_{NO_2^-}$ at $(NO_2^-)/(H_2O_2)$ ratios below unity, shown in Fig. 4, may be ascribed to the reaction

$$OH + H_2O_2 = H_2O + HO_2 \qquad (6)$$

which would be expected to compete with (1) at high (H_2O_2). According to the results in oxygenated solution (see below) the HO_2 chiefly disappears by reducing NO_2 back to nitrite

$$HO_2 + NO_2 = HNO_2 + O_2 \qquad (7)$$

The increase in $(-1/G_{NO_2^-})$ shown in Figs. 4 and 8 at low $(NO_2^-)/(H_2O_2)$, as well as the decrease in $G_{H_2O_2} - G_{NO_2^-}$, may be shown to agree with those expected from the mechanism, including (6) and (7), if $k_1/k_6 = 55 \pm 20$. The best value of F, obtained from the intercept of a plot of $G_{H_2O_2} - G_{NO_2^-}$ against an appropriate function of $(NO_2^-)/(H_2O_2)$, appears to be 0.47. We believe the value 0.45, obtained from hydrogen yield measurements, is more reliable; in any case, the difference is within the probable errors. The corrections in the values of $R + 2E$ and k_2/k_3, due to introduction of (6) and (7), are insignificant.

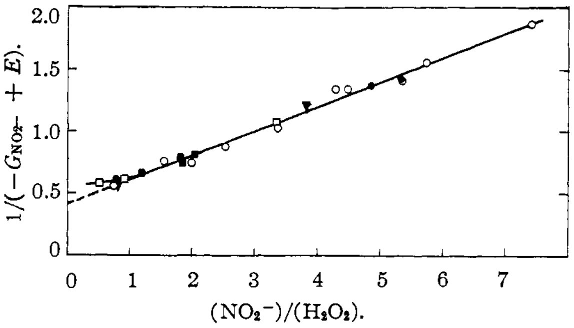

Fig. 8.—Nitrite disappearance in KNO_2–H_2O_2 mixtures, plotted as suggested by equation (e). Values of E read from curve drawn in Fig. 7.

The above mechanism, based on the idea that the main competition between NO_2^- and H_2O_2 is for the H atom, explains the results in full detail. An alternative mechanism may be set up on the hypothesis that the main competition is for OH (reactions (1) and (6)). The HO_2 formed in (6) must then be assumed to oxidize nitrite, while the NO_2 formed in (1) is all reduced back to nitrite. Now when O_2 is added to the solution much HO_2 is formed, and if this radical acted to oxidize nitrite, the oxidation yield at high (O_2) should approach a finite value of the order of $R + E$. The experiments on oxygenated solutions were performed primarily to test this mechanism. The yield of nitrite oxidation actually approached zero at high (O_2) (Fig. 6). Other experiments (Table II) showed that the addition of air to a KNO_2–H_2O_2 mixture reduced the nitrite oxidation yield. The mechanism for the deaerated solutions which postulates competition for OH (but not for H) is therefore inadmissible. We believe that the mechanism consisting of reactions (1)–(7) is the only one, consistent with the data, which can be obtained on the basis of a free radical theory of water decomposition by radiation.

TABLE II

COMPARISON OF NITRITE DISAPPEARANCE YIELDS IN AERATED AND DEAERATED NO_2^-–H_2O_2 MIXTURES

$(NO_2^-)_0 = 680\ \mu M$

Av. $\left(\frac{NO_2^-}{H_2O_2}\right)$	$-G_{NO_2^-}$ Aerated	Deaerated (from Fig. 8)
4.78	0.58	0.63
3.48	0.68	0.79
2.04	0.78	1.11
0.82	1.17	1.61

Nitrite Solutions Containing Oxygen.—Since OH radicals do not react with oxygen, they must react with NO_2^-, by (1), to give NO_2, whether O_2 is present or not. The H atoms may reduce nitrite by (2), or may react with O_2 to form HO_2

$$H + O_2 = HO_2 \qquad (8)$$

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[13] E. J. Hart, THIS JOURNAL, 76, 4312 (1954).

The yield of nitrite oxidation (Fig. 6) over the range studied depends only on the ratio of the concentrations of oxygen and nitrite. This indicates that the two solutes are competing for some intermediate. Among all the plausible intermediates (OH, H, NO, NO_2, NO_3, HO_2) only the H atom can reasonably be supposed to react readily with both O_2 and NO_2^-. We therefore believe that the course of the reaction is determined chiefly by competition between (2) and (8). Since the yield of nitrite oxidation approaches zero at low $(NO_2^-)/(O_2)$, the HO_2 formed in (8) must reduce back to nitrite the NO_2 formed in (1), by reaction (7) or by an equivalent process. When (2) occurs instead of (8), some nitrite is oxidized. Thus in the presence of oxygen, the NO formed in (2) does not always reduce NO_2 by (4), but undergoes some other reaction. This might be a reaction with oxygen, or with HO_2. Various reactions may be postulated to follow (1), (2), (8) and (7), leading to different kinetic expressions; the data are neither extensive enough nor reproducible enough to distinguish between the various possibilities.

The ratio of the rate constants for the main competing reactions, k_2/k_8, cannot be assigned a definite value until the mechanism is better known. The competition, however, is clearly in full swing when the $(NO_2^-)/(O_2)$ ratio is unity, so that k_2 and k_8 must be of the same order of magnitude. Since we have shown that k_3 and k_2 are of the same order, it follows that H atoms react at comparable rates with H_2O_2 and with O_2. This conclusion is important in considering the radiation chemistry of solutions of oxygen and hydrogen peroxide.

At low $(NO_2^-)/(O_2)$, HO_2 forms at a greater rate than NO_2 because of the existence of reaction (*E*). The excess HO_2 apparently does not react with nitrite, and disappears by reaction with itself.

$$HO_2 + HO_2 = H_2O_2 + O_2 \qquad (9)$$

Consequently, the total H_2O_2 yield (Fig. 5) is somewhat higher at low (NO_2^-) than the yield of H_2O_2 coming directly from water decomposition (Fig. 7). At higher (NO_2^-), however (2 m*M* and above in the air-saturated solutions), where the rate of formation of HO_2 is smaller, all the HO_2 is used up by (7) or other reactions, none is left to disappear by (9), and the total H_2O_2 yield becomes equal to that formed directly from the water, $F + E$. The constancy of the observed H_2O_2 yield in the air-saturated solutions above 2 m*M* NO_3^- confirms the previous finding that the magnitude of E does not change as the nitrite concentration is increased above this level.

Significance of the Primary Peroxide Yield.—Values of the primary molecular peroxide yield from water irradiated with γ-rays or X-rays, $F + E$, are available for dilute solutions of Fe^{++},[14] Br^-,[15] Cl^-,[16] HCOOH[13] and now NO_2^-. In all cases, the peroxide yield is higher than the hydrogen yield, but may vary from about 0.5 to 0.8 depending upon the concentration of the reducing agent and, in some cases, the acidity of the solution. The hydrogen yield does not seem to be appreciably affected by these solutes. There is no evidence that the total net yield of water decomposition, $2F + 2E + R$, varies with the nature or concentration of reducing agent present. The reducing agent appears to divert to itself some of the oxidizing power of the irradiated water which, in the absence of the reducing agent, would appear as molecular H_2O_2. On the free radical theory, the result suggests that OH radicals, formed in fairly close proximity to one another, which would have an appreciable probability of combining to H_2O_2 in the absence of reducing agent, react with the reducing agent when it is present, so that the molecular peroxide yield is lowered while the apparent "free radical yield" R is increased by an equivalent amount. Since the effect of the reducing agent is manifested at high dilutions, this model requires that the dimensions of the "hot spots," or regions in which a group of OH appears, must be larger than generally supposed.

Such a model would predict that the functional dependence of the decrease in E on the solute concentration should be of the same type for all reducing solutes. Now Sworski[15,16] has found that in bromide and chloride solutions (at *p*H 0.4–2) the decrease in E is proportional to the cube root of the concentration up to 0.01 *M*, and shows no sign of levelling off to a constant value. In the nitrite solutions, however, we have seen that the yield has already levelled off at 0.002 *M*, and shows no appreciable further change at higher concentrations. It may be significant that all the bromide and chloride data were obtained in acid solutions, while all the nitrite data were obtained in neutral solutions. Evidently more work is required before the production of molecular peroxide in irradiated water can be completely understood.

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[14] F. S. Dainton and H. C. Sutton, *Trans. Faraday Soc.*, **49**, 1011 (1953).

[15] T. J. Sworski, THIS JOURNAL, **76**, 4687 (1954).

[16] T. J. Sworski, *Radiation Research*, in press.