γ Radiolysis of Liquid Ethanol. Yields of Hydrogen and Free Ions.

Solvated Electron Rate Constants¹

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The initial hydrogen yield from pure ethanol at 20° is $G(H_2)_0 = 5.9$; the free ion yield is $G(e_{solv})_{fi} = 1.7$. Most of the values reported earlier were lower than these and seem to have been affected by impurities in the alcohol. The dose dependence of the hydrogen yields and the yields of hydrogen and nitrogen from nitrous oxide solutions agree with calculations based on $G(H_2)_0 = 5.9$, $G(e_{solv})_{fi} = G(H_2)_{fi}^{\max} = G(N_2)_{fi}^{\max} = 1.7$, using independently measured values of the rate constants. For the free ion reaction, 1.0 nitrogen molecule is formed for each solvated electron scavenged by nitrous oxide in ethanol. Rate constant ratios for reactions of solvated electrons were determined by competition kinetics. Using the previously reported² value $k(e_{-solv} + CH_3CHO) = 4 \times 10^9 M^{-1} \sec^{-1}$, the following values of k for other solutes were obtained at 20°, in units of $10^9 M^{-1} \sec^{-1}$: N₂O, 7; C₂H₅OH₂⁺, 29; C(NO₂)₄, 19; CCl₄, <9; n-C₃H₇Br, ≤ 1.3 . Pulse-spectroscopic measurements gave higher values for the last three compounds: C(NO₂)₄, 35; CCl₄, 11; n-C₃H₇Br, 3.0.

Introduction

Development of the theory of radiation chemistry requires accurate knowledge of the yields of intermediates and final products in irradiated systems. To this end several systems have been, and continue to be, intensively studied. One such system is liquid ethanol.²⁻¹³

For a number of years the initial yield of hydrogen from the γ radiolysis of liquid ethanol at room temperature has been thought to be $G(H_2)_0 = 5.0 \pm 0.1^{2,6,8-11}$ and the most widely accepted free ion yield has been $G(e_{solv})_{fi} = 1.0 \pm 0.1.^{8-10, 12, 18}$ However, higher values of the hydrogen⁵ and free ion^{2,6,11} yields have been reported and the hydrogen yield has been found to increase in the presence of a trace of acid.^{11,14} The acid-sensitive intermediate has a G value of 0.8 in ethanol that gives an "initial" $G(H_2) = 5.1$.¹¹ Two possible interpretations of the results seem to be: (a) the ethanol contains a trace of electron-scavenging impurity, and absolutely pure ethanol would give $G(H_2)_0 = 5.9$ and $G(e_{solv})_{fi} = 1.7$ or (b) $G(H_2)_0 = 5.0$, $G(e_{solv})_{fi} \approx 1.0$ and the unidentified acid-sensitive species X has a yield $G(X) \approx 0.8$.¹⁵ The present work was undertaken to try to choose between these alternatives. At the same time the unexpectedly low rate constant reported for the reaction between electrons and carbon tetrachloride in ethanol⁸ has been investigated as a possibly related problem.

Since this project was begun articles have appeared which support $G(e_{solv})_{fi} = 1.7$,² and 1.0.^{12,13} The continuing large magnitude of the discrepancy makes it seem progressively more serious.

Experimental Section

Materials and Sample Preparation. Absolute ethanol from the Reliance Chemical Co. was subjected to the purification method described earlier.¹⁶ However, a subsequent uv spectroanalysis of this alcohol using a 10-cm cell indicated trace amounts of carbonyl compounds. Therefore, absolute ethanol from the U. S. Industrial Chemical Co. was used. Analysis of this alcohol by the above method established an upper limit of impurities such as carbonyl compound and benzene at $10^{-5} M$. Analysis provided by the U. S. Industrial Chemical Co. indicated the impurity levels as follows: water 50 ppm, benzene <1 ppm, methanol 2.5 ppm, acetaldehyde <1 ppm, and halogen compounds <1 ppm.

The ethanol was treated with KOH under vacuum and condensed in a trap at -196° while being evacua-

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ted. After thorough degassing the ethanol was finally recondensed in a storage bulb. The system handling ethanol contained greaseless Hoke values.

Nitrous oxide was purified by passing it through a concentrated aqueous solution of KOH and subsequently passing it through a column packed with silica gel. Finally the gas was passed through KOH pellets, thoroughly degassed, and stored in a reservoir. Acetaldehyde was purified by fractional distillation using a 70-cm column packed with glass helices. The middle fraction was introduced into a storage bulb and degassed by pumping initially at -78° and finally at room temperature. The storage bulb was ultimately maintained at -78° .

Carbon tetrachloride and *n*-propyl bromide were purified by treatment with KHCO₃ followed by thorough washing with triply distilled water. They were degassed by repeated freeze-pump-thaw cycles. Tetranitromethane was also purified by the above method; however, in this case solutions of $C(NO_2)_4$ in ethanol were prepared immediately after purification and used as soon as possible.

Hydrogen chloride was passed over copper foil, thoroughly degassed, and stored in a Pyrex bulb. Hydrogen chloride, carbon tetrachloride, and *n*-propyl bromide were always recondensed and pumped on at -196° before use. The storage bulbs for ethanol and all other reagents were protected from light by aluminum foil.

Most samples were prepared by standard vacuum techniques. For acetaldehyde solutions the acetaldehyde was introduced into the sample cell by condensation at -78° , followed by the ethanol. The sample cell was gently vibrated to allow thorough mixing, cooled to -196° , and then sealed off under vacuum. This procedure was adopted to avoid freezing the pure acetaldehyde, which causes it to polymerize.

Tetranitromethane, potassium hydroxide, and sulfuric acid were added by introducing their solutions in ethanol into sample cells provided with a side arm, which was then sealed off. The volume of solutions thus introduced was generally 0.05–0.5 ml. The solution was degassed by freeze-pump-thaw cycles and then the required extra ethanol was distilled into the sample cell. The 5-ml samples were contained in 7-ml cells.

Irradiations. Irradiations were done at 20° in a ⁶⁰Co Gammacell 220 (Atomic Energy of Canada Ltd). The dose rate was $4 \times 10^{17} \text{ eV/g min.}$

The yields of gaseous products were determined by refluxing the sample in a vacuum line and passing the gases so obtained through two cold traps kept at -196° . The pressure and volume of the products were measured in a Toepler-McLeod gauge, and the gases were then analyzed by gas chromatography. A 2-m molecular sieve column, helium carrier gas, and a thermal conductivity detector were used. The yield of each gas



Figure 1. Hydrogen yield as a function of dose. The solid curve was calculated using eq II.



Figure 2. Hydrogen and nitrogen yields from nitrous oxide solutions in ethanol: \bigcirc , $G(N_2)$; \triangle , $g(H_2)$; \square , $G(N_2) + g(H_2)$. The solid curves at $N_{N_{20}} < 10^{-3}$ were calculated using eq III and IV.

was calculated from the chromatogram, with calibrations for each gas.

Pulse Radiolysis. For pulse-radiolysis experiments the solutions of carbon tetrachloride were prepared by vacuum technique. The pure ethanol and solutions containing propyl bromide and tetranitromethane were deoxygenated by bubbling argon through them. The 1.0- μ sec pulses of 1.7-MeV electrons imparted 5 \times 10¹⁶ eV/ml to the samples. The temperature was 20°.

Results

The hydrogen yield from ethanol decreases with increasing dose (Figure 1). The initial yield deduced from mechanistic considerations (see Discussion) is $g(H_2) = 5.9$. For the rest of the experiments the dose used was $1 \times 10^{18} \text{ eV/ml}$, unless otherwise stated.

The yields of hydrogen and nitrogen from nitrous oxide solutions in ethanol are shown in Figure 2. The reported nitrogen yields are based on the total energy absorbed by the solution and are designated by $G(N_2)$. The hydrogen yields from the solutions are calculated on the basis of the energy absorbed by the solvent only and are designated by $g(H_2)$. The hydrogen yield decreases and the nitrogen yield increases with increasing nitrous oxide concentration. The sum of the nitrogen



Figure 3. Hydrogen yields from solutions containing acetaldehyde, \bigcirc , tetranitromethane, \triangle , and $C_2H_5OH_2^+$ from sulfuric acid, \Diamond . The line through the acetaldehyde points was calculated from eq II. The concentrations of the oxonium ions $C_2H_5OH_2^+$ were calculated on the basis of $k_{diss}(H_2SO_4) =$ 1.7×10^{-3} in ethanol.

and hydrogen yields increases with increasing solute concentration.

Figure 3 represents the effects of sulfuric acid, acetaldehyde, and tetranitromethane on the yield of hydrogen. Acetaldehyde is itself a product of radiolysis of ethanol and it was estimated that after a dose of $1 \times 10^{18} \text{ eV/ml}$ had been absorbed the accumulated concentration of acetaldehyde in the sample was 5.2×10^{-5} M. The aldehyde is an electron scavenger and it interferes with reactions of other added solutes. In the case of acetaldehyde as solute, the time-averaged concentration of acetaldehyde would be $2.6 \times 10^{-5} M$ higher than that initially added. The curve for the effect of the concentrations of acetaldehyde on the yield of hydrogen in Figure 3 was calculated using a method described later.

The yield of hydrogen decreases with the increase in the concentration of aldehyde or tetranitromethane (Figure 3). The yield of hydrogen from solutions of sulfuric acid in ethanol increases with acid concentration. Similar experiments with hydrochloric acid gave lower hydrogen yields presumably due to the formation of ethyl chloride.¹¹

The concentrations of $C_2H_5OH_2^+$ in the acid solutions in Figure 3 were computed on the basis that the dissociation constant of sulfuric acid in ethanol was $k_{diss} =$ 1.7×10^{-3} . This value of the dissociation constant was extrapolated from reported values of dissociation constants in methanol, $k_{diss}(HCl) = 0.25$,¹⁷ and $k_{diss}^ (H_2SO_4) = 0.028$,¹⁸ and the value for HCl in ethanol, $k_{diss}(HCl) = 0.015$.¹⁹

The effects of carbon tetrachloride and n-propyl bromide on the yield of hydrogen, both in the absence



Figure 4. Hydrogen yields from solutions containing halides. Open points, no KOH added; closed points, KOH added (8 mM in CCl₄ and 0.8 mM in *n*-C₈H₇Br solutions): carbon tetrachloride, \bigcirc , 9 × 10¹⁷ eV/ml; \blacklozenge , 3 × 10¹⁷ eV/ml; \blacklozenge , 9 × 10¹⁷ eV/ml; *n*-propyl bromide, $\triangle \blacklozenge$, 9 × 10¹⁷ eV/ml.

and presence of potassium hydroxide, are represented in Figure 4. The yield of hydrogen in basic solutions of the halides decreases with the halide concentration. In the absence of alkali, however, the hydrogen yield remains practically unchanged at solute concentrations less than $5 \times 10^{-4} M$.

Figure 5 represents the effects of aldehyde and tetranitromethane on the yields of nitrogen and hydrogen from solutions of nitrous oxide in ethanol. At a fixed concentration of nitrous oxide, the yields of nitrogen and hydrogen decrease with the increasing concentration of acetaldehyde or tetranitromethane.

Figure 6 represents the effects of carbon tetrachloride and *n*-propyl bromide on the yields of nitrogen and hydrogen from nitrous oxide solution in ethanol, both in the absence and the presence of dilute potassium hydroxide. Figure 6 also shows the effect of dose on the vields from the ternary solutions. The nitrogen and hydrogen yields decrease with increase in the concentration of the halide. For a given concentration of nitrous oxide and carbon tetrachloride, $G(N_2)$ decreases and $q(H_2)$ increases with increasing dose in the absence of alkali (Figure 6A). In the presence of alkali there is no dose effect, and $g(H_2)$ decreases steadily with increasing carbon tetrachloride concentration. At a fixed concentration of nitrous oxide and n-propyl bromide, $G(N_2)$ decreases with increasing dose in the absence of alkali; however, there is practically no change in $g(H_2)$ with dose (Figure 6B). For a given concentration of n-propyl bromide and nitrous oxide in the presence of alkali the corresponding values of

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Figure 5. Competition of nitrous oxide with acetaldehyde (A) and tetranitromethane (B). Open points, 1.2×10^{-8} $M N_2O$; closed points $1.0 \times 10^{-2} M N_2O$; \bigcirc , $G(N_2)$; \triangle , $g(H_2)$. The curves for $G(N_2)$ were calculated using the competition rate constants listed in Table I.



Figure 6. Competition of nitrous oxide with carbon tetrachloride (A) and n-propyl bromide (B). Open points, no KOH added; closed points, KOH added (8 mM in CCl₄ and 0.8 mM in n-C₃H₇Br solutions). The curves for $G(N_2)$ were calculated using $k(e^{-}_{solv} + N_2O) = 7 \times 10^9 M^{-1} sec^{-1}$, $k(e^{-}_{solv} + CCl_4) = 9 \times 10^9 M^{-1} sec^{-1}$ and $k(e^{-}_{solv} +$ n-C₃H₇Br) = 1.3 $\times 10^9 M^{-1} sec^{-1}$; $[N_2O] = 2.2 \times 10^{-3}$ and $1.0 \times 10^{-2} M$ for the CCl₄ solutions and $[N_2O] = 1.0 \times$ $10^{-3} M$ for the n-C₃H₇Br solutions: $O G(N_2)$; $\Delta g(H_2)$; (A) at $9 \times 10^{17} eV/ml O$, Δ , $2.2 \times 10^{-3} M N_2O$; Θ , Δ , $1.0 \times 10^{-2} M N_2O$; \bullet , A, $1.0 \times 10^{-3} M N_2O$; at $33 \times 10^{-17} eV/ml \Phi\Phi$, ΔA , $1.0 \times 10^{-3} M N_2O$; (B) $1.0 \times 10^{-3} M N_2O \odot$, $M N_2O \odot \Phi$, ΔA , $9 \times 10^{17} eV/ml$; Φ , A, $33 \times 10^{17} eV/ml$.

 $G(N_2)$ are higher than those obtained in the absence of alkali, whereas $g(H_2)$ does not change.

The yield of nitrogen increases and that of hydrogen decreases with increase in concentration of nitrous oxide in solutions of sulfuric acid in ethanol (Figure 7A).



Figure 7. Competition of sulfuric acid with nitrous oxide (A) and carbon tetrachloride (B): \bigcirc , $G(N_2)$; $\triangle \blacktriangle$, $g(H_2)$; \Box , $G(N_2) + g(H_2)$; open points $[C_2H_3OH_2^+] = 0.7 \times 10^{-3} M$; closed points $[C_2H_4OH_2]^+ = 3.3 \times 10^{-3} M$. The curve for $G(N_2)$ was calculated using the competition rate constants listed in Table I.

The total yield of $(N_2 + H_2)$ remains unchanged up to $1 \times 10^{-2} M N_2O$ and then increases. The yield of hydrogen from 1 mM and 10 mM sulfuric acid solutions remains practically unchanged with the addition of up to $10^{-3} M$ carbon tetrachloride and then decreases as the halide concentration is increased.

Typical oscilloscope traces of the decay of the solvated electron absorption are represented in Figure 8. Figure 8A refers to pure ethanol, whereas B and C refer to $1.1 \times 10^{-4} M$ n-propyl bromide and $1.0 \times 10^{-4} M$ n-propyl bromide plus $8 \times 10^{-3} M$ KOH, respectively. The half-lives of the solvated electrons in these solutions were 3.8, 1.4, and 1.6 μ sec, respectively. The half-life of solvated electrons in pure ethanol containing $8 \times 10^{-3} M$ KOH was 6.2 μ sec. The value of the rate constant $k(e^{-}_{solv} + S)$ is calculated from eq. I.

$$k(e_{solv} + S) = \frac{0.69}{[S]} \left(\frac{1}{t_{1/2}} - \frac{1}{t_{1/2}} \right)$$
 (I)

where $t_{1/2}^{*}$ is the electron half-life in the presence of solute S at concentration [S] and $t_{1/2}^{0}$ is the half-life in the neutral or basic solvent, as appropriate. The above results give $k(e_{solv} + n-C_3H_7Br) = 2.8 \times 10^9$ $M^{-1} \sec^{-1}$ in the neutral sample and $3.2 \times 10^9 M^{-1} \sec^{-1}$ in the basic sample. The values in the presence and absence of base are essentially the same, with an average of $3.0 \times 10^9 M^{-1} \sec^{-1}$.

Rate constants were similarly determined for the reactions of solvated electrons with tetranitromethane and carbon tetrachloride. The values are listed in Table I.



Figure 8. Typical oscilloscope traces of the decay of the solvated electron absorption, pulse dose $\approx 5 \times 10^{16} \text{ eV/g}$, sweep speed 1 μ sec/cm: A, pure ethanol; B, 1.1 $\times 10^{-4} M$ n-C₃H₇Br; C, 1.1 $\times 10^{-4} M n$ -C₃H₇Br + 8 $\times 10^{-3} M$ KOH.

Table I:	Rate	Constants	for	Reactions of	e	_{solv} in Ethanol
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	$k(e^{-k_0}) + k$	S). $10^9 M^{-1}$ sec	n -1
Solute	N ₂ O com- petition ^a	Pulse	Aqueous pulse ^e
CH ₃ CHO	(Assume 4)	4^{f}	3.5
N_2O	7		6.6
$C_2H_5OH_2^+$	$29 \ (>20)^b$	$\geq 20^{b \cdot d}$	22
$C(NO_2)_4$	19	35	46
CCl_4	<9	110	30
n-C ₃ H ₇ Br	≤ 1.3	3.0°	8.5
Napthalene		4.5^{g}	5.4

^a Based on the assumed value for CH₃CHO. ^b The value $k(e_{solv} + acid) = 2.0 \times 10^{10} M^{-1} sec^{-1}$ would be obtained from the competition if the gross concentration of added sulfuric acid were used in the calculation. We used $k_{diss}(H_2SO_4) = 1.7 \times 10^{-3}$ in ethanol at 20°. The value $k(e_{solv} + H^+) = 2.0 \times 10^{10} M^{-1} sec^{-1}$ reported from a pulse study^d was obtained by assuming the dissociation to H⁺ and HSO₄⁻ to be complete. The HCl solutions might have been contaminated by C₂H₅Cl (see ref 11). ^c In neutral or basic solution. ^d I. A. Taub, D. A. Harter, M. C. Sauer, Jr., and L. M. Dorfman, J. Chem. Phys., **41**, 979 (1964). ^e See ref 20. ^f See ref 2. ^g G. L. Bolton, private communication.

Discussion

Pure Ethanol. The present work combined with that of Fletcher and coworkers² demonstrates that $G(\mathbf{H}_2)_0 =$

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5.9 and $G(e^{-}_{solv})_{fi} = 1.7$. The effects previously attributed to an acid-sensitive species X,¹⁵ and the earlier reported "initial" hydrogen yield of $5.0 \pm 0.1^{6.8-11}$ and free ion yield ≈ 1.0 were apparently caused by traces of impurities that react with solvated electrons. The ethanol used in the present experiments was of the highest purity that we have obtained thus far (see Experimental Section). The elimination of greased stopcocks from the vacuum system may also have reduced the possibilities of contamination.

The curve drawn through the hydrogen yields in Figure 1 was calculated from the expression

$$GH(H_2) = 5.9 - 1.7 \left(\frac{k_5 [CH_3 CHO]}{k_2 + k_5 [CH_3 CHO]} \right)$$
 (II)

where 5.9 = $G(H_2)_0$, 1.7 = $G(H_2)_{fi}$, $k_2 = 1.2 \times 10^5$ sec⁻¹,² $k_5 = 4 \times 10^9 M^{-1} \sec^{-1}$,² and [CH₃CHO] is the average acetaldehyde concentration present during the radiolysis. The aldehyde is a radiolysis product and its yield is $G(CH_3CHO] = G(H_2) - 2.3.^9$

Since we are concerned here with trace quantities of scavengers, only the free ions are involved in the competitions. This portion of the mechanism can be represented as follows.

$$mC_{2}H_{5}OH \longrightarrow C_{2}H_{5}OH_{2}+_{solv} +$$

 $e^{-}_{solv} + CH_3CHOH$ (1)

$$e^{-}_{solv} \longrightarrow C_2 H_5 O^{-}_{solv} + H$$
 (2)

$$H + C_2 H_5 OH \longrightarrow H_2 + CH_3 CHOH$$
 (3)

$$C_2H_5OH_2^+{}_{solv} + C_2H_5O^-{}_{solv} \longrightarrow nC_2H_5OH$$
 (4)

$$e^{-}_{solv} + CH_3CHO \longrightarrow CH_3CHO^{-}_{solv}$$
 (5)

 $CH_3CHO_{solv} + C_2H_5OH_2^+_{solv} \longrightarrow$

$$CH_3CHOH + C_2H_5OH$$
 (6)

Nitrous Oxide Solutions. At the dose used to study these solutions, $1 \times 10^{18} \text{ eV/ml}$, in the absence of solute the hydrogen yield was 5.1 and the average acetaldehyde concentration during the irradiation was 2.6 \times 10^{-5} M. Upon addition of nitrous oxide reaction 7 competes with (2) and (5).

$$e^{-}_{solv} + N_2 O \longrightarrow N_2 O^{-}_{solv}$$
 (7)

$$N_2O_{solv} \longrightarrow N_2 + O_{solv}$$
 (8)

The curves through the nitrogen and hydrogen yields in Figure 2 at nitrous oxide concentrations $\leq 10^{-3} M$ were calculated from eq III and IV, respectively. At these concentrations only the free ions participate in the scavenging kinetics.

$$G(N_2) = 1.7 \left(\frac{k_7 [N_2 O]}{k_2 + k_5 [CH_3 CHO] + k_7 [N_2 O]} \right)$$
(III)

$$g(H_2) = 5.9 - 1.7 \times \left(\frac{k_5 [CH_3 CHO] + k_7 [N_2 O]}{k_2 + k_5 [CH_3 CHO] + k_7 [N_2 O]} \right)$$
(IV)

The value of k_7 is 7 \times 10⁹ M^{-1} sec⁻¹ (see later). The curve through the $[G(N_2) + g(H_2)]$ points over this concentration region in Figure 2 represents the sum of eq III and IV.

The agreement between the experimental and the calculated yields is satisfactory.

At solute concentrations $> 10^{-3} M$ scavenging occurs in the spurs. The kinetics of spur reactions has been treated earlier¹¹ and does not require discussion here.

Other Binary Solutions. The hydrogen yields from the acetaldehyde solutions (Figure 3) were similar to those from the nitrous oxide solutions (Figure 2), and those from the acid solutions (Figure 3) were similar to the combined $(H_2 + N_2)$ yields from the nitrous oxide solutions (Figure 2). The curves drawn for the acid and acetaldehyde results are simply the nitrous oxide curves shifted horizontally by factors equal to $k(e^{-solv} + N_2O)/k(e^{-solv} + S)$ that were determined from the competition studies discussed later.

The tetranitromethane and carbon tetrachloride solutions gave hydrogen yields greater than those from the acetaldehyde solutions (Figures 3 and 4). These results are contrary to what would be expected from the relative values of the rate constants shown in Table I; values for aqueous solutions²⁰ are given for comparison. Carbon tetrachloride in ethanol forms hydrochloric acid in a radiation-sensitized chain reaction.²¹ Although the chain length would be short in the present dilute solutions [$G(\text{HCl}) \approx 100$ in 4 M CCl₄²¹ and the concentrations shown in Figure 4 are 10^{-4} to $10^{-1} M$], sufficient hydrochloric acid was formed to increase the hydrogen yields. This was confirmed by the fact that $g(\text{H}_2)$ decreased when the solutions were made alkaline (Figure 4).

The formation of hydrobromic acid from *n*-propyl bromide²² and of nitrous acid from tetranitromethane explains the high hydrogen yields from those solutions in the absence of alkali (Figures 4 and 3, respectively). The electron scavenging efficiency of the acid formed is greater than that of the added organic solute (Table I). Acid formation in the tetranitromethane solutions was less serious than that in the halide systems.

$$e^{-}_{solv} + RX \longrightarrow R + X^{-}_{solv}$$
 (9)

$$e^{-}_{solv} + C_2 H_5 O H_2^+_{solv} \longrightarrow C_2 H_5 O H + H$$
 (10)

The formation of acid explains the abnormally low efficiency of electron scavenging reported for carbon tetrachloride by Adams and Sedgwick.⁸

Electron Scavenging Competitions. Rate Constants. Competitions were run between nitrous oxide and other solutes to determine relative values of $k(e^{-}_{solv} + S)$. Results were plotted according to the expression

$$\frac{G(N_2)_0}{G(N_2)} = 1 + \frac{k_s[S]}{k_{N_2O}[N_2O]}$$
(V)

where $G(N_2)_0$ is the yield in the absence of a second



Figure 9. Kinetic analysis of competition of nitrous oxide with acetaldehyde and tetranitromethane for electrons: open points, $1.2 \times 10^{-2} M N_2O$; filled points, $1.0 \times 10^{-2} M N_2O$. Competitor S: Δ , \blacktriangle , acetaldehyde; \bigcirc , \blacklozenge , tetranitromethane.



Figure 10. Kinetic analysis of competition between nitrous oxide and the halides: CCl₄ (A), $9 \times 10^{17} \text{ eV/ml}$: O, $[N_2O] =$ $2.2 \times 10^{-3} M_i \rightarrow -$, $[N_2O] = 1.0 \times 10^{-2} M_i$; 33×10^{17} $eV/ml; \langle \rangle, [N_2O] = 1.1 \times 10^{-3} M_i$; C₃H₇Br (B), $[N_2O] =$ $1.0 \times 10^{-3} M$: O, $9 \times 10^{17} \text{ eV/ml}; \langle \rangle, 33 \times 10^{17} \text{ eV/ml}.$ The dashed lines represent the rate constants obtained by the pulse-spectroscopic technique.

solute and $G(N_2)$ is the yield in the presence of concentration [S] of the second solute. Plots for acetaldehyde and tetranitromethane are shown in Figure 9. The value $k(e_{solv} + CH_3CHO) = 4 \times 10^9 M^{-1} \text{ sec}^{-1}$ obtained from pulse measurements by Fletcher and coworkers² was then used to obtain the absolute values of the rate constants listed in Table I.

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The competitions of nitrous oxide with acetaldehyde. tetranitromethane, and sulfuric acid were well behaved and they were described by eq V. However, the halide systems were complicated by the formation of acid. This was demonstrated by the effects of dose and the addition of base (Figures 6 and 10). The addition of base complicates the system further, because nitrous oxide can also form nitrogen by a chain process in irradiated alkaline solutions.23 The rate constants given for CCl_4 and $n-C_8H_7Br$ in the competition column of Table I were obtained from the solutions in which no base was added and which were given a dose of 9×10^{17} eV/ml; the values are upper limits because no correction was made for the acid formed. That an appreciable amount of acid was formed in the carbon tetrachloride solutions is indicated by the high hydrogen yields (Figure 6A). The acid effect in the n-propyl bromide competition was almost negligible, as indicated by the similar hydrogen yields in the presence and absence of base (Figure 6B).

Rate Constant Values. Pulse Radiolysis and Competition Kinetics. The values of $k(e^{-}_{solv} + S)$ obtained for tetranitromethane, carbon tetrachloride, and *n*-propyl bromide by the pulse-spectroscopic technique were significantly larger than those obtained from the competition with nitrous oxide (Table I). This type of difference has been noted for halides before²⁴ and might be due to an electron exchange reaction such as²⁵

$$RX_{solv} + N_2O \longrightarrow RX + N_2O_{solv}$$
 (11)

The effect is not due to the production of acid in the pulse experiments because the same value of the rate constant was obtained in the presence and absence of an excess of alkali ($k = 11.5 \pm 1.5$ for CCl₄ and 3.0 ± 0.2 for n-C₃-H₇Br, in units of 10⁹ M^{-1} sec⁻¹). The comparison of the two techniques merits further investigation.

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Mechanism of the Radiation-Induced Dechlorination of

1,1,1-Trichloro-2,2-bis(p-chlorophenyl)ethane in Alcoholic Solution

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1,1,1-Trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT) undergoes dechlorination to 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (DDD) in γ -irradiated 2-propanol solution. The large *G* yields obtained indicate a chain mechanism for the process. Reduction in yield in the presence of small concentrations of free-radical scavengers shows the participation of free radicals as chain carriers, while the dependence of yield on dose rate is consistent with chain termination *via* bimolecular reaction of these radicals. A detailed mechanism is proposed for the reaction.

In the presence of aliphatic alcohols containing a carbinol hydrogen, carbon tetrachloride undergoes radiolytic dechlorination to chloroform and hydrochloric acid with high G yields,² indicating a chemical chain reaction. Since carbon tetrachloride may be considered a structural model for DDT it was of interest to extend the study of chlorinated hydrocarbons to solutions of DDT. In preliminary experiments⁸ it was in fact found that DDT underwent radiolytic chain dechlorination in 2-propanol solution similar to that of carbon tetrachloride. In the present communication details of the reaction mechanism are examined.

Experimental Section

Materials. DDT (City Chemical Corp. and Matheson Coleman and Bell, p,p-DDT) was recrystallized twice from petroleum ether (mp 107.5-109°). 2-Propanol (Baker spectroscopic grade) was used as received. The only detectable impurity was acetone

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