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THE CHAIN FORMATION OF ALDEHYDES IN THE RADIOLYTIC OXIDATION OF ALIPHATIC ALCOHOLS

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Abstract—The effect of dose rate on the yields of aldehyde, hydrogen peroxide and hydrogen in oxygen-saturated methanol, ethanol, 1-propanol, 2-propanol and 1-butanol was studied. A reaction mechanism to explain the results is proposed and discussed. It is concluded that the viscosities of the various alcohols play an important role in determining the length of the chain reactions.

During an investigation of the γ-radiolysis of oxygen-saturated 1-propanol[1] it was found that the formation of the product propionaldehyde could not be adequately explained by considering only the molecular (G = 2.0) and radical (G = 4.8) yields.[2] In order to explain the high yield of this product obtained in oxygen-saturated 1-propanol, the occurrence of a short chain reaction was advanced. From the published literature it was concluded that this chain reaction was also operative, though to a lesser extent, in ethanol, but it was not unambiguously identified in methanol. It was thus of importance to establish whether the chain reaction also occurred in other aliphatic alcohols, and whether the structure or chain length of the various alcohols has an influence on the length of the chain reaction. We therefore decided to study the effect of dose rate on the yield of aldehyde formed in methanol, ethanol and 1-propanol, and to extend the study further to 2-propanol and 1-butanol.

EXPERIMENTAL

Materials. The alcohols were all Merck *pro analysi* quality and were further purified by fractionation on a Nester-Faust spinning-band column, retaining only middle fractions, after refluxing with 2,4-dinitrophenyl hydrazine for approximately two hours.

Irradiations. The oxygenated samples were irradiated by means of a Gammabeam 650 irradiator (Atomic Energy of Canada Limited). The dose rates, depending on the geometry of the sources, were determined by making use of the Fricke dosimeter, taking $G(Fe^{3+}) = 15.6$.

Analyses. The determination of hydrogen has been described elsewhere.[1] Formaldehyde was determined by the method of Bricker and Johnsen,[3] and hydrogen peroxide by the method of Eisenberg.[4] Acetaldehyde, propionaldehyde and butyraldehyde were determined by a modification of the 2,4-dinitrophenylhydrazone method of Johnson and Scholes.[5] Acetone was determined by gas chromatography employing a flame ionization detector and a 2 m × 3 mm stainless steel column packed with 10% XF 1150 on Chromosorb P. All products were determined in a region where they were independent of dose, and received a total dose of $\sim 10^{18}$ eV ml^{-1}. Each value represents the average of at least three determinations.

RESULTS

The alcohols methanol, ethanol, 1-propanol, 2-propanol and 1-butanol were irradiated at different dose rates and the yields of the corresponding aldehydes, hydrogen gas and hydrogen peroxide, which together form the major products of oxygen-saturated solutions, were determined. In the case of methanol all these products were found to be independent of dose rate between 2.6×10^{18} eV ml^{-1} min^{-1} and 1.4×10^{15} eV ml^{-1} min^{-1}. The following G values were found:

$$G(HCHO) = 3.5; \quad G(H_2O_2) = 3.4 \quad \text{and} \quad G(H_2) = 1.4.$$

The yields of hydrogen peroxide and hydrogen agree quite well with the values of 3.1 and 1.9 respectively, obtained by Choi and Lictin.[6] On the other hand, in the case of formaldehyde, a large discrepancy exists, as these authors obtained G(HCHO) = 10.1 at a dose rate of 1.07×10^{16} eV ml^{-1} min^{-1} and a total dose of 1.9×10^{18} eV ml^{-1}. Their results are, however, difficult to understand as a G value as high as 10 strongly suggests a chain reaction, but both the results of Hayon and Weiss[7] and the present detailed study indicate that the yield of formaldehyde is independent of dose rate.

In the case of 2-propanol the results of various workers are also at variance with each other. Hughes and Makada,[14] for example, found that although a chain reaction was responsible for the formation of acetone in oxygenated acid solution, there were no indications of such a reaction in neutral and alkaline solutions. On the other hand, the results of Radlowski and Sherman[11] revealed that in the oxidation of neutral 2-propanol by carbon tetrachloride, a sharp increase in G(acetone) took place when the solution was saturated with air and G values of over a hundred were obtained. Similarly, a chain reaction has been implicated in the formation of acetone in the oxidation of alkaline 2-propanol solutions by dialkylperoxide.[13] The work of Burchill and Ginns[10] has furthermore clearly shown that chain reactions do occur in the radiation-induced oxidation of neutral aqueous solutions of 2-propanol by hydrogen peroxide. The present results are consistent with those of both Sherman and Burchill and Ginns, and it would appear the Huges and Makada possibly did not study the reaction in neutral and alkaline solutions in great detail, since only two values are given in their paper (see Fig. 2 and Table IV of Ref. 14). The values of G(acetone) = 7 they do give

Table 1. Product yields in oxygen-saturated ethanol

Dose rate ($\times 10^{17}$ eV ml^{-1} min^{-1})	$G(CH_3CHO)$	$G(H_2O_2)$	$G(H_2)$
12.80	6.7	3.6	1.7
5.80	7.4	3.7	1.6
1.53	8.6	3.7	1.7
0.84	9.0	3.9	1.7
0.44	10.2	4.0	1.6
0.15	10.8	4.2	1.6
0.06	12.2	4.7	1.7

in their paper seem to indicate, however, that a chain reaction did in fact start to take place.

The yields of the major products obtained in ethanol, 1-propanol, 2-propanol and 1-butanol as a function of dose rate are given in Tables 1–4.

Table 2. Product yields in oxygen-saturated 1-propanol

Dose rate ($\times 10^{17}$ eV ml^{-1} min^{-1})	G(C_2H_5CHO)	G(H_2O_2)	G(H_2)
13.0	5.7	3.6	1.4
5.8	6.2	4.9	1.3
1.5	6.7	6.3	1.3
0.3	7.0	7.0	1.3
0.15	10.0	10.5	1.3
0.06	14.1	13.0	1.4

DISCUSSION

In the previous investigation of the radiolytic oxidation of 1-propanol, the high yield of propionaldehyde was explained by postulating a chain reaction, even though the effect of dose rate could not be studied due to the lack of a suitable radiation source. The present results clearly show that in all the alcohols studied, with the exception of methanol, the yields of aldehyde and hydrogen peroxide are to a greater or lesser extent dependent on the radiation intensity. We conclude, therefore, that chain reactions are responsible for the formation of these products and suggest the following mechanism to explain the results obtained in the aliphatic alcohols.

$$ROH \rightsquigarrow ROH^{+} + e^{-} \qquad (1)$$

$$ROH^{+} + ROH \longrightarrow ROH_2^{+} + \dot{R}OH + e \qquad (2)$$

$$e^{-} + ROH_2^{+} \longrightarrow ROH + H\cdot \qquad (3)$$

$$e^{-} + n\ ROH \longrightarrow e^{-}_{solv} \qquad (4)$$

$$e^{-}_{solv} + O_2 \longrightarrow O_2^{-} \qquad (5)$$

$$\cdot H + O_2 \longrightarrow HO_2\cdot \qquad (6)$$

$$HO_2\cdot \xrightleftharpoons{pK=4.8} H^{+} + O_2^{-} \qquad (7)$$

$$HO_2\cdot + ROH \longrightarrow \dot{R}OH + H_2O_2 \qquad (8)$$

$$2HO_2\cdot \longrightarrow H_2O_2 + O_2 \qquad (9)$$

$$\dot{R}OH + O_2 \longrightarrow R(\dot{O}_2)OH \qquad (10)$$

Table 4. Product yields in oxygen-saturated 1-butanol

Dose rate ($\times 10^{17}$ eV ml^{-1} min^{-1})	G(C_3H_7CHO)	G(H_2O_2)	G(H_2)
11.5	3.4	0.6	0.47
5.2	4.8	1.7	1.3
3.0	5.8	2.0	1.5
1.4	8.0	2.6	1.8
0.76	9.7	3.4	1.9
0.39	15.4	5.3	2.6
0.13	17.3	6.0	2.5
0.05	27.0	5.4	3.2

$$R(\dot{O}_2)OH + ROH \longrightarrow R(OOH)OH + \dot{R}OH \qquad (11)$$

$$R(\dot{O}_2)OH + HO_2\cdot \longrightarrow R(OOH)OH + O_2 \qquad (12)$$

$$2R(\dot{O}_2)OH \longrightarrow R(OOH)OH + R'CHO + O_2 \qquad (13)$$

$$2R(OOH)OH \longrightarrow R'CHO + H_2O_2 \qquad (14)$$

$$2R(OOH)OH \longrightarrow R'COOH + H_2O \qquad (15)$$

The chain leading to the formation of aldehyde and hydrogen peroxide is propagated by reactions (8), (10) and (11) and terminated by reactions (12)–(15). With decreasing dose rate the steady-state concentration of $\dot{R}OH$ radicals should also decrease, favouring chain propagation. This is found experimentally to be true of the yields of aldehyde and hydrogen peroxide in all the alcohols studied, whith the exception of methanol in which no chain reaction was observed. The scheme also predicts that approximately equal amounts of hydrogen peroxide and aldehyde are formed simultaneously. Rather surprisingly, this was only found for 1-propanol. Several reasons can be advanced to explain this finding. Alan and Beck,[9] for instance, found that in aqueous ethanol solutions the reaction

$$(CH_3)_2\dot{C}OH + H_2O_2 \longrightarrow (CH_3)_2CO + H_2O + OH \qquad (16)$$

is responsible for the disappearance of hydrogen peroxide by a chain process. It is possible that, with increasing hydrogen peroxide concentration, the peroxide starts to react with the radicals present in the system. Another possibility is that, with recreasing G(−alcohol), the hydrogen peroxide starts competing with solvated electrons for oxygen:

$$e^{-}_{solv} + O_2 \longrightarrow O_2^{-}; \quad k_2 = 1.3 \times 10^{10}\ M^{-1} s^{-1} \qquad (5)$$

$$e^{-}_{solv} + H_2O_2 \longrightarrow OH + OH\ ; \quad k_2 = 1.2 \times 10^{10}\ M^{-1} s^{-1}. \qquad (17)$$

Table 3. Product yields in oxygen-saturated 2-propanol

Dose rate ($\times 10^{17}$ eV ml^{-1} min^{-1})	G(CH_3CHO) (1)	G(CH_3COCH_3) (2)	G(1 + 2)	G(H_2O_2)	G(H_2)
26.3	3.9	4.5	8.4	4.8	1.6
12.8	5.7	5.3	11.0	5.0	1.5
5.8	6.1	5.4	11.5	6.1	1.5
3.4	7.0	6.8	13.8	7.0	1.5
1.5	6.6	7.0	13.6	9.7	1.5
0.84	8.1	9.7	18.8	11.8	1.5
0.05	11.4	17.9	29.3	—	1.6
0.01	12.7	18.7	31.4	—	1.5

The hydroxyl radicals formed in reactions (5) and (17) will lead to further $\dot{R}OH$ radicals, resulting in the formation of one molecule of hydrogen peroxide for every two molecules of aldehyde. From the results on 1-butanol it does seem that, at high conversions, oxygen is being used up. This would cause an increase in the yield of hydrogen gas as all the hydrogen atoms are not scavenged by the oxygen. Experimentally it was found that the yield of hydrogen increases rapidly at low dose rates.

Effects of dose rate. The overall reaction kinetics could not be solved algebraically, assuming steady states for the various radicals. It was therefore not possible to derive a simple expression for the dependence of the aldehyde yield on dose rate in order to test the proposed mechanism by comparing the calculated values with those obtained experimentally. For an ideal biradical-terminated chain reaction, a plot of log (G) vs log (dose rate) should give a straight line with slope = −0.5. For all the alcohols studied, such a plot reveals deviation from ideal behaviour (see Fig. 1).

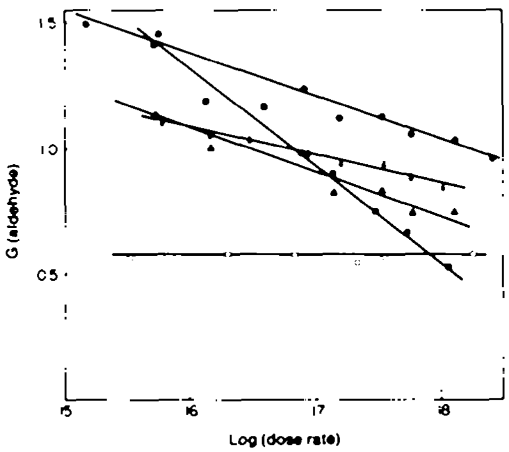

Fig. 1. Influence of dose rate on the yield of aldehyde for various alcohols. ○, methanol; ↑, ethanol; ▲, 1-propanol; ●, 2-propanol; ■, 1-butanol.

The following slopes were obtained for the various alcohols:

Table 5. Exponent of dose rate for aldehyde formation

Alcohol	Exponent	Viscosity
methanol	0	0.60
ethanol	−0.22	1.20
1-propanol	−0.33	2.26
2-propanol	−0.40	2.45*
1-butanol	−0.76	2.90

*Determined relative to 1-propanol.

In the case of methanol, no dose-rate dependence of either the formaldehyde or hydrogen peroxide yield was observed in the present investigation. This is in contradiction with the results of Habersbergerova *et al.*[11] who found that these products did show a slight dependence on dose rates at very low dose-rate values. The reason for this discrepancy is not clear, but from the published literature it would appear that great uncertainty exists as to whether any chain reactions are operative in this system.

Although a linear relationship exists between the yields of the various aldehydes and the inverse of the dose rate, the results show that chain termination does not occur solely through a bimolecular process. By plotting G(aldehyde) as a function of $(1/D)^{1/2}$ it can be observed, especially at low dose rates, that unimolecular processes become increasingly important. A similar effect was observed by Burchill and Ginns[10] in the radiation-induced oxidation of 2-propanol by hydrogen peroxide in aqueous solution. One such process could involve the transfer of an electron from the alcohol radical to the electron-accepting oxygen molecule. Asmus *et al.*[12] have shown that various alcohol radicals can transfer an electron to nitrobenzene in aqueous solution. As the electron affinity of molecular oxygen is very similar to that of nitrobenzene, it is conceivable that electron transfer to molecular oxygen is in competition with addition of the oxygen to the alcohol radical.

Effect of viscosity. From Fig. 1 it can be observed that G(aldehyde) increases with increasing alcohol chain length. In addition, it was found that for a specific chain length the branched alcohol (2-propanol) yields a higher G value than the straight-chain alcohol (1-propanol). Radlowski and Sherman[13] ascribed this effect, which was also found in the oxidation of the propanols by carbon tetrachloride, as due to the higher energy (~4 kcal) required for the homolytic scission of the primary C–H bond in the case of the straight-chain alcohol. However, if we compare the straight-chain alcohols, it can be seen that the bond-dissociation energies of the C–H bonds do not differ to such an extent as to explain the rather drastic increase in G(aldehyde) with increasing chain length.

We therefore suggest that the yield of aldehyde is determined by the viscosity of the medium. If we plot the magnitude of aldehyde formation (the exponent of

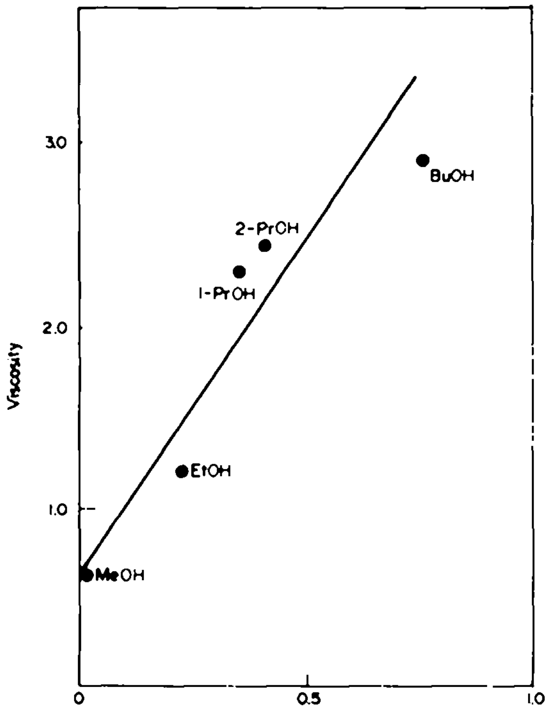

Fig. 2. Yield of aldehyde as a function of viscosity for various aliphatic alcohols.

the slope) against the viscosity, it can be seen (Fig. 2) that, even though there is some deviation from an ideal linear dependency, there exists a direct relationship between the viscosity of the specific alcohol and its yield of aldehyde. An increase in the alcohol chain-length is paralleled by an increase in the viscosity, and this would cause a decrease in the chain termination reactions which are diffusion-controlled. Reactions (8), (10) and (11) should therefore be favoured over reactions (12)–(15). Viscosity effects would be enhanced at low dose rates where the radical concentrations become relatively small, reducing the probability of chain termination through radical–radical processes. If we compare the experimental yields, we find that the kinetic chain length of aldehyde for the various alcohols is much more pronounced at low dose rates than at high dose rates.

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