The Radiolysis of Water Vapor and a Surface-Catalyzed Isotope-Exchange Reaction

Helen W. Richter* and R. F. Firestone

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. Received February 5, 1981

Abstract: The steady-state radiolysis of deuterium oxide vapor has been examined using protium, perprotiopropane, or mixtures of these two as free-radical scavengers. Tritiated water was used as an internal radiation source, and glass irradiation vessels were employed. D atoms are produced in the radiolytic decomposition of D_2O, and HD is formed by reaction of this species with the added radical scavengers. It was assumed previously that the yield of HD molecules could be equated with the yield of radiolytically produced D atoms. However, the experimental results of the present investigation demonstrate conclusively that when H_2 is used as a radical scavenger there are two pathways for HD formation: (1) homogeneous scavenging of the radiolytically produced D atoms by H_2, as expected, and (2) heterogeneous combination of H atoms produced in the scavenging reaction ($D + H_2 \rightarrow HD + H$) with D atoms adsorbed on the vessel surface, where the adsorbed D atoms are generated by a surface-catalyzed isotope-exchange reaction between H atoms adsorbed from the volume and D_2O. From the results of this investigation, it appears that the yield of D atoms produced in the radiolysis of D_2O is $G_D = 7.0$ atoms/100 eV absorbed energy, i.e., the $G(HD)$ found in experiments using propane as the radical scavenger. G_{D_2} is shown to be 0.65 molecules/100 eV.

Water vapor was one of the first systems whose radiation chemistry was examined, following the discovery of radioactivity.[1] The first investigation employing modern techniques was that of Firestone, reported in this journal in 1957.[2] The activity in this area was quite vigorous for several years, and two reviews were published.[3] Interest in this system continues, with a number of papers on water-vapor radiolysis[4–8] and on photo-ionization and photodissociation[10–12] appearing in the last few years.
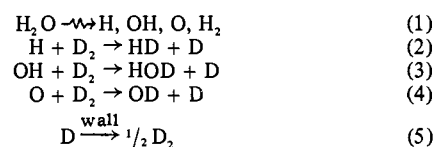
The ultimate products of the primary and secondary processes occurring during the radiolysis of water vapor are hydrogen atoms, hydroxyl radicals, oxygen atoms, and hydrogen molecules. When pure water vapor is treated with ionizing radiation, low steady-state concentrations of hydrogen, oxygen, and hydrogen peroxide result.[3] Little information about the radiolytic phenomena occurring in the water vapor can be gained from these yields; however, the perturbing action of small concentrations of reactive additives presents a path for examining the intermediates produced in irradiated water vapor.

The yield of hydrogen atoms from the direct radiolysis of water vapor, G_D or G_H, is a matter of great interest and significance in radiation chemistry, per se. Firestone[2] examined the hydrogen atom yield in the radiolysis of protium oxide vapor with deuterium added as a radical scavenger. G_H, the yield of H atoms from the primary and secondary radiolytic processes, was equated with $G(HD)$, the measured yield of HD molecules per 100 eV absorbed energy, on the basis of the mechanism given in Scheme I. A value of 13.1 ± 0.3[13] was obtained for $G(HD)$.
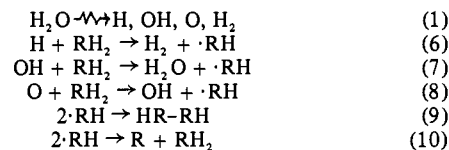
In a study of the radiolysis of deuterium oxide vapor with protium added as the radical scavenger, Bibler and Firestone[13] obtained a value for $G(HD)$, equated with G_D, of 13.1 ± 0.3, the same as in the protium oxide system within experimental error. The values obtained for $G(HD)$ were found to be independent of dose rate, temperature, and mole fraction of hydrogen additive over an appreciable range of values of these parameters. It was further observed that as the reaction temperature was increased beyond this region of constancy, $G(HD)$ increased rapidly. This increase was attributed to the onset of a chain reaction propagated by reactions of hydrogen atoms with water molecules.

Baxendale and Gilbert[14] examined the radiolysis of protium oxide vapor with small added amounts of methanol, ethanol, cyclohexane, or ether and of deuterium oxide with methanol, propane, or protium. With protium oxide, a value of 8.0 ± 0.7 was obtained for $G(H_2)$. By assuming a mechanism analogous to that of Firestone, Scheme II, $G(H_2)$ was equated with G_H. With

Scheme I

$$H_2O \rightsquigarrow H, OH, O, H_2 \qquad (1)$$
$$H + D_2 \rightarrow HD + D \qquad (2)$$
$$OH + D_2 \rightarrow HOD + D \qquad (3)$$
$$O + D_2 \rightarrow OD + D \qquad (4)$$
$$D \xrightarrow{\text{wall}} {}^1/_2 D_2 \qquad (5)$$

Scheme II

$$H_2O \rightsquigarrow H, OH, O, H_2 \qquad (1)$$
$$H + RH_2 \rightarrow H_2 + \cdot RH \qquad (6)$$
$$OH + RH_2 \rightarrow H_2O + \cdot RH \qquad (7)$$
$$O + RH_2 \rightarrow OH + \cdot RH \qquad (8)$$
$$2 \cdot RH \rightarrow HR\text{-}RH \qquad (9)$$
$$2 \cdot RH \rightarrow R + RH_2 \qquad (10)$$

deuterium oxide, $G(HD)$ in the presence of methanol or propane was 7.0 while in the presence of protium $G(HD) = 10.5$ was obtained. The radiolysis of deuterium oxide vapor in the presence of propane as a radical scavenger was carefully studied by Johnson and Simic,[15] who obtained $G(HD) = 7.6$, which was equated with

(1) Duane, W.; Scheuer, O. *C. R. Hebd. Seances Acad. Sci.* **1913**, *156*, 466–7. Günther, P.; Holzapfel, L. *Z. Phys. Chem., Abt. B* **1939**, *42*, 346–58.

(2) Firestone, R. F. *J. Am. Chem. Soc.* **1957**, *79*, 5593–8.

(3) Anderson, A. R. In "Fundamental Mechanisms in Radiation Chemistry"; Ausloos, P., Ed.; Interscience Publishers: New York, 1968; Chapter 5. Dixon, R. S. *Radiat. Res. Rev.* **1970**, *2*, 237–96.

(4) Burns, W. G.; Winter, J. A.; Barton, R. A.; Anderson, A. R., presented at the Chemical Institute of Canada, American Chemical Society Joint Meeting, Toronto, May 1970. Burns, W. G.; Marsh, W. R. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 197–215.

(5) Boyd, A. W.; Willis, C.; Lalor, G. C. *Can. J. Chem.* **1972**, *50*, 83–92. Boyd, A. W.; Willis, C.; Miller, A. D. *Ibid.* **1973**, *51*, 4048–55, 4056–61. Willis, C.; Boyd, A. W. *Int. J. Radiat. Phys.* **1976**, *8*, 71–111.

(6) Gordon, S.; Mulac, W. A. *Int. J. Chem. Kinet. Symp. No. 1*, **1975**, 289–99.

(7) Ohno, S.; Nagayama, H.; Okazaki, K.; Sato, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2153–7.

(8) Sennhauser, E. S.; Armstrong, D. A. *Radiat. Phys. Chem.* **1978**, *12*, 115–23.

(9) Quickenden, T. I.; Irving, J. A.; Sangster, D. F. *J. Chem. Phys.* **1978**, *69*, 4395–402. Quickenden, T. I.; Trotman, S. M.; Irvin, J. A.; Sangster, D. F. *J. Chem. Phys.* **1979**, *71*, 497–501.

(10) Mentall, J. E.; Möhlmann, G. R.; Guyon, P. M. *J. Chem. Phys.* **1978**, *69*, 3735–9.

(11) Hilton, P. R.; Nordholm, S.; Hush, N. S. *Chem. Phys. Lett.* **1979**, *64*, 515–8.

(12) Sworski, T. J.; Hochanadel, C. J.; Ogren, P. J. *J. Phys. Chem.* **1980**, *84*, 129–34.

(13) Bibler, N. E.; Firestone, R. F. *J. Phys. Chem.* **1972**, *76*, 621–30.

(14) Baxendale, J. H.; Gilbert, G. P. *Discuss. Faraday Soc.* **1963**, *36*, 186–92; *J. Am. Chem. Soc.* **1964**, *86*, 516.

*Address correspondence to this author at the Department of Chemistry, Mellon College of Science, Carnegie-Mellon University, Pittsburgh, PA 15213.

G_D, assuming the mechanism in Scheme II.

These conflicting results presented a dilemma: when organic compounds were used as radical scavengers in the radiolysis of water vapor the hydrogen atom yield determined was 7–8 atoms/100 eV, whereas when hydrogen was used as a radical scavenger the yield determined was 10–13 atoms/100 eV. Obviously, both values cannot be correct and it is apparent that either there is in the case of the organic scavengers a reaction suppressing the hydrogen atom yield, or there is in the case of the hydrogen scavengers a reaction enhancing the yield of the HD molecules.

Several possible explanations of the difference in the hydrogen and organic additive systems have been advanced,[2] including the production of extra HD with the hydrogen additive via chemical quenching of low-lying triplet excited states of water by the hydrogen, resulting in isotope exchange, or reduction of the hydrogen yield in the organic additive systems via deactivation of a hydrogen atom precursor by the organic additive. However, none of these explanations were considered adequate. The present report presents the results of an investigation of the radiolysis of deuterium oxide vapor using protium, propane, or mixtures of protium and propane as radical scavengers. The results obtained disagree substantially with the mechanism given in Scheme I. A mechanism for HD production is presented which rationalizes the results obtained, and which explains the difference in the apparent G_D for organic and hydrogen radical-scavenger experiments, thereby resolving a long-standing dilemma in radiation chemistry.

Experimental Methods and Materials

Reagents. Tritium deuterium oxide (TOD)/deuterium oxide was prepared from mixtures of tritium (ORNL, Union Carbide Corp., Oak Ridge, TN) and deuterium (Matheson Gas Products, C.P. Grade, ≥99.5 atom % D_2) by passage of the mixture over CuO at 400 °C. The water obtained was diluted with carefully purified[16] D_2O, generously provided by Dr. E. J. Hart of The Argonne National Laboratory. Research grade protium (certified to have no impurities detectable by mass spectrometry, with a threshold for most gases of 2 ppm) was obtained from Matheson. Research grade propane was obtained from the Phillips Petroleum Co. (specified to be 99.97 mol % propane, 0.03 mol % isobutane; gas-chromatographic analysis indicated propene was ≤1 ppm). Hydrogen deuteride for mass spectrometer calibration solutions was from Merck, Sharpe and Dohme of Canada, Ltd. (specified to be ≥49 atom % deuterium; mass spectrometric analysis indicated 0.84 mol % D_2).

Dosimetry. For water activity determinations, a Packard Tri-carb Liquid Scintillation Spectrometer (Model 3310, Packard Instrument Co., Inc.), with standards from New England Nuclear, was used. Liquid scintillation cocktails were prepared with Preblend 3a30 from Research Products International Corp. (PPO and POPOP with *para*-dioxane solvent.) Multiple determinations yielded specific activities of 1.29 ± 1%, 6.65×10^{-2} ± 0.5%, and 3.51×10^{-2} ± 0% Ci/g for three water preparations. Experimental dose rates were varied by the mixing of aliquots of one of the preparations with pure D_2O on the sample preparation vacuum system. Absorbed doses were computed by assuming an average β-particle energy of 5.73×10^3 eV,[17] and that greater than 99% of the energy of the tritium β particles is adsorbed by the D_2O.[18] The volume of the water aliquot introduced into the irradiation vessel could be determined with an accuracy of ±0.5%.

Preparation of Reaction Vessels and Reaction Mixtures. The vacuum systems were entirely grease free. Irradiation vessels were constructed using 250-mL Pyrex or fused-silica spherical bulbs, in the manner described previously.[13] Four vessel pretreatment procedures were used. Procedure 1 (Pyrex vessels) consisted of a distilled water rinse of a new vessel. Following attachment of the break-seal, the vessel was baked (i) in air for 3 h at 150 °C, (ii) in vacuo for 12 h at 500 °C, and (iii) in vacuo for 12 h at 440 °C.[2] For procedure 2 (Pyrex vessels), vessels were rinsed with two cleaning solutions: (i) an aqueous solution of 25 mL of HF, 100 mL of HNO_3, and 10 g of Alconox in a total volume of 250 mL[19] and (ii) a 10:1 mixture of concentrated HNO_3 and 30% H_2O_2 (Caution: this solution should be prepared and used promptly, since the

Table I. Experimental Conditions and Results of the Protium-Additive Experiments[a]

expt no.	dose × 10^{-16}/ eV cm^{-3}	[H$_2$] × 10^{-17}/ molecules cm^{-3}	G(HD)	G(D$_2$)	β(D/T)	vessel cleaning procedure[b]
40	2.78	1.03	13.0	0.53	1.94	2
9	2.86	1.06	13.7			1
12	7.00	2.59	10.6	0.29	1.62	1
10	7.37	2.73	12.3	0.46	1.66	1
11	9.26	3.43	11.0	0.35	1.65	1
16	9.33	3.46	11.4	0.39	2.07	2
15	12.0	4.44	11.8	0.46	2.08	2
14	17.2	6.37	9.2	0.25	1.47	1
13	17.8	6.59	10.2	0.29	1.63	1

[a] Reaction temperature for experiment 40 was 418 K. All other experiments in this table were performed at 385 K. The [D_2O] were between 1.58×10^{19} and 1.65×10^{19} molecules cm^{-3}, except for experiment 40, which used 4.15×10^{19} molecules cm^{-3}. The dose rates were between 1.56×10^{11} and 1.69×10^{11} eV cm^{-3} s^{-1}, except for experiment 40, which used 2.14×10^{11} eV cm^{-3} s^{-1}. [b] See Experimental Section for description of the procedures.

concentrated solution will explode after ~15 min). The vessel was rinsed with distilled water after each solution, and finally with triply-distilled water. The bake-out was the same as for procedure 1. Procedure 3 (silica vessel) was a treatment designed by Elmer et al.[20] to replace the hydroxyl groups on the surfaces of porous glasses with fluorine atoms. Following a brief baking in air, the vessel was baked in vacuo at 500 °C for ≥4 h. Procedure 4 (silica vessel) consisted of a 3-min soak in 5% HF followed by 12 rinses with triply-distilled water. This etching should remove a layer of SiO_2 of about 100-nm depth from the vessel surface.[21] The vessel was then baked in vacuo at 200 °C for 3 h.

Protium-additive reaction samples were prepared as previously described.[2] Propane-additive samples were prepared by condensing a propane aliquot into the irradiation vessel, where the water was already frozen at -196 °C. Propane pressures were determined by using a Pace differential pressure transducer with a linear range of 0–6 torr (Model P7D, with a Carrier Demodulator Model CD-10, Whittaker Corp., North Hollywood, CA). Protium-/propane-additive samples were prepared by introduction of the protium into the vessel already containing the propane and water aliquots. The frozen samples were thawed rapidly by a 60-s immersion in a fluidized sandbath[13] at 350 °C and were then placed in a temperature-controlled oven (±1 °C control): the rapid thawing permitted irradiation times as short as 100 min to be measured accurately. Radiolysis was terminated by immersion of the vessel in liquid nitrogen. Irradiation times from 97 to 26 000 min were used, with temperatures between 385 and 418 K.

Product Collection and Analysis. The hydrogen present following irradiation was collected by pumping the gas from the reaction vessel (immersed in liquid N_2) through a liquid N_2 cooled U-tube filled with activated silica gel into a micro-gas burette by means of a diffusion pump and Toepler pump in series. In blank runs with mixtures containing tritiated water, 30 ppb or less of the water (i.e., ≤10 ng of D_2O) was collected with the hydrogen. Hydrogen volumes between 8 μL and 3 mL (STP) were transferred quantitatively: with volumes less than 8 μL, extraneous gas was collected with the hydrogen, e.g., in blank runs with 2 μL of gas, 105% was collected. The isotopic composition of the hydrogen was determined by using an extensively modified CEC-21-620 mass spectrometer equipped with an isotope-ratio accessory (Consolidated Electrodynamics Corp., Pasadena, CA). Concentrations of HD in H_2 as low as 0.5% could be measured with ±2% precision; concentrations of D_2 in H_2 of 0.05% could be analyzed with ±10% precision. The tritium content of the hydrogen was determined as described previously,[13] assuming that 34.9 eV is required for formation of an ion pair in N_2.[22]

Results

Deuterium oxide vapor was irradiated with the use of tritiated water (TOD) as an internal source of β rays ([D_2O]/[TOD] ≥ 2000). Four sets of experiments were performed in the tem-

(15) Johnson, G. R. A.; Simic, M. *J. Phys. Chem.* **1967**, *71*, 1118–23.

(16) Hart, E. J.; Gordon, S.; Hutchinson, D. A. *J. Am. Chem. Soc.* **1953**, *75*, 6165–9.

(17) Pillinger, W. L.; Hentges, J. J.; Blair, J. A. *Phys. Rev.* **1961**, *121*, 232–3.

(18) Dorfman, L. M. *Phys. Rev.* **1954**, *95*, 393–6.

(19) Dye, J. L.; DeBacker, M. G.; Dorfman, L. M. *J. Chem. Phys.* **1970**, *52*, 6251–8. Feldman, L. H.; DeWald, R. R.; Dye, J. L. *Adv. Chem. Ser.* **1965**, *50*, 163–72.

(20) Elmer, T. H.; Chapman, I. D.; Nordberg, M. E. *J. Phys. Chem.* **1963**, *67*, 2219–22.

(21) Osborne, J. F.; Larrabee, G. B.; Harrap, V. *Anal. Chem.* **1967**, *39*, 1144–8.

(22) Jesse, W. P.; Sadauskis, J. *Phys. Rev.* **1955**, *97*, 1668–70.

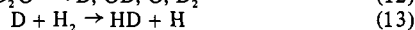(23) Polanyi, J. C. *J. Chem. Phys.* **1955**, *23*, 1505–13.

perature-independent region for $G(HD)$:[13] (i) protium-additive experiments, (ii) propane-additive experiments, (iii) experiments with both propane and protium added, and (iv) protium-additive experiments in which a very low dose rate was employed and the irradiation vessel surface was varied.

Protium-Additive Experiments. The conditions and results of the protium-additive experiments are given in Table I. The kinetic isotope separation factor, $\beta(D/T)$, is defined by

$$\beta(D/T) = f_T[G(HD) + 2G(D_2)]/G(T) \tag{11}$$

where f_T is the fraction of the hydrogen atoms in the water vapor which are tritium. The effects of dose and vessel surface pretreatment were examined.

Scheme III

$$D_2O \xrightarrow{\text{\Large$\sim\!\!\wedge\!\!\sim$}} D, OD, O, D_2 \tag{12}$$
$$D + H_2 \rightarrow HD + H \tag{13}$$
$$OD + H_2 \rightarrow HOD + H \tag{14}$$
$$O + H_2 \rightarrow OH + H \tag{15}$$
$$OH + H_2 \rightarrow H_2O + H \tag{16}$$
$$H \xrightarrow{\text{wall}} {}^1/_2 H_2 \tag{17}$$
$$H + D_2 \rightarrow HD + D \tag{18}$$
$$H + HD \rightarrow H_2 + D \tag{19}$$

On the basis of the homogeneous mechanism for HD production given in the introduction, the reactions in Scheme III are expected to occur. Because of the long lifetime of the H atom with respect to recombination at the vessel surface, reaction 18 will affect hydrogen product yields, even at relatively low conversions of H_2: as the dose is increased $G(D_2)$ will decrease and $G(HD)$ will increase, while $G(HD) + 2G(D_2)$ remains constant. At sufficiently high dose, reactions 20–22 must be added to Scheme III to de-

$$D + HD \rightarrow D_2 + H \tag{20}$$

$$OD + HD \rightarrow D_2O + H \tag{21}$$

$$O + HD \rightarrow OD + H \tag{22}$$
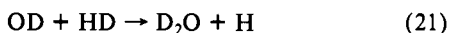
scribe the expected mechanism (the corresponding reactions with D_2 need not be considered since $G(HD)/G(D_2) > 10$, while the corresponding rate constants are similar[23]). Reaction 20, the reverse of reaction 18, will be more than offset by reaction 18. Reactions 21 and 22 reduce $G(HD)$ and $G(HD) + 2G(D_2)$. At the highest conversion used ([HD]/[H₂] = 0.06), roughly 3% of the OD radicals can react via reaction 21; thus, assuming that $G(OD) \approx G(D)$, $G(HD)$ will be reduced by $\leq 3\%$. Since $G(O) \approx G(D_2)$, the effect of reaction 22 should be negligible. In summary, as the absorbed dose is increased $G(HD) + 2G(D_2)$ will decrease by less than 3%, while $G(D_2)$ decreases and $G(HD)$ increases as a result of reaction 18.

$G(HD)$, $G(D_2)$, and $\beta(D/T)$ are plotted vs. dose in Figure 1. $G(D_2)$ decreased with increasing dose, as expected from the contribution of reaction 18; vessel pretreatment had no appreciable effect. $G(HD)$ showed a steady *decrease* with dose; the magnitude of the decrease was much larger than the possible 3% due to reaction 21. The vessel pretreatment had no effect. As a result of the decreases in both $G(D_2)$ and $G(HD)$, $G(HD) + 2G(D_2)$ declined instead of remaining constant. The kinetic isotope separation factor was dramatically affected by the vessel pretreatment: $\beta(D/T)$ increased by about 25% when the pretreatment was switched from a simple rinse with H_2O (procedure 1) to washing with strong solutions (procedure 2). No such dependence is predicted by Scheme III. With procedure 1, $\beta(D/T)$ decreased with increasing dose.

Comparing pairs of experiments with essentially identical conditions gives average $G(HD)$ of 13.3 ± 2.6%, 11.5 ± 7.4%, 11.2 ± 1.8%, and 9.7 ± 5.1%. These standard deviations are much larger than expected from the known precision of the mass-spectrometric analyses and other experimental manipulations. From Figure 1, it is observed further that the higher $G(HD)$ were accompanied by higher $G(D_2)$, in comparable pairs of experiments; this correlation is not an artifact of the measurements, and is not predicted by Scheme III. The $G(HD)$ and $G(D_2)$ obtained at lower doses are in agreement with published values.[13]
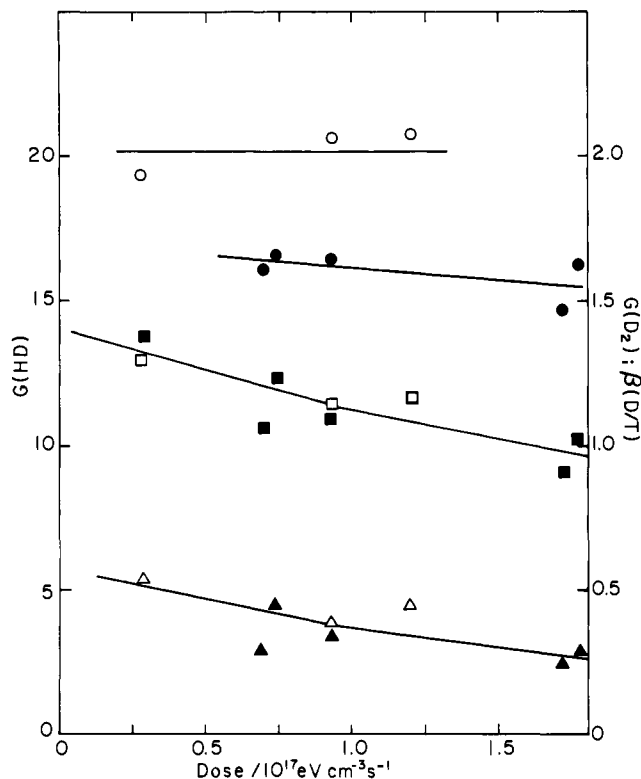
Figure 1. Dependence of the hydrogen product yields and the kinetic isotope separation factor on absorbed dose in the protium-additive experiments. (■, □) $G(HD)$; (▲, △) $G(D_2)$; (●, ○) $\beta(D/T)$. Reaction vessels for (■, ▲, ●) were cleaned by procedure 1; vessels for (□, △, ○) were cleaned by procedure 2. Other experimental parameters are given in Table I.

Table II. Experimental Conditions and Results of the Propane-Additive Experiments[a]

expt no.	dose × 10⁻¹⁶/ eV cm⁻³	[C₃H₈] × 10⁻¹⁷/ molecules cm⁻³	$G(HD) + G(D_2)$
28	0.130	6.05	7.05
27	0.329	6.03	7.48
26	0.767	6.02	6.62
25	1.49	6.00	7.45
24	2.97	6.02	7.20
22	3.09	6.61	7.70
23	3.13	6.48	7.60
29	7.85	5.94	7.03
31	35.1	5.74	6.06
30	7.81	2.94	6.72
32	5.78	1.34	6.38
33	7.78	0.474	5.51

[a] The irradiation temperature was 418 K. The [D₂O] were between 4.09 × 10¹⁹ and 4.24 × 10¹⁹ molecules cm⁻³. The dose rates were between 2.23 × 10¹¹ and 2.37 × 10¹¹ eV cm⁻³ s⁻¹.

Propane-Additive Experiments. The conditions and results of the propane-additive experiments are given in Table II. Only the sum of hydrogen product yields, $G(HD) + G(D_2)$, was determined (by volume measurement). Two series of measurements were performed: (i) with $[C_3H_8]_0$ constant, the absorbed dose was varied, and (ii) with the dose constant, $[C_3H_8]_0$ was varied.

In analogy with Scheme II, the expected mechanism is given in Scheme IV ($\cdot C_3H_7$ denotes both the 1- and 2-propyl radicals). At sufficiently high doses, reactions 28–30 must be included to indicate the scavenging radicals by product alkenes.

As seen in Figure 2, the total hydrogen product yield dropped significantly only at the highest dose used. The average value obtained for $G(HD) + G(D_2)$ for doses $<3 \times 10^{17}$ eV cm⁻³ was 7.27 ± 1.6%; in experiments 22, 23 and 24, which were run under

Table III. Experimental Conditions and Results of the Protium-/Propane-Additive Experiments[a]

expt no.	dose rate/ 10^{11} eV cm^{-3} s^{-1}	$[C_3H_8] \times 10^{-14}$/ molecules cm^{-3}	$[H_2] \times 10^{17}$/ molecules cm^{-3}	G(HD)	G(D$_2$)	β(D/T)
40	2.14	0	2.87	13.0	0.53	1.94
80	2.12	0.570	2.82	11.1	0.44	1.77
70-1	2.13	1.18	2.86	11.4	0.48	1.79
70-2[b]	2.13	1.17	2.79	9.13	0.50	1.67
72-1	1.05	1.19	2.83	11.6	0.49	1.62
72-2[b]	1.04	1.17	2.77	9.09	0.51	1.51
71-1[b]	2.12	1.18	5.67	9.52	0.45	1.79
71-2[b]	2.12	1.17	5.63	9.42	0.40	1.71
71-3[b]	2.13	1.18	5.52	9.09	0.41	1.70
60	2.08	5.04	2.86	8.78	0.52	1.66
55	0.177	14.7	2.58	6.90	0.57	
50	2.11	36.3	2.88	7.62	0.63	1.63

[a] The irradiation temperature was 418 K. The [D$_2$O] were 4.09×10^{19} to 4.15×10^{19} molecules cm^{-3}. The absorbed doses were between 2.70×10^{16} and 2.78×10^{16} eV cm^{-3}. All vessels were cleaned by procedure 2 (see Experimental Section). [b] These reactions were carried out in the same reaction vessel.

Scheme IV

$$D_2O \rightsquigarrow D,\ OD,\ O,\ D_2 \tag{12}$$
$$D + C_3H_8 \rightarrow HD + \cdot C_3H_7 \tag{23}$$
$$OD + C_3H_8 \rightarrow HOD + \cdot C_3H_7 \tag{24}$$
$$O + C_3H_8 \rightarrow OH + \cdot C_3H_7 \tag{25}$$
$$\cdot C_3H_7 + \cdot C_3H_7 \rightarrow C_3H_6 + C_3H_8 \tag{26}$$
$$\cdot C_3H_7 + \cdot C_3H_7 \rightarrow C_6H_{14} \tag{27}$$
$$D + C_3H_6 \rightarrow \cdot C_3H_6D \tag{28}$$
$$OD + C_3H_6 \rightarrow \cdot C_3H_6OD \tag{29}$$
$$O + C_3H_6 \rightarrow \cdot C_3H_6O \tag{30}$$
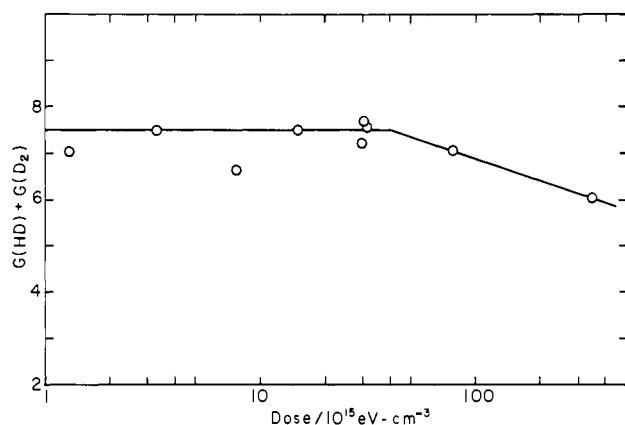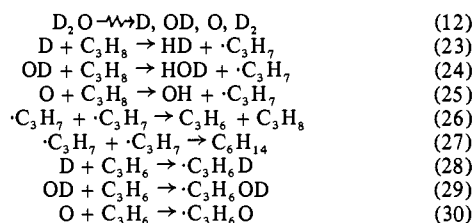
Figure 2. Dependence of the hydrogen product yield on absorbed dose in the propane-additive experiments. Propane concentration was held constant, with $[C_3H_8]_0 \approx 6 \times 10^{17}$ molecules cm^{-3}. Other experimental parameters are given in Table II.

essentially identical conditions, an average G(HD) + G(D$_2$) of 7.5 ± 1.7% was obtained. Thus, the precision of the measurements corresponded to the precision of the experimental manipulations. In the experiments with $[C_3H_8]_0$ held constant, the total hydrogen yield (Table II) decreased substantially only when $[C_3H_8]_0$ was reduced below 3×10^{17} molecules cm^{-3}. The decreases in the total hydrogen yield which occur when $[C_3H_8]_0$ is decreased or when the dose is increased are the expected result, since in each case $[C_3H_6]_f/[C_3H_8]_0$ is increased, boosting the efficiency of reaction 28 with respect to reaction 23.

The value obtained for the total hydrogen yield under conditions of dose and $[C_3H_8]_0$ where reaction 28 does not interfere, i.e., G(HD) + G(D$_2$) = 7.5, agrees with reported values. In the protium-/propane-additive experiments to be discussed shortly, G(D$_2$) = 0.63 was obtained in the experiment with the highest $[C_3H_8]_0$, in agreement with the work of Johnson and Simic.[15] Thus, assuming that G_D = G(HD), the present experiments give G_D = 6.9 for propane-additive experiments.

Protium-/Propane-Additive Experiments. The conditions and results of the experiments with both protium and propane added are given in Table III. The major additive was protium, at about
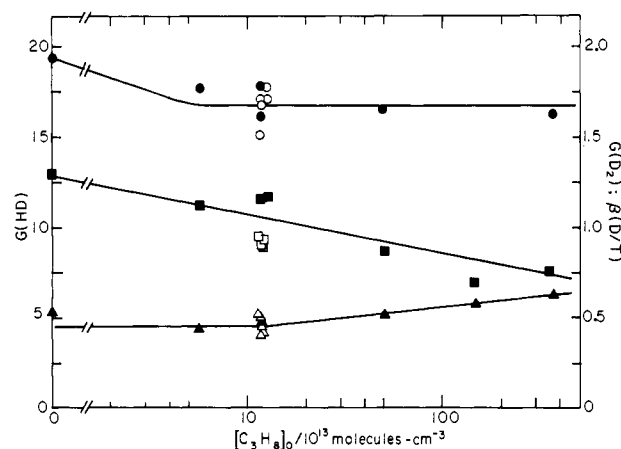
Figure 3. Dependence of the hydrogen product yields and the kinetic isotope separation factor on $[C_3H_8]_0$ in the experiments with protium and propane added. ($\blacksquare$, $\square$) G(HD); ($\blacktriangle$, $\triangle$) G(D$_2$); ($\bullet$, $\bigcirc$) β(D/T). Open symbols denote reactions performed in the same reaction vessel; filled symbols indicate the vessels were randomly chosen. All vessels were cleaned by procedure 2 prior to each experiment. Other experrimental parameters given in Table III.

0.7 mol %; $[C_3H_8]_0/[H_2]$ was varied from 0–0.013. The effects of $[C_3H_8]_0/[H_2]$, dose rate, and method of vessel selection ("random" selection or repeated use of the same vessel) were examined. All vessels were cleaned by procedure 2.

The anticipated mechanism for homogeneous production of HD includes Scheme III and reactions 31 and 32, which will be

$$H + C_3H_8 \rightarrow H_2 + \cdot C_3H_7 \tag{31}$$

$$H + C_3H_6 \rightarrow \cdot C_3H_7 \tag{32}$$
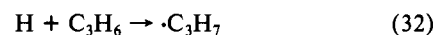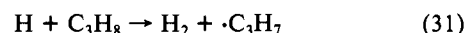
followed by reactions 26 and 27 of Scheme IV. In the experiment with the highest $[C_3H_8]_0$, it was estimated that 99% of the H atoms would be scavenged homogeneously via reactions 31 and 32. It should be noted that these reactions only approximate the H atom scavenging reactions, since even in the experiment with the largest $[C_3H_8]_0$ the number of H atoms produced is larger than the number of propane molecules present.

In Figure 3, G(HD) is plotted as a function of $[C_3H_8]_0$. The most striking feature is that G(HD) drops quickly with the first additions of propane. With $[C_3H_8]_0/[H_2]$ = 0.013, G(HD) has already dropped to 7.6, which is nearly the value obtained in experiments with propane alone added. Clearly, this strong dependence of G(HD) on $[C_3H_8]_0$ is not predicted by the anticipated mechanism. From Figure 3, it is seen that G(D$_2$) increases with increasing $[C_3H_8]_0$. G(D$_2$) at low $[C_3H_8]_0$ is the same as that seen in the protium-additive experiments at low dose; with increasing $[C_3H_8]_0$, G(D$_2$) approaches the value reported for experiments with only propane added,[15] i.e., 0.65 molecules/100 eV.

5156 *J. Am. Chem. Soc., Vol. 103, No. 17, 1981*

Richter and Firestone

This result would be expected since C_3H_8 can block reaction 18 by reducing the steady-state concentration of H atoms. With the first addition of C_3H_8, $\beta(D/T)$ dropped from the value of about 2.0 seen in the experiments with H_2 alone added (and procedure 2 used for vessel cleaning) to a value of about 1.7, which was not affected appreciably by further additions of C_3H_8.

Three sets of experiments were performed with $[C_3H_8]_0$ constant. The conditions were the same except that set-71 had twice the protium concentration of set-70, and set-72 had a dose rate half that of set-70. Experiments 70-1 and 70-2, identical except for the reaction vessel used, gave $G(HD) = 10.3 \pm 11\%$. Experiments 72-1, and 72-2, identical except for the vessel, gave $G(HD) = 10.3 \pm 13\%$. Set-71 experiments, identical in all respects including the reaction vessel, gave $G(HD) = 9.3 \pm 2\%$. For all the experiments in which the same reaction vessel was used, wherein the dose rate and $[H_2]$ were varied, an average of 9.25 $\pm 2\%$ was obtained for $G(HD)$. These results show clearly that a tremendous decrease in experimental scatter in $G(HD)$ was obtained when the same reaction vessel was used repeatedly. Experiments using the same vessel gave a scatter of about $\pm 2\%$, roughly the precision of the mass-spectrometric isotope analyses, while those using arbitrary vessel selection gave a scatter of about $\pm 12\%$, the same range seen in the protium-additive experiments. Such a dependence of the experimental precision on the method of vessel selection cannot be rationalized by the expected mechanism. $G(D_2)$ was not affected by vessel selection.

The constancy of $G(HD)$ in experiments where the same reaction vessel is used demonstrates there is no dependence of the HD yield on $[H_2]$, $[C_3H_8]_0/[H_2]$, or the dose rate. This lack of dependence would be expected from the homogeneous mechanism for HD production. The lack of dependence on $[H_2]$ demonstrates that neither the propane nor the product alkenes, which are much more reactive than the parent alkanes, scavenge a significant number of D atoms. Using the value of Westenberg and de Haas[24] for the rate constant of reaction 13 and the value of Kazmi, Diefendorf, and LeRoy[25] for reaction 23, one computes that C_3H_8 can scavenge only 1.8% of the D atoms at the highest $[C_3H_8]_0$ used.

Low Dose Rate/Protium-Additive Experiments. The experimental conditions and results are given in Table IV. The dose rates used were lower by a factor of 20 than those elsewhere in this investigation; the lowest dose rate was lower by a factor of 250 than the lowest dose rate of Firestone and Bibler.[2,13] Five different vessels were used: three Pyrex vessels cleaned by procedure 2 prior to each irradiation, and two silica vessels cleaned by procedure 3 or by procedure 4 prior to each irradiation. The effects of variation of the absorbed dose and of protium concentration were examined ($[HD]_f/[H_2]_0$ ranged from 0.0016–0.017). The reaction mechanism expected assuming homogeneous production of HD molecules is the same as that in the protium-additive experiments at higher dose rates, given essentially by Scheme III.

In the studies of Firestone and Bibler[2,13] and in the present investigation with dose rates greater than 1.5×10^{10} eV cm^{-3} s^{-1}, the $G(HD)$ obtained with protium additive were close to 13. Firestone and Bibler reported no dependence of $G(HD)$ on the dose rate. In the present series, exceedingly low dose rates were used, such that an irradiation period of 2 weeks gave less than 2% conversion of the protium. For three experiments performed in the same Pyrex vessel, with the same dose rate and dose ($[H_2]$ was sufficient to scavenge all D atoms), the average $G(HD)$ was $8.39 \pm 1.1\%$. This value is strikingly different from the values obtained at higher dose rates in the present study, as well as the average value of 13.3 reported by Bibler and Firestone.[13] An additional experiment performed in the same vessel, using a dose rate lowered by an additional factor of 2, gave an even lower $G(HD)$, to wit, 6.9 molecules/100 eV. This is the same as the G_D obtained from the propane-additive experiments of the present

(24) Westernberg, A. A.; de Haas, N. *J. Chem. Phys.* **1967**, *47*, 1393–406.
(25) Kazmi, H. A.; Diefendorf, R. F.; LeRoy, D. J. *Can. J. Chem.* **1963**, *41*, 690–4.

Table IV. Experimental Conditions and Results of the Low Dose Rate/Protium-Additive Experiments[a]

expt no.	vessel surface	dose × 10^{-15}/ eV cm^{-3}	$[H_2]$ × 10^{-17}/ molecules cm^{-3}	$G(HD)$	$G(D_2)$
P17	Pyrex[b]	7.44	1.01	8.38	0.44
P16	Pyrex[b]	7.59	1.02	8.26	0.44
P13	Pyrex[b]	7.89	0.407	8.53	0.46
P12	Pyrex[b]	2.66	0.526	7.98	0.67
P14	Pyrex[b]	8.48	0.353	5.01	0.45
P15	Pyrex[b]	2.35	1.06	6.93	0.44
P21	Pyrex[c]	5.37	1.00	7.85	0.44
P31	Pyrex[c]	5.17	1.00	7.89	0.41
SF4	silica[d]	7.33	1.04	8.17	0.45
SF3	silica[d]	8.22	1.06	8.33	0.45
SF2	silica[d]	7.85	0.407	7.38	0.46
SF1	silica[d]	7.96	0.393	5.17	0.47
S4	silica[e]	8.15	1.00	7.09	0.44
S1	silica[e]	2.63	0.781	8.29	0.42
S2	silica[e]	2.61	0.541	9.13	
S3	silica[e]	7.85	0.370	6.91	0.40

[a] The irradiation temperature was 398 K. The $[D_2O]$ were between 1.78×10^{19} and 1.87×10^{19} molecules cm^{-3}. The dose rates were between 7.62×10^9 and 7.90×10^9 eV cm^{-3} s^{-1}, except for experiment P15 which used 4.03×10^9 eV cm^{-3} s^{-1}. [b] Experiments P12–P17 were carried out in the same Pyrex reaction vessel, which was cleaned by procedure 2 prior to each experiment. [c] Experiments P21 and P31 used two other Pyrex vessels, also cleaned by procedure 2. [d] For experiments SF1–SF4, a single silica vessel was cleaned by procedure 3 prior to each experiment. [e] For experiments S1–S4, a single silica vessel was cleaned by procedure 4 prior to each experiment.
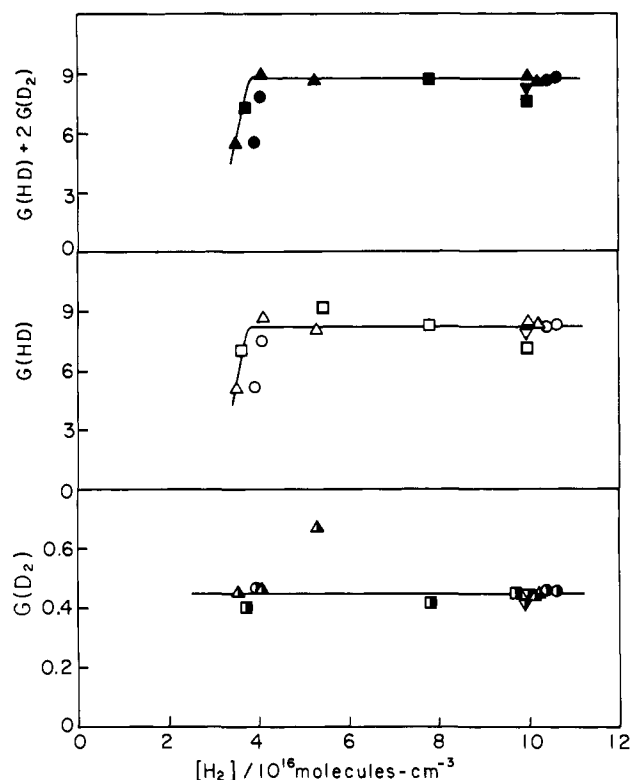
investigation. The unavoidable conclusion is that $G(HD)$ is strongly dependent on the dose rate in the protium-additive experiments at sufficiently low dose rates. This behavior cannot be explained by the homogeneous mechanism for hydrogen isotope production given in Scheme III.

With regard to the influence of the vessel surface on the hydrogen product yields, consider first the P1 set of experiments, all performed in the same Pyrex vessel. With $[H_2]$ sufficient to scavenge all D atoms, $G(HD)$ was $8.39 \pm 1.1\%$. The observed uncertainty corresponds to the uncertainty of the mass-spectrometric isotope analyses. For two additional experiments carried out in two other Pyrex vessels, the $G(HD)$ obtained were 7.85 and 7.89, which are about 6% less than the value obtained with the P1 set vessel. Thus, $G(HD)$ depends substantially on the particular Pyrex vessel used, a dependence which is not expected from Scheme III. $G(D_2)$ was not affected by vessel selection. In the SF set of experiments, the single silica vessel used was treated by a procedure designed to replace the surface hydroxyl groups with florine atoms prior to each irradiation (procedure 3 in the experimental section). In experiments with $[H_2]$ sufficient for D-atom scavenging, $G(HD)$ was $8.25 \pm 0.9\%$, a very reproducible value. For the S-set experiments, the surface of a single silica vessel was etched to a depth of roughly 100 nm prior to each irradiation (procedure 4). The values obtained for $G(HD)$ when $[H_2]$ was sufficient gave an average of $8.17 \pm 8.8\%$. This large scatter in $G(HD)$ is similar to that obtained when a wide variety of Pyrex vessels was used. The values obtained for $G(D_2)$, using silica vessels, were constant, and were the same as the values obtained by using Pyrex vessels.

As the absorbed dose is increased, it is expected that $G(D_2)$ will decrease, $G(HD)$ increase, and $G(HD) + 2G(D_2)$ remain constant, as discussed previously. In Figure 4, these product yields are plotted vs. the absorbed dose for all the low dose rate experiments with sufficient H_2 present. For the P1-set experiments (performed in the same vessel), $G(D_2)$ decreased slightly, $G(HD)$ increased slightly, and $G(HD) + 2G(D_2)$ remained constant with increasing dose, which is the predicted pattern. With the S1-set experiments, it was observed that $G(D_2)$ remained constant while $G(HD) + 2G(D_2)$ and $G(HD)$ *decreased* with increasing dose: these trends are opposite to those observed with the P1-set ex-

A Surface-Catalyzed Isotope-Exchange Reaction

J. Am. Chem. Soc., Vol. 103, No. 17, 1981 5157
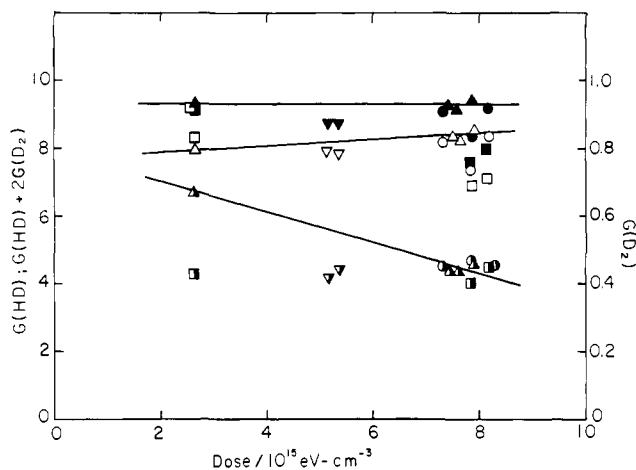
Figure 4. Dependence of the values of $G(HD)$, $G(D_2)$, and $G(HD) + 2G(D_2)$ on the absorbed dose in the low dose rate/protium-additive experiments. Open symbols refer to $G(HD)$, half-filled symbols refer to $G(D_2)$, and filled symbols refer to $G(HD) + 2G(D_2)$: (△, ▲, ▲) experiments P12–P17 (excluding P15, which has a lower dose rate, and P14 which has a low [H_2]) in a single Pyrex vessel; (▽, ▼, ▼) experiments P21 and P31 in two different Pyrex vessels; (□, ◨, ■) experiments S1–S4 in a silica vessel etched with HF; and (○, ◑, ●) experiments SF1–SF4 in a silica vessel with a fluorinated surface. The dose rates used were $(7.6–7.9) \times 10^9$ eV cm^{-3} s^{-1}. Other experimental parameters are given in Table IV.

periments, but are the same as those found in the high dose rate, Pyrex-vessel experiments.

If the concentration of the protium radical scavenger is reduced, a point will be reached where H_2, in competition with diffusion to the vessel surface, cannot scavenge all the D atoms homogeneously. The D atoms diffusing to the vessel surface can combine either with another adsorbed D atom or with an adsorbed H atom to produce D_2 or HD, respectively, requiring the addition of reactions 33 and 34 to Scheme III to complete the expected

$$D \xrightarrow{\text{wall}} {}^1\!/_2 D_2 \tag{33}$$

$$D \xrightarrow{\text{wall}} {}^1\!/_2 HD \tag{34}$$

mechanism. The corresponding wall reaction of OD need not be considered, since k_{14} is substantially larger than k_{13}: $k(OH + H_2)$ is 1.2×10^{-13} cm^3 molecule^{-1} s^{-1} at 418 K,[26] while k_{13} is 7.7 $\times 10^{-15}$ cm^3 molecule^{-1} s^{-1}.[24] O atoms will be lost to the vessel surface even before D atoms, since $k_{15} = 2.5 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1},[27] leading to a reduction in the yield of H atoms; however, this is not expected to affect $G(HD)$. Thus, while $G(HD)$ is expected to decrease, $G(HD) + 2G(D_2)$ should remain constant and $G(D_2)$ should increase when [H_2]$_0$ is reduced. In Figure 5, the product yields from the low dose rate experiments are plotted vs. [H_2]. In the S-set experiments, neither $G(HD)$ nor $G(HD) + 2G(D_2)$ changed with [H_2] (within the experimental scatter), and $G(D_2)$ values remained constant. With the Pyrex and SF sets of experiments, a sharp drop in $G(HD)$ occurs when [H_2] is taken below 4×10^{16} molecules cm^{-3}, the expected trend. However, in contrast to the expected constant value, a sharp drop in $G(HD) + 2G(D_2)$ also occurs parallel to the decrease in $G(HD)$. No increase in $G(D_2)$ with decreasing [H_2] was observed; indeed, the values obtained were quite constant (the point at 5×10^{16} molecules cm^{-3}, experiment P12, is high as a result of the lower absorbed dose employed). With regard to experiment P12, which received the lowest dose of any sample in this investigation, it is interesting to note that the $G(D_2)$ obtained was 0.67, which is, within experimental precision, equal to the value obtained in propane-additive experiments,[15] and is the same as the limiting value obtained in the protium/propane experiments of the present investigation.

(26) Wilson, W. E., Jr. *J. Phys. Chem. Ref. Data* **1972**, *1*, 535–73.
(27) Westenberg, A. A.; de Haas, N. *J. Chem. Phys.* **1969**, *50*, 2512–16.

Figure 5. Dependence of $G(HD)$, $G(D_2)$, and $G(HD) + 2G(D_2)$ on the protium scavenger concentration in the low dose rate/protium-additive experiments. Open symbols refer to $G(HD)$, half-open symbols refer to $G(D_2)$, and closed symbols refer to $G(HD) + 2G(D_2)$: (△, ▲, ▲) experiments P12–P17 in a single Pyrex vessel (excluding P15, which has a lower dose rate); (▽, ▼, ▼) experiments P21 and P31 in two different Pyrex vessels; (□, ◨, ■) experiments S1–S4 in a silica vessel etched with HF; and (○, ◑, ●) experiments SF1–SF4 in a silica vessel with a fluorinated surface. The dose rates used were $(7.6–7.9) \times 10^9$ eV cm^{-3} s. Other experimental parameters are given in Table IV.

Summary of the Results. In the discussions of each of the four series of experiments, the results were examined with regard to mechanisms in which HD molecules are produced in homogeneous reactions. Several inconsistencies were noted, and the major points are as follows:

(i) The apparent G_D from D_2O radiolysis is different when measured by using H_2 or C_3H_8 radical scavengers, as has been reported previously.

(ii) In experiments using H_2 as a scavenger, including the protium-/propane-additive experiments, the deviation in $G(HD)$ when reaction vessels are "randomly" chosen is substantially larger than that expected from the known experimental uncertainties. In contrast, with certain pretreatment procedures, the precision of the $G(HD)$ values obtained with Pyrex and silica vessels when a single irradiation vessel is used repeatedly *is* of the expected size. With the propane-additive experiments, the precision of $G(HD)$ was of the expected size, even with random selection of vessels. These observations indicate that in experiments using H_2, $G(HD)$ is influenced by the irradiation vessel surface.

(iii) In the protium-/propane-additive experiments, it was observed that $G(HD)$ is sharply reduced by very small concentrations of C_3H_8. The results demonstrate that propane very efficiently deactivates a precursor of HD and that propane does not compete with H_2 for this precursor. This behavior indicates that C_3H_8 may reduce $G(HD)$ via the homogeneous scavenging of H atoms which would otherwise recombine at the vessel surface and lead to the production of "extra" HD molecules.

(iv) At very low dose rates ($<1.5 \times 10^{10}$ eV cm^{-3} s^{-1}), $G(HD)$ in protium-additive experiments is dependent on the dose rate. With decreasing dose rate, $G(HD)$ approaches the value of the propane-additive experiments.

(v) In the protium-additive experiments at higher dose rates, $G(D_2)$ decreases with increasing dose, as expected from the ho-

5158 *J. Am. Chem. Soc., Vol. 103, No. 17, 1981*

Richter and Firestone

mogeneous mechanism; however, $G(HD)$ also decreases, leading to a decrease in $G(HD) + 2G(D_2)$, a result which is inconsistent with the homogeneous mechanism. In the low dose rate/protium-additive experiments, similar trends were observed with the S-set experiments (HF-etched silica vessel); however, with the P1-set experiments (Pyrex vessel), the trends in the hydrogen yields with dose were those expected from the homogeneous mechanism.

(vi) In the protium-additive experiments at higher dose rates, it was determined that the kinetic isotope separation factor, β-(D/T), varied with the Pyrex vessel pretreatment. In the protium-/propane-additive experiments, it was observed that the first addition of C_3H_8 resulted in a substantial decrease in β(D/T). These observations indicate that in the protium-additive experiments HD is being produced by at least two reactions, each having a different kinetic isotope separation factor. The reactions are related to the vessel surface and to the steady-state concentration of H atoms.

(vii) In the low dose rate/protium-additive experiments, it was expected that as $[H_2]$ was decreased below the critical level for essentially 100% scavenging of D atoms, $G(HD)$ would decrease and $G(D_2)$ increase, while $G(HD) + 2G(D_2)$ would remain constant. The observed behavior in the Pyrex and SF sets of experiments was that $G(HD)$ did decrease with decreasing $[H_2]$; however, the $G(D_2)$ did not increase, and in fact, the values were quite constant. Thus, $G(HD) + 2G(D_2)$ decreased, as though D atoms were being lost at the vessel surface.

In conclusion, these results establish that in D_2O radiolysis experiments using protium as a radical scavenger the vessel surface plays an important role in the production of HD molecules, giving a substantial contribution to the measured $G(HD)$. Further, it is the H atoms produced via reactions 13–16 which interact with the surface to produce "extra" HD molecules, resulting in an apparent G_D in protium radical-scavenger experiments which is substantially larger than the apparent G_D determined in propane radical-scavenger experiments.

Discussion

In view of the several observations implicating the recombination of H atoms at the vessel surface as a source of "extra" HD molecules in D_2O-vapor radiolysis employing H_2 as a radical scavenger, it is appropriate to examine the character of the silicate surfaces being used (Pyrex is a borosilicate glass). It is well-known that the surface of a silicate material which has been exposed to moisture is covered with silanol groups ($\equiv$Si—OH) of at least three types,[28] and that water molecules are physically adsorbed on the surface.[29] These surface hydroxyl groups can be completely deuterated (to give $\equiv$Si—OD) via an isotope-exchange reaction which is accomplished simply by repeated evacuation at room temperature followed by exposure to D_2O;[30,31] in the infrared-spectroscopic studies of Benesi and Jones,[30] transitions attributed to adsorbed HOD molecules were observed along with those of the newly formed $\equiv$Si—OD groups.

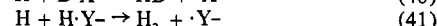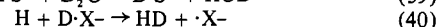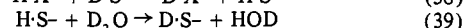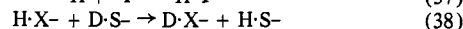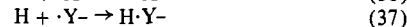The occurrence of exchange reactions between molecular hydrogen and H atoms chemically incorporated in silicate surfaces was reported as early as 1935 by Farkas and Farkas,[32] who examined the exchange of D_2 with H atoms contained in fused silica surfaces at high temperatures (700 °C). More recently, Annis, Clough, and Eley[33] have determined that on borosilicate glass the energy of activation for the D_2/surface-H-atom exchange reaction (yielding HD product) is 21.5–23.6 kcal/mol, where the reaction was first order in D_2. Infrared spectroscopic studies of this exchange reaction made by Peri[34] on a dry silica Aerogel and by

Low and Ramasubramanian[31] on a porous Vycor glass have established that the exchange occurs between the molecular hydrogen and the hydroxyl groups on the surface, which could be represented by reaction 35 (a Langmuir–Rideal mechanism).

$$D_2 + \equiv Si—OH \rightarrow HD + \equiv Si—OD \qquad (35)$$
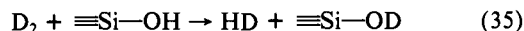
Sagert and Ponteau[35] have determined that if molecular hydrogen is dissociated by adsorption on catalysts such as platinum (intermingled in the silicate material), isotope exchange occurs at low temperatures: the exchange occurs between the adsorbed H atom and deuterated surface hydroxyl groups.

Scheme V

$$\begin{array}{ll} H + \cdot X- \rightarrow H\cdot X- & (36) \\ H + \cdot Y- \rightarrow H\cdot Y- & (37) \\ H\cdot X- + D\cdot S- \rightarrow D\cdot X- + H\cdot S- & (38) \\ H\cdot S- + D_2O \rightarrow D\cdot S- + HOD & (39) \\ H + D\cdot X- \rightarrow HD + \cdot X- & (40) \\ H + H\cdot Y- \rightarrow H_2 + \cdot Y- & (41) \end{array}$$

Clearly, in the present experiments we are dealing with a silicate surface covered with deuterated surface hydroxyl groups and saturated with physically adsorbed D_2O molecules. In the radiolysis experiments using protium, neither high temperature nor catalysts are needed to give adsorbed hydrogen *atoms*. Thus, on the basis of the known isotope-exchange reactions catalyzed by silicate surfaces just discussed, an exchange reaction between adsorbed, radiolytically produced H atoms and surface $\equiv$Si—OD groups appears not only reasonable, but inevitable. The experimental results obtained in the present study clearly show that when the radiolytically generated H atoms recombine at the deuterium oxide saturated surface of the silicate vessels, isotope exchange can occur between the H atoms from the volume and *chemisorbed* D_2O molecules, i.e., the $\equiv$Si—OD groups. The result is that both H_2 and HD molecules can be produced when the H atoms recombine at the vessel surface. The following explicit model, taken together with a small number of qualitative characteristics, presents a framework within which the observed behavior can be understood. The reactions occurring in the protium radical-scavenger experiments will include reactions 12–16, 18, and 19 of Scheme III, and the isotope exchange reactions in Scheme V, where $\cdot X-$, $\cdot Y-$, and $\cdot S-$ represent surface adsorption sites. The combinations of reactions 36 and 38–40 and of 37 and 41 may be represented by reactions x and y:

$$H \xrightarrow{\text{wall}} {}^1/_2 HD \qquad (x)$$

$$H \xrightarrow{\text{wall}} {}^1/_2 H_2 \qquad (y)$$
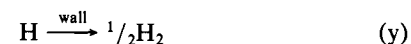
When protium and propane are used together as scavengers, reactions 31 and 32 must also be considered. Reactions 36–41 describe the "recombination" of H atoms at the vessel surface. Three types of surface sites are indicated: X– and Y– sites, which can adsorb H atoms from the volume, and the S– sites which are surface-hydrogen-containing groups, whose identity is not specified (presumably, they are the surface $\equiv$Si—OD and $\equiv$Si—OH groups). The X– and Y– sites differ in that H atoms adsorbed on X– sites can undergo isotope exchange with D atoms bound as D·S–. D and H atoms adsorbed on both the X– and Y– sites combine with H atoms from the vessel volume, according to the Langmuir concept of atomic recombination.[36] The deactivated exchange sites, H·S–, are regenerated by reaction with D_2O. The rationalization of the experimental results within the framework of this mechanism is now presented.

The Value of G_D. The present investigation confirmed the large difference between G_D determined by using protium as a radical scavenger and the value obtained by using propane, which has been reported in the literature. The mechanism including HD production in the H_2 scavenger experiments via the surface-

(28) Hair, M. L. "Infrared Spectroscopy in Surface Chemistry"; Marcel Dekker, Inc.: New York, 1967; p 82.

(29) Eitel, W. "Silicate Science"; Academic Press: New York, 1964; Vol. I.

(30) Benesi, H. A.; Jones, A. C. *J. Phys. Chem.* **1959**, *63*, 179–82.

(31) Low, M. J. D.; Ramasubramanian, N. *J. Phys. Chem.* **1966**, *70*, 2740–6.

(32) Farkas, A.; Farkas, L. *Trans. Faraday Soc.* **1935**, *31*, 821–4.

(33) Annis, G. S.; Clough, H.; Eley, D. D. *Trans. Faraday Soc.* **1958**, *54*, 394–9.

(34) Peri, J. B. *J. Phys. Chem.* **1966**, *70*, 2937–45.

(35) Sagert, N. H.; Ponteau, R. M. *Can. J. Chem.* **1971**, *49*, 3411–17.

(36) Laidler, K. J. "Chemical Kinetics"; McGraw-Hill Book Co., Inc.: New York, 1965; Chapter 6.

catalyzed isotope-exchange reactions rationalizes this difference, using known characteristics of silicate surfaces.

Based on the surface-catalyzed isotope-exchange mechanism, the maximum possible value of $G(HD)$ (when reaction 18 does not contribute substantially) in the H_2 scavenger experiments is

$$G(HD)_{max} = G_D + G(H)/2 = G(HD)_{homog} + G(H)/2 \quad (42)$$

Presumably, the yield of HD from homogeneous reactions is given by the $G(HD)$ determined in the C_3H_8 scavenger experiments, i.e., $G(HD)_{homog} = 6.9$. $G(H)$ is given by

$$G(H) = 2(G_D + G_{D_2}) \quad (43)$$

obtained by combining the mass-balance relationship

$$G_D + 2G_{D_2} = G_{OD} + 2G_O \quad (44)$$

with eq 45, based on the mechanism:

$$G(H) = G_D + G_{OD} + 2G_O \quad (45)$$

Thus, $G(H) = 15.0$ and $G(HD)_{max} = 14.4$. The average value found by Bibler and Firestone[13] for $G(HD)$ was 13.1: values as high as 14.6 were obtained. In this investigation, $G(HD)$ as high as 13.7 were obtained. Thus, the surface-catalyzed isotope-exchange mechanism very successfully rationalizes the difference in $G(HD)$ obtained when H_2 or C_3H_8 are used as radical scavengers, and explains how such large $G(HD)$ can be obtained with an H_2 scavenger.

Dependence of $G(HD)$ on Vessel Selection. As described by Scheme V, the vessel surface possesses both X– and Y– sites, where only X– sites are capable of undergoing isotope exchange with the D atoms held in the S– sites. Thus, assuming an abundance of the D·S– species, the yield of HD molecules from the surface reaction is given by

$$G(HD)_{surface} = F_X(G_H/2) = F_X(G_D + G_{D_2}) \quad (46)$$

where F_X is the fraction of adsorbed H atoms which are on X– sites. With the use of the average $G(HD)$ of Bibler and Firestone,[13] a value of 6.2 is obtained for $G(HD)_{surface}$, which corresponds to an average value of 0.83 for F_X in their experiments. A given vessel possesses a fixed value of the ratio F_X: if the vessel preparation procedure does not alter F_X, the measured $G(HD)$ for identical experimental conditions will be constant when the same vessel is used. However, since F_X may vary substantially from vessel to vessel, random selection of vessels leads to the large variation seen in $G(HD)$, even under identical experimental conditions. Thus, the inclusion of *two* types of adsorption sites accounts for the variability in $G(HD)$ with random vessel selection.

With regard to the surface preparation procedures examined, both procedures 1 and 2 (see experimental section) for Pyrex vessels apparently yielded constant F_X values for each vessel. With the silica vessels, procedure 3 (producing a fluorinated surface) yielded constant F_X; however, procedure 4, in which a substantial layer of the vessel surface was removed prior to each experiment, apparently produced a different F_X after each treatment, just as is found when different vessels are used.

In the protium-additive experiments, it was noted that high $G(HD)$ were usually accompanied by high $G(D_2)$, where the effect was not due to experimental uncertainty. This is explained if adsorbed hydrogen atoms combine with one another to a limited extent, as in reactions 47 and 48. Thus, in experiments where

$$D·X– + H·Y– \rightarrow HD + ·X– + ·Y– \quad (47)$$

$$2D·X– \rightarrow D_2 + 2·X– \quad (48)$$
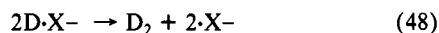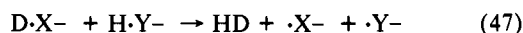
F_X is large, $G(HD)$ is large and reaction 48 can occur more frequently. This atomic recombination of adsorbed atoms is analogous to reactions in the Bonhoeffer–Farkas mechanism for parahydrogen conversion.[36]

Effect of Small Concentrations of C_3H_8. In the protium-/propane-additive experiments, it was observed that the addition of very small quantities of propane resulted in a dramatic decrease in $G(HD)$: further increases in $[C_3H_8]_0$ resulted in $G(HD)$ which were very near the values found with propane alone. The initial

decrease occurred at values of $[C_3H_8]_0/[H_2]$ where C_3H_8 could scavenge susbtantially less than 1% of the D atoms, as discussed previously. According to the proposed mechanism, very small $[C_3H_8]_0$ reduce $G(HD)$ by scavenging H atoms and thereby preventing production of HD in the surface reactions. Thus, $G(HD)$ in these experiments depends on $[C_3H_8]_0$, but not on $[H_2]/[C_3H_8]_0$. The effect of increasing $[C_3H_8]_0$ on $G(D_2)$ was explained previously in terms of a reduction in the steady-state [H].

Dependence of $G(HD)$ on Dose Rate. In the present investigation, it was determined that for dose rates less than 1.5×10^{10} eV cm^{-3} s^{-1}, $G(HD)$ *does* depend on the dose rate. Furthermore, it was observed that with decreasing dose the $G(HD)$ approach the value obtained in experiments employing only propane. Dose-rate dependence is predicted by the mechanism which includes the surface-catalyzed isotope-exchange reaction in the following manner. The total rate of loss of H atoms at the vessel surface, v_s, is a sum of the rates of loss on the X– and Y– sites:

$$v_s = v_X + v_Y \quad (49)$$

With the use of the Langmuir adsorption isotherm,[36] the rate of H-atom recombination at the X– sites is

$$v_X = k_X K_X [H]^2/(1 + K_X[H]) \quad (50)$$

and eq 49 becomes

$$v_s = k_X K_X [H]^2/(1 + K_X[H]) + k_Y K_Y [H]^2/(1 + K_Y[H]) \quad (51)$$

(k_X and k_Y are the first-order recombination rate constants, and K_X and K_Y are the adsorption equilibrium constants). The fraction of H atoms that recombine on the X– sites is given by:

$$F_X = v_X/(v_X + v_Y) = [1 + (k_Y K_Y/k_X K_X)(1 + K_X[H])/(1 + K_Y[H])]^{-1} \quad (52)$$

Thus, F_X is dependent on the steady-state hydrogen-atom concentration, which is a function of dose rate, and $G(HD)$ can depend on the dose rate. If K_Y is considerably larger than K_X, F_X will decrease rapidly when [H] falls below the level required for saturation of the X– sites, and $G(HD)_{surface}$ would decrease with decreasing dose rate. At sufficiently high dose rates, $K_X[H]$ and $K_Y[H]$ can become large with respect to unity, and F_X becomes independent of dose rate (a similar expression results if $K_X = K_Y$):

$$F_X = k_X/(k_X + k_Y) \quad (53)$$

Thus, Firestone and Bibler[2,13] saw no dose-rate dependence in $G(HD)$ because their experimental conditions satisfied the requirement for eq 53. In the low dose rate experiments of the present investigation, general eq 52 applies.

Effect of Dose on Product Yields. Both the homogeneous and the surface-catalyzed isotope-exchange mechanisms predict that as the dose is increased, $G(D_2)$ will decrease and $G(HD)$ increase, while $G(HD) + 2G(D_2)$ remains constant (via reaction 18). In the protium-additive experiments at higher dose rates, it was found that $G(D_2)$ did decrease; however, $G(HD)$ also *decreased* so that $G(HD) + 2G(D_2)$ decreased with increasing dose. These trends can be rationalized by using the results of Green et al.[37] on the behavior of the surface recombination coefficient, ϵ,[38] of the hydrogen atom with respect to the treatment of a silica recombination surface (the first-order surface-recombination rate constant is directly proportional to ϵ). It was observed that (i) ϵ increases with temperature, (ii) the surface exhibits "memory" in that the ϵ measured immediately after cooling to room temperature are the same as the ϵ measured at the high temperature, and (iii) when the surface was heated to >400 °C, it exhibited a very persistent "memory" which was retained on exposure to water vapor, and which was erased only by prolonged exposure to atomic hydrogen. This increased activity and persistent memory are attributed to

(37) Green, M.; Jennings, K. R.; Linnett, J. W.; Schofield, D. *Trans. Faraday Soc.* **1959**, *55*, 2152–61.

(38) Benson, S. W. "The Foundations of Chemical Kinetics"; McGraw-Hill Book Co., Inc.: New York, 1960; p 447.

the irreversible dehydration of silica surfaces which has been found to occur upon heating at greater than 400 °C.[39,40] In the present investigation, all vessel pretreatment procedures except procedure 4 included prolonged heating in vacuo at greater than 400 °C. Thus, if the recombination sites formed by the preheating promote isotope exchange, e.g., if X– sites are formed by preheating, larger doses will result in the reversible inactivation of these sites and F_X will decrease. Thus, with increasing dose, $G(HD)_{surface}$ will decrease, $G(D_2)$ will be reduced by reaction 1, and by a lower frequency for reaction 48, and the observed, overall effect of decreases in $G(HD)$, $G(D_2)$, and $G(HD) + 2G(D_2)$ with increasing dose will be generated.

In the P1-set of the low dose rate experiments, the trends in $G(HD)$, $G(D_2)$, and $G(HD) + 2G(D_2)$ with increasing dose followed the path expected without a consideration of exchange-site deactivation. This observation fits very well within the framework just constructed: the doses were smaller by a factor of 10 than those used in the protium-additive experiments at higher dose rates, so that the proportion of exchange sites inactivated prior to the termination of the experiment is small. In the S set of the low dose rate experiments, the trends in hydrogen product yields were the same as those in the protium-additive experiments at higher dose rates, which would appear to be in conflict with the P1-set results; however, a consideration of the vessel pretreatment resolves this apparent conflict. In the S set, silica vessels were baked at 200 °C for 3 h: Green et al.[37] observed that when the silicate surface was heated to <400 °C, the increased values of ϵ were reduced to the original value simply by exposure of the surface to a moist hydrogen *molecule* stream. Thus, in the S-set experiments, the value of F_X would decrease simply by the increasingly long exposure to moist H_2 corresponding to increasing dose, and the same effects would be observed as in the higher dose rate experiments.

Thus, the inclusion of the observations of Green et al.[37] in the reaction mechanism for HD production completely rationalizes the rather complex behavior observed in the yields of the hydrogen products with increasing dose.

The Kinetic Isotope Separation Factor. In the protium-additive experiments, it was determined that $\beta(D/T)$ varied substantially with the Pyrex vessel pretreatment. Two conclusions can be drawn: (i) HD is produced in more than one reaction, and (ii) the vessel surface plays an intimate role in the production of HD. In the protium-/propane-additive experiments, it was observed that $\beta(D/T)$ decreased from 1.94 with no propane present to 1.63 at the highest $[C_3H_8]_0$ tested. Thus, it may be assumed that the weighted average of the isotope separation factors for homogeneously and surface produced HD is 1.94, while $\beta(D/T)$ for homogeneously produced isotopes is 1.63. It is of interest to note that the $\beta(D/T)$ obtained in propane-additive experiments was 1.6.[41]

Dependence of the Hydrogen Product Yields on $[H_2]$. In the low dose rate/protium-additive experiments, it was found when

$[H_2]$ was decreased that $G(HD)$ and $G(HD) + 2G(D_2)$ decreased, while $G(D_2)$ remained constant. As $[H_2]$ is reduced, an increasing number of D atoms will reach the vessel surface and reactions 54–56 must be added to Scheme V. Each time reaction 54 occurs,

$$D + \cdot X- \rightarrow D\cdot X- \qquad (54)$$

$$D + \cdot Y- \rightarrow D\cdot Y- \qquad (55)$$

$$H + D\cdot Y- \rightarrow HD + \cdot Y- \qquad (56)$$
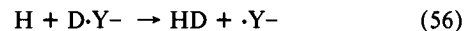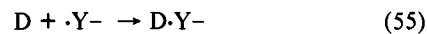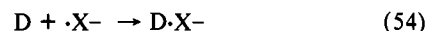
one less HD will be produced since the isotope exchange of reaction 38 is circumvented. As long as most hydrogen atoms reaching the surface are H atoms, $G(D_2)$ will not be affected substantially, and $G(HD) + 2G(D_2)$ will decrease along with $G(HD)$. Thus, the surface-catalyzed isotope-exchange mechanism explains the observed behavior, which could not be rationalized with the use of the homogeneous mechanism.

Mechanism in the Chain Region. As reported in detail by Bibler and Firestone,[2,13] at higher temperatures (218–381 °C) HD and D_2 are produced in chain reactions involving attack of H atoms on the D_2O molecules. It is highly unlikely that an exchange reaction between molecular hydrogen and surface $\equiv$Si—OD groups, i.e., reaction 57, is contributing to the chain reactions since

$$H_2 + \equiv Si-OD \rightarrow HD + \equiv Si-OH \qquad (57)$$
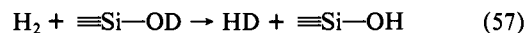
the equivalent thermal reaction described by Annis et al.[33] proceeded only very slowly at temperatures as low as 380 °C. In view of the slow rate of the thermally initiated exchange at the temperatures employed by Bibler and Firestone, it must be concluded that the chain reaction proceeds as described except that termination of H atoms at the vessel wall must also include the reactions in Scheme V.

Conclusion

The results of the present investigation establish that the difference in the $G(HD)$ obtained from the radiolysis of heavy water vapor when H_2 or C_3H_8 is used as a scavenger of D atoms is a direct result of a surface-catalyzed isotope-exchange reaction in the H_2-additive experiments. The H atoms produced in the process of D atom scavenging by H_2 readily undergo isotope exchange at the deuterated vessel surface, leading to the production of "extra" HD molecules. Thus, it appears that G_D from D_2O radiolysis is given by $G(HD)$ in the C_3H_8-additive experiments, i.e., $G_D \sim 7$.

Beyond the explanation of the very basic difference between the values assigned to G_D by experiments using H_2 or C_3H_8, the proposed mechanism rationalizes a host of results which are not consistent with the previously accepted homogeneous mechanism for HD production. The very high value of $G(HD)$ obtained with an H_2 additive, which is disfavored by the energetics of the water vapor system, is explained. This investigation resolves the conflict regarding the yield of hydrogen atoms from water vapor radiolysis, a number whose value is a matter of great interest and substantial significance in radiation chemistry, per se, and whose determination has been in progress for the last 25 years.

(39) Young, G. J. *J. Colloid. Sci.* **1958**, *13*, 67–85.
(40) White, M. L. In "Clean Surfaces"; Goldfinger, G., Ed.; Marcel Dekker, Inc.: New York, 1970; p 361.
(41) Richter, H. W.; Firestone, R. F. *J. Phys. Chem.*, submitted for publication.