used ethylene in liquid cyclopentane and $G(H_2)$ decreased from 5.2 in pure cyclopentane without reaching a well-defined lower limit. Assuming simple competition between ethylene and cyclopentane to yield ethane (via $C_2H_5 + RH \rightarrow C_2H_6 + R$) or hydrogen we obtain by conventional stationary-state kinetics from Holroyd's results limiting values of $G(C_2H_6)$ approximating 1.0, 0.80, and 0.9 at 28, 15, and 0°, respectively. Since $G(H_2) + G(C_2H_6)$ is constant at each temperature, one may conclude that G(H, thermal) $\cong$ 0.9. This supports the low yield of thermal H atoms based upon our own measurements.[35]

The correlation between the yields $2\Delta G(C_5H_8) \approx \Delta G(C_5H_9I)$ for cyclopentane suggests interdependent mechanisms for the formation of these products. The substantial constancy of $G(HI) + G(CH_4)$ indicates that the organic counterparts of these products are not

(34) R. A. Holroyd, J. Phys. Chem., **66**, 730 (1962).

(35) Holroyd did not draw the same conclusion. He assumed that his $G(H_2)$ = 5.2 for pure cyclopentane was low because of H-atom scavenging by product cyclopentene, for which the final concentration approximated 10^{-3} M. This same concentration of ethylene, however, produced no detectable effect. The value of $G(H_2)$ in Table II for pure cyclopentane agrees with Holroyd's value.

included among those reported. In cyclohexane it is also clear that $G(H_2)$, $G(C_6H_{10})$, and $G(C_6H_{11}I)$ behave qualitatively the same with respect to concentration of methyl iodide while again $G(HI) + G(CH_4)$ is constant and requires other conjugate organic products and an independence of the ion recombination process.

According to Dyne and Stone[7] the only organic products from γ-radiolysis are cyclohexene and bicyclohexyl- and cyclohexylhexene-1, and the yields of these hydrogen-deficient products accounted for 99% of $G(H_2)$. These products cannot account for the large absorption in the 200 mμ regions observed in the present work in excess of that required for $G(C_6H_{10})$ determined by v.p.c. analysis in irradiated pure cyclohexane. It appears to be a nonconjugated olefinic product and our results show that this excess absorption can be accounted for, at least in part, by an olefin boiling around 65° and resulting from C–C bond rupture since it is neither 1,3- nor 1,4-cyclohexadiene. Finally, it would have been very remarkable if no C–C bonds were broken by radiolysis of cycloalkanes since it is a rather efficient process in linear and branched alkanes.[12,21]

The Radiolysis of Deaerated Aqueous Solutions of 2-Propanol Containing Nitrous Oxide[1]

BY J. T. ALLAN AND C. M. BECK

Deaerated aqueous solutions of 2-propanol containing nitrous oxide were irradiated with 2.5 Mev. electrons and the yields of nitrogen, hydrogen, acetone, and hydrogen peroxide measured as a function of pH, solute concentration, and radiation dose rate. The effects of additional solutes on the product yields were also investigated. The results have been interpreted on the basis of the primary formation of two reducing species in irradiated water—the hydrated electron and a species which behaves as a hydrogen atom. The yields, reactivity, and possible modes of formation of these species have been discussed.

Introduction

In general the radical species formed in the radiation-induced decomposition of water have been referred to as "H" and "OH." The radicals were assumed to result from reactions between water molecules and the charged intermediates[2] produced according to

$$H_2O \rightsquigarrow H_2O^+ + e^- \qquad (1)$$
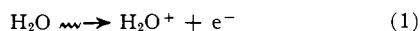
or from excited water molecules formed by recombination of the electrons and the positively charged parent ions.[3] Later studies[4-9] indicated the existence of two different forms of reducing species in aqueous systems, which led to a re-evaluation of previous considerations concerning reactions of the charged intermediates with suitable acceptors.[10] Chemical[4-9,11,12] and physical[13,14]

(1) This work is supported, in part, by the U. S. Atomic Energy Commission.

(2) D. E. Lea, "Actions of Radiations on Living Cells," Cambridge University Press, 1946.

(3) M. Burton, J. L. Magee, and A. H. Samuel, J. Chem. Phys., **20**, 760 (1952); H. A. Samuel and J. L. Magee, ibid., **21**, 1080 (1953).

(4) E. Hayon and J. Weiss, Proc. Intern. Conf. Peaceful Uses At. Energy, **29**, 80 (1958).

(5) J. H. Baxendale and G. Hughes, Z. physik. Chem., **14**, 306 (1958).

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

(7) J. T. Allan and G. Scholes, Nature, **187**, 218 (1960).

(8) F. S. Dainton and D. B. Peterson, ibid., **186**, 878 (1960).

(9) P. Kelly and M. Smith, J. Chem. Soc., 1487 (1961).

(10) (a) G. Stein, Discussions Faraday Soc., **12**, 227, 289 (1952); (b) H. Frohlich and R. L. Platzman, Phys. Rev., **92**, 1152 (1953); (c) J. Weiss, Nature, **174**, 78 (1954); (d) R. L. Platzman, Radiation Res., **2**, 1 (1955); (e) J. Weiss, Experientia, **12**, 7, 280 (1956).

investigations have now established that radiation-produced electrons constitute the major portion of the so-called "H" radicals in aqueous media and that these may give rise to hydrogen atoms by reaction with H_3O^+. The charged reducing species (hydrated electron or negative polaron[15]) is referred to here as e_{aq}^-.

Allan and Scholes[7] showed that, in addition to hydrated electrons, another reducing species was produced independently in a yield of $G \sim 0.6$. This was presumed to be a hydrogen atom and to be formed by the decomposition of an excited water molecule according to

$$H_2O^* \longrightarrow H + OH \qquad (2)$$

H_2O^* could presumably result from direct excitation or from ion recombination.[3] To distinguish this independently formed species from the hydrogen atom produced in the reaction

$$e_{aq}^- + H_3O^+ \longrightarrow H + H_2O \qquad (3)$$
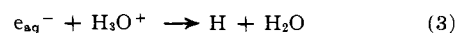
it will be referred to as H^α. The existence of H^α has since been confirmed by other workers using different aqueous organic systems.[11,16] For ^{60}Co-γ and electron

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

(12) G. Czapski and H. A. Schwarz, ibid., **66**, 471 (1962).

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

(14) J. P. Keene, Nature, **197**, 47 (1963).

(15) J. Weiss, ibid., **186**, 751 (1960).

(16) (a) J. Rabani, J. Am. Chem. Soc., **84**, 868 (1962); (b) J. Rabani and G. Stein, J. Chem. Phys., **37**, 1865 (1962).
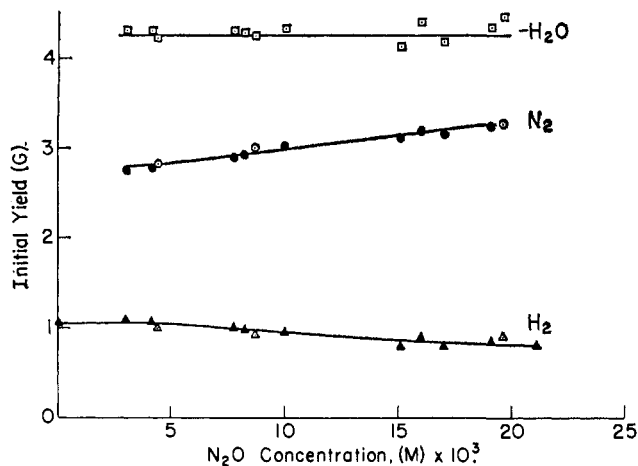
Fig. 1.—Dependence of the N_2 and H_2 yields on N_2O concentration in deaerated solutions of 10^{-2} M 2-propanol irradiated with 2.5 Mev. electrons at pH 5.90: ●, △, 0.5×10^{-6} amp.; ○, △, 0.5×10^{-7} amp.

Fig. 2.—Plot of pH dependence of the N_2 and H_2 yields in deaerated solutions of 10^{-2} M 2-propanol and 10^{-2} M N_2O irradiated with 2.5 Mev. electrons.

irradiations of aqueous solutions under neutral conditions of pH (5–7) the apparent yields of water decomposition and of "H" radicals are generally accepted to be $G(-H_2O) = 3.80$ and $G("H") = 2.90$, respectively.[17] Since H^α is formed to the extent of $G(H^\alpha) = 0.6$, Allan and Scholes concluded that the yield of hydrated electrons under these conditions should be $G(e_{aq}^-) = 2.30$. Czapski and Allen[18] subsequently showed, however, that in solutions containing O_2 and H_2O_2 the yield of hydrated electrons was $G = 2.85 \pm 0.15$. To explain these contradictory observations regarding the relative yields of e_{aq}^- and H^α the following explanations have been proposed: (a) Hayon[19] has suggested that O_2 may react with the H^α precursor in such a way as to convert it to a hydrated electron. (b) Lifschitz,[20] from studies of the deuterium isotope effect in H_2O-D_2O solutions of sodium formate, obtained data which were incompatible with the formation of H^α via reaction 2. It was concluded that H^α may result from the "spur" reactions 1, 4, and 5

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH \qquad (4)$$

$$H_3O^+ + e_{aq}^- \longrightarrow H + H_2O \qquad (5)$$
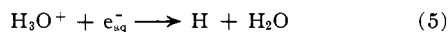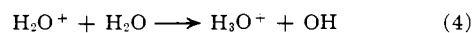
and that in solutions containing efficient electron scavengers, the formation of H^α would be suppressed.

Further studies by Rabani and Stein[16b] indicated that the accepted yield of "H" radicals was unreliable, since they calculated $G(e_{aq}^-)$ and $G(H^\alpha)$ to be, respectively, 2.65 and 0.55 in neutral solutions containing 2-propanol and acetone.

In the following presentation we submit data obtained from chemical studies of electron-irradiated aqueous solutions containing 2-propanol and N_2O. This work was undertaken in order to determine: (a) whether or not H^α is produced in the presence of an efficient electron scavenger (N_2O); (b) the yields of the reducing species, $G(e_{aq}^-)$ and $G(H^\alpha)$, and of $G(-H_2O)$ as a function of electron scavenger concentration; (c) the relative rate constants for reactions of e_{aq}^- with certain added solutes.

(17) A. O. Allen, "The Radiation Chemistry of Water and Aqueous Solutions," D. Van Nostrand Co., Inc., New York, N. Y., 1961, p. 46.
(18) G. Czapski and A. O. Allen, J. Phys. Chem., 66, 262 (1962).
(19) E. Hayon, Nature, 196, 533 (1962).
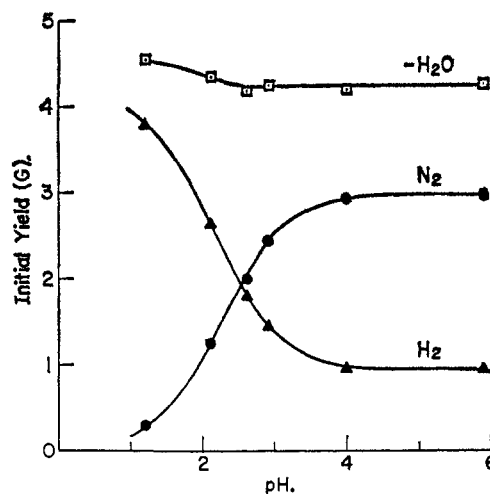(20) C. Lifschitz, Can. J. Chem., 40, 1903 (1962).

Experimental

Solutions were prepared from distilled water which had been redistilled from acidified dichromate and alkaline permanganate and then given a final distillation. The pH of the water was usually in the range pH 5.9 ± 0.2. Other pH values were obtained using sulfuric acid or sodium hydroxide; no buffers were used. 2-Propanol (Fisher certified reagent) was redistilled from 2,4-dinitrophenylhydrazine to remove trace amounts of acetone. Other solutes were the best grade obtainable and were used without additional purification. Nitrous oxide (Matheson Co., Inc.) was purified by several trap to trap distillations in a mercury-free vacuum line, the line being evacuated for 5 min. after each freezing at $-196°$. A sample prepared in this manner and analyzed by mass spectrometry contained no impurity.

Irradiations were carried out with 2.5 Mev. electrons from a Van de Graaff accelerator. The beam current was varied between 0.5×10^{-8} and 0.5×10^{-6} amp.

Solutions were degassed by the standard freezing–pumping technique, a predetermined amount of N_2O transferred into the vessel, and then shaken and equilibrated at $24°$ for several hours prior to irradiation. The concentration of N_2O in the solution was determined from the distribution constant C_{N_2O} in vapor/C_{N_2O} in water $= 1.63 \pm 0.05$ which was calculated for the experimental temperature ($24°$) from data available on the dependence of solubility and of Henry's coefficient for N_2O in water as a function of temperature and pressure.

The gaseous products were collected by means of a toepler pump after passing through two traps cooled to -78 and $-196°$, respectively. The collection procedure was repeated four times after additional shakings were given to the solution. The gases retained in the traps were distilled from trap to trap (three times) and any additional N_2 and H_2 collected after each distillation. The gas samples were subsequently analyzed by mass spectrometry. Acetone was quantitatively determined by the microcolorimetric technique developed by Berntsson[21] and hydrogen peroxide was measured using the iodide technique.[22]

Results

The measured products in the electron irradiation of deaerated aqueous solutions of 2-propanol and N_2O were nitrogen, hydrogen, hydrogen peroxide, and acetone. Unless otherwise stated, the product yields were a linear function of the radiation dose. Doses of up to 10^{17} e.v./ml. were employed. G-Values were obtained from yield–dose plots representing at least four determinations.

Figure 1 shows the dependence of the yields of N_2 and H_2 as a function of N_2O concentration in neutral solutions of 10^{-2} M 2-propanol irradiated with 2.5

(21) S. Berntsson, Anal. Chem., 28, 1337 (1956).
(22) A. O. Allen, C. J. Hochanadel, J. A. Ghormley, and T. W. Davis, J. Phys. Chem., 56, 575 (1952).

Mev. electrons at a beam current of 0.5×10^{-6} amp. At N$_2$O concentrations lower than $\sim 5 \times 10^{-3}$ M the measured yield of H$_2$, $G(\text{H}_2) = 1.05$, was identical with the yield obtained for 2-propanol solutions containing no added N$_2$O.[7] The yield of N$_2$ in the range 3 to 5 $\times$ 10^{-3} M was $G(\text{N}_2) = 2.80 \pm 0.1$. Increasing the N$_2$O content to 2×10^{-2} M led to a decrease, $\Delta G = 0.25$, in the yield of H$_2$ and to an increase, $\Delta G = 0.50$, in the N$_2$ yield. For solutions containing 10^{-1} M 2-propanol and 3×10^{-3} M N$_2$O the yields were $G(\text{N}_2)$ 2.88 and $G(\text{H}_2)$ 1.10.

In acidified 10^{-2} M 2-propanol solutions at pH 1.20 the H$_2$ yield decreased linearly from $G(\text{H}_2)$ 4.00 to 3.50 and the N$_2$ yield increased from zero to $G(\text{N}_2)$ 0.70 over the N$_2$O concentration range 0 to 2.27×10^{-2} M.

Figure 2 is a plot of $G(\text{N}_2)$ and $G(\text{H}_2)$ as a function of pH for 10^{-2} M 2-propanol solutions containing 10^{-2} M N$_2$O. Increasing the pH led to higher yields of N$_2$ and lower yields of H$_2$; the limiting values, $G(\text{H}_2)$ 0.95 and $G(\text{N}_2)$ 2.98, were reached at pH ~ 5.

In the presence of 0.1 N NaOH (pH ~ 13) the yields were found to be $G(\text{H}_2)$ 0.55 and $G(\text{N}_2)$ 10.6. The high yield of N$_2$ was indicative of a chain process in the alkaline solutions; yields were therefore determined at various radiation intensities (beam currents). The results are given in Table I. The dose range was re-

TABLE I

N$_2$ AND H$_2$ YIELDS IN 10^{-2} M 2-PROPANOL–10^{-2} M N$_2$O SOLUTIONS IRRADIATED AT pH ~ 13 (0.1 N NaOH) WITH 2.5 MEV. ELECTRONS

Beam current, amp.	$G(\text{H}_2)$	$G(\text{N}_2)$
0.5×10^{-5}	0.52 ± 0.05	6.4 ± 0.2
$.5 \times 10^{-6}$	$.52 \pm .05$	$10.6 \pm .3$
$.5 \times 10^{-7}$	$.53 \pm .05$	$16.4 \pm .5$
$.5 \times 10^{-8}$	$.61 \pm .05$	21.0 ± 2.0

duced at lower intensities to ensure that the measured values were initial yields and that acetone did not reach a sufficient concentration to compete with N$_2$O for the hydrated electrons. The yields of acetone were measured in solutions containing 10^{-2} M 2-propanol and 10^{-2} M N$_2$O at various pH values and with different radiation dose rates. These results are summarized in Table II.

TABLE II

YIELDS OF ACETONE IN 10^{-2} M 2-PROPANOL–N$_2$O SOLUTIONS IRRADIATED WITH 2.5 MEV. ELECTRONS

pH	Beam current, amp.	N$_2$O concn., M	$G(\text{acetone})$
1.20	0.5×10^{-6}	10^{-2}	2.82
1.20	$.5 \times 10^{-6}$	2×10^{-2}	2.87
1.20	$.5 \times 10^{-8}$	10^{-2}	3.30^a
2.85	$.5 \times 10^{-6}$	10^{-2}	2.40
5.90	$.5 \times 10^{-6}$	10^{-2}	2.27
5.90	$.5 \times 10^{-6}$	2×10^{-3}	2.35
5.90	$.5 \times 10^{-8}$	10^{-2}	3.05^a

^{a} Nonlinear yield–dose relationships. G-values were initially lower.

The molecular yields of H$_2$O$_2$ were determined in 10^{-2} M 2-propanol–N$_2$O solutions at pH 5.90 using N$_2$O concentrations in the range 4.3×10^{-3} to 1.96×10^{-2} M and electron beam currents of 0.5×10^{-6}, 0.5×10^{-7}, and 0.5×10^{-8} amp. The initial yield of H$_2$O$_2$ was $G^M(\text{H}_2\text{O}_2)$ 0.56 ± 0.03 in all cases. However, at beam currents lower than 0.5×10^{-6} amp. the H$_2$O$_2$ reached a steady-state concentration in the dose range
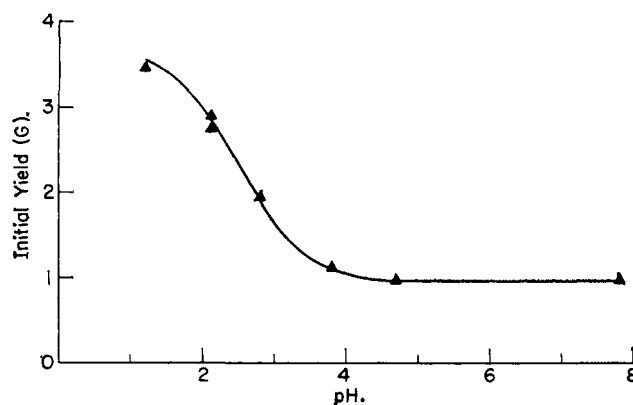

Fig. 3.—Plot of pH dependence of the H$_2$ yields in deaerated solutions of acetaldehyde irradiated with 2.5 Mev. electrons.

investigated (doses $< 10^{17}$ e.v./ml.). The steady-state concentration was 10^{-5} M at 0.5×10^{-8} amp. and increased with increasing dose rate.

Effect of Added Solutes. Acetone.—Table III gives the measured yields of N$_2$ and H$_2$ in 10^{-2} M 2-propanol–N$_2$O solutions containing 0.94×10^{-2} M acetone. The solutions were irradiated at pH 5.90 with a beam current of 0.5×10^{-6} amp. The acetone concentration (0.94×10^{-2} M) was the analytically determined amount present in the solutions just prior to irradiation and represents the amount remaining after evacuation of an initially 10^{-2} M solution.

TABLE III

INITIAL YIELDS OF N$_2$ AND H$_2$ IN IRRADIATED 10^{-2} M 2-PROPANOL–N$_2$O SOLUTIONS (pH 5.90) CONTAINING 0.94×10^{-2} M ACETONE

N$_2$O concn., M	$G(\text{N}_2)$	$G(\text{H}_2)$
5.02×10^{-3}	1.12	0.87
7.03×10^{-3}	1.53	.82
1.04×10^{-2}	1.76	.85

Acetaldehyde.—The measured yields of N$_2$ and H$_2$ in 10^{-2} M 2-propanol solutions containing 10^{-2} M N$_2$O and 10^{-2} M acetaldehyde irradiated at pH 5.90 were, respectively, $G(\text{N}_2)$ 2.14 and $G(\text{H}_2)$ 0.90.

Figure 3 shows the pH dependence of $G(\text{H}_2)$ in deaerated solutions of 10^{-2} M acetaldehyde irradiated with 2.5 Mev. electrons (0.5×10^{-6} amp.). The curve which is drawn represents the theoretical pH dependence taking a value of 1.69 for the ratio of the rate constants of reaction 3 and the competing reaction of acetaldehyde with hydrated electrons, calculated from the results obtained with the 2-propanol–N$_2$O–acetaldehyde system.
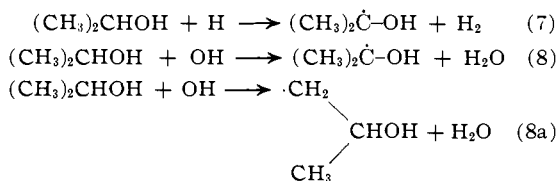
Discussion

Dainton and Peterson[8,23] have shown from studies of the γ-radiolysis of aqueous N$_2$O solutions that N$_2$O has a high reactivity toward e_{aq}^-, the products of the reaction being nitrogen and an oxidizing species, presumably OH (or O$^-$).

$$\text{N}_2\text{O} + e_{aq}^- \longrightarrow \text{N}_2 + \text{OH} + \text{OH}^- \qquad (6)$$
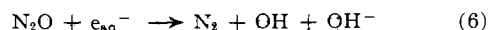
Hydrogen atoms undergo a relatively slow reaction with N$_2$O; thus in the presence of 2-propanol the reaction sequence may be represented by reaction 6 together with the processes

(23) F. S. Dainton and D. B. Peterson, Proc. Roy. Soc. (London), A267, 443 (1962).

$$(CH_3)_2CHOH + H \longrightarrow (CH_3)_2\dot{C}\text{-}OH + H_2 \quad (7)$$

$$(CH_3)_2CHOH + OH \longrightarrow (CH_3)_2\dot{C}\text{-}OH + H_2O \quad (8)$$

$$(CH_3)_2CHOH + OH \longrightarrow \cdot CH_2$$
$$\diagdown$$
$$\qquad\qquad\qquad\qquad\qquad CHOH + H_2O \quad (8a)$$
$$\diagup$$
$$\qquad\qquad CH_3$$

The organic free radicals produced in reactions 7 and 8 and in reaction 8a will be referred to as R and R′, respectively. Subsequent dismutation reactions of these radicals accounts for the formation of acetone. Assuming that all the hydrated electrons react with the N_2O, this system provides a convenient method for the determination of the yields of e_{aq}^- and H^α since, according to the above mechanism, $G(e_{aq}^-) = G(N_2)$ and $G(H^\alpha) = G(H_2) - G^M(H_2)$.
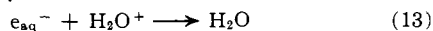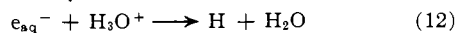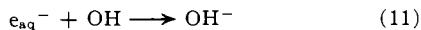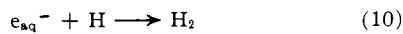
In neutral solutions of 2-propanol and N_2O (Fig. 1) the yield of H_2 was consistently greater than the maximum value for molecular hydrogen formation, i.e., $G^M(H_2)$ 0.45, indicating that H^α is produced even in the presence of comparatively high concentrations of N_2O.

The molecular yield of hydrogen as determined in deaerated solutions of $3 \times 10^{-3} M$ $CuSO_4$ containing $2 \times 10^{-2} M$ N_2O was found to be $G^M(H_2)$ 0.25 ± 0.05. The decrease in $G(H_2)$ with increasing N_2O concentration can therefore be ascribed wholly to the scavenging of molecular hydrogen precursors by N_2O and, since the reaction between H atoms and N_2O is generally considered to be a slow process, these observations are consistent with the view that the molecular hydrogen yield arises, at least in part, from reactions of electrons, the most predominant of which is presumably

$$e_{aq}^- + e_{aq}^- \longrightarrow H_2 \quad (9)$$
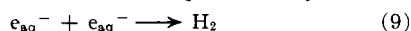
That this reaction does in fact yield hydrogen was recently demonstrated by Dorfman and Taub.[24] The yield of H^α in the system is $G(H^\alpha)$ 0.60 ± 0.05 and is constant for $10^{-2} M$ 2-propanol solutions containing 0.3 to $2.1 \times 10^{-2} M$ N_2O.

The N_2 yield is a composite function of the scavenging by N_2O of electrons in the bulk of the solution together with some scavenging of electrons in the spurs. On the assumption that the reduction in $G^M(H_2)$ is due only to scavenging of reaction 9, the contribution to $G(N_2)$ would be twice the decrease in $G(H_2)$. The results given in Fig. 1 show that the ratio $\Delta G(N_2)/\Delta G(H_2)$ is in fact close to 2, from which it might be inferred therefore that scavenging by N_2O of other

$$e_{aq}^- + H \longrightarrow H_2 \quad (10)$$

$$e_{aq}^- + OH \longrightarrow OH^- \quad (11)$$

$$e_{aq}^- + H_3O^+ \longrightarrow H + H_2O \quad (12)$$

$$e_{aq}^- + H_2O^+ \longrightarrow H_2O \quad (13)$$

spur reactions does not occur to any significant extent over the range of N_2O concentration investigated. In view of the large concentration dependence of $G(N_2)$ observed by Dainton and Peterson using solutions of N_2O, such a conclusion would be surprising unless the determining factor in the scavenging of back reaction 11 is the reaction of 2-propanol with OH radicals (8 and 8a) rather than the scavenging of electrons by N_2O according to reaction 6. Allowing for contributions to $G(N_2)$ from scavenging of reaction 9 the yield of hydrated electrons in the bulk of the solution is G-(e_{aq}^-) 2.80 ± 0.1 and is independent of N_2O concentra-

tion over the range investigated. Also given in Fig. 1 are the yields of net water decomposition, calculated from the expression

$$G(-H_2O) = G(N_2) + 2G(H_2) - G(H^\alpha) \quad (A)$$

The yield, $G(-H_2O)$ 4.25 ± 0.15, is constant over the range of N_2O concentration indicated.

In $10^{-1} M$ 2-propanol solutions containing $3 \times 10^{-3} M$ N_2O the yields of N_2 and H_2 are somewhat higher than those obtained using $10^{-2} M$ 2-propanol. This effect probably results from additional scavenging by 2-propanol of hydrogen atoms and OH radicals which normally undergo spur reactions such as 10 and 11.

The N_2O concentration dependence of $G(N_2)$ and $G(H_2)$ in acidified solutions is attributed to a simple competition between H_3O^+ ions and N_2O for the hydrated electrons, reactions 3 and 6. The increase in $G(N_2)$ over the concentration range is somewhat greater than the decrease in $G(H_2)$, indicating that the competition can also occur in the spurs and thus reduce $G^M(H_2)$ which under these conditions of pH is normally produced according to reaction 9 and/or reactions 3 and 14

$$H + H \longrightarrow H_2 \quad (14)$$
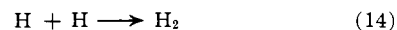
A correction for this effect may be made using the value of $k_3/k_6 = 1.64$ obtained from a kinetic treatment of the results presented in Fig. 2. Values for net water decomposition were then obtained from expression A. The yield was constant, $G(-H_2O)$ 4.50 ± 0.10, over the range 0.2 to $2.3 \times 10^{-2} M$ N_2O.

The influence of pH on the gas yields is shown in Fig. 2. The results are explained on the basis of a simple competition between reactions 3 and 6. Values for $G(-H_2O)$ were obtained from expression A assuming $G(H^\alpha)$ to be independent of pH and correcting for the small change in $G^M(H_2)$ (0.35 to 0.45) on increasing the pH from neutral to acid solutions at pH 1.20. The curves drawn through the $G(H_2)$ and $G(N_2)$ values in Fig. 2 were obtained from relationships B and C, respectively. The competition kinetics are expressed in terms of the measured H_2 yields by the relationship

$$\frac{G(e_{aq}^-)}{G(H_2) - G(H^\alpha) - G^M(H_2)} = \frac{k_6[N_2O]}{k_3[H^+]} + 1 \quad (B)$$

A plot of the left-hand side of expression B vs. $[N_2O]/[H^+]$ yields a straight line and a value for the ratio of rate constants of $k_3/k_6 = 1.64$. The yield of N_2 under these conditions is given by

$$G(N_2) = \frac{G(e_{aq}^-)}{1 + (k_3[H^+]/k_6[N_2O])} \quad (C)$$

The theoretical curve calculated from this expression is seen to be in good agreement with the experimental points (Fig. 2). The slight deviation at pH 1.20 is partially a result of a salt effect which favors reaction 3 and amounts to a reduction of approximately 6% in the value of k_3/k_6.
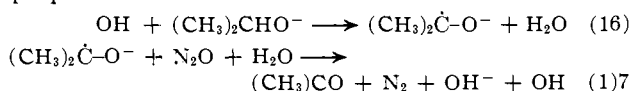
In the presence of 0.1 N NaOH (pH ∼13) the yield of hydrogen in $10^{-2} M$ 2-propanol-$10^{-2} M$ N_2O solutions is reduced to $G(H_2) = 0.55 ± 0.05$. This effect has been attributed[25] to the introduction of reaction 15 in competition with reaction 7.

(24) L. M. Dorfman and I. A. Taub, *J. Am. Chem. Soc.*, **85**, 2370 (1963).

(25) J. T. Allan, M. G. Robinson, and G. Scholes, *Proc. Chem. Soc.*, 381 (1962); M. S. Matheson and J. Rabani, *Radiation Res.*, **19**, 180 (1963).

$$H^\alpha + OH^- \longrightarrow e_{aq}^- \qquad (15)$$
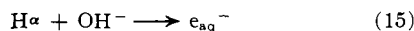
The radiation-induced chain reaction which results in high yields of N$_2$ has been attributed[26] to the interaction of N$_2$O with the radical produced from the 2-propanol ion

$$OH + (CH_3)_2CHO^- \longrightarrow (CH_3)_2\dot{C}-O^- + H_2O \quad (16)$$
$$(CH_3)_2\dot{C}-O^- + N_2O + H_2O \longrightarrow$$
$$(CH_3)CO + N_2 + OH^- + OH \quad (1)7$$

The $G(N_2)$ values given in Table I do not satisfy the simple kinetic relationship which may be derived on the basis of reactions 16 and 17 alone, i.e.

$$G(N_2)_{measd} = G(e_{aq}^-) + \frac{k_{16}(N_2O)}{\sqrt{D}}$$

where D = dose rate. This is not surprising since only 87% of the 10^{-2} M 2-propanol is present as the 2-propanol ion at pH 13[27]; thus reactions 8 and 8a will constitute chain-breaking processes as well as interactions of the radicals R and R' and their respective radical ions. A rough kinetic interpretation of the results gives a value for the electron yield of $G(e_{aq}^-)$ 3.7 ± 0.3. Taking into account the contributions to this yield from reaction 15 and from scavenging of molecular hydrogen precursors at 10^{-2} M N$_2$O, the yield of hydrated electrons in the bulk of the solution at pH 13 may be taken as 3.1 ± 0.3.

In aqueous 2-propanol solutions irradiated in vacuo with ^{60}Co γ-rays or with low dose rate (e.g., 0.5 × 10^{-8} amp.) electron radiations the molecular hydrogen peroxide is present in a low stationary-state concentration in both neutral and acidified solutions. The disappearance of H$_2$O$_2$ is accounted for by a chain process, initiated by reaction of the organic radical R (and possibly R') with H$_2$O$_2$ according to

$$(CH_3)_2\dot{C}-OH + H_2O_2 \longrightarrow (CH_3)_2CO + H_2O + OH \quad (18)$$
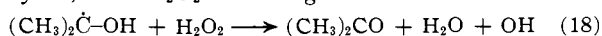
This effect also accounts for the higher yields of acetone observed in solutions irradiated at low dose rates (Table II) and for the nonlinearity of the acetone yield–dose dependencies which were obtained.

The suggestion[23] that the oxidizing species produced in reaction 6 is an OH or O$^-$ radical is confirmed by equating the acetone yields presented in Table II to the yields of H (and H$^\alpha$) and OH radicals which are produced under the corresponding conditions of pH and dose rate. H atoms react with 2-propanol according to reaction 7 and yield organic radicals R, which on dismutation give acetone via

$$2(CH_4)_2\dot{C}-OH \longrightarrow (CH_3)_2CO + (CH_3)_2CHOH \quad (19)$$
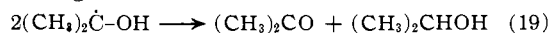
The formation of diol from combination of R radicals apparently does not occur.[16b,28] Hydroxyl radicals, however, undergo a less specific dehydrogenating reaction with 2-propanol and yield both R and R' radicals according to reactions 8 and 8a, respectively.[28] This has been shown to be small (~2% reaction at the methyl group) in the case of H atoms.[29] Since not all reactions of R and R' yield acetone, the following equation may be derived

$$G(\text{acetone}) = \frac{G(H)}{2} + \frac{FG(OH)}{2} \quad (D)$$

where F is constant and represents the fraction of OH radicals which lead ultimately to acetone formation. In 10^{-2} M 2-propanol–10^{-2} M N$_2$O solutions irradiated at pH 5.9 with a beam current of 0.5 × 10^{-6} amp., $G(e_{aq}^-) = 3.00$ $G(H^\alpha) = 0.6$, $G^M(H_2) = 0.35$, $G^M(H_2O_2) = 0.56$, and $G(OH) = 3.10$. The measured yield of acetone was G 2.30; thus assuming that each e_{aq}^- leads to an OH radical via reaction 6, the fraction F is calculated to be 0.66. The yields of acetone calculated in this manner from (D), and taking into account reaction 18 at the low dose rate, agree to within 0.1 G with the experimentally determined values at the other pH's shown in Table II.

Effect of Added Solutes.—The presence of an additional electron scavenger in the 2-propanol–N$_2$O system should result in a competition between the added solute and N$_2$O for the radiation-produced electrons and thus lead to a decrease in the yield of nitrogen.

In the case of acetone the competing reaction is

$$(CH_3)_2CO + e_{aq}^- \longrightarrow [(CH_3)_2CO]^- \quad (20)$$
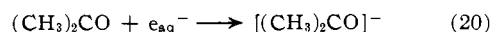
and the competition kinetics may be represented by the relationship

$$\frac{G(e_{aq}^-)}{G(N_2)} = \frac{k_{20}[(CH_3)_2CO]}{k_6[N_2O]} + 1 \quad (E)$$

The yields of N$_2$ and H$_2$ in the 10^{-2} M 2-propanol–0.94 × 10^{-2} M acetone–N$_2$O system were determined for several N$_2$O concentrations and the data (Table III) plotted according to eq. E. The yield of hydrated electrons was determined from

$$G(-H_2O) = G(e_{aq}^-) + 2G(H_2) - G(H^\alpha) \quad (F)$$

assuming $G(-H_2O)$ 4.25 and $G(H^\alpha)$ 0.60. A linear relationship was obtained which yielded a value for the ratio of rate constants of $k_6/k_{20} = 1.02$, from which it may be inferred that $k_3/k_{20} = 1.67$.

For the 2-propanol–N$_2$O system containing acetaldehyde as the added electron scavenger the ratio of rate constants for the competing reactions 6 and

$$CH_3CHO + e_{aq}^- \longrightarrow [CH_3CHO]^- \quad (21)$$
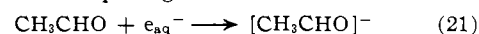
was derived from a kinetic equation similar to (E) and gave $k_6/k_{21} = 2.35$. This, however, does not take into account the fact that acetaldehyde in aqueous solution enters into the equilibrium reaction

$$CH_3CHO + H_2O \rightleftarrows CH_3CH(OH)_2 \quad (22)$$
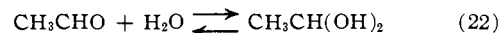
At room temperature (24°) the ratio of the diol to aldehyde form is 1.27:1.[30] In 10^{-2} M acetaldehyde solutions, therefore, only 0.44 × $10^{-2} M$ is present as CH$_3$-CHO. On the assumption that reaction of the hydrated electrons with CH$_3$CH(OH)$_2$ does not compete with reaction 21, the value k_6/k_{21} becomes 2.35 × 0.44 = 1.03. Thus acetaldehyde is as equally efficient in scavenging electrons as acetone.

The pH dependence of the hydrogen yields for de-aerated aqueous solutions of acetaldehyde irradiated with 2.5 Mev. electrons is shown in Fig. 3. The reactions which determine the H$_2$ yield in this system are

$$CH_3CHO + H \longrightarrow CH_3\dot{C}O[\dot{C}H_2CHO] + H_2 \quad (23)$$
$$CH_3CHO + H \longrightarrow CH_3\dot{C}HOH \quad (24)$$
$$CH_3CH(OH)_2 + H \longrightarrow$$
$$CH_3\dot{C}(OH)_2[\dot{C}H_2CH(OH)_2] + H_2 \quad (25)$$

(26) G. Scholes, M. Simic, and J. J. Weiss, 36th Ann. Discussions Faraday Soc., Notre Dame, Ind., September, 1963.

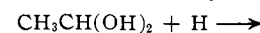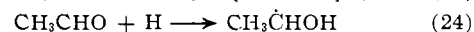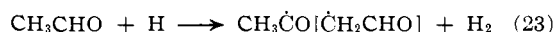(27) C. F. Wells, Discussions Faraday Soc., **29**, 219 (1960).

(28) J. T. Allan, M. G. Robinson, and G. Scholes, unpublished results.

(29) J. T. Allan, unpublished results.

(30) R. P. Bell and J. C. Clunie, Trans. Faraday Soc., **48**, 439 (1952).

together with reactions 3 and 21. In terms of the reaction kinetics, $G(H_2)$ is given by the relationship

$$G(H_2) = G^M(H_2) + \left\{ G(H^\alpha) + \frac{G(e_{aq}{}^-)}{1 + (k_{21}(CH_3CHO)/k_3(H^+))} \right\} P$$

where

$$P = \frac{k_{23} + k_{25}([CH_3CH(OH)_2]/[CH_3CHO])}{k_{23} + k_{24} + k_{25}([CH_3CH(OH)_2]/[CH_3CHO])}$$

and is constant at constant temperature.

The rate constant ratio for reactions 3 and 21, calculated from the values of k_3/k_6 and k_6/k_{21}, is $k_3/k_{21} = 1.69$. Values of $G(e_{aq}{}^-)$ may be determined from the $G(-H_2O)$ yields shown in Fig. 2. The constant, $P = 0.87$, represents the fraction of hydrogen atoms leading to hydrogen formation and was evaluated from data obtained at pH 1.20 where the influence of various additives, i.e., acetic acid and 2-propanol, on $G(H_2)$ were investigated. Substituting this information in the expression above we obtain a theoretical pH dependence for $G(H_2)$ which, as can be seen from Fig. 3, agrees well with experimental findings.

Conclusions

The radiation chemistry of the systems described above are readily interpreted on the basis of the primary formation of two reducing species, $e_{aq}{}^-$ and H^α. H^α undergoes the reactions normally attributed to hydrogen atoms, e.g., reactions 7, 15, and 24, and its identification as such is supported by the reaction kinetic studies of Rabani and Stein.[16] These hydrogen atoms may arise from the decomposition of excited molecules,[7] H_2O^*, formed either by ion recombination in the spurs or by the direct excitation of surrounding water molecules, or possibly from the spur

reactions 4 and 5.[20] However, the data presented above show that the yield of H^α is unaffected by relatively high concentrations of electron scavengers such as H_3O^+, N_2O, acetone, and acetaldehyde.

In systems containing 10^{-2} M 2-propanol and N_2O the yield of hydrated electrons in the bulk of the solution was found to be $G(e_{aq}{}^-) = 2.80 \pm 0.1$ under neutral conditions of pH. Thus since H^α is present in a yield of $G(H^\alpha) = 0.60$, these observations are consistent with the views expressed earlier by Rabani and Stein; i.e., that $G("H")$ is actually 3.40 ± 0.15 in aqueous 2-propanol and not 2.90 as has been generally accepted.

The results shown in Fig. 1 suggest that under similar conditions of pH the electron yield in the bulk of an O_2-saturated solution should be $G(e_{aq}{}^-)$ 2.80 ± 0.1, as was observed by Czapski and Allen[18] using the O_2-H_2O_2 system. This assumes, however, that the determining factor in the production of G 2.80 electrons in the 2-propanol and 2-propanol-N_2O systems is not scavenging of OH radicals by 2-propanol according to reactions 8 and 8a, which may not necessarily apply.

Czapski and Allen concluded from their results that the electron yield which they determined constituted all of the reducing species produced in the solution and thus challenged the existence of H^α in oxygenated solutions. However, recent studies by Scholes, et al.,[31] using solutions of O_2 and formate have shown that H^α is formed in the presence of oxygen and enters into competing reactions with O_2 and formate.

It seems fairly certain, therefore, that the two reducing species are formed in irradiated aqueous solutions although some questions remain concerning their respective yields. In particular, more investigations are necessary in order to elucidate the problems relating to oxygenated systems.

(31) G. Scholes and M. Simic, Nature, 199, 276 (1963).

Studies with a Single-Pulse Shock Tube. III. The Thermal Isomerization of Methyl Isocyanide

By Assa Lifshitz, H. F. Carroll, and S. H. Bauer

The thermal isomerization of methyl isocyanide to acetonitrile has been investigated behind reflected shocks over the temperature range 710–860°K. The heated mixture consisted of 2% methyl isocyanide in argon. The reaction products were analyzed by vapor phase chromatography. The first-order rate constants obtained in this temperature region are higher by a factor of about 10^6 when compared to the lower temperature (~500°K.) values. An Arrhenius extrapolation and Slater's equation for the dependence of (k/k^∞) on temperature were used to compare the high with the low temperature data.

Introduction

The thermal isomerization of methyl isocyanide has been studied recently by Schneider and Rabinovitch[1] over the temperature region 450–530°K. and over a wide range of (k/k^∞). These investigators also recently reported their work on the isomerization of methyl-d_3 isocyanide.[2] It was shown that the reaction is homogeneous and unimolecular. Owing to the relatively small number of degrees of freedom, the limiting first-order rate constant was reached only at pressures

of around 8 atmospheres; its value is

$$k_{uni}{}^\infty = 10^{13.6} \exp(-38,400/RT)$$

This paper is a continuation of our study of unimolecular reactions at the high temperatures attainable in shock tubes. Although the high pressure unimolecular limit could not be reached in the present glass shock tube, due to the excessive pressures which would be necessary, our data may be compared with those of Schneider and Rabinovitch by means of the equation given by Slater on the influence of temperature on (k/k^∞).

(1) F. W. Schneider and B. S. Rabinovitch, J. Am. Chem. Soc., 84, 4215 (1962).
(2) F. W. Schneider and B. S. Rabinovitch, ibid., 85, 2365 (1963).