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γ-Radiolysis of a Binary Mixture of Methanol and Water. The Formation of Formaldehyde in the Radiolysis of Liquid Methanol

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The γ radiolysis of a binary mixture of methanol and water over a wide concentration range has been investigated. The observed yields of products are expressed as a linear function of the electron fraction of methanol in the mixture. The yields of molecular hydrogen were also determined. Analyzing the results on reasonable assumptions, one could obtain for neutral water, $G^{\mathrm{w}}_{e^-_s}=2.3—2.5$ and $G^{\mathrm{w}}_{\mathrm{OH}}\geq 2.6$. It was concluded that, in the radiolysis of methanol, formaldehyde may be produced through the decomposition of CH_2OH radicals in the spur region, not by the disproportionation of these radicals.

Liquid methanol and water have been long-term subjects of the most extensive study in radiation chemistry, with plenty of information being accumulated, especially for water.[1,2] The radiolysis of liquid methanol is more complicated than that of water and there remain some unsolved problems.

This work was initiated with the hope of obtaining more detailed information about reactions involving the initial species produced in irradiated methanol using precise data on aqueous systems. Although methanol is frequently used as a radical scavenger in the radiolysis of water, few studies on binary mixtures over a wide concentration range have been reported so far.[3,4]

We obtained some interesting results not only on the radiolysis mechanism of methanol but also on that of water, which will be presented in this paper.

Experimental

Extra-pure grade methanol supplied by the Wako Pure Chemical Co. was purified and dried as described previously.[5] Reagent grade anhydrous ferric chloride was used (as a scavenger) without further purification. Water was triply distilled according to Allen's description.[1]

A definite amount of purified water was pipetted into an irradiation ampoule and degassed thoroughly on a vacuum line before adding degassed methanol by distillation. Methanol-water mixtures containing ferric chloride were prepared beforehand and degassed in a small refluxing apparatus.

Irradiation ampoules were made of hard or Pyrex glass and were cleaned carefully as described previously.[5] Irradiation was carried out at room temperature with ^{60}Co γ rays at a dose rate in the vicinity of 1.5×10^{17} eV/$ml\cdot$min based on a ferrous sulfate dosimeter taking $G(\mathrm{Fe(III)})=15.5$. The dose rate was corrected for the electron density of each mixture.

The radiolysis products, hydrogen, carbon monoxide, methane, ethylene glycol and formaldehyde, were determined by methods previously used.[5] Hydrogen peroxide was determined by the Ghormely method.[6]

Results

Yields of Products. In Fig. 1 the observed yields of the main products, hydrogen, ethylene glycol and formaldehyde, were plotted as a function of the electron fraction of methanol, x, in the mixture. $G(H_2)$, $G(C_2H_6O_2)$ and $G(CH_2O)$ all appear to decrease linearly with increasing concentration of water, the yields for pure methanol being determined as 4.92, 2.95 and 2.15, respectively. (The symbol, G, is the yield as expressed by the number of molecules produced per 100eV of absorbed energy.) It should be noted that the extrapolated $G(CH_2O)$ to $x=0$ is not zero but 0.60. No hydrogen peroxide was detected for all mixtures investigated. Several separate experiments definitely indicated that no hydrogen peroxide was present even immediately after irradiation.[7] The yields of carbon monoxide and methane also show a linear dependence, the extrapolated G values to $x=0$ being zero (not shown in Fig. 1).

The observed yields can be expressed by such

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

[2] A. O. Allen, *Radiat. Res., Suppl.* **4**, 54 (1964).

[3] W. R. McDonell, *J. Chem. Phys.*, **23**, 208 (1955).

[4] Z. Schweiner, I. Janocský and J. Bednář, *Coll. Czech. Chem. Commun.*, **31**, 43 (1966).

[5] H. Seki and M. Imamura, *J. Phys. Chem.*, **71**, 870 (1967).

[6] C. J. Hochanadel, *ibid.*, **56**, 587 (1952).

[7] This series of experiments was carried out by Miss R. Maki.

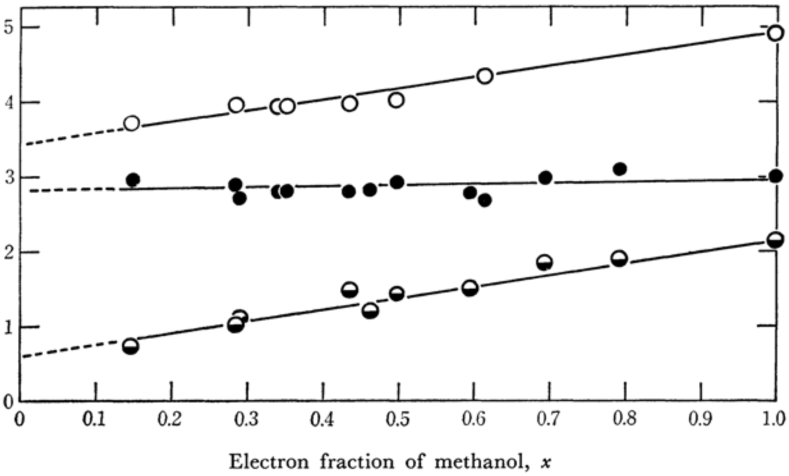

Fig. 1. Yields of hydrogen (○), ethylene glycol (●) and formaldehyde (◒) in methanol-water mixtures irradiated with γ rays.

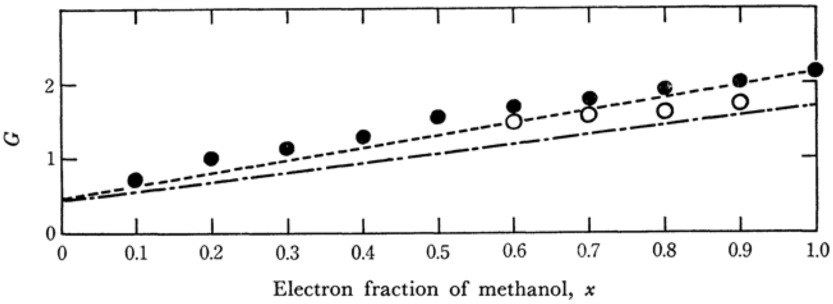

Fig. 2. Yields of the total gas (●) and hydrogen (○) in methanol-water mixtures containing 5×10^{-2} M $FeCl_3$.
----: the line connecting $G^{w}_{H_2}$ and $G_{H_2}+G_{CO}+G_{CH_4}$
·—·: the line connecting $G^{w}_{H_2}$ and G_{H_2}

linear functions of x as

$$G(H_2) = 1.52x + 3.40 \quad (A)$$

$$G(C_2H_6O_2) = 0.15x + 2.80 \quad (B)$$

$$G(CH_2O) = 1.55x + 0.60 \quad (C)$$

Yields of Molecular Hydrogen. The yield of molecular (unscavengeable) hydrogen, G_{H_2}, from γ-irradiated liquid methanol has been determined as 1.6,[8] 1.8[9] and 1.9.[10] We also determined G_{H_2} to be 1.7, using ferric chloride as a scavenger, in good agreement with published data. The yields of molecular methane and carbon monoxide were determined at the same time. Their sum is about 0.3, in agreement with the result of Choi and Lichtin.[10]

The yield of total gas as well as that of hydrogen was also determined for methanol-water mixtures containing 5×10^{-2}M of ferric chloride. The yields are plotted in Fig. 2 as a function of x. Although the plots are not linear, the extrapolated values are very close to the yield of molecular hydrogen from water, $G^{w}_{H_2}$,[11] at $x=0$, and close to the total yield of the molecular gases from methanol, $G_{H_2}+G_{CO}+G_{CH}$, and G_{H_2} at $x=1$. These results apparently indicate that the formation of molecular hydrogen from methanol or water is not prevented at all by the presence of water or methanol, respectively.

Discussion

As early as 1955, McDonell reported the γ radiolysis of methanol-water mixtures, in which only the yields of ethylene glycol and formaldehyde were determined.[3] The variations in yields are similar to the present ones, but there are some differences.

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[8] J. H. Baxendale and F. W. Mellows, *J. Am. Chem. Soc.*, **83**, 4720 (1961).

[9] G. E. Adams and J. H. Baxendale, *ibid.*, **80**, 4125 (1958).

[10] S. U. Choi and N. N. Lichtin, *ibid.*, **86**, 3948 (1964).

[11] $G^{w}_{H_2}=0.4$ in Ref. 2 and 0.4—0.45 in Proc. 5th Informal Conf. Radiation Chemistry of Water (Univ. Notre Dame 1966), p. 27.

The variation in $G(C_2H_6O_2)$ is linear from 100% methanol ($G=2.9$) down to 30%, the linear portion of the curve to 100% water being extended $G=2.5$. The variation in $G(CH_2O)$ is also linear over the entire range. However, the yield for pure methanol is $G=1.3$ and the extrapolated yield to 100% water is zero.

Recently Schweiner *et al.* observed non-linear variation in $G(H_2)$ for methanol-water mixtures.[4] They assumed that the probability of localization of part of the absorbed energy, leading to hydrogen formation from methanol is higher for a methanol molecule than for a water molecule. No such a deviation from linearity is observed for $G(H_2)$ as well as for other yields in the present study (Fig. 1). The slight deviation observed for G_{H_2} (Fig. 2) might be due, at least in part, to some effect of the relatively high concentration of ferric chloride used, no further discussion being given here.

Equations (A), (B) and (C) could be analyzed on the reasonable assumptions described below.

Hydrogen Yield. Hydrogen is formed by three processes: molecular, ionic and radical processes. Molecular hydrogen is formed separately from methanol and water, the yields of which are represented as G_{H_2} and $G^{w}_{H_2}$, respectively. As mentioned in Results (Fig. 2). G_{H_2} and $G^{w}_{H_2}$ are not affected by the presence of water and methanol, respectively. The independent of $G^{w}_{H_2}$ of the presence of methanol is also supported by results from the radiolysis of aqueous solutions of CD_3OH (0.01—1.0 M).[12] Similar results were obtained in the radiolysis of 2-propanol solutions in D_2O containing nitrous oxide, in which $G(D_2)$ was found constant (0.33) over the concentration range 0.01—1.0 M 2-propanol.[13]

Irradiation of methanol and water produces both solvated electrons and hydrogen atoms. The solvated electrons which arise from methanol and water are assumed to form hydrogen atoms through Reactions (1)—(3).

$$e^-_{solv} + CH_3OH_2^+ \rightarrow H\cdot + CH_3OH \qquad (1)$$

$$e^-_{solv} + CH_3OH \rightarrow H\cdot + CH_3O^- \qquad (2)$$

$$e^-_{solv} + H_3O^+ \rightarrow H\cdot + H_2O \qquad (3)$$

Protonated methanol, $CH_3OH_2^+$, is assumed to form through an ion-molecule reaction similar to that in the gas phase.

$$\begin{aligned} &CH_3OH^+ + CH_3OH \rightarrow \\ &\qquad CH_3OH_2^+ + CH_3O\cdot,\ CH_2OH\cdot \qquad (4)\end{aligned}$$

The hydrogen atoms produced directly both from methanol and water, and indirectly through Reactions (1)—(3) abstract hydrogen atoms from methanol to form hydrogen.

$$CH_3OH + H\cdot \rightarrow H_2 + CH_2OH\cdot \qquad (5)$$

Reactions (1) and (2) have been assumed to take place by Baxendale and Mellows,[8] the former being commonly accepted as the principal reaction of the solvated electron in liquid methanol. Reaction (2) has sometimes also been assumed to be the principal reaction.[14] Although the rate constant of Reaction (2) is less than $10^4\ M^{-1}\ sec^{-1}$,[15] this reaction may become more or less important in the high concentration range of methanol studied.

These assumptions lead to the expression for the yield of hydrogen from the mixtures

$$\begin{aligned} G(H)_2 &= x(G_{H_2} + G_{e^-_s} + G_H) \\ &\quad + (1-x)(G^{w}_{H_2} + G^{w}_{e^-_s} + G^{w}_{H}) \\ &= x(G_{H_2} + G_{e^-_s} + G_H - G^{w}_{H_2} - G^{w}_{e^-_s} - G^{w}_{H}) \\ &\quad + (G^{w}_{H_2} + G^{w}_{e^-_s} + G^{w}_{H}) \qquad (a)\end{aligned}$$

Here, the primary yields with superscript w refer to water, those without w to methanol.

Comparison of Eq. (a) with Eq. (A) gives the relations

$$G_{H_2} + G_{e^-_s} + G_H = 4.92 \qquad (i)$$

$$G^{w}_{H_2} + G^{w}_{e^-_s} + G^{w}_{H} = 3.40 \qquad (ii)$$

The yield of molecular hydrogen from neutral water seems well-established at 0.4—0.45.[11] The primary yield of hydrogen atoms from neutral water has also been established at 0.55—0.65.[2,16,17] From Eq. (ii), therefore, the yield of hydrated electrons, $G^{w}_{e^-_s}$, is claculated to be 2.3—2.5.

The yield of hydrated electrons has repeatedly been reported. Czapski and Allen[18] reported 2.85, Allan and Beck[19] 2.80 and Sawai[20] 2.77. Lower values have also been reported: 2.65 by Rabani and Stein,[21] 2.6 by Hochanadel and Casey,[22] 2.45 by Head and Walker,[17] 2.3 by Scholes and Simic,[23] Hayon[24] and Seddon and Allen.[25] A recent study of Russell and Freeman

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12) R. Nagai and M. Imamura, to be published.

13) F. S. Dainton, A. R. Gibbs and D. Smithies, *Trans. Faraday Soc.*, **62**, 3170 (1966).

14) J. Teplý and A. Habersbergerová, *Coll. Czech. Chem. Commun.*, **32**, 1350 (1966). For ethanol, J. J. J. Myron and G. R. Freeman, *Can. J. Chem.*, **43**, 1484 (1965); J. W. Fletcher and G. R. Freeman, *ibid.*, **45**, 635 (1967).

15) M. Anbar and P. Neta, *Intern. J. Appl. Radiation Isotopes*, **18**, 493 (1967).

16) E. Hayon, *J. Phys. Chem.*, **68**, 1242 (1964).

17) D. A. Head and D. C. Walker, *Nature*, **207**, 517 (1965); *Can. J. Chem.*, **45**, 2051 (1967).

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

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

20) T. Sawai, This Bulletin, **39**, 955 (1966).

21) J. Rabani and G. Stein, *J. Chem. Phys.*, **37**, 1865 (1966).

22) C. J. Hochanadel and R. Casey, *Radiation Res.*, **25**, 198 (1965).

23) G. Scholes and M. Simic, *Nature*, **199**, 276 (1962).

24) E. Hayon, *Trans. Faraday Soc.*, **61**, 123 (1965).

25) W. A. Seddon and A. O. Allen, *J. Phys. Chem.*, **71**, 1914 (1967).

gave a "free ion" yield $G^{w}_{e_s^-}=2.7$ according to their model.[26] The current value of 2.3—2.5 for the yield of the hydrated electron is in agreement with those of the lower group. In the present study, however, a plausible reaction which lowers the yield can be taken into account,

$$e^-_{solv} + H_2O_2 \rightarrow OH\cdot + OH^- \qquad (6)$$

which might also be responsible for the absence of hydrogen peroxide in the system. Reaction (6) produces OH radicals, which consecutively give CH_2OH radicals through reaction with methanol. However, as will be discussed in a latter section, the majority of CH_2OH radicals do not give formaldehyde but ethylene glycol in the bulk. The excess yield of formaldehyde observed upon extrapolation of the plot of $G(CH_2O)$ to $x=0$ (Fig. 1) is not accounted for by Reaction (6). Thus the possibility of Reaction (6) may be excluded. The excess yield of formaldehyde will be explained in a latter section.

Equation (i) indicates that the total yield of hydrogen from pure methanol is 4.92, which is the experimental value and is less than the "true" value of 5.40 deduced from the methanol-nitrous oxide system.[5] The discrepacny between these two values has been discussed previously;[5] a few experiments show that the values of $G(H_2)+G(N_2)$ obtained from methanol-waterm ixtures containing nitrous oxide fall on the line connecting $G=5.4$ $(x=1)$ and 3.4 $(x=0)$.

Ethylene Glycol Yield. Ethylene glycol is produced, except for a minor portion by a molecular process, by a combination reaction of CH_2OH radicals

$$2CH_2OH\cdot \rightarrow C_2H_6O_2 \qquad (7)$$

Hydroxymethyl radicals are produced through the reaction of methanol with all radicals, R·, produced in the solution (H· (including H· produced by Reactions (1)—(3)), OH·, $CH_3\cdot$, $CH_3O\cdot$ and $CH_2OH\cdot$)

$$CH_3OH + R\cdot \rightarrow CH_2OH\cdot + RH \qquad (8)$$

It is sometimes assumed that some CH_2OH radicals give rise to the formation of formaldehyde through the disproportionation reaction

$$2CH_2OH\cdot \rightarrow CH_2O + CH_3OH \qquad (9)$$

On the basis of the assumptions made above, the yield of ethylene glycol in the present system can be expressed as

$$G(C_2H_6O_2) = x\left(G_{C_2H_6O_2} + \frac{\alpha}{2}G_R\right) + (1-x)\frac{\alpha}{2}(G^{w}_{e_s^-} + G^{w}_{H} + G^{w}_{OH})$$

$$= x\left[G_{C_2H_6O_2} + \frac{\alpha}{2}G_R - \frac{\alpha}{2}(G^{w}_{e_s^-} + G^{w}_{H} + G^{w}_{OH})\right] + \frac{\alpha}{2}\left(G^{w}_{e_s^-} + G^{w}_{H} + G^{w}_{OH}\right) \qquad (b)$$

The molecular yield of ethylene glycol from pure methanol, $G_{C_2H_6O_2}$, has been determined as 0.09[27]—0.1.[10] The factor, α, represents the fraction of CH_2OH radicals which produce ethylene glycol

$$\alpha = k_7/(k_7 + k_9)$$

The superscript w refers to water, as before.

Comparing Eq. (b) with Eq. (B), one obtains the relations

$$\alpha(G^{w}_{e_s^-} + G^{w}_{H} + G^{w}_{OH}) = 5.60 \qquad (iii)$$

$$\alpha G_R = 5.72 \qquad (iv)$$

In the preceding section, we came to the conclusion that $G^{w}_{e_s^-}=2.3-2.5$ depending upon the values of $G^{w}_{H_2}$ and G^{w}_{H}. It is easily found, however, that, from Eqs. (ii) and (iii),

$$G^{w}_{OH} \geq 2.6$$

because α should not exceed unity.

On the other hand, the total yield of radicals from methanol has been determined experimentally as 6.2,[10] which is in agreement with other results.[8] If the value of 6.2 is used for G_R in Eq. (iv), α is calculated to be 0.92. The rate-constant ratio of disproportionation to combination of CH_2OH radicals, k_9/k_7, is then 0.087.[28] Applying $\alpha=0.92$ to Eq. (iii), one obtains $G^{w}_{OH}=3.0$, which is higher than the value quoted by Allen ($G=2.2$).[2]

Daniels and Wigg[29] reported $G^{w}_{OH}=2.53\pm0.10$ for NO_3^- solution, and similar and higher values have also been reported by Hochanadel and Casey[22] (2.59 for $CO+H_2$ solution), by Seddon and Sutton[30] (2.9 for NO solution) and by Sawai[20] (3.0 for 2-propanol+NO_3^- solution). Although it is not possible to give a satisfactory account for the discrepancy at present, it should be emphasized that α is close to unity, *i. e.*, the contribution of the disproportionation reaction of CH_2OH radicals to the formation of formaldehyde is rather small.

Formaldehyde Yield. As described in Results, no hydrogen peroxide was detected in

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[26] J. C. Russell and G. R. Freeman, *J. Chem. Phys.*, **48**, 90 (1968).

[27] M. Imamura and H. Seki, *Sci. Papers Inst. Phys. Chem. Res.*, **59**, 146 (1965).

[28] No such a rate-constant ratio seems to have been reported for the CH_2OH radical, the results for several alkyl radicals being published. *Cf.*, J. A. Kerr and A. F. Trotman-Dickenson, "Progress in Reaction Kinetics," Vol. 1, ed. by G. Porter, Pergamon Press, Oxford (1961), p. 105; J. O. Terry and J. H. Futrell, *Can. J. Chem.*, **45**, 2327 (1967), and the papers cited therein. It is to be noted that k_9/k_7 has been assumed to be ≈ 0.2 for CH_2OH radicals in the aqueous medium. (P. Kelly and M. Smith, *J. Chem. Soc.*, **1961**, 1487).

[29] M. Daniels and E. E. Wigg, *Science*, **153**, 1533 (1966); *J. Phys. Chem.*, **71**, 1024 (1967).

[30] W. A. Seddon and H. C. Sutton, *Trans. Faraday Soc.*, **59**, 2323 (1963).

the present system. Similar results have been found for the deaerated neutral ethanol solution,[31] which was ascribed to the efficient secondary decomposition of hydrogen peroxide. In the present study, the extrapolated value of $G(CH_2O)$ to $x=0$ is 0.60 (Fig. 1), which is very close to the value for $G^{w}_{H_2O_2}$.[2] We therefore assume that this excess yield of formaldehyde results from the reaction of the CH_2OH radical with hydrogen peroxide produced molecularly from water.

$$CH_2OH\cdot + H_2O_2 \rightarrow CH_2O + H_2O + OH\cdot \quad (10)$$

A similar reaction has been suggested for C_2H_4OH radicals.[25] The occurrence of Reaction (10) does not reduce $G(C_2H_6O_2)$ because OH radicals will regenerate CH_2OH radicals.

An alternative explanation for the absence of hydrogen peroxide might be given by assuming reaction occurs between the precursor of molecular hydrogen peroxide and methanol. It does not seem that the precursor of molecular hydrogen peroxide in the radiolysis of water has been well-defined, some species other than OH radicals being proposed.[32,33] Such a reaction being assumed to occur, the possibility of OH radical being the precursor of molecular hydrogen peroxide can be excluded also from the fact that an excess yield of aldehyde is close to the value corresponding to $G^{w}_{H_2O}$. If OH radical is the precursor of molecular hydrogen peroxide, scavenging the radical with methanol in the spur region would give rise to the formation of a CH_2OH radical, most of which forms ethylene glycol as discussed in the preceding section. No further discussion on the nature of the precursor is given here.

Several reaction mechanisms for the formation of formaldehyde in the radiolysis of methanol have been discussed. Of possible mechanisms, the disproportionation reaction of CH_2OH radicals (Reaction (9)) has been ruled out as mentioned above. The disproportionation reaction of CH_3O radicals has also been proposed, especially to explain the increasing yield of formaldehyde in the radiolysis of liquid methanol by high LET (linear energy transfer) radiations[34,35]

$$2CH_3O\cdot \rightarrow CH_2O + CH_3OH \quad (11)$$

In fact, the isotopic composition of hydrogen produced by γ radiolysis of CH_3OD shows that $HD > H_2$,[36] indicating the primary yield of the CH_3O radical is greater than that of the CH_2OH radical. If Reaction (11) is responsible for the increasing yield of formaldehyde in the dense ionization tracks of the high LET radiations, the isotopic composition of the hydrogen produced in such systems should also show a tendency similar to that observed for γ radiolysis. This is not the case, but it was found that $H_2 > HD$ for radiolysis with recoiled α, ^{7}Li-particles.[36] Therefore, the second possibility as represented by Reaction (11) may be unimportant.

The remaining possibilities are molecular detachment[37,38]

$$CH_3OH \rightarrow CH_2O + H_2 \quad (12)$$

and thermal decomposition of CH_2OH radicals[37]

$$CH_2OH\cdot \rightarrow CH_2O + H\cdot \quad (13)$$

Both reactions have been proposed for the photolysis of methanol vapor. Phibbs and Darwent found that the activation energy of Reaction (13) is 29 kcal/mol, and pointed out that the reaction is increasingly important above 400°C.[37]

It may be reasonable, from the above discussions, to assume that in the radiolysis of liquid methanol, formaldehyde may be produced molecularly (in the spur region) by Reaction (13) and/or Reaction (12). The increasing yield of formaldehyde in radiolysis with high LET radiations may therefore be explained by assuming thermal spikes in these radiation tracks, which will promote Reaction (13) to produce formaldehyde in a higher yield. Similar processes have also been proposed by McDonell and Gordon.[39]

Now, the observed yield of formaldehyde can be expressed as

$$\begin{aligned} G(CH_2O) &= xG_{CH_2O} + (1-x)G^{w}_{X} \\ &= x(G_{CH_2O} - G^{w}_{X}) + G^{w}_{X} \end{aligned} \quad (c)$$

Here, G^{w}_{X} corresponds to $G^{w}_{H_2O_2}$, as mentioned above. From Eq. (C) and Eq. (c), the molecular yield of formaldehyde from pure methanol is 2.15.

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[31] G. G. Jayson, G. Scholes and J. Weiss, *J. Chem. Soc.*, **1957**, 1358.

[32] M. Anbar and I. Pecht, *J. Chem. Phys.*, **44**, 3635 (1966).

[33] G. Hughes and C. Willis, *Discussions Faraday Soc.*, **36**, 223 (1963).

[34] L. M. Theard and M. Burton, *J. Phys. Chem.*, **67**, 59 (1963).

[35] M. Imamura, S. U. Choi and N. N. Lichtin, *J. Am. Chem. Soc.*, **85**, 3565 (1963).

[36] H. Seki and M. Imamura, *J. Chem. Phys.*, **48**, 1866 (1968).

[37] M. K. Phibbs and B. deB. Darwent, *ibid.*, **18**, 495 (1950).

[38] R. P. Porter and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **81**, 2307 (1959); R. F. Pottie, A. G. Harrison and F. P. Lossing, *Can. J. Chem.*, **39**, 102 (1961).

[39] W. R. McDonell and S. Gordon, *J. Chem. Phys.*, **23**, 208 (1955).