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Radical Yields in the Radiolysis of Neutral Aqueous Solutions

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The determination of the yields of the two reducing species and the OH radical in the radiolysis of neutral aqueous solutions was undertaken, using deaerated 2-propanol aqueous solutions containing potassium nitrate or hydrogen peroxide as electron scavengers. Irradiation was carried out with ^{60}Co γ-rays, and the hydrogen, nitrite ion, acetone, hydrogen peroxide and pinacol so produced were analyzed. The hydrogen yield decreases upon the addition of hydrogen peroxide or nitrate ions. The yield of hydrogen atoms is found to be 0.61 ± 0.03 by subtracting the molecular yield of hydrogen from the total hydrogen yield in the solutions containing enough scavengers. The yield of nitrite ions increases with an increase in the concentration of nitrate ions, and decreases with an increase in the concentration of acetone and with a decrease in the pH value. The acetone yield increases sharply with an increase in the quantity of nitrate ions and reaches a plateau value in the concentration range of nitrate ions higher than 1×10^{-2} M. In the presence of potassium nitrate of 1×10^{-2} M, pinacol is not formed, and the yield of hydrogen peroxide is less than the molecular yield of hydrogen peroxide. On the basis of these results, radiolysis mechanisms are elucidated and the yields of the hydrated electron and the OH radical of a neutral solution are found to be 2.77 ± 0.03 and 3.0 respectively. The relative rate constants, $k_{\mathrm{H}+\mathrm{NO}_3^-}/k_{\mathrm{H}+(\mathrm{CH}_3)_2\mathrm{CHOH}}$ and $k_{\mathrm{e}^-_{\mathrm{aq}}+(\mathrm{CH}_3)_2\mathrm{CO}}/k_{\mathrm{e}^-_{\mathrm{aq}}+\mathrm{NO}^-_3}$, are found to be 0.18 and 0.78.

Recent experimental evidence obtained by many investigators[1-5] in radiation chemical studies of dilute aqueous solutions has indicated that two forms of reducing species are produced in irradiated aqueous solutions. From chemical

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[1] E. Hayon and J. Weiss, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy*,, **29**, 80 (1958).

[2] N. F. Barr and A. O. Allen, *J. Phys. Chem.*, **63**, 928 (1959).

[3] J. Weiss, *Nature*, **186**, 751 (1960).

[4] J. Weiss, G. Scholes and J. Holian, ibid., **191**, 1386 (1961).

[5] A. O. Allen and E. Hayon, *J. Phys. Chem.*, **65**, 2181 (1961).

and physical investigations[6-17] it has been established that the major part of the reducing species is a hydrated electron, which is referred to as e^-_{aq}. The other reducing species is presumed to be a hydrogen atom. The yields of the two reducing species, Ge^-_{aq} and G_H, have been measured using different aqueous systems.[6,8,10] Allan and Beck,[11] using deaerated 2-propanol solutions containing nitrous oxide, found the yields to be 2.80±0.1 and 0.6±0.1. More recently, however, from the radiolysis of aqueous methanol - sodium nitrate solutions, Allan[12] obtained $Ge^-_{aq}=2.80\pm0.15$ and $G_{OH}=2.95$, while Adams et al.,[13] calculating the primary radical yields in neutral and alkaline solutions from the results of the pulse radiolysis of ferrocyanide solutions, obtained $G_{OH}=3.2$, $G_{e^-_{aq}}=3.16$, and $G_H=0.6$ to 0.8.

The present investigation was undertaken in order to determine the yields of the two reducing species and of the OH radical under neutral conditions in the gamma radiolysis of deaerated 2-propanol aqueous solutions containing potassium nitrate or hydrogen peroxide.

Experimental

The Preparation of Samples and the Irradiation.—2-Propanol was distilled, and the middle fraction was checked by gas chromatography prior to use. Other reagents of the GR grade were used without further purification. Solutions were prepared using water triply-distilled from acidic permanganate, dichromate and alkaline permanganate. The pH of the solutions was in the range between 5.6 and 5.7. In some experiments the pH of solutions was varied by adding sulfuric acid, sodium bicarbonate or sodium hydroxide. Solutions (20 ml.) degassed by the standard freezing-pumping technique were irradiated by ^{60}Co γ-rays at room temperature. The meansurements were made at least three times. The dose rate mainly employed was 2.42×10^{17} eV./ml.hr. Dosimetry was carried out with a usual ferrous dosimeter.

Analysis.—The hydrogen was analyzed by gas chromatography (Yanagimoto GCG-220) by using a molecular sieve 5A column (2m.) at room temperature and by using argon as the carrier gas. The acetone was determined by the spectrophotometric method[18] (Shimadzu QR-50 and Cary Model 14). The analysis of nitrite ion was made on the basis of the absorption at 525 mμ by using the method of sulfanilic acid and α-naphthylamine.[19] For the 2-propanol - hydrogen peroxide system, hydrogen peroxide was determined by the method developed by Ghormley,[20] while for the potassium nitrate - 2-propanol system the reduction of ceric ion was used for the determination of hydrogen peroxide. Pinacol was identified by a hydrogen-flame ionization detector using glycerol and PEG-6000 columns, and was determined from acetone obtained by the reaction with lead tetraacetate.[21]

Results

Deaerated 2-Propanol Aqueous Solutions Containing Hydrogen Peroxide.—Deaerated aqueous solutions containing various concentrations of hydrogen peroxide were irradiated and the amounts of hydrogen, acetone and hydrogen peroxide produced were determined. As for the organic product, only acetone was determined.

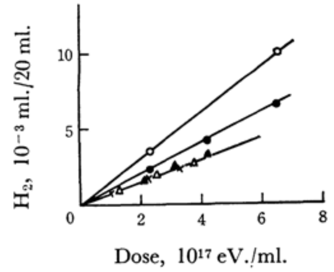

Fig. 1. Yields of H_2 in the radiolysis of deaerated aqueous solutions of 2.5×10^{-2} M 2-propanol containing various concentrations of H_2O_2 at pH 5.6.
[H_2O_2], ○ : 0, ● : 1.0×10^{-4} M,
△ : 5.0×10^{-4} M, ▲ : 1.0×10^{-3} M,
× : 2.4×10^{-3} M

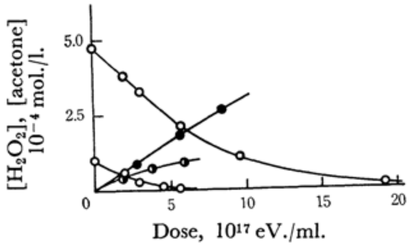

Fig. 2. Yields of acetone and disappearance of H_2O_2 in the radiolysis of deaerated aqueous solutions of 2.5×10^{-2} M 2-propanol containing H_2O_2 at pH 5.6.
○ : H_2O_2,
◑ : Acetone in 1×10^{-4} M H_2O_2 soln.
● : Acetone in 4.8×10^{-4} M H_2O_2 soln.

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[6] J. T. Allan and G. Scholes, *Nature*, **187**, 218 (1960).

[7] E. Collinson, F. S. Dainton, D. R. Smith and S. Tazuké, *Proc. Chem. Soc.*, 140 (1962).

[8] G. Czapski and A. O. Allen, *J. Phys. Chem.*, **66**, 262 (1962).

[9] J. Rabani, *J. Am. Chem. Soc.*, **84**, 868 (1962).

[10] J. Rabani and G. Stein, *J. Chem. Phys.*, **37**, 1865 (1962).

[11] J. T. Allan and C. M. Beck, *J. Am. Chem. Soc.*, **86**, 1483 (1964).

[12] J. T. Allan, *J. Phys. Chem.*, **68**, 2697 (1964).

[13] G. E. Adams, J. W. Boag and B. D. Michael, *Trans. Faraday Soc.*, **61**, 492 (1965).

[14] E. Hayon, ibid., **61**, 723 (1965).

[15] G. Czapski and H. A. Schwalz, *J. Phys. Chem.*, **66**, 471 (1962).

[16] E. J. Hart and J. W. Boag, *J. Am. Chem. Soc.*, **84**, 4090 (1962).

[17] J. P. Keene, *Nature*, **197**, 47 (1963).

[18] S. Berntsson, *Anal. Chem.*, **28**, 1337 (1956).

[19] F. D. Snell and C. T. Snell, "Colorimetric Method of Analysis," Vol. II, D. Van Nostrand Co., New York (1961), p. 802.

[20] A. O. Allen, C. J. Hochanadel, J. A. Ghormley and J. W. Paris, *J. Phys. Chem.*, **56**, 575 (1952).

[21] E. Bear, J. M. Grosheintz and H. O. L. Fischer, *J. Am. Chem. Soc.*, **61**, 1384 (1939).

The formation of hydrogen is linear with the dose, as is shown in Fig. 1. Figure 2 shows the plots of the production of acetone and the disappearance of hydrogen peroxide versus the dose. They are dependent on the hydrogen peroxide concentration below 1×10^{-4} M. The variations in G-values with hydrogen peroxide concentration are given in Fig. 3. As the hydrogen peroxide concentration increases, the hydrogen yield decreases and the yields of acetone formation and of the disappearance of hydrogen peroxide increase, while at higher concentrations of hydrogen peroxide, these yields reach constant values. The constant $G(H_2)$ is 1.06±0.02, a value which is in agreement with the results obtained by Allan et al.[6,11] and Stein et al.[10]

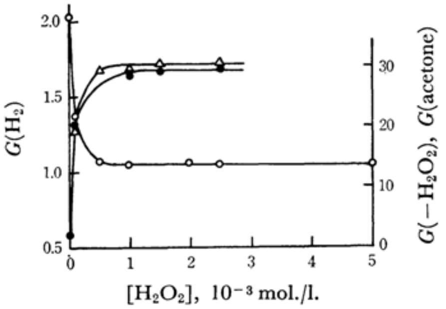

Fig. 3. Effects of H_2O_2 concentration on $G(H_2)$, G(acetone) and $G(-H_2O_2)$ in the radiolysis of deaerated aqueous solutions of 2.5×10^{-2} M 2-propanol at pH 5.6.

○: H_2, ●: acetone, △: $-H_2O_2$

Deaerated 2-Propanol Aqueous Solutions Containing Potassium Nitrate.—The deaerated 2-propanol aqueous solutions containing nitrate ions were irradiated under various conditions, and the amounts of hydrogen, nitrite ion, acetone, pinacol and hydrogen peroxide produced were determined.

The formations of the H_2, NO_2^- and $(CH_3)_2CO$ are linear with the dose up to 2.5×10^{17} eV./ml. Above this dose, however, the rate of nitrite ion formation becomes slightly slower. The initial yields were obtained from the slopes of the straight lines.

The effects of potassium nitrate, 2-propanol and pH on the yields of hydrogen, nitrite ion and acetone are shown in Fig. 4 and in Tables I and II.

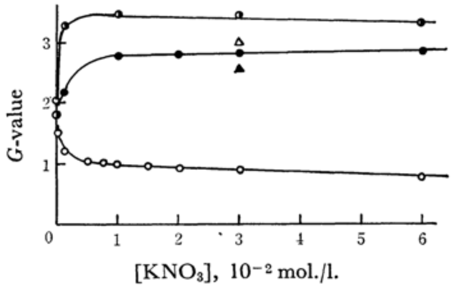

Fig. 4. Effects of KNO_3 concentration on $G(H_2)$, $G(NO_2^-)$ and G(acetone) in the radiolysis of deaerated aqueous solutions of 2×10^{-2} M 2-propanol at pH 5.6.

○: H_2, ●: NO_2^-, ◑: acetone, ▲: NO_2^- in aerated, △: acetone in aerated

TABLE I. EFFECTS OF 2-PROPANOL CONCENTRATION ON $G(NO_2^-)$ IN THE RADIOLYSIS OF DEAERATED SOLUTIONS OF 1×10^{-2} M KNO_3 AT pH 5.6

2-Propanol concn., M	$G(NO_2^-)$
2×10^{-2}	2.80±0.02
4×10^{-2}	2.81±0.02
6×10^{-2}	2.77±0.02
10×10^{-2}	2.77±0.03

TABLE II. EFFECTS OF pH ON $G(H_2)$, $G(NO_2^-)$ AND G(acetone) IN THE RADIOLYSIS OF DEAERATED SOLUTIONS OF 2×10^{-2} M 2-PROPANOL AND 1×10^{-2} M KNO_3

pH	$G(H_2)$	$G(NO_2^-)$	G(acetone)
3.0	1.25±0.02	1.39±0.01	4.5±0.2
4.0		2.45±0.02	3.8±0.2
5.0	1.00±0.02	2.77±0.02	3.6±0.2
5.6	1.02±0.02	2.80±0.04	3.5±0.1
6.5—6.7	1.02±0.02	2.80±0.02	3.4±0.1
7.3		2.80±0.02	3.4±0.1
9.5	1.00±0.02	2.79±0.05	3.4±0.1
11	0.99±0.03	3.36±0.08	

pH 3—5, $KNO_3=2\times10^{-2}$ M

As the potassium nitrate concentration increases, the hydrogen yield decreases from 2.05 to 0.79 at the nitrate concentration of 6×10^{-2} M, while, on the other hand, the nitrite yield increases from 2.20 to 2.89. The acetone yield increases sharply at first and then decreases slowly. At the constant concentration of nitrate of 1×10^{-2} M, the nitrite yield slightly decreases with an increase in the amount of 2-propanol and reaches a constant value at 2.77±0.03. These yields are independent of the pH from 5.6 to 9.5; at pH 11 the nitrite yield shows a higher value, below pH 5.0 it shows a lower value, and the hydrogen and acetone yields decrease with an increase in the pH. The nitrite yield also decreases in the presence of such other electron scavengers as oxygen and acetone as is shown in Fig. 4 and Table III. The hydrogen peroxide

TABLE III. EFFECTS OF ACETONE CONCENTRATION ON $G(H_2)$ AND $G(NO_2^-)$ IN THE RADIOLYSIS OF DEAERATED SOLUTIONS OF 2×10^{-2} M 2-PROPANOL AND 1×10^{-2} M KNO_3 AT pH 5.6

$(CH_3)_2CO$, M	$G(H_2)$	$G(NO_2^-)$
0	1.02±0.02	2.80±0.04
2.8×10^{-3}		2.20±0.03
4.3×10^{-3}		2.03±0.05
8.5×10^{-3}	1.00±0.03	1.58±0.01

yield is plotted as a function of the dose in Fig. 5. It is very low in the absence of nitrate ions, but in the presence $G(H_2O_2)=0.5$. Pinacol and acetone are detected in the absence of nitrate ions by means of a hydrogen-flame ionization detector, whereas in solutions containing nitrate ions, pinacol can not be detected. The formation of pinacol is shown in Fig. 6, from which the yield is found to be about 0.2.

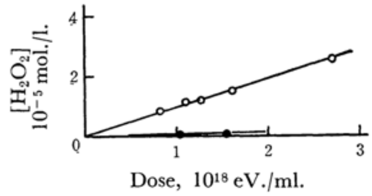

Fig. 5. Yields of H_2O_2 in the radiolysis of deaerated aqueous solutions of 2×10^{-2} M 2-propanol at pH 5.6.

●: KNO_3 not added, ○: KNO_3 1×10^{-2} M

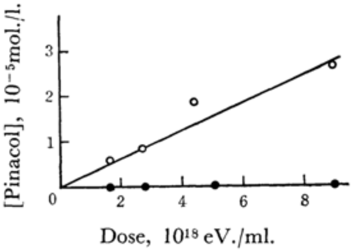

Fig. 6. Yields of pinacol in the radiolysis of deaerated aqueous solutions of 2×10^{-2} M 2-propanol at pH 5.6.

○: KNO_3 not added, ●: KNO_3 1×10^{-2} M

Discussion

Deaerated 2-Propanol Aqueous Solutions Containing Hydrogen Peroxide.—The radiolysis of water can be expressed as follows:

$$H_2O \rightsquigarrow H,\ e^-_{aq},\ OH,\ H_2,\ H_2O_2, \tag{1}$$

In the presence of 2-propanol, H atoms and OH radicals react with the solute, mainly according to 2 and 3:

$$(CH_3)_2CHOH + H \rightarrow (CH_3)_2COH + H_2 \tag{2}$$

$$(CH_3)_2CHOH + OH \rightarrow (CH_3)_2COH + H_2O \tag{3}$$

The rate constant for the reaction of the H atom with 2-propanol is 2×10^7 M^{-1} sec^{-1},[22] and that of OH is 1.74×10^9 M^{-1} sec^{-1}.[23] Acetone is formed by the following reactions:[10,11]

$$(CH_3)_2COH + H_2O_2 \rightarrow (CH_3)_2CO + OH + H_2O \tag{4}$$

$$2(CH_3)_2COH \rightarrow (CH_3)_2CO + (CH_3)_2CHOH \tag{5}$$

Dimerization was also suggested by Stein et al.[10] as the possible disappearance reaction of the organic radical.

It is well known that hydrogen peroxide is a good electron scavenger. In the presence of hydrogen peroxide, it reacts with the hydrated electron in competition with the hydrogen ions:

$$H_2O_2 + e^-_{aq} \rightarrow OH + OH^- \tag{6}$$

$$H^+ + e^-_{aq} \rightarrow H \tag{7}$$

Both reactions, 6 and 7, are very fast; the rate constants of these reactions have been determined by Hart et al.[24] to be 1.2×10^{10} M^{-1} sec^{-1} and 2.3×10^{10} M^{-1} sec^{-1} respectively. On the other hand, hydrogen peroxide reacts with the hydrogen atom and the hydroxyl radical according to:

$$H_2O_2 + H \rightarrow OH + H_2O \tag{8}$$

$$H_2O_2 + OH \rightarrow HO_2 + H_2O \tag{9}$$

Both reactions, however, are relatively slow, and the rate constants, k_8 and k_9, are 4×10^7 [25] and 4.5×10^7 M^{-1} sec^{-1} [26] respectively. Therefore, the reactions 7, 8 and 9 can be ignored in systems which contain 2-propanol of 2.5×10^{-2} M and hydrogen peroxide of the 1×10^{-3} M-5×10^{-3} M range, and the hydrogen yield can be expressed by the following equation:

$$G(H_2) = G_{H_2} + G_H \tag{10}$$

The yield of the hydrogen atom, G_H, in the radiolysis of water can be calculated from the values of the total hydrogen yield, $G(H_2)$, and the molecular yield of hydrogen, G_{H_2}. From the results of Fig. 3, G_H is caluculated to be 0.61 ± 0.02 by using the value of $G_{H_2}=0.45$.[27,28]

The G values of acetone formation and of the disappearance of hydrogen peroxide are higher in the presence of higher concentrations of hydrogen peroxide. It seems that the chain reactions 3 and 4 occur, as suggested by Rabani et al.[10] The decrease in the rates of acetone formation and of hydrogen peroxide disappearance in the dilute solutions of hydrogen peroxide may be due to the competition of the reactions 4 and 5.

Deaerated Aqueous 2-Propanol Solutions Containing Potassium Nitrate.—*Hydrogen Yield.*—It is known that nitrate ion is a good electron scavenger; the rate constant of the scavenging was found by Hart et al.[29] to be 1.1×10^{10} M^{-1} sec^{-1}.

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[22] $k(H+NO_3^-)=1\times10^7$ M^{-1} sec^{-1} (G. Navon and G. Stein, *J. Phys. Chem.*, **69**, 1384 (1965)), k(H+2-propanol)/$k(H+NO_3^-)$ =2 (Ref. 31).

[23] J. K. Thomas, *Trans. Faraday Soc.*, **61**, 702 (1965).

[24] S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani and J. K. Thomas, *Discussions Faraday Soc.*, **36**, 193 (1963).

[25] J. K. Thomas, *J. Phys. Chem.*, **67**, 2593 (1963).

[26] H. A. Schwarz, ibid., **66**, 255 (1962).

[27] A. O. Allen, "The Radiation Chemistry of Water and Aqueous Solutions," D. Van Nostrand Co., New York (1961).

[28] T. Sawai, Y. Shinozaki and G. Meshitsuka, *Tokyo Metropolitan Isotope Res. Center, Ann. Report*, **3**, 65 (1964).

[29] J. K. Thomas, S. Gordon and E. J. Hart, *J. Phys. Chem.*, **68**, 1524 (1964).

The nitrate ion is reduced to the nitrite ion by reaction with the hydrated electron, but the details are not clear:

$$e^-_{aq} + NO_3^- \rightarrow NO_2^- \qquad (11)$$

The hydrated electron reacts also with the hydrogen ion to give the H atom (reaction 7). In the presence of higher concentrations of nitrate ions, on the other hand, the reaction of the H atom with NO_3^- should be considered. It has been proposed that the H atom reduces the nitrate ion to the nitrite ion by the reactions 12 and 13:30)

$$H + NO_3^- \rightarrow NO_2 + OH^- \qquad (12)$$

$$2NO_2 + H_2O \rightarrow NO_3^- + NO_2^- + 2H^+ \qquad (13)$$

The decrease in $G(H_2)$ with an increase in the nitrate ion concentration (Fig. 4) can be explained by the competition of the reactions 7, 11, 2 and 12.

The hydrogen yield in this system will be given by:

$$G(H_2) = G_{H_2} + \left(G_H + Ge^-_{aq}\frac{k_7[H^+]}{k_7[H^+]+k_{11}[NO_3^-]}\right) \times \frac{k_2[ROH]}{k_2[ROH]+k_{12}[NO_3^-]} \qquad (14)$$

In the range of $k_7[H^+] \ll k_{11}[NO_3^-]$,

$$G(H_2) = G_H + \frac{G_H}{1+\dfrac{k_{12}[NO_3^-]}{k_2[ROH]}} \qquad (15)$$

According to the Eq. 15, $G(H_2)$ is plotted versus $(G(H_2) - G_{H_2})[NO_3^-]/[ROH]$ in Fig. 7. A straight line is obtained, and from the intercept $G_H + G_H$ is found to be 1.06±0.03, a value in good agreement with the results in the 2-propanol-hydrogen peroxide system. The ratio of the rate constants, k_{12}/k_2, is also calculated from the slope to be 0.18; this value is a little lower than the value, 0.5, given by Scholes et al.31)

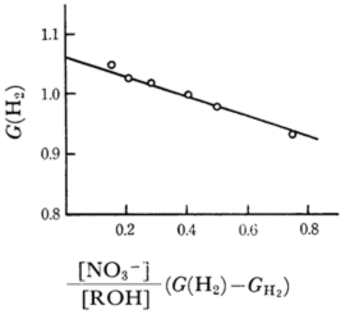

Fig. 7. Dependences of KNO_3 concentration on $G(H_2)$ in the radiolysis of deaerated aqueous solutions of 2×10^{-2} M 2-propanol at pH 5.6.

Nitrite Yield.—The radiolysis of aqueous nitrate solutions has been studied, but the reaction mechanisms are not clear.30,32,33) As for the reaction of the hydrated electron with the nitrate ion, the following reactions, 16 and 17, have been examined:

$$e^-_{aq} + NO_3^- \rightarrow NO_2 + 2OH^- \qquad (16)$$

$$e^-_{aq} + NO_3^- \rightarrow NO_2^- + OH + OH^- \qquad (17)$$

If the reaction 16 is predominant, $G(NO_2^-)$ has to be approximately equal to 1/2 Ge^-_{aq}. However, the present result shows $G(NO_2^-) = 2.8$, which is near the reported values of Ge^-_{aq} instead of half of them. From the studies of the radiolysis of sodium nitrate ice, Kevan34) has shown that NO_2 is not formed via a reaction with the electron. If a nitrite ion is produced directly by the reaction 17, the increase in $G(H_2)$ and the decrease in $G(NO_2^-)$, with the decrease in pH equal one other. As Table II shows, however, this is not the case.

As possible reactions, the followings were suggested by Allan:12)

$$e^-_{aq} + NO_3^- \rightarrow NO_3^{2-} \qquad (18)$$

$$NO_3^{2-} + (CH_3)_2COH \rightarrow (CH_3)_2CO + NO_2^- + OH^- \qquad (19)$$

The NO_3^{2-} radical ion has been tentatively identified by electron paramagnetic resonance studies of the radical species produced in the irradiated potassium nitrate crystal.35)

In neutral solutions containing high concentrations of 2-propanol and nitrate ions, all hydrated electrons are scavenged by nitrate ions and the reaction 12 can be ignored; $G(NO_2^-)$ is equal to Ge^-_{aq}, on the basis of the reactions 18 and 19. From the results noted in Table I, the value of the hydrated electron yield is given as $Ge^-_{aq} = 2.77 \pm 0.03$, which is in good agreement with the finding of Allan et al.11,12) $G(NO_2^-)$ does not change with the pH value from 5.0 to 9.5; therefore, Ge^-_{aq} is constant in this pH range. The changes in $G(NO_2^-)$ with the variation in the nitrate ion concentration is about half that of $G(H_2)$, as is shown in Table IV. The nitrite ion formation by the

TABLE IV. EFFECTS OF KNO_3 CONCENTRATION ON $\Delta G(NO_2^-)$ AND $-\Delta G(H_2)$ IN THE RADIOLYSIS OF DEAERATED SOLUTIONS OF 2×10^{-2} M 2-PROPANOL AT pH 5.6

KNO_3 concn., M	$\Delta G(NO_2^-)$	$-\Delta G(H_2)$
1.0×10^{-2}	0	0
1.5×10^{-2}		0.02
2.0×10^{-2}	0.03	0.07
3.0×10^{-2}	0.05	0.10
6.0×10^{-2}	0.09	0.23

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30) J. Bednar, "Proc. Titany Symposium Rad. Res. Chem.," Akademiai Kiado, Budapest (1964), p. 325.

31) A. Appleby, G. Scholes and M. Simic, *J. Am. Chem. Soc.*, **85**, 2891 (1963); G. Scholes and M. Simic, *J. Phys. Chem.*, **68**, 1738 (1964).

32) H. A. Mahlman and J. W. Boyle, *J. Chem. Phys.*, **27**, 1434 (1957).

33) H. A. Mahlman, ibid., **32**, 601 (1960).

34) L. Kevan, *J. Phys. Chem.*, **68**, 2590 (1964).

35) J. Cunningham, ibid., **66**, 972 (1962).

reaction of the H atom with nitrate may arise via the reactions 12 and 13.

In the presence of acetone, $G(NO_2^-)$ decreases by the following competitive reactions:

$$e^-_{aq} + NO_3^- \rightarrow NO_3^{2-} \qquad (18)$$

$$e^-_{aq} + (CH_3)_2CO \rightarrow (CH_3)_2CO^- \qquad (20)$$

In terms of the reaction kinetics, the yield of nitrite is written as follows:

$$G(NO_2^-) = Ge^-_{aq}\frac{k_{18}[NO_3^-]}{k_{18}[NO_3^-]+k_{20}[R_2CO]} + 1/2\, G_H\frac{k_{12}[NO_3^-]}{k_{12}[NO_3^-]+k_2[ROH]} \qquad (21)$$

By introducing the numerical values of $G_H=0.6$, $k_{12}/k_2=0.18$, $[NO_3^-]=1.0\times 10^{-2}$ M, and $[ROH]=2.0\times 10^{-2}$ M, one can obtain the following relation:

$$\frac{1}{G(NO_2^-)-0.02} = \frac{1}{Ge^-_{aq}}1+\left(\frac{k_{20}[R_2CO]}{k_{18}[NO_3^-]}\right) \qquad (22)$$

In Fig. 8, $1/G(NO_2^-)-0.02$ is plotted as a function of $[R_2CO]$, and $G(NO_2^-)$ and k_{20}/k_{18} are found from the intercept and the slope of the straight line to be 2.8 and 0.78 respectively. The ratio of the rate constants, k_{20}/k_{18}, is in agreement with the results obtained using the pulse radiolysis technique.[36,37]

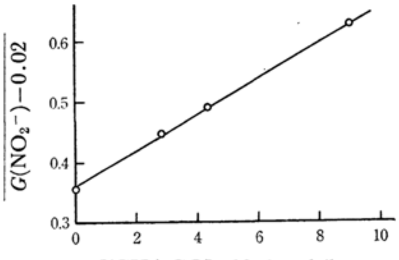

Fig. 8. Variations of $G(NO_2^-)$ with $(CH_3)_2CO$ concentration in the radiolysis of deaerated aqueous solutions of 2×10^{-2} M 2-propanol, 1×10^{-2} M KNO_3.

Acetone Yield.—In the potassium nitrate 1×10^{-2} M-2-propanol 2×10^{-2} M system, all the H atom and OH radicals react with 2-propanol to give organic radicals, and all the hydrated electrons are scavenged by nitrate ions. The yield of hydrogen peroxide is slightly lower than that of the molecular hydrogen peroxide in water radiolysis (Fig. 5); the results of Fig. 6 indicate that the dimerization of organic radicals can be neglected.

The mechanisms of the acetone formation can be written as follows:

$$(CH_3)_2COH + NO_3^{2-} \rightarrow (CH_3)_2CO + NO_2^- + OH^- \qquad (19)$$

$$(CH_3)_2COH + H_2O_2 \rightarrow (CH_3)_2CO + OH + H_2O \qquad (4)$$

$$2(CH_3)_2COH \rightarrow (CH_3)_2CO + (CH_3)_2CHOH \qquad (5)$$

On the basis of the reactions, 2, 3, 4, 5 and 19, G(acetone) is given by:

$$\begin{aligned} G(\text{acetone}) &= G(NO_2^-)+G_{H_2O_2}-G(H_2O_2)+ \\ &\quad 1/2[G_H+G_{OH}+G_{H_2O_2}-(G(NO_2^-)+ \\ &\quad G_{H_2O_2}-G(H_2O_2))] \\ &= 1/2[G(NO_2^-)+G_H+G_{OH}] \\ &\quad +G_{H_2O_2}-G(H_2O_2) \end{aligned} \qquad (23)$$

By using the numerical values of $G_{H_2O_2}-G(H_2O_2)=0.2$, $G(NO_2^-)=2.8$, $G_H=0.6$ and $G(\text{acetone})=3.4$, G_{OH} can be calculated from Eq. 23 to be 3.0.

Radical Yields.—From the radiolysis of the deaerated neutral solutions of 2-propanol containing hydrogen peroxide or potassium nitrate, the primary radical yields have been obtained:

$$G_{OH}=3.0,\ Ge^-_{aq}=2.77\pm 0.03,$$
$$G_H=0.61\pm 0.03$$

These values are relatively high. Recently Hayon[14] obtained $G_{OH}=2.25$, $Ge^-_{aq}=2.3$ and $G_H=0.55$ from the radiolysis of dilute solutions containing various solutes, and suggested that the radical scavenger concentration was important in the measurement of the radical yields. Since relatively higher concentrations of scavengers were used in the present experiments, the higher values obtained may be due to reactions similar to those postulated by Dainton et al.[38] to account for the increase in radical yields at high and low pH values:

$$(H_2O^+ + H_2O^-) + NO_3^- \rightarrow NO_3^{2-} + OH + H^+ + H_2O \qquad (24)$$

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