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APPENDIX

Asymptotic solutions to the energy equation must reduce to known results when $N_{Re_w} = 0$. Furthermore since the energy equation is linear, it should be possible by superpositior to construct a more general solution which applies to the thermal entrance region.

Clearly the asymptotic solutions given previously reduce exactly to well-known solutions for linear wall temperature. However it may not be quite so obvious that superposition can be used to describe the thermal entrance region. Therefore a very brief discussion will be given to illustrate how this may be done. It is necessary to neglect field forces; thus the momentum and energy equations are uncoupled.

Assume that an entrance section is attached to a system of porous parallel plates so that the velocity distribution entering the thermal test section is fully developed. Consider axial conduction negligible, and for simplicity neglect viscous dissipation, although this can be included without difficulty. If $x_1 = 0$ is the entrance to the test section, then the wall temperature distribution is the same as that in Equation (12), and the fluid entrance temperature is uniform and equal to a constant. Once the basic problem is solved, the entrance temperature distribution can be generalized to arbitrary $T(0, \eta)$.

Let

$$T = T_w + \overline{U}\,\phi_2(\eta) + G(x_1, \eta)$$

and by allowing the asymptotic functions F or ϕ_2 to account for all inhomogeneities one obtains Equation (15), and

$$\overline{U} f' \frac{\partial G}{\partial x_1} + 2V_{1w} f \frac{\partial G}{\partial \eta} = \frac{4}{N_{Pe}} \frac{\partial^2 G}{\partial \eta^2}$$

together with homogeneous boundary conditions

$$G(x_1, 1) = \frac{\partial G}{\partial \eta}(x_1, 0) = 0$$

These equations represent the flat plate linear wall temperature analogue of the constant wall temperature problem discussed by Yuan and Finkelstein (*33*) and can be reduced immediately to a Sturm-Liouville system by separation of variables. An identical procedure can be used for the tube problem.

Free-Radical Yields in *n*-Alcohols Resulting from Gamma Irradiation

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The physical interaction of radiation with matter results in the formation of chemically reactive species. For organic liquids the precursors of most of the chemical products found as a result of irradiation are predominantly free radicals. The yield or G-value (molecules formed/100 electron volt absorbed) for free-radical formation for various organic compounds is a quantity of fundamental interest since, if the identities of the radicals are known in addition to their yield, the overall chemical effect of radiation may be predicted. Many investigators have reversed the procedure and have predicted G-values from the quantity and nature of the final products. Obviously it is desirable to check such results by direct measurements for free-radical formation, and such measurements have been reported in the literature for various compounds. The method most suitable for liquid-phase reactions utilizes some well-known specific reactions for free radicals such as the interaction with highly reactive solutes termed "scavengers." To be useful such reactions must remove all radicals from the system before they may undergo secondary reactions. The stable free-radical diphenylpicrylhydrazyl (DPPH) has been used for this purpose with, however, widely varying results (*4, 6, 7, 16*). These results are also inconsistent with values re-

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ported by other methods. These inconsistencies apparently discouraged earlier researchers from applying this technique to alcohols. It should be noted that these experiments were carried out in the presence of oxygen, and apparently no attempts were made to dry the samples thoroughly. The present investigation was undertaken to improve the technique with the scavenger DPPH.

The purposes of the current work are to establish the significant criteria involved in the use of DPPH as a scavenger and to measure the free-radical yields in several normal aliphatic alcohols under the influence of gamma radiation. The series of *n*-alcohols was chosen for study because of its practical interest and because results of other investigations were available for comparison.

THEORETICAL CONSIDERATIONS

With the assumption that the predominant chemically active species formed by the interaction of radiation with an alcohol are free radicals according to the following reaction

$$M \overset{K_o}{\rightsquigarrow} R \tag{1}$$

the more significant subsequent reactions in the system may be represented by the following:

$$R + M \xrightarrow{k_2} R' + P_1 \tag{2}$$

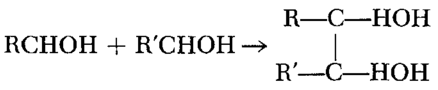
$$R + R \xrightarrow{k_3} P_2 \tag{3}$$

Equation (2) represents radical attack upon unconsumed reactants, and it must be a chain transfer reaction producing an additional radical (R') without a net change in the radical concentration. Since alcohols are not known to polymerize, hydrogen abstraction is a likely example of this reaction:

$$RCHOH + R'CH_2OH \rightarrow R'CHOH + RCH_2OH$$

The resulting radicals are very similar, if not identical, to the original radical.

Reaction (3) represents radical-radical combination, the chain-termination step, which is a very high free-energy reaction. In an alcohol system this reaction may result in the formation of glycols:



$$RCHOH + R'CHOH \rightarrow \begin{array}{l} R\text{—}C\text{—}HOH \\ \quad\;\; | \\ R'\text{—}C\text{—}HOH \end{array}$$

In addition, molecular rearrangement with the emission of hydrogen is possible, as in the formation of formaldehyde in a methanol system (*11*), but the energy requirements must be highly specific. It was shown by McDonell that proportionately few radicals undergo rearrangements. Furthermore, reaction of the radicals with one of the above-mentioned products, for example, the glycols or aldehydes, is possible, but because of the low concentrations, probability of success is very low.

In an efficient scavenger system the predominant reaction is expected to be the one between the radical and the scavenger molecules. The kinetic process may be described by the reaction

$$R + S \xrightarrow{k_1} P_3 \tag{4}$$

When the overall kinetic scheme is considered, the rate of change of radical concentration as obtained from Equations (1), (3), and (4) is given by

$$\frac{d(R)}{dt} = K_o - k_1(R)(S) - k_3(R)^2 \tag{5}$$

where the values in parentheses are the concentrations of the materials represented by the same letters in the above equations, and the k's are the corresponding rate constants. The rate of change of scavenger concentration from Equation (4) is given by

$$\frac{d(S)}{dt} = -k_1(R)(S) \tag{6}$$

The stationary, or steady state concentration of radicals (R_{st}) may be evaluated by setting the rate of change of radicals in Equation (5) equal to zero. The resulting expression may then be solved for R_{st} where

$$R_{st} = \frac{-k_1S + \sqrt{(k_1S)^2 + 4k_3K_o}}{2k_3} \tag{7}$$

Only the positive square root term is meaningful. The differential equation which results from substituting Equation (7) into Equation (6) may be solved to give the relation below, where S_o is the initial value of the scavenger concentration:

$$-\frac{2k_3t}{k_1^2} = (S - S_o) + \sqrt{S^2 + \frac{4k_3K_o}{k_1^2}} - \sqrt{S_o^2 + \frac{4k_3K_o}{k_1^2}} + \frac{4k_3K_o}{k_1} \left[\ln \frac{S\left(\sqrt{S_o^2 + \frac{4k_3K_o}{k_1^2}} + \sqrt{\frac{4k_3K_o}{k_1^2}}\right)}{S_o\left(\sqrt{S^2 + \frac{4k_3K_o}{k_1^2}} + \sqrt{\frac{4k_3K_o}{k_1^2}}\right)} \right] \tag{8}$$

In addition to the above analysis, it is possible to assume an ideal scavenger model, whereby only Reactions (1) and (4) need be considered. Thus, the only reactions occurring are the radical initiation and scavenger reactions. An analysis similar to the above gives the following linear relation between the scavenger concentration and reaction time:

$$S - S_o = -K_ot \tag{9}$$

This ideal model for the scavenger mechanism is likely to apply over a range of scavenger concentration between a maximum, $S_{max.}$, above which the direct interaction between the radiation and the scavenger becomes significant, and a minimum, S_c, commonly referred to as the *critical concentration* (*7, 17*), below which the concentration of the scavenger is too small to remove all the radicals, and side reactions become competitive. It may be shown mathematically that Equation (8) reduces to Equation (9) as S approaches S_o. The above analyses apply only below $S_{max.}$, since interaction between the scavenger and the radiation has not been included in either of the kinetic models.

Thus, by plotting the scavenger concentration, S, vs. the reaction time, t, the slope at $t = 0$ may be obtained. This should be equal to K_o which, in turn, is equal to the rate of formation of the radicals. The entire irradiation curve may be analyzed by various curve-fitting techniques from which approximate values of the rate constants k_1 and k_3 may be evaluated. The analysis of the scavenger system may be accomplished by measuring the slope of the tangent of the "S" vs. "t" curve at $S = 0$ (provided $S_c < S_o < S_{max.}$) to obtain K_o, and fitting Equation (8) to the entire irradiation curve to evaluate k_1 and k_3. However, the validity of this analysis depends upon the assumptions that only radical species react with the scavenger (*15*), the concentration of radicals is uniform throughout the system (*6, 7*), and a 1 to 1 stoichiometric factor exists between the radicals and the scavenger (*3, 16*).

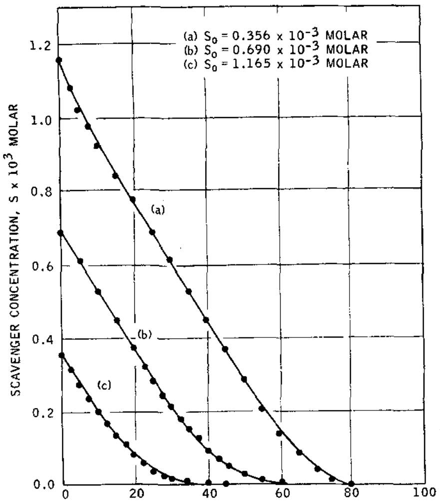


Fig. 1. Irradiation of methyl alcohol: degassed methanol-DPPH solutions (intensity = 198,200 roentgens/hr., temperature 25°C).

EXPERIMENTAL PROCEDURE AND PRELIMINARY RESULTS

The selection of the scavenger depends upon the analytical techniques available for accurate measurement of its concentration in addition to its properties as a free radical trapping agent. The main requirements are compatibility with the system and rapid rate of reaction with the radicals. Diphenylpicrylhydrazyl (DPPH) was selected since its concentration may be determined readily and accurately by photometric techniques in the visible region at 515 μ. The extinction coefficient of each alcohol-DPPH system was determined by preparing calibration curves and noting that Beer's law of light absorption was obeyed.

The purest commercially available alcohols were predried, distilled twice, dried with aluminum-amalgam, distilled, dried again with lime, and finally redistilled. During each distillation the collected product cut was within ± 0.1°C. of the boiling point.

The alcohols were degassed for 1 hr. in a closed glass system. After degassing, without exposure to the atmosphere, the alcohol was mixed with a predetermined amount of vacuum-dried DPPH in the solution flask. This flask was sealed and placed on a shaker for agitation to facilitate complete dissolution, after which it was attached to a closed vacuum filtering apparatus and the filtrate was collected in a vacuum flask. The filtered solution was then transferred to a specially constructed glass tube filling train (*18*), also operated under vacuum with facilities for nitrogen purge to avoid contact with air. The reaction tubes were cylindrical Pyrex vessels, 10 cm. long, 11 mm. I.D., with only one opening at the top through which a 12 cm. long, 5 mm. I.D. neck was extended. These tubes were filled to the neck and sealed with a torch. Enough solution was prepared to provide samples for a complete run including duplicates and blanks. Degradation checks were made by measuring the optical density of unirradiated samples prior to the irradiations (blank A) and after the completion of the irradiations (blank B). When a decrease in optical density greater than 0.2% of the original was observed between blanks A and B, the experiment was considered unsatisfactory because of excessive degradation caused by contaminants. When an increase in optical density was observed from blank A to B, the experiment was also considered unsatisfactory because of nonuniform concentrations among samples which may have occurred as a result of nonuniform pressure or temperature control during the tube-filling step, resulting in excessive alcohol evaporation.

Analyses were made within 5 min. after the sample tubes were opened to the atmosphere and usually immediately after irradiation. Samples, while not in use, for example, prior to irradiation or after irradiation but before analysis, were stored in a cold room at 4°C. All samples were shielded from light by tinted or aluminum-foil wrapped glassware. The samples were irradiated in a cobalt-60 gamma source which has been described in detail by Hayward and Bretton (*9*).

The compatibility of the DPPH with the alcohol was determined by preparing solutions under various conditions, storing these for prolonged periods of time, and periodically measuring the optical density.

A degradation process was noted involving reaction with water, the rate of which is temperature dependent. At room temperature, in the presence of water, an initial large degradation rate was observed, followed by a decrease to a value equal to the steady degradation rate observed in water-free samples. The initial high rate apparently proceeded until all the moisture was consumed, and its average magnitude varied directly with the initial moisture content. The steady degradation rate seemed to be owing to the presence of oxygen since a very low rate of change of DPPH concentration was observed even in the completely dried samples. At low temperatures (4°C.), the large initial degradation was eliminated, and the observed rate of DPPH concentration change was equal to the rate of steady degradation. The values of this steady degradation were 5.6×10^{-6} moles/liter/hr. at 4°C., 29.6×10^{-6} moles/liter/hr. at room temperature when shielded from light, and 37.2×10^{-6} moles/liter/hr. when exposed to light.

The rate of reaction of DPPH with free radicals may be assumed to be rapid on the basis of the experience reported by previous authors (*2, 8*) who have also discussed the details of the technique. This assumption has been confirmed experimentally in this work as evidenced by the large rate constants for the scavenger reaction given below. The efficiency of the DPPH scavenger in removing all radicals was also checked by analyzing qualitatively the irradiated samples for glycols and aldehydes, which have been reported by previous authors (*10, 12, 13*) to be the major reaction products. These analyses were made on vacuum distillates of the irradiated sample with the highly colored and possibly interfering DPPH retained in the still flask. No glycols or aldehydes were observed in samples when the DPPH concentration was above approximately 0.2×10^{-3} mole/liter, indicating high scavenger efficiency. On the other hand, the qualitative tests indicated

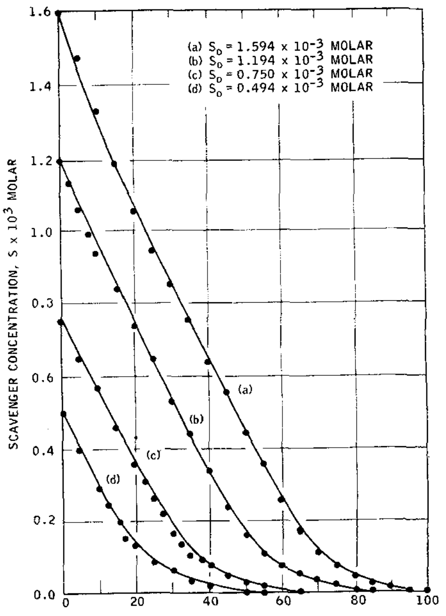


Fig. 2. Irradiation of ethyl alcohol: degassed ethanol-DPPH solutions (intensity = 200,600 roentgens/hr., temperature 25°C).

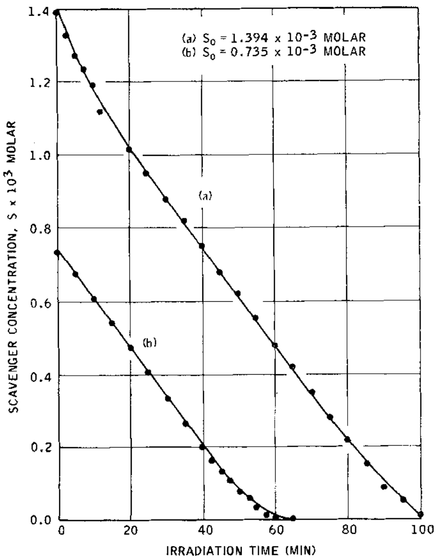


Fig. 3. Irradiation of *n*-propyl alcohol: degassed *n*-propanol-DPPH solutions (intensity = 196,500 roentgens/hr., temperature 25°C).

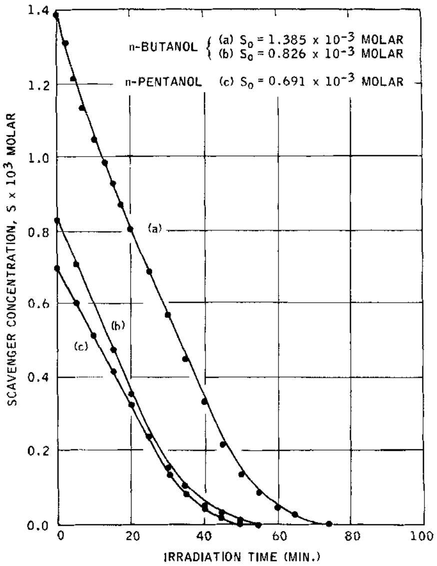


Fig. 4. Irradiation of *n*-butyl and *n*-pentyl alcohols: degassed alcohol-DPPH solutions (intensity = 196,000 roentgens/hr., temperature 25°C).

the presence of these products when the DPPH concentration was low, as shown in Table 1.

The photometric technique is satisfactory only if other compounds in the system do not interfere with the absorption at the characteristic wavelength. It was observed that the reaction between the radicals and DPPH is such that the absorption curves, over an extended wavelength region, of samples irradiated for varying time intervals, intersected in an isosbestic point at about 400 μ. This indicates that the products absorbing light were formed in amounts proportional to the extent of irradiation. Thus, a calibration was necessary for these absorbing products to permit the subtraction of their contribution from the measured optical density. This was made possible by the assumption that no product was present prior to irradiation and that the only absorbing material was the product at infinite irradiation. If one also assumes that the light absorption owing to the product obeys Beer's law, then the magnitude of this contribution may be approximated as $t_\infty D_\infty / t$, where D_∞ was the measured optical density at infinite time t_∞. This value was subtracted from the measured optical density at all irradiation times to obtain the corrected values, which then were converted to DPPH concentration with the aid of the appropriate calibration.

TABLE 1. ANALYTICAL RESULTS TO DETERMINE SCAVENGER EFFICIENCY

S_0 (mole/liter)	Irrad. time (min.)	S (mole/liter)	Results of qualitative analyses*	
			Glycols	Aldehydes
0.15×10^{-3}	20	0.02×10^{-3}	+	+
0.45×10^{-3}	20	0.38×10^{-3}	—	—
0.82×10^{-3}	20	0.55×10^{-3}	—	—
0.82×10^{-3}	60	0.15×10^{-3}	+	+

* (+) indicates the presence, (—) the absence of the indicated product.

The presence of oxygen was found to have a very significant effect on the course of reactions. The data indicate that the rate of scavenger depletion is greater by a factor of three when an excess of oxygen is present (alcohol saturated at room temperature). This suggests a chain mechanism involving the radical and oxygen, perhaps via the hydroperoxide, resulting in products such as olefins, water, hydroxyl radicals, or additional radicals through interaction with unreacted alcohol, all of which tend to react with the DPPH. No attempts were made to verify the identity of these products.

TABLE 2. TABULATED VALUES OF THE CALCULATED RATE CONSTANTS

Alcohol	Initial DPPH concentration $S_o \times 10^3$ (mole/liter)	$(K_o \times 10^5) \pm 5\%$ (mole/liter/min.)	$k_1 \times 10^5$ (mole/liter/min.)	$k_3 \times 10^5$ (mole/liter/min.)
Methanol	0.690	1.62	0.776 ± 50%	19.2 ± 33%
	0.356	1.60	1.00 ± 26%	35.6 ± 21%
Ethanol ($I\gamma$ ~ 196,000 roentgen/hr.)	0.750	1.97	1.52 ± 38%	100 ± 30%
	0.494	1.97	1.96 ± 29%	153 ± 41%
Ethanol ($I\gamma$ ~ 45,000 roentgen/hr.)	0.728	0.463	2.04 ± 34%	172 ± 52%
Ethanol ($I\gamma$ ~ 262,000 roentgen/hr.)	0.932	2.66	1.57 ± 21%	105 ± 29%
Propanol	0.738	1.34	1.00 ± 18%	9.11 ± 16%
Butanol	0.826	2.34	1.08 ± 13%	50.3 ± 62%
Pentanol	0.693	1.79	0.975 ± 24%	14.9 ± 32%

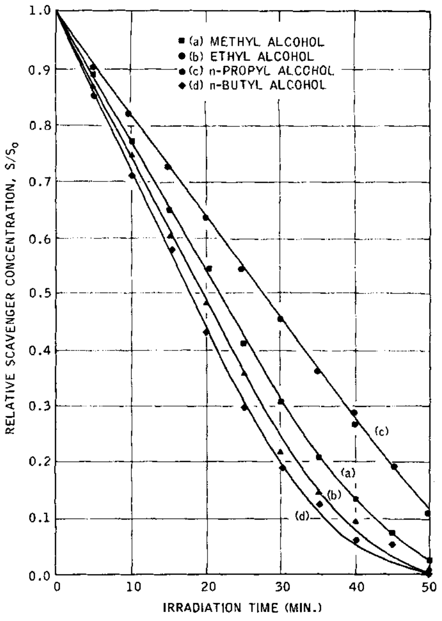


Fig. 5. Comparison of experimental data with theoretical curves (degassed solutions).

DISCUSSION OF THE RESULTS

Figures 1 to 4 are the irradiation curves for methyl, ethyl, *n*-propyl, and *n*-butyl, plus *n*-pentyl alcohols, respectively. It may be noted that between $S = 1.0 \times 10^{-3}$ mole/liter and $S = 0.2 \times 10^{-3}$ mole/liter, the curves are straight lines. This is referred to as the *ideal region*. The slope of this line provides the value of K_o, which, as postulated above is the rate of formation of free radicals. Above $S = 1.0 \times 10^{-3}$ mole/liter, the curves deviate from a straight line with the slope becoming steeper, indicating a faster rate of DPPH consumption than during the ideal region and indicating the direct interaction between the radiation and scavenger. Below $S = 0.2 \times 10^{-3}$ mole/liter, the curves again deviate from a straight line, gradually decreasing in slope. This is the region where the scavenger concentration is below the critical value and the competition for the radicals between the various termination reactions becomes significant.

A nonlinear regression computation, using an IBM-704 digital computer, was performed on the scavenger consumption Equation (8). The best obtainable values of the rate constants were calculated and are tabulated in Table 2. Figure 5 compares the experimental data with the theoretical curves obtained with these constants. The large deviations associated with each of the constants result from the scatter of the data and the limitation of the exactness of the fit with two mathematically arbitrary constants (k_1 and k_3). It is noteworthy that with the mean value of the rate constants, a theoretical curve not deviating by more than 2% from the experimental data was obtained. This agreement seems very satisfactory when one considers normal experimental errors.

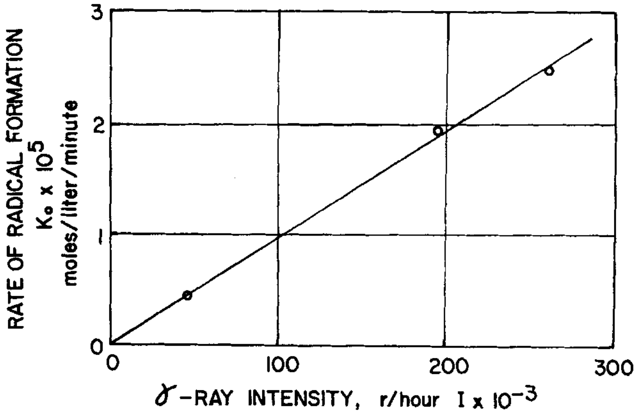


Fig. 6. Effect of intensity of radical formation rate (degassed ethanol-DPPH solutions).

Irradiation curves for ethyl alcohol were obtained at three different irradiation intensities. Theoretically, the rate of formation of radicals is proportional to the intensity

$$K_o = K_{10} I_Y \qquad (10)$$

where K_{10} is a proportionality constant. A plot of K_o vs. I_Y (Figure 6) gives a straight line through the origin with a slope "K_{10}" $\approx 10^{-8}$ which is comparable in magnitude to the values obtained by Chapiro (*6*). If his results are extended, it may be concluded that at intensities higher than about 30,000 roentgen/hr., the distribution of radicals throughout the bulk is uniform. This justifies the validity of the assumption made above in the kinetic analysis.

The free-radical yields have been evaluated in terms of G-values and are tabulated with other values found in the literature in Table 3 (*1, 2, 5, 11, 12, 14, 16*). Satisfactory agreement is observed indicating the validity of the scavenger technique in comparison to the other more complicated methods. It is also interesting to note that good agreement in order of magnitude is also obtained for the irradiation of samples which had not been degassed. Previous authors reported their results over broad ranges, since they were unable to obtain reproducible results. This shortcoming, however, was not realized in the current experimentation, indicating the superiority of the scavenger technique as employed in this investigation.

The alcohols with an even number of carbon atoms are more susceptible to irradiation attack than either of the adjacent alcohols with an odd number of carbons. This is in agreement with the findings of McDonell and Newton

TABLE 3. RESULTS OF RADICAL YIELDS
G-values

	Current work		Literature data			
Alcohol	Degassed	With air	Degassed	Reference	With air	Reference
Methanol			6.5	(*1*) $S(Fe^{+3}) + PA$	19.7	(*5*) *PO*
	6.26	14.5	5.87	(*14*) $S(I_2) + PA$	10-20	(*16*) S(DPPH), *PO*
			7.67*	(*12*) *PA*		
Ethanol	7.76	17.6	9.0	(*2*) *PA*		
			8.19	(*12*) *PA*	25	(*2*) *PA*
n-Propanol	5.12	5.12	7.30*	(*12*) *PA*	10-20	(*16*) S(DPPH), *PO*
n-Butanol	8.81	24.0	8.53*	(*12*) *PA*		
n-Pentanol	6.70	14.8				

* Using 28 mev. helium ions; all others are with γ-rays.
Symbols describing method used to obtain the results: $S(X)$ = scavenger technique with X scavenger, PA = product analysis technique, PO = polymerization initiation technique.

(*12*), who also postulated that "an even-odd effect" in the radiolysis of the alcohols may exist. The relatively high G-values of ethanol and butanol indicate why these substances are useful protective agents against irradiation damage.

CONCLUSIONS

Under the influence of gamma radiation, the initial free-radical yields have been measured by the scavenger technique for the five normal aliphatic alcohols, methyl, ethyl, propyl, *n*-butyl, and *n*-pentyl. Diphenylpicrylhydrazyl was used as the scavenger. The effect of temperature was measured over a 120°C. range, and in the case of ethanol, the radiation intensity was varied between 44,500 and 225,000 roentgen/hr.

The radical yields were found to be independent of temperature for each of the alcohols. The presence of oxygen in the irradiation system could not be tolerated because a portion of the radicals was oxygenated, probably to hydroperoxide radicals. These peroxides, in turn, formed additional radicals, possibly by a chain mechanism, so that the apparent yield of radicals was between two and three times the actual yield.

The experimental data for scavenger depletion were well fitted by an assumed mechanism consisting of the following reactions:

$$M \rightsquigarrow R \tag{1}$$

$$R + S \xrightarrow{k_1} P_3 \tag{4}$$

$$R + R \xrightarrow{k_3} P_2 \tag{3}$$

It was shown that the extent to which the radical-radical reaction proceeds at DPPH concentrations above 0.2×10^{-1} mole/liter is insignificant. The concentration region above this value was described by an ideal model, and is characterized by a straight-line irradiation curve. The slope of this line was shown to be equivalent to the rate of radical formation. At about 1.0×10^{-3} mole/liter of DPPH, a limiting concentration was noted above which the direct effect of the radiation upon the scavenger molecules became pronounced. The lower limit of the ideal model was at 0.2×10^{-3} mole/liter, which is referred to as the *critical scavenger concentration*.

The effect of radiation intensity on the rate of radical formation was found to be linear. Owing to the large deviations associated with the calculated rate constants "k_1" and "k_3", no significant prediction could be made on their radiation intensity dependence.

The effect of the radiation was greater for the alcohols with an even number of carbon atoms than for those with an odd number. This increased reactivity might be materialized in a protective phenomenon against radiation damage.

The scavenger technique for measuring radical yields is a satisfactory means of determining radiation effects. It is essential that a scavenger compatible with the medium and efficient in trapping the radicals be selected. DPPH was compatible with the dry alcohols, but reacted relatively rapidly with any residual water left by purifications. Analysis of the scavenger concentration was accomplished by photometric technique in the visible region at 515 μ, once it was shown that in the DPPH-radical reaction a proportionate amount of light absorbing product was formed per amount of destroyed scavenger.

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NOTATION

D_∞ = optical density owing to product at infinite irradiation
I_Y = intensity of gamma radiation, (roentgen/hr.)
k_1 = rate constant for scavenging reaction [mole/liter (min.)]
k_2 = rate constant for chain transfer reaction [mole/liter (min.)]
k_3 = rate constant for radical-radical reaction [mole/liter (min.)]
K_o = rate of radical formation or rate constant for radical formation reaction ($K_o = k_o M I_Y$), mole/liter/min.
M = concentration of irradiated reactant (alcohol), (mole/liter)
P = concentration of product of a reaction between R and other species present (mole/liter)
R = concentration of radical species formed by irradiating M (mole/liter)
S = concentration of scavenger species (DPPH) (mole/liter)
S_o = initial scavenger concentration (mole/liter)
t_∞ = infinite irradiation time (min.), selected as that time when the irradiation curve became horizontal
t = irradiation time (min.)

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