

The Mechanism of Hydrogen Formation in the γ Radiolysis of 1,4-Dioxane and Its Mixtures with Water

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In the γ irradiation of pure liquid 1,4-dioxane, $G(\text{H}_2) = 1.31$ was obtained. The hydrogen yield is suppressed to a limit of $G(\text{H}_2) \approx 1.0$ by the H atom scavenger 1-hexene and by the electron scavengers N_2O and $c\text{-C}_4\text{F}_8$. Consequently, $G(\text{H}_2) \approx 1.0$ is attributed to molecular elimination from directly excited dioxane molecules. The yield of scavengeable electrons, as determined with N_2O and 0.1 N H_2SO_4 , corresponds to $G = 3.1\text{--}3.4$. Thus $G(\text{H}_2) \approx 0.3$ results from H atoms produced with $\sim 10\%$ efficiency in the neutralization of dioxane cations by electrons. An enhancement of $G(\text{H}_2)$ by NH_3 is observed that indicates proton transfer from a dioxane cation to give NH_4^+ , which on neutralization by an electron presumably yields H with unit efficiency. Water is considerably less effective than NH_3 in the enhancement of $G(\text{H}_2)$; the results suggest that the specific rate of proton transfer to H_2O is less than that to NH_3 in liquid dioxane. As the water-dioxane composition is varied over the whole range, $G(\text{H}_2)$ passes through a maximum. Such behavior is related to a change in the yield of free solvated electrons with change in the dielectric constant of the medium. The presence of dioxane in cyclohexane causes a suppression of $G(\text{H}_2)$, which is restored by the addition of methanol or NH_3 . The results indicate that positive charge is transferred from cyclohexane cations to dioxane and that the added base scavenges cations of both cyclohexane and dioxane with about equal efficiency.

Introduction

In a preliminary communication, $G(\text{H}_2) = 1.4$ was reported for radiolysis of pure dioxane;² such a value is significantly smaller than the values generally observed for saturated ethers, alcohols, and hydrocarbons.³ The small hydrogen yield in dioxane radiolysis cannot be attributed, as in the case of unsaturated compounds, to self-scavenging of hydrogen atoms. On the contrary, reaction of H with dioxane to give H_2 should be relatively efficient. Consequently, the low hydrogen yield must reflect a low probability of formation of H and H_2 in the primary processes. The aim of the present study was to clarify the mechanism of formation of the small hydrogen yield obtained in the radiolysis of 1,4-dioxane. The study of water-dioxane mixtures yielded somewhat surprising results of special interest.

Experimental Section

Materials. The 1,4-dioxane (Matheson Coleman and Bell spectroscopic reagent) was passed through a column of activated alumina to remove peroxides. Then it was refluxed over sodium under an atmosphere of dried nitrogen for ~ 16 hr and subsequently was distilled from sodium on a 3-ft Nester-Faust spinning-band column. The middle third of the distillate was retained and stored in a drybox under dry nitrogen. The uv spectrum of this dioxane has been reported.²

Methanol (Fisher) was refluxed with dinitrophenylhydrazine and sulfuric acid for approximately 24 hr and then was distilled on the Nester-Faust spinning-band column; both operations were carried out under dried nitrogen. The middle third of the distillate was re-

tained for use. Methanol-*d* (Merck Sharp and Dohme) was used as received. Cyclohexane (Fisher spectro-analyzed) was passed through a column of silica gel and stored over sodium. 1-Hexene (Aldrich Chemical Co.) was used after being passed through a column of activated alumina.

Ammonia, perfluorocyclobutane, and nitrous oxide, all obtained from Matheson Co., were purified by three trap-to-trap distillations under vacuum with rejection of head and tail fractions; the gases were stored on the vacuum line, and prior to use they were pumped for at least 30 min at -196° . Deuterium oxide (Columbia Organic Chemicals, 99.5%) was distilled from an alkaline permanganate solution and then was redistilled once in a system protected from atmospheric water and carbon dioxide by a drying tube containing sodium hydroxide. Triply distilled water used in all aqueous experiments was kindly supplied by Farhataziz. All other chemicals were of reagent grade and used as received.

Procedures. The solution (5 ml) to be irradiated was placed in a 13-mm o.d. Pyrex reaction tube fitted with a standard-taper joint and break-seal. The reaction tube was attached to a vacuum line, and the solution was thoroughly degassed by successive freeze-pump-

(1) The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-589.

(2) R. R. Hentz, F. W. Mellows, and W. V. Sherman, *J. Phys. Chem.*, **71**, 3365 (1967).

(3) M. Haissinsky and M. Magat, "Radiolytic Yields," Pergamon Press Ltd., London, 1961.

thaw cycles. Gaseous solutes were admitted into an evacuated bulb of known volume to a desired pressure, and the gas was condensed into the reaction tube containing degassed solution at 77°K. The reaction tube then was sealed and was allowed to warm to room temperature; when a gaseous solute was present, the reaction tube was shaken vigorously for ~10 min to ensure equilibration.

Samples were irradiated in a 4-kc ^{60}Co source. Over the period of the work, dose rates received by Fricke-dosimeter solutions, based on $G(\text{Fe}^{3+}) = 15.6$, were $(1.82\text{--}1.64) \times 10^{18} \text{ eV ml}^{-1} \text{ min}^{-1}$. The dose received by a particular solution was calculated by correction for the electron density relative to that of the dosimeter.

After radiolysis the reaction tube was attached to a vacuum line. Gas products were collected with a Toepler pump, using two or three freeze-pump-thaw cycles, at -196 and -77° and their pressure was measured in a calibrated volume. The -196° fraction was analyzed for H_2 , O_2 , N_2 , CH_4 , and CO by gas chromatography using a Gow-Mac 9677 matched-thermistor detector, a column of molecular sieve (Linde 5A) at room temperature, and helium as the carrier gas; the -77° fraction was analyzed with a Consolidated 21-103A mass spectrometer. Hydrogen isotopes also were analyzed with the mass spectrometer. In a number of experiments, mass spectrometry was used as a cross-check on the gas chromatographic analyses. The agreement was better than $\pm 5\%$.

Determination of Gas Solubilities. Because there was a dead volume above the liquid sample in the sealed reaction tube, calculation of the concentration of gaseous solutes required a determination of the gas solubilities. The solubilities were determined with the simple apparatus shown in Figure 1. The solvent (100 ml) was placed in bulb A and was degassed by repeated pumping (*via* stopcock 1) and shaking. With stopcock 1 closed, the solvent was allowed to equilibrate and the vapor pressure was measured with the manometer. Next, stopcock 2 was rotated to close off bulb A, and bulb B was evacuated and then filled with gas to a measured pressure. Stopcock 1 was closed, and the gas was condensed in the limb of B by cooling in liquid nitrogen. Stopcock 2 then was rotated, and the contents of A were tipped into B by raising A *via* the flexible tube. After closure of bulb A with stopcock 2, the contents of B were allowed to warm to room temperature and were equilibrated by vigorous shaking. Because the volume bounded by stopcocks 1 and 2 was previously measured (530 ml), measurement of the pressure permitted calculation of the Ostwald solubility coefficient, β .⁴ Values of β for NH_3 , N_2O , and C_2F_6 in dioxane and for NH_3 in cyclohexane were determined to be, with $\sim 10\%$ accuracy, 17, 2.8, 1.3, and 2.0, respectively, at $\sim 24^\circ$. For N_2O , values of β equal to 2.8 and 1.3 were obtained at electron fractions

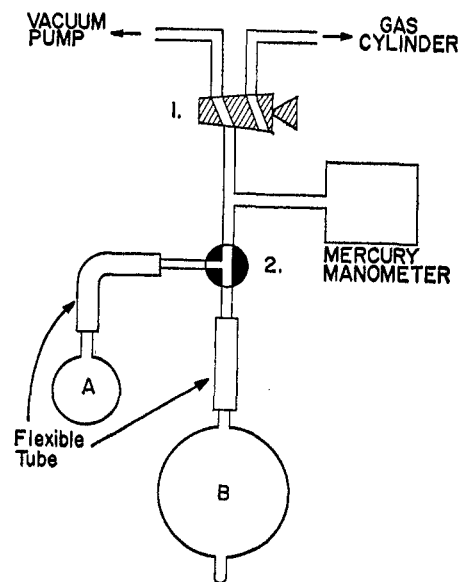


Figure 1. Apparatus for the determination of gas solubilities.

of water equal to 0.1 and 0.5, respectively. Gas concentrations in the irradiated liquids were calculated using these β values and a dead-space volume estimated to be equal to the volume occupied by the solution.

Results

Pure Dioxane. Gas products identified in the radiolysis of dioxane were hydrogen, carbon monoxide, ethylene, and traces ($G < 0.05$) of methane and ethane. No dose dependence of hydrogen and carbon monoxide yields was observed over the range 3.6×10^{18} to $4.9 \times 10^{20} \text{ eV ml}^{-1}$. $G(\text{H}_2) = 1.31 \pm 0.04$ and $G(\text{CO}) = 0.18 \pm 0.03$ represent the results of eight experiments over this dose range. $G(\text{C}_2\text{H}_4)$ decreased with increasing dose over the same range; G values at the lowest and highest doses were 1.58 and 0.50, respectively. At a dose of $4.3 \times 10^{21} \text{ eV ml}^{-1}$, the hydrogen and carbon monoxide yields also were lower; such a dose gave values of $G(\text{H}_2) = 0.99$, $G(\text{CO}) = 0.08$, and $G(\text{C}_2\text{H}_4) = 0.20$.

Dioxane-Water Mixtures and the Effect of Solutes. The dependence of radiolysis yields (dose = $1.1 \times 10^{20} \text{ eV ml}^{-1}$) on the electron fraction, F , of added water is shown in Figure 2. The effect of dose was checked for $F = 0.1$ and 0.5; no dose dependence was observed over the range from 9.2×10^{18} to $1.1 \times 10^{20} \text{ eV ml}^{-1}$. Essentially identical yields of total hydrogen and other products were obtained with D_2O in place of H_2O ; the isotopic composition of the hydrogen yields is presented in Table I. A further enhancement of hydrogen yields was observed in H_2O -dioxane mixtures with 0.1 *N* sulfuric acid present (Figure 2). The value of $G(\text{H}_2) = 4.1 \pm 0.2$ is essentially independent of the amount of water present over the range $F = 0.1\text{--}0.9$.

(4) β equals the ratio at equilibrium of the molar concentration of gas in the liquid phase to that in the gas phase.

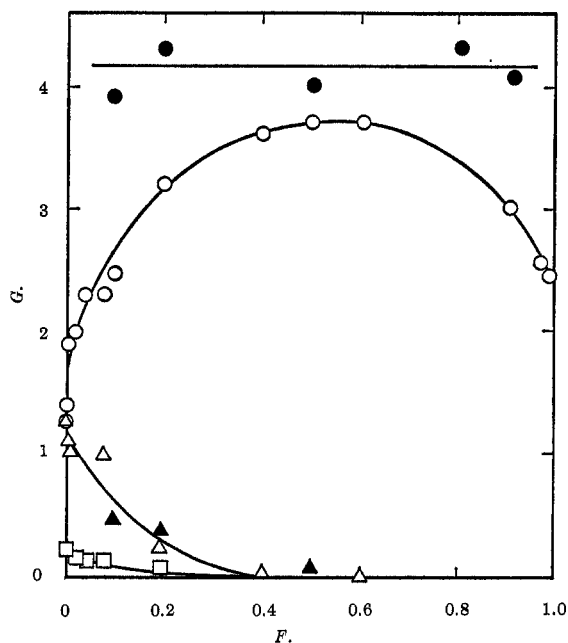


Figure 2. Yields in the radiolysis of dioxane-water mixtures (\circ , $G(\text{H}_2)$; Δ , $G(\text{C}_2\text{H}_4)$; \square , $G(\text{CO})$) and in the presence of $0.1 \text{ N H}_2\text{SO}_4$ (\bullet , $G(\text{H}_2)$; \blacktriangle , $G(\text{C}_2\text{H}_4)$). Note: $M = 55.5F$ and mole fraction $X = 4.8F/(1 + 3.8F)$. F denotes the electron fraction of water.

Table I: Isotopic Composition of the Hydrogen Yields from D_2O -Dioxane Mixtures^a

$F(\text{D}_2\text{O})$	$G(\text{H}_2)$	$G(\text{HD})$	$G(\text{D}_2)$
0	1.31
0.1	0.97 ^b	1.53 ^b	0.04
0.2	0.77	1.99	0.08
0.6	0.29	2.97	0.25
0.8	0.18	2.95	0.31

^a Dose = $1.1 \times 10^{20} \text{ eV ml}^{-1}$. ^b Essentially identical results were obtained for a dose = $9.2 \times 10^{18} \text{ eV ml}^{-1}$.

The effect of added ammonia on $G(\text{H}_2)$ was qualitatively similar to that of water but, as shown in Figure 3, a given concentration of ammonia up to 1 M (upper limit attainable at convenient working pressures) caused a significantly greater enhancement of $G(\text{H}_2)$. The presence of both water and ammonia had an additive effect on $G(\text{H}_2)$; thus the addition of 0.07 and 0.2 M NH_3 to a solution containing water at $F = 0.1$ increased $G(\text{H}_2)$ from 2.5 to 2.8 and 2.9 , respectively.

The effect of nitrous oxide in pure dioxane and in solutions containing 0.1 and 0.5 electron fraction of water is shown in Figure 4. The initial slope of the $G(\text{N}_2)$ vs. $[\text{N}_2\text{O}]$ curve increases with increasing water content, although similar values of $G(\text{N}_2)$ are attained near 0.25 M . The depression of $G(\text{H}_2)$ by a given concentration of nitrous oxide increases with water concentration; in all three solutions, $G(\text{H}_2)$ approaches a limiting value of 1.0 at higher N_2O concentrations.

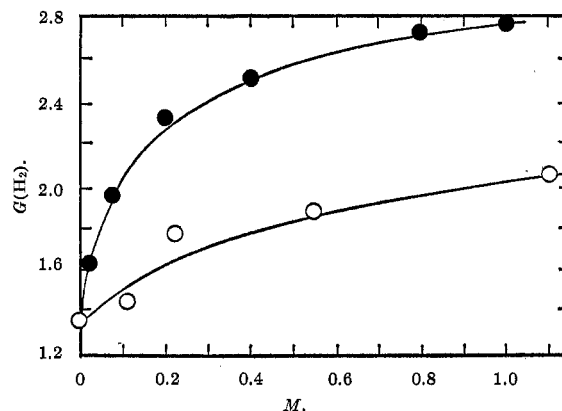


Figure 3. Hydrogen yields from dioxane as a function of the molarity, M , of ammonia (\bullet) or H_2O (\circ).

A similar enhancement of $G(\text{N}_2)$ was not found with ammonia present in place of water. Radiolysis of a solution containing $7.5 \times 10^{-2} \text{ M N}_2\text{O}$ and 1.0 M NH_3 gave $G(\text{N}_2) = 2.13$, essentially the same as that of a solution containing N_2O alone, and $G(\text{H}_2) = 1.14$.

The presence of 0.1 M benzene had no significant effect on $G(\text{H}_2)$ from dioxane. The effects of 1-hexene, perfluorocyclobutane, and iodine are shown in Table II. A concentration of 10^{-2} M iodine reduced $G(\text{H}_2)$ in solutions containing 0.1 and 0.2 electron fraction of water to 1.98 and 2.57 , respectively.

Table II: Effect of Solutes on the Hydrogen Yield from Dioxane^a

Solute	Concn., M	$G(\text{H}_2)$
None	...	1.31
1-Hexene	0.064	1.08
	0.100	1.19
	0.160	0.95
	0.320	0.96
	0.640	1.02
<i>c</i> - C_4F_8	0.028	1.12
	0.057	1.08
	0.110	1.09
Iodine	0.010	1.26
	0.100	1.13

^a Dose rate = $1.8 \times 10^{18} \text{ eV ml}^{-1} \text{ min}^{-1}$; total dose = $2.7 \times 10^{19} \text{ eV ml}^{-1}$.

Hydrogen Yields in Cyclohexane-Dioxane Mixtures. A progressive decrease in $G(\text{H}_2)$ was observed with increasing concentration of dioxane in cyclohexane (Figure 5). For solutions containing up to 0.05 M dioxane, the presence of 1 M methanol essentially restored $G(\text{H}_2)$ to the value of 5.4 ± 0.1 for pure cyclohexane. At higher dioxane concentrations, as shown in Figure 5, 1 M methanol only partly restored the hydrogen yield. Ammonia had a similar effect. The

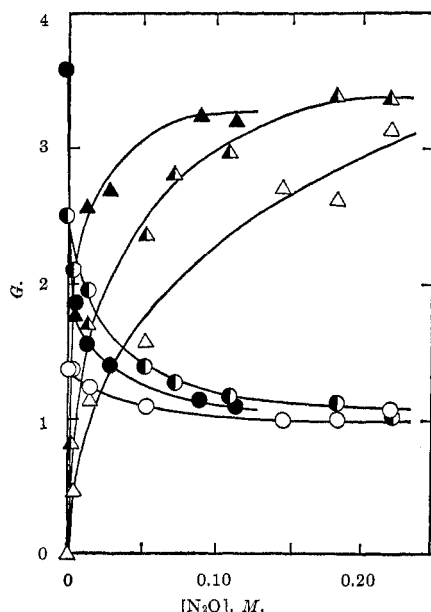


Figure 4. Hydrogen and nitrogen yields from dioxane and its mixtures with water as a function of the molarity of nitrous oxide: $F = 0$: \circ , $G(\text{H}_2)$; \triangle , $G(\text{N}_2)$; $F = 0.10$: \bullet , $G(\text{H}_2)$; \blacktriangle , $G(\text{N}_2)$; $F = 0.50$: \bullet , $G(\text{H}_2)$; \blacktriangle , $G(\text{N}_2)$.

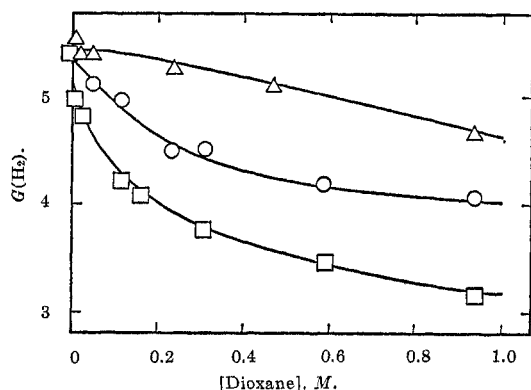


Figure 5. Effect of methanol or ammonia on $G(\text{H}_2)$ from solutions of dioxane in cyclohexane: \square , $G(\text{H}_2)$ (with dioxane as the only solute); \circ , $G(\text{H}_2)$ (with 0.13 M ammonia present); \triangle , $G(\text{H}_2)$ (with 1.0 M methanol present).

presence of 0.13 M ammonia restored $G(\text{H}_2)$ in solutions containing up to 0.024 M dioxane to the value for pure cyclohexane; at higher dioxane concentrations, the same concentration of ammonia only partly restored $G(\text{H}_2)$.

Figure 6 shows the isotopic composition of hydrogen yields from cyclohexane solutions containing 1.0 M methanol- d and various dioxane concentrations. In the absence of dioxane, the hydrogen yield was 30% HD and 70% H_2 , as compared with 28% HD and 72% H_2 obtained by Buchanan and Williams⁵ for cyclohexane containing 1.1 M $\text{C}_2\text{H}_5\text{OD}$. The yield of HD remains approximately constant with increasing dioxane concentration; thus the decrease in $G(\text{H}_2)$ almost completely accounts for the decrease in total hydrogen yield.

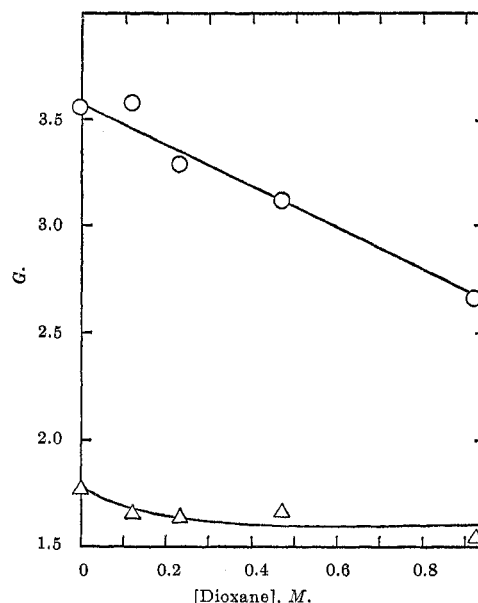
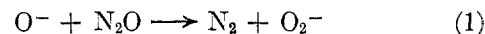


Figure 6. Isotopic composition of the hydrogen yields from cyclohexane solutions of dioxane and 1.0 M methanol- d : \circ , $G(\text{H}_2)$; \triangle , $G(\text{HD})$.

Discussion

Dioxane. The formation of N_2 in radiolysis of dioxane with added N_2O , as shown in Figure 4, is considered evidence for the formation of scavengeable electrons. $G(\text{N}_2)$, at corresponding concentrations of N_2O , is 20–50% lower than values obtained in cyclohexane.^{6–8} Such a result may be attributable to suppression of the secondary reaction



because of enhanced H abstraction by O^- from the more labile CH bonds in dioxane; if so, $G(\text{N}_2)$ in dioxane may correspond more closely to the yield of scavenged electrons. Attainment of a limiting $G(\text{H}_2) \approx 1.0$ with increase in N_2O concentration indicates that, unlike the situation in cyclohexane and other saturated solvents, only a small fraction ($\sim 24\%$ corresponding to $\Delta G \approx -0.3$) of the hydrogen yield can be suppressed by N_2O . Thus with the assumption of a total $G(e^-) \approx 3$, only 10% of the scavengeable electrons ultimately yield H_2 .

The effect of $c\text{-C}_4\text{F}_8$ on $G(\text{H}_2)$ was studied for confirmation of the N_2O results. The bond strengths of CF and HF are 152⁹ and 136¹⁰ kcal mol⁻¹, respectively. Consequently, abstraction of H from dioxane should

(5) J. W. Buchanan and Ff. Williams, *J. Chem. Phys.*, **44**, 4377 (1966).

(6) G. Scholes and M. Simic, *Nature*, **202**, 895 (1964).

(7) W. V. Sherman, *J. Chem. Soc., A*, 599 (1966).

(8) S. Sato, R. Yugeta, K. Shinsaka, and T. Terao, *Bull. Chem. Soc. Jap.*, **39**, 156 (1966).

(9) M. M. Bibby and G. Carter, *Trans. Faraday Soc.*, **59**, 2455 (1963).

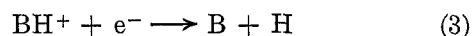
(10) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

remain the predominant fate of thermal H at the concentrations of $c\text{-C}_4\text{F}_8$ used. Rajbenbach¹¹ has concluded that suppression of $G(\text{H}_2)$ by $c\text{-C}_4\text{F}_8$ in radiolysis of $n\text{-C}_6\text{H}_{14}$ is attributable to the scavenging of electrons. The suppression of $G(\text{H}_2)$ in dioxane radiolysis by concentrations of $c\text{-C}_4\text{F}_8$ up to the maximum attainable at atmospheric pressure is shown in Table II. The results are consistent with the conclusions drawn from the N_2O experiments.

An olefin such as 1-hexene ($\text{IP} = 9.46 \text{ eV}^{12}$) does not scavenge electrons and cannot undergo charge transfer with an unexcited dioxane ($\text{IP} = 9.13 \text{ eV}^{12}$) cation. However, addition of thermal H to olefins is rapid,¹³ and, therefore, the suppression of $G(\text{H}_2)$ by added 1-hexene to a limiting value of ~ 1.0 (cf. Table II) is consistent with a value of $G(\text{H}) \approx 0.3$ in the radiolysis of dioxane. Coincidence of the limiting values obtained with 1-hexene and the electron scavengers suggests that electrons are precursors of thermal H; i.e., it appears that the $\sim 10\%$ of scavengeable electrons that ultimately yield H_2 do so *via* the formation of thermal H. The results presented in Table II for I_2 as the solute, which presumably can scavenge both electrons and H, also are consistent with the view presented.

The major portion of the hydrogen yield obtained in γ radiolysis of dioxane, corresponding to $G(\text{H}_2) \approx 1.0$, apparently is formed in a molecular elimination process which does not have an electron precursor. Decomposition of a directly excited state is suggested as the source of this hydrogen yield, designated as $G^*(\text{H}_2)$. Failure of 0.1 M benzene to affect $G(\text{H}_2)$ requires that such an excited state have a lifetime less than $\sim 10^{-10}$ sec, assuming a diffusion-controlled excitation transfer. As expected, 0.1 M benzene ($\text{IP} = 9.24 \text{ eV}^{12}$) must have no effect on the ionic processes responsible for $G(\text{H}_2) \approx 0.3$, and benzene must be a less efficient scavenger of H than 1-hexene.

As shown in Figure 3, addition of NH_3 to dioxane produces an increase in $G(\text{H}_2)$. In accordance with the arguments of Williams,¹⁴ such an effect is interpreted in terms of the reaction sequence



in which RH represents a solvent molecule and B represents a basic solute; reaction 3 is assumed to occur in each such neutralization (i.e., H is formed with unit efficiency). The yield of free ion pairs in dioxane is given by Hummel and Allen¹⁵ as $G_{\text{fi}} = 0.04$. Consequently, the enhanced yield of hydrogen must result from a competition between reaction 2 and the rapid recombination (yielding H with only 10% efficiency) of those sibling cation-electron pairs of the solvent ($\sim 99\%$) whose members do not escape from their

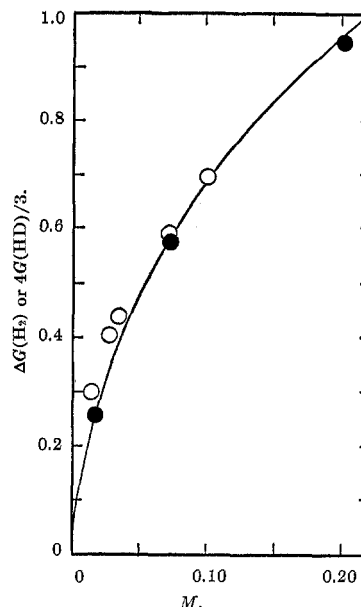


Figure 7. The enhancement of the hydrogen yield, $\Delta G(\text{H}_2)$, vs. the molarity of NH_3 in dioxane (●) compared with the yield of the proton transfer, $4G(\text{HD})/3$, vs. the molarity of ND_3 in cyclohexane (○). (Cf. ref 14.)

mutual coulombic fields (hence are designated as geminate or coupled).

The presence of 0.075 M N_2O in a 1 M NH_3 solution gave the same $G(\text{N}_2) = 2.13$ as was obtained from 0.075 M N_2O in dioxane alone, but $G(\text{H}_2)$ was reduced to a value of 1.14 from $G(\text{H}_2) = 2.75$ in 1 M NH_3 solution without N_2O . Apparently the presence of 1 M NH_3 has a negligible effect on G_{fi} and on the over-all evolution of electron-neutralization processes which determines the efficiency of electron scavenging by a given concentration of N_2O .¹⁶ Thus the observed reduction of $G(\text{H}_2)$ by 0.075 M N_2O in the 1 M NH_3 solution results from the scavenging of electrons in coupled ion pairs and replacement of the electron in reaction 3 by an anion which does not yield H or H_2 on neutralization by NH_4^+ .

In Figure 7, the enhancement of $G(\text{H}_2)$ by NH_3 in dioxane is compared with Williams' results¹⁴ for the yield of solvent cations scavenged by proton transfer to ND_3 in $c\text{-C}_6\text{H}_{12}$, this yield being taken as the measured $G(\text{HD})$ multiplied by $4/3$. The comparison indicates

(11) L. A. Rajbenbach, *J. Amer. Chem. Soc.*, **88**, 4275 (1966).

(12) K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962).

(13) See, e.g., J. L. McCrumb and R. H. Schuler, *J. Phys. Chem.*, **71**, 1953 (1967).

(14) F. Williams, *J. Amer. Chem. Soc.*, **86**, 3954 (1964).

(15) A. Hummel and A. O. Allen, *J. Chem. Phys.*, **44**, 3426 (1966).

(16) Presumably, the evolution of electron-neutralization processes is governed largely by the dielectric constant, ϵ , of the medium. See, e.g., ref 14 and G. R. Freeman and J. M. Fayadh, *J. Chem. Phys.*, **43**, 86 (1965). Assuming ϵ of the solution to be the molecular average of the component values, $\epsilon \approx 3.5$ is obtained for 1 M NH_3 in dioxane as compared to $\epsilon = 2.2$ for pure dioxane.

that the efficiency of ammonia as a scavenger of solvent cations is essentially the same in these two solvents of nearly equal dielectric constant.

Dioxane-Water Mixtures. Interpretation of the radiation chemistry of dioxane-water mixtures is fraught with difficulties. Both the dielectric constant¹⁷ and the structure of the solution^{17,18} undergo a continuous change with change in mixture composition. Because of the strong hydrogen-bonding propensities of water and dioxane, the solution structure at any composition appears to be determined by the equilibria between various water-dioxane complexes, the monomers, and "polymers" of water. At the water-rich end of the composition range, the radiation chemistry of dioxane-water mixtures involves the complications of water radiation chemistry as modified in several important respects by the presence of relatively large concentrations of dioxane. At the dioxane-rich end of the composition range, the radiation chemistry involves those complexities peculiar to a solvent of low dielectric constant.^{14,19} In view of the complex character of water-dioxane mixtures, a detailed interpretation of the results obtained in this initial study is not attempted. Instead, the results are rationalized in terms of a general model which can be elaborated by further experimentation.

Somewhat surprisingly, as shown in Figure 3, water is considerably less effective than ammonia in the enhancement of hydrogen yields. Such a difference in behavior must be ascribed to a difference in the efficiency with which NH_3 and H_2O convert solvent cations into H atoms *via* reactions 2 and 3. The behavior of water, in particular, may be related to the manner in which water molecules are bound in the dioxane solutions, *i.e.*, to the structure of the solutions. At the lower H_2O concentrations, then, either the scavenging efficiency *via* reaction 2 is greatly reduced relative to that of NH_3 or reaction 3 occurs in a small fraction of the neutralizations. The latter explanation requires that the ratio of hydrogen-yield enhancements obtained in an NH_3 solution and an H_2O solution of the same concentration be independent of concentration and that a comparatively small limiting yield of $G(\text{H}_2)$ be approached at high concentrations of water; neither condition is satisfied by the data (see Figures 2 and 3). It is concluded that in dioxane solutions the value of k_2 for water as B is less than for NH_3 , which results in a reduction of the efficiency with which reaction 2 competes with neutralization of the dioxane cation of a coupled ion pair.²⁰

As the water concentration is increased, a greater fraction of the dioxane cations of coupled ion pairs would be scavenged in reaction 2 for a fixed value of k_2 ; the efficiency of such scavenging may be a complicated function of water concentration owing to concomitant changes in the value of k_2 as the solution structure changes. Another, perhaps more important, contri-

bution to an increase in $G(\text{H}_2)$ is the increase in direct ionization of water molecules which have other water molecules as nearest neighbors. Such a process leads, in every case, to H_3O^+ which on neutralization by the coupled electron is assumed to give H with unit efficiency. Thus an increase in $G(\text{H}_2)$ occurs which is determined by the fraction of total ionization occurring in water molecules.

At 25°, the dielectric constant of a dioxane-water mixture¹⁷ is only 10.1 at a mole fraction of water $X = 0.5$ ($F = 0.17$) and is 31.2 at $X = 0.8$ ($F = 0.45$). Consequently, a pronounced increase in G_{fi} must occur as water concentration is increased from $F = 0.45$ to 1. Such an increase in G_{fi} may account for the passage of $G(\text{H}_2)$ through a maximum near $F = 0.55$ (Figure 2). At the dose rates used, all free electrons will react either with small concentrations of impurities for which the specific rate of reaction is diffusion controlled or possibly with dioxane at a considerably smaller specific rate or both. If the net effect of such reactions is to yield less than one molecule of H_2 per free electron, as seems very likely, then the processes which tend to increase $G(\text{H}_2)$ on addition of water to dioxane are counteracted by the increase in G_{fi} . In solutions of $F > 0.9$, corresponding to dioxane concentrations below $\sim 1 M$, the continuing decrease in $G(\text{H}_2)$ must be almost entirely a manifestation of the radiation chemistry of dilute aqueous solutions.

As N_2O concentration is increased in pure dioxane (Figure 4), the gradual increase in $G(\text{N}_2)$ and complementary decrease in $G(\text{H}_2)$ are characteristic of the scavenging of electrons from coupled ion pairs.⁶⁻⁸ With water present at $F = 0.1$, the scavenging efficiency of N_2O is increased, as reflected in the greater rates of increase and decrease of $G(\text{N}_2)$ and $G(\text{H}_2)$, respectively. Because little increase in G_{fi} would be expected ($\epsilon \approx 6.0$), the enhanced scavenging efficiency must be related almost entirely to an increase in the lifetimes of coupled ion pairs, owing to the somewhat larger dielectric constant.^{14,19} The enhancement of N_2O scavenging efficiency is still more pronounced at $F = 0.5$. In addition to a further increase in the lifetimes of coupled ion pairs, a significant contribution of G_{fi} to $G(\text{N}_2)$ would be expected in this solution with $\epsilon \approx 35$. The present results are not adequate for disclosure of such a contribution. For all three solvent mixtures represented in Figure 4, $G(\text{N}_2)$ appears to be approaching an upper

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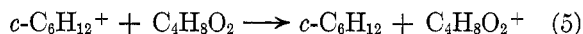
(20) The lower k_2 for water may be related to its lower proton affinity. A. P. Altshuller, *J. Amer. Chem. Soc.*, **77**, 3480 (1955), gives the gas-phase proton affinity of ammonia as 202 kcal mol⁻¹; that for water has been determined by V. L. Tal'roze and E. L. Frankevich, *ibid.*, **80**, 2344 (1958), to be 169 kcal mol⁻¹.

limit near 3.4, which may represent the yield of scavengeable electrons. The approach of $G(\text{H}_2)$ to a lower limit near unity in all three solvents (Figure 4) appears to be a coincidental result of the approximate equality of $G^*(\text{H}_2) = 1$ in dioxane radiolysis and the sum of H and H_2 "primary" yields in water radiolysis.²¹

The constancy of $G(\text{H}_2) = 4.1$ in 0.1 *N* H_2SO_4 solutions from $F = 0.1$ to 0.9 indicates that the yield of scavengeable electrons plus $G^*(\text{H}_2)$ in dioxane radiolysis approximates the sum of "primary" yields of e_{aq}^- , H, and H_2 in water radiolysis. The value of $G(\text{H}_2) = 4.1$ at $F = 0.9$ ($\sim 1 M$ dioxane) is near that expected for a water solution containing 0.1 *N* H_2SO_4 and an organic additive to convert all H into H_2 .²² At $F = 0.1$, for which ϵ and G_{fi} are small, 0.1 *N* H_2SO_4 must efficiently scavenge the electrons (with formation of H) of coupled ion pairs. Subtraction of $G^*(\text{H}_2) = 1$ from the value of $G(\text{H}_2) = 4.1$ gives $G = 3.1$ as the yield of scavenged electrons. Such a value is in reasonable agreement with the value of $G = 3.4$ obtained as the yield of scavengeable electrons with N_2O .

Another interesting aspect of the radiolysis of water-dioxane mixtures is evident in the isotopic composition of the hydrogen yields obtained with D_2O (Table I). Multiplication of $G^*(\text{H}_2) = 1$ by $1 - F$ gives values in rather close agreement with the measured values of $G(\text{H}_2)$. Such a result, particularly at $F(\text{D}_2\text{O}) = 0.1$ for which use of the electron fraction assumption is not critical, indicates that H atoms from dioxane (which would form H_2 in reaction 4) make little or no contribution to the enhanced hydrogen yield. The results of Baxendale and Rodgers,²³ obtained at $F(\text{D}_2\text{O}) < 0.05$, unequivocally support such a conclusion. Thus any HD_2O^+ formed in reaction 2 must undergo several exchanges with D_2O molecules prior to neutralization; alternatively, another mechanism may be involved such as that suggested by Baxendale and Rodgers.²³

Cyclohexane-Dioxane Mixtures. Cyclohexane has an ionization potential of 9.88 eV.¹² Consequently, transfer of charge from a cyclohexane cation to dioxane is exothermic and, therefore, is expected to occur on each encounter; the transfer of a proton also may be possible. Because of the low efficiency with which ionic processes yield hydrogen in dioxane, corresponding to $G_1(\text{H}_2) \approx 0.3$ as compared to a value of $G_1(\text{H}_2) \approx 3$ in cyclohexane,⁶⁻⁸ charge transfer to dioxane (reaction 5)



will result in a reduction in $G(\text{H}_2)$ greater than that expected on the basis of an electron fraction partition

of the absorbed energy. In fact, because $G(\text{H}_2) = 1.3$ for dioxane as compared to $G(\text{H}_2) = 5.4$ for cyclohexane, any process that results in preferential localization of deposited energy on dioxane molecules will contribute to a reduction in $G(\text{H}_2)$ of the mixture.

Addition of dioxane to cyclohexane has the expected effect on $G(\text{H}_2)$ as shown in Figure 5. That the reduction in $G(\text{H}_2)$ is attributable to ionic processes only is shown by the effects of methanol and ammonia on $G(\text{H}_2)$ of the dioxane-cyclohexane mixtures. Such basic solutes (as shown for NH_3 in Figure 7) should scavenge cations of both cyclohexane and dioxane with about equal efficiency and, *via* reactions 2-4, yield a molecule of H_2 for each cation scavenged. If neutralization of a cyclohexane cation by an electron yields H or H_2 with unit efficiency, conversion of a cyclohexane cation to the protonated basic solute (reaction 2) has no effect on the hydrogen yield; however, replacement of a dioxane cation by the protonated basic solute exactly offsets the effect of reaction 5 on the hydrogen yield.

As shown in Figure 5, addition of ammonia or methanol to dioxane-cyclohexane mixtures enhances the hydrogen yield. When the concentration of added base is large relative to that of dioxane, $G(\text{H}_2)$ is restored to the value for pure cyclohexane; such is the case for 0.13 *M* NH_3 and 1 *M* CH_3OH in solutions of less than 0.024 and 0.05 *M* dioxane, respectively. It is clear that a simple competition between dioxane and base for cyclohexane cations is not involved; if this were the case, the curves in Figure 5 for a fixed concentration of base would converge at large dioxane concentrations. As expected, the base must scavenge cations of both cyclohexane and dioxane with about equal efficiency. Thus the fraction of total cations scavenged by a fixed concentration of base is independent of the composition of the cyclohexane-dioxane mixture. Such behavior is confirmed by the approximate constancy of $G(\text{HD})$ shown in Figure 6 for 1 *M* CH_3OD and dioxane concentrations up to $\sim 1 M$. The net effect of increasing dioxane concentration is that an increasing fraction of those cations *not* scavenged by 1 *M* CH_3OD undergo reaction 5; the resultant decrease in $G(\text{H}_2)$ necessarily corresponds to the decrease in total hydrogen yield.

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