halogen molecule and two from the original electron pair bond, O–H in the case of water and C–H in the case of the paraffin hydrocarbon. In this kind of bridge the proton would be nearer to the O or C atom of its original electron pair bond than to the halogen atom of the halogen molecule. The resulting structures would be either rings or chains.

The enhanced absorption of light that has been found to take place when the halogen molecules Cl_2, Br_2 or I_2 are dissolved in water[10] or paraffin hydrocarbons[11] could be interpreted in terms of these structures as well as the electron donor–acceptor complexes previously postulated.[11] Our explanation suggests that in these solutions $\bar{\epsilon}$ for these halogens may also depend upon the temperature.

The halogen molecule, of course, also reacts with water to form significant amounts of the species $H^+ + X^- + HOX$ where X is Cl, Br or I. This fact and the absorption of light by HOX and X_3^- should not be overlooked in interpreting absorption spectra of water solutions of these halogens.[10]

The simultaneous existence of several different kinds of hydrogen bridges between certain solutes and solvents also is suggested. In the case of O_2 (or Cl_2, Br_2 or I_2) dissolved in an alcohol[16] there could form a 1:1 complex in the form of a ring consisting of one molecule of the solute and one molecule of the solvent. This complex would be made up of two different kinds of hydrogen bridges in the ring, one hydrogen bridge like that between O_2 (or Cl_2, Br_2 or I_2) and water and the other hydrogen bridge like that between O_2 (or Cl_2, Br_2 or I_2) and a paraffin hydrocarbon. Similarly there could form in these solutions a chain complex consisting of one molecule of the solute and two molecules of the solvent. In these solutions also $\bar{\epsilon}$ for the molecular form of the solute may, therefore, be found to depend upon the temperature.

[16] A. V. Munck and J. F. Scott, *Nature*, **177**, 587 (1956).

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION AND SCHOOL OF NUCLEAR SCIENCE AND ENGINEERING, ARGONNE NATIONAL LABORATORY]

The Radiation Chemistry of Water Vapor. The Indirect Effect on Deuterium and the Exchange of D-Atoms with Water Molecules[1]

BY RICHARD F. FIRESTONE[2]

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An investigation of the tritium β-ray induced exchange between deuterium gas and water vapor containing tritium–water has been made in order to measure the radical-pair and water decomposition yields in irradiated water vapor. A value for the radical-pair yield of 11.7 ± 0.6 radical pairs/100 e.v. has been determined. The exchange takes place *via* a chain mechanism above 150°. Evidence for the chain-propagating step $D + HOH = H + DOH$ is presented. An apparent activation energy of 18 ± 1 kcal./mole is assigned to this reaction. Results from the radiolysis of pure water vapor indicate an upper limit of 0.02 for $G(H_2)$.

Introduction

Most of the known chemical effects of ionizing radiation on liquid water have been rationalized with free radical mechanisms and by considering the different track densities of densely and sparsely ionizing particles. Much attention has been directed toward measurement of the so-called molecular product and free-radical yields in water solutions.[3] The observed increase in the ratio of the former to the latter as heavier and more densely ionizing particles are employed has been partially explained by considering the initial spatial distribution of reactive intermediates (ions, free-radicals, excited molecules). In the case of light particles distances between "spurs," or regions of high local intermediate concentration scattered along the particle's trajectory, are large on the average, and escape from the "spur" effectively guarantees detection of an intermediate by reaction with an appropriate solute.[3] Thus, the free radical yield, or yield of intermediates free to react with solute molecules is relatively large in the case of γ-rays and energetic β-rays. On the other hand, intermediates formed in the much more closely spaced spurs of α-particle or nuclear recoil-ion tracks have a correspondingly lesser chance of escape and subsequent reaction with the solute. Consistent with this reasoning it is to be expected that a large decrease in density of the reaction medium should, by virtue of a resulting decrease in track densities and an increase in diffusion rates, promote an increase in the free radical yield at the expense of both the molecular product yield and of those fast track reactions, if any, which merely re-form water in denser media.

This investigation of the tritium β-ray induced decomposition of water vapor in samples 1000-fold less dense than liquid water demonstrates, as anticipated, that a much greater proportion of reactive species are free to react with "solute molecules" in the gas phase. In mixtures of tritium–water vapor at pressures of 1000 mm. and deuterium gas at mole fractions in the range 10^{-3} to 10^{-2}, the rate of hydrogen deuteride formation appears to be equal, below 150°, to the rate of formation of hydrogen atoms. The magnitude of $G(HD)$ observed (11.7 ± 0.6 molecules/100 e.v.) indicates that the detectable water decomposition yield as well as the free radical yield is considerably greater in water vapor than in liquid water.

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] Morley Chemical Laboratory, Western Reserve University, Cleveland 6, Ohio.

[3] E. J. Hart, *Radiation Research*, **1**, 53 (1954).

Experimental

Deuterium gas supplied by the Stuart Oxygen Company was used without further purification except to pass it through a liquid nitrogen trap. All deuterium used in this work was drawn from a 2-liter storage flask, F, shown schematically in Fig. 1. Mass spectrometric analysis showed this gas to contain 0.18 mole % H_2, 1.11 mole % HD and 98.68 mole % D_2. The tritium–water was prepared by E. J. Hart by a method previously described. The tritium–water was assayed for tritium content by the following procedure: (1) conversion of a known weight of water to hydrogen by passage over metallic zinc; (2) dilution of the hydrogen with methane to a pressure of approximately 1 atm. in an ionization chamber; (3) measurement of the ion current produced by tritium decay in the diluted gas sample with a recording vibrating-reed electrometer. Tritium water was stored in reservoir tube, R, of Fig. 1 in solutions approximately 10^{-3} *N* in ferrous sulfate and 0.8 *N* in sulfuric acid in order to minimize the steady-state concentration of hydrogen peroxide formed by constant radiolysis of the liquid. Triply distilled water[5] was used for all dilutions of the original stock of tritium–water.

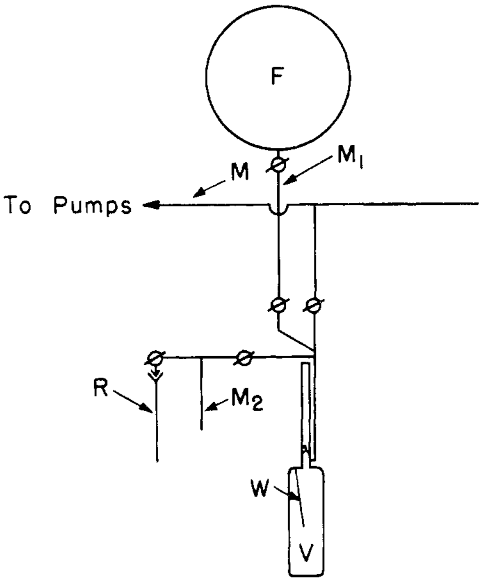

Fig. 1.—Schematic diagram of vacuum system used to prepare TOH–HOH–D_2 samples.

The cylindrical Pyrex reaction vessels were treated as follows before admission of reactants, in order to minimize evolution of foreign gases from the walls during experimental runs. Each vessel was washed with distilled water and baked in air for approximately 3 hr. at 500° before attachment to the vacuum system. After evacuation each vessel was pumped and baked for at least 12 hr. at 510° followed by 12 hr. at 440°. The glass vacuum system shown in Fig. 1 was maintained at pressures of the order of 10^{-6} mm. (indicated by a Phillips gage on the manifold, *M*) with an oil diffusion pump backed by a conventional high-vacuum mechanical forepump. After thorough outgassing of the tritium water by means of several freezing-pumping-melting cycles, a known quantity of water was distilled into a graduated and calibrated metering tube, M_2. The water was then distilled into the reaction vessel, V, by immersing the base of V in liquid nitrogen. V was then opened to the pumps, and any non-condensable gases were pumped out of V with the water held at liquid nitrogen temperature. The system was then closed to the pumps, and a quantity of deuterium gas was introduced to V *via* metering tube M_1. V was then sealed off with a gas–oxygen flame near its point of attachment to the system, and immersed in a constant temperature bath at the desired temperature. A Dow–Corning 550 silicone oil-bath was used at temperatures of 165° and below. Temperature control was maintained with an Amplitrol temperature regulator (Thermoelectric Company, Dubuque, Iowa) using an iron–constantan thermocouple inserted in thermocouple well, W, as the sensing device for the regulator. Periodic measurements of the well temperature also were made with this thermocouple. Samples irradiated above 165° were maintained at constant temperature by complete immersion of the vessels in the equilibrium vapor of appropriate organic liquids at their boiling points.[6] The maximum uncertainty of temperatures reported in Table I is ±1% of the stated value.

Collection of the gas for isotopic analysis was carried out by attaching the vessels, V, to another section of the vacuum line (not shown in Fig. 1) *via* the break-seal tube shown in Fig. 1. The gas was transferred with a Toepler pump through a trap cooled in Dry Ice–acetone slush to remove water. Gas samples were collected by pressing them from the Toepler pump into 5 mm. o.d. glass tubes fitted with $^5/_{20}$ male ground joints at their open ends. These collection tubes fitted a $^5/_{20}$ female joint, equipped with a small mercury cup at its upper end and mounted *via* one passage of a three-way stopcock above the compression chamber of the Toepler pump. After pressing the gas into a collection tube, the stopcock was closed, and the tube was lifted slightly from its seat in the female joint, allowing the gas within to adjust itself to atmospheric pressure by drawing mercury part of the way up the tube. Filled collection tubes were kept open end-down in small bottles of mercury while awaiting isotopic analysis. The quantity of gas collected was determined by compressing it into several known volumes on another vacuum system and reading the resulting pressures on an attached manometer. The controlling relay of the automatic Toepler pump was triggered by changes in capacitance of two copper coils caused by the rise and fall of the mercury instead of the conventional device of allowing the mercury to make or break the circuit directly. This method of control avoided equilibration of isotopic mixtures of hydrogen which might have been induced by sparking between the mercury and the direct electrical contacts of a conventional Toepler relay circuit.

Isotopic analysis of the hydrogen gas samples was performed on a 60-degree, sector-type, direction-focusing mass spectrometer designed by and constructed under the direction of Dr. D. A. Hutchison at the Argonne National Laboratory. Analysis of gases produced from irradiated samples of pure water vapor was performed on a micro gas analysis apparatus especially fitted for chemical analysis of volumes of the order of 10 mm.^{3} (STP).[7] Portions of several of these samples also were analyzed mass spectrometrically as a qualitative check on the chemical method.

$G(-D_2)$ (molecules of deuterium disappearing/100 e.v. absorbed) was calculated for each sample by means of the expression $G(-D_2) = (1 - f)\ (\%D_2)^0 VN/(2.24 \times 10^4 D)$, where $f = (\%D_2)/(\%D_2)^0$. $(\%D_2)^0$ is the initial mole % deuterium, *V* is the volume of gas collected (cc., STP), *N* is Loschmidt's number, and *D* is the dosage (e.v.). The dosage was calculated using 5.69 kev. for the average β-particle energy. Thus, $D = (7.59 \times 10^{17})tsg$, where *t* is the heating time (hr.), *s* is the specific activity of the tritium water (curies/g.), and *g* is the quantity of tritium–water present (g.). Hydrogen deuteride yields were calculated from the expression $G(\text{HD}) = (\Delta\%\text{HD})\ VN/(2.24 \times 10^4 D)$. At vapor densities employed in sample vessels used in this work, it is estimated that over 99% of the tritium β-particles are absorbed by the water vapor. This estimate is based on data reported by Dorfman for absorption of tritium β-particles in homogeneous tritium–protium gas mixtures.[8] Precision of *G* values reported is limited by the precision of the mass spectrometer data. Since all *G* values were obtained by difference between two mass spectrometer data, the experimental uncertainty decreases in proportion to the magnitude of the $1 - f$ values, *i.e.*, to the fraction of deuterium exchanged. The maximum uncertainty in $G(-D_2)$ for samples with $1 - f > 0.05$ is estimated to be approximately ±5%. The maximum uncertainty in $G(\text{HD})$ for such samples is probably about ±10%.

Three lots of tritium–water, differing in specific activity, were used. Since some degree of enrichment in tritium con-

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(4) E. J. Hart, *J. Phys. Chem.*, **56**, 594 (1952).

(5) E. J. Hart, S. Gordon and D. A. Hutchison, THIS JOURNAL, **74**, 5548 (1952); **75**, 6165 (1953).

(6) F. Bessinger and V. Pretorius, *J. Chem. Educ.*, **33**, 330 (1956).

(7) D. G. Madley and R. F. Strickland-Constable, *The Analyst*, **78**, 122 (1953).

(8) L. M. Dorfman, *Phys. Rev.*, **95**, 393 (1954).

tent of the reservoir might be expected as samples are removed by evaporation, an attempt was made to determine its significance to the data reported here. Comparison of exchange yields calculated by assuming equal specific activity for all samples from each lot of water, regardless of the order in which they were prepared, fails to show a significant trend toward higher yields in the later samples. Comparison of the specific activity of the reservoir of tritium–water used for samples 3, 14 and 16 and a sample of equal volume removed by evaporation indicated an enrichment of the reservoir of approximately 4% may have occurred in the distillation. However, water from samples 11 and 15 was found to have the same specific activity as the reservoir from which they were distilled. It appears that only the exchange yields of samples 3, 14 and 16, prepared from a reservoir of small relative volume, are likely to reflect uncertainties comparable in magnitude to those attributed to the mass spectrometer data.

Results and Discussion

Radiolysis of Pure Water Vapor.—Small quantities of gas were collected when Pyrex tubes of tritium water vapor were heated and when tubes of ordinary water vapor were exposed to gamma-radiation from a 400-curie Co^{60} source. The chemical composition of gases formed in the several samples (Table I) varied widely, but almost all contained hydrogen, nitrogen, carbon dioxide, carbon monoxide and traces of oxygen. Carbon dioxide content varied from zero to 50%, the higher values occurring in samples from vessels which were not rigorously baked out by the procedure described above before filling. Hydrogen content varied from 20 to 46% with the greater amounts, though not always the higher percentages, present in gases from unbaked vessels. Nitrogen content varied from 8 to 78% without regard to pre-treatment of the vessel. Variation in carbon monoxide content was roughly parallel to that of carbon dioxide over a range from zero to 11%.

TABLE I

APPARENT 100 E.V. YIELDS OF H_2 IN PURE WATER VAPOR

Pre-treatment of vessel	Quantity of water, g.	Temp., °C.	Irradn. time, hr.	Dosage, e.v. × 10^{-21}	Apparent $G(H_2)$
Flamed[a]	0.10	109	21.3	0.1[b]	0.25
Flamed, baked in air	.10	109	17.1	.1[b]	.14
Flamed, baked in air	.10	110	21.8	.1[b]	.15
Baked *in vacuo*	.10	110	19.3	.1[b]	.015
Flamed[c]	.77	116	19.2	.094[d]	1.4
Baked *in vacuo*[e]	.18	121	141	1.65[d]	0.021

[a] Silica vessel. [b] γ-Radiation. [c] 1-liter Pyrex flask. [d] Tritium β-rays. [e] Tube type I; all other vessels were tube type II, unless otherwise indicated.

In order to compare these data with other available data from the radiolysis of water vapor,[9,10] apparent $G(H_2)$ values have been calculated and are reported in Table I. Comparison of the present results of the radiolysis of pure water vapor with those of Günther and Holzapfel, and Duane and Scheuer is of questionable significance because of important differences among the three reaction systems represented. Nevertheless, comparison permits several interesting observations. Duane and Scheuer irradiated water vapor with α-particles at 170° by mixing it with radon at three atmospheres total pressure. Their results indicated a maximum ion-pair yield for hydrogen of approximately 0.02, which corresponds to an upper limit for $G(H_2)$ of approximately 0.06. Günther and Holzapfel, on the other hand, report an ion-pair yield greater than unity for hydrogen ($G(H_2) > 3$) in the xenon-sensitized, X-ray-induced decomposition of water vapor at 40°. The latter work was carried out using an external source of X-rays focused through a thin aluminum window in the side of the compression chamber of a silica McLeod gage. Mixtures of xenon and water vapor were irradiated within this chamber. Total pressures were in the vicinity of 460 mm. with xenon in approximately sevenfold excess. Outgassing of the walls of their reaction chamber was apparently carried out by prolonged pumping on the chamber at the reaction temperature, although the outgassing temperature is not stated explicitly. The greatest apparent $G(H_2)$ found in the present investigation is 1.4. This value is calculated from the hydrogen yield in a mixture of gaseous products consisting of 49% hydrogen, 32% carbon dioxide, 17% nitrogen, and about 1% oxygen. It also should be noted that the total inner surface area of this vessel was the greatest of the lot. The data of Table I show a sharp decrease in apparent $G(H_2)$ to a value of 0.02 for samples irradiated in vessels which were carefully outgassed. Thus, it appears that rigorous outgassing of the vessel walls is necessary in order to measure the quantity of gas genuinely formed by radiation-induced decomposition of water vapor, at least under conditions employed in the present investigation. The present results suggest that the net radiation-induced decomposition of water vapor is less than that of liquid water exposed to a variety of ionizing radiations.[11] This low yield can be at least partially explained by assuming, as Duane and Scheuer first suggested, that rapid back reactions prevent extensive decomposition in the gas phase, similar to the explanation given for the low sensitivity of pure liquid water to light-particle irradiation.[12,13] The ion-pair yield reported by Günther and Holzapfel appears much too large, although the total amount of hydrogen produced in each of their runs was quite small (of the order of 1 mm.³). These amounts are small enough to be attributed to gases evolved from the walls of their reaction chamber. It is also possible that foreign gases, possibly xenon or traces of mercury, in some way inhibited the back reactions in their system.

Exchange Yields in Water Vapor–Deuterium Mixtures.—Data reported in Table II show that in all mixtures of tritium water vapor and deuterium gas the rate of hydrogen deuteride formation was equal within ± 10% to the rate of disappearance of deuterium. These data represent experimental runs at temperatures from 84 to 278°. The fraction of deuterium exchanged varies from 4.93 to 29.9%. Absence of dependence of $G(-D_2)$ and $G(HD)$ on deuterium concentration indicates that deuterium is a completely efficient scavenger for the reaction species involved when present at mole fractions in the range 0.005 to 0.01. Reaction

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[9] P. Günther and L. Holzapfel, *Z. physik. Chem.*, **B42**, 346 (1939).

[10] W. Duane and O. Scheuer, *Le Radium*, **10**, 33 (1913).

[11] A. O. Allen, *J. Phys. Chem.*, **52**, 479 (1948).

[12] A. O. Allen, *ibid.*, **52**, 479 (1948).

[13] A. O. Allen, C. J. Hochanadel, J. A. Ghormley and T. W. Davis, *ibid.*, **56**, 575 (1952).

TABLE II

100 E.V. YIELDS IN TRITIUM β-RAY INDUCED EXCHANGE BETWEEN HOH AND D_2 IN GASEOUS TOH–HOH–D_2 MIXTURES

Sample[a]	Dosage,[b] e.v. × 10^{-19}	Temp., °C.	Vapor density, mg./ml.	Mole fraction $D_2 \times 10^3$	$1 - f$	$G(-D_2)$	$G(HD)$	$\Delta\%H_2$
1-III	1.97(0.674)[b]	84	0.300	9.08	0.067	10	10	−0.1
2-I	1.97(0.980)	106	.437	9.21	.0732	11.8	11.8	0.0
3-II	1.68(1.80)	125	.774	8.37	.0772	12.7	12.7	.0
4-I	2.18(8.22)	130	.773	4.68	.0941	12.3	11.6	.2
5-I	2.47(8.22)	139	.773	9.78	.0493	12.0	11.9	.0
6-I	2.16(8.22)	140	.777	4.84	.0850	11.6	11.3	.4
7-I	5.65(8.22)	140	.773	4.93	.202	10.8	10.1	1.2
8-I	7.58(8.22)	140	.777	4.90	.299	11.8	10.5	2.9
9-I	2.14(8.22)	150	.773	4.78	.0961	13.1	12.9	0.2
10-I	2.14(8.22)	165	.773	4.91	.100	14.1	13.9	.2
11-II	0.322(1.74)	196	.774	8.28	.0197	16.7	17.7	− .2
12-II	1.40(8.27)	197	.775	8.71	.0809	16.7	16.7	.1
13-II	1.27(8.28)	228	.774	6.70	.203	35.4	32.7	1.1
14-II	0.882(1.80)	232	.774	8.50	.116	37.0	36.3	0.2
15-II	0.233(1.74)	254	.774	8.64	.057	71	71	− .1
16-II	0.251(1.80)	278	.774	8.79	.103	130	128	.1

[a] Roman numerals indicate type of reaction vessel; tube type I is 51 mm. o.d. and has volume of 238 cc.; tube type II is 41 mm. o.d. and has volume of 128 cc.; tube type III is 57 mm. o.d. and has volume of 330 cc. [b] Dosage rates (e.v./l./min. × 10^{-17}) are given in parentheses.

times varied from 18.2 hr. (sample 16-II) to 148 hr. (sample 1-III) with no apparent effect on the 100 e.v. exchange yields. Apparent changes in mole % protium are reported in the last column of Table II. These represent differences between initial and final mole % protium and are reliable within about one order of magnitude. They serve to show, however, that no significant amounts of protium were formed during the irradiations. The expected trend toward increasing amounts of protium with increasing values of $1 - f$ is apparent.

No exchange occurred in the absence of tritium-water. A mixture of ordinary water and deuterium prepared in a manner identical with sample 16-II was heated 18.6 hr. at 277°; mass spectrometric analysis showed no change in isotopic composition of the gas as a result of prolonged heating in contact with water vapor.

Within experimental uncertainty, $G(-D_2)$ and $G(HD)$ are independent of temperature below approximately 150°. Reference to Fig. 2 shows a gradual increase in exchange rate with temperature, beginning at about 150°; and a much more rapid increase in the linear region above 200°. The sharp change in slope and the magnitude of $G(-D_2)$ at the higher temperatures indicate operation of a chain mechanism above 150°. The only molecular species detectable in gases recovered from reaction mixtures were protium, hydrogen deuteride, deuterium and traces of nitrogen ($<1\%$), regardless of the irradiation temperature. The apparently random variation of $G(-D_2)$ among samples irradiated below 150° is within reasonably estimated limits of precision for these data. Thus, $G(-D_2)$ for non-chain, temperature-independent exchange is accepted as 11.7 ± 0.6 molecules per 100 e.v., an average of all $G(-D_2)$ values reported below 150°. This value is designated as $G(-D_2)^0$ in Fig. 3, which illustrates the temperature dependence of exchange yields from which the non-chain, temperature-independent yield, $G(-D_2)^0$, has been subtracted. An apparent activation energy of 18 ± 1 kcal./mole is obtained for the temperature-sensitive reaction(s) involved in the exchange between deuterium and water vapor.

No indication of sensitivity of the exchange yields to variations in dosage rate was found in either the non-chain or chain regions. A fivefold difference in dosage rates between samples 11-II and 12-II at 196 and 197°, respectively, had no effect on exchange yields; nor did a similar variation between samples 13-II and 14-II at 228 and 232°. Comparison of $G(-D_2)$ among samples absorbing energy at different rates below 150° also fails to disclose any dependence upon dosage rate.

Limitations imposed on size and shape of the reaction tubes by the outgassing procedure discouraged investigation of possible effects of large changes in the surface/volume ratio. Within narrow limits (0.7 to 1.1), the exchange rates were insensitive to the surface/volume ratio of the vessels. Packing of the vessels with Pyrex wool or other material was not attempted because of uncertainty in determining the amount of energy absorbed by the packing material relative to that absorbed by the water vapor.

Mechanism of Exchange.—Formation of hydrogen deuteride must be caused, at least in part, by the direct action of hydrogen atoms. However, it is conceivable that ion-molecule reactions are directly responsible for hydrogen deuteride formation. One mechanism for direct ion–molecule contribution to the hydrogen deuteride yield is the hypothetical reaction sequence

$$HOH^+ + D_2 = H_2OD^+ + D \qquad (8)$$

$$H_2OD^+ + e^- = HD + OH \qquad (9)$$

Reaction 8 is analogous to the reasonably well-established reaction 10.[14,15] However, at mole fractions in the range 10^{-3} to 10^{-2}, deuterium cannot play a significant role of interaction with ions unless it possesses a cross section at least 100 to

$$HOH^+ + HOH = H_3O^+ + OH \qquad (10)$$

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(14) H. D. Smyth and D. W. Mueller, *Phys. Rev.*, **43**, 116 (1933).

(15) M. M. Mann, A. Hustrulid and J. T. Tate, *ibid.*, **58**, 340 (1940).

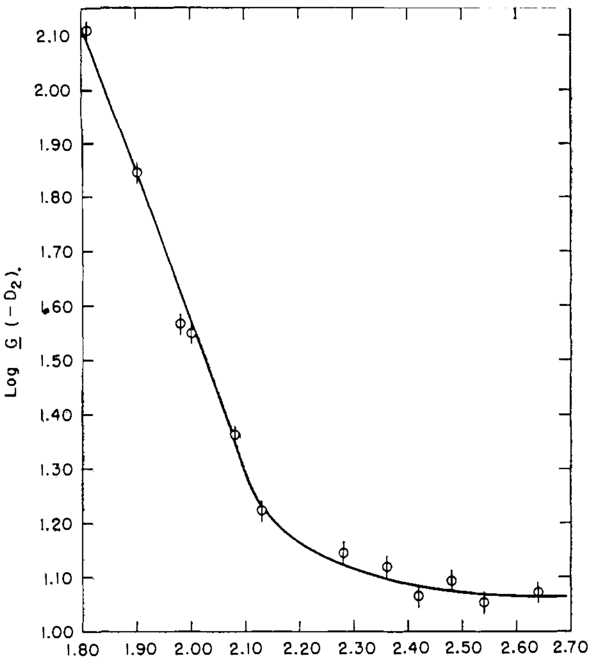

Fig. 2.—Temperature dependence of $G(-D_2)$.

1000 times as great as water for the reaction in question. This is, of course, also true concerning interaction with electrons, and there is no known evidence for such a condition in either case. Furthermore, even under favorable conditions for reaction 8, the probability of hydrogen deuteride formation in reaction 9 is, *a priori*, only about $^2/_3$, if a molecular product is formed. Considering the relatively large order of energies released by positive ion-electron combinations, reaction 9 would seem more likely to produce atoms and radicals in the absence of a third body. Other mechanisms involving ion–molecule steps in the direct formation of hydrogen deuteride appear to suffer from one or more of the same deficiencies.

If the major role of ions is assumed to result in the ultimate formation of free radicals according to the frequently postulated net-reaction 1

$$\mathrm{HOH} \rightsquigarrow \mathrm{H} + \mathrm{OH} \qquad (1)$$

all observations can be consistently rationalized by means of a free-radical mechanism. In the non-chain region (below 150°), hydrogen deuteride appears to be formed simply by reaction of hydrogen atoms with deuterium (reaction 2).

$$\mathrm{H} + \mathrm{D_2} = \mathrm{HD} + \mathrm{D} \qquad (2)$$

Consistently, other necessary reaction steps proposed are

$$\mathrm{OH} + \mathrm{D_2} = \mathrm{DOH} + \mathrm{D} \qquad (3)$$

and a deuterium atom recombination step represented by reaction 6 and/or reaction 7

$$\mathrm{D}(+\mathrm{s}) = {}^1/_2\mathrm{D_2}(+\mathrm{s}) \qquad (6)$$

$$\mathrm{D} + \mathrm{D}(+\mathrm{M}) = \mathrm{D_2}(+\mathrm{M}) \qquad (7)$$

where S represents any active surface and M any effective third body. The chain reaction can be explained with either of the chain-propagating steps

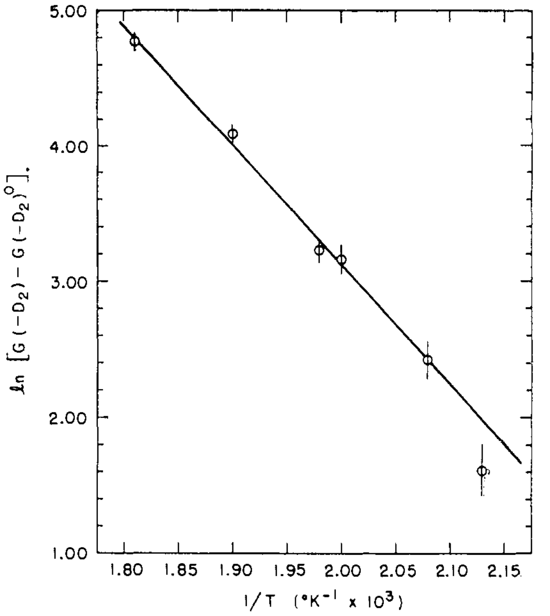

Fig. 3.—Temperature dependence of $[G(-D_2) - G(-D_2)^0]$.

$$\mathrm{D} + \mathrm{HOH} = \mathrm{H} + \mathrm{DOH} \qquad (4)$$

$$\mathrm{D} + \mathrm{HOH} = \mathrm{HD} + \mathrm{OH} \qquad (5)$$

Reaction 5 is improbable for two reasons; it is 16 kcal./mole endothermic, and it is known that hydrogen atoms formed in a Wood's tube do not react with water vapor to form hydrogen.[16,17] Reaction 4 is 1.7 kcal./mole exothermic, and good evidence for its participation in the exchange between deuterium atoms and water vapor has been reported.[16,18]

Since the radiation-source atoms (T) were distributed uniformly throughout the reaction mixtures, the reaction mixtures were of low density, and because the local density of ions formed by tritium β-particles is relatively low, it appears reasonable to assume that the reaction system represents a close approach to one in which a uniform distribution of reactive intermediates exists in both space and time, *viz.*, the "high background" case in the terminology of Magee.[19] Assuming, then, steady-state conditions for deuterium and protium atoms and hydroxyl radicals, rate law I, based upon reaction steps 1, 2, 3, 4 and 6, is $G(\mathrm{HD}) = k_1 + 2k_1k_4(\mathrm{HOH})/k_6(\mathrm{S})$. If second-order D-atom recombination is assumed (reaction 7), rate law II is $G(\mathrm{HD}) = k_1 + k_4(\mathrm{HOH})\ [k_1/k_7(\mathrm{M})I_\mathrm{a}]^{1/2}$. In either case, $G(\mathrm{HD})$ in the non-chain region is equal to $k_1 = G(-\mathrm{D_2})^0 = G(-\mathrm{H_2O}) = 11.7 \pm 0.6$ molecules/100 e.v. It follows that $[G(-\mathrm{D_2}) - G(-\mathrm{D_2})^0]$ is equal to the second term in one of the above rate laws. Again in either case, the apparent activation energy of 18 ± 1 kcal./mole can be assigned tentatively to reaction 4, since the

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(16) K. H. Geib and E. W. R. Steacie, *Z. physik. Chem.*, **B29**, 215 (1935).

(17) E. Boehm and K. F. Bonhoeffer, *ibid.*, **119**, 389 (1926).

(18) A. Farkas and H. W. Melville, *Proc. Roy. Soc.* (*London*), **A157** 625 (1936).

(19) J. L. Magee. THIS JOURNAL, **73**, 3270 (1951).

thermal activation energies of reactions 1, 6 and 7 can be assumed to be very small or zero.

Geib and Steacie[16] report a lower limit of about 6 kcal./mole for reaction 4 obtained from measurements of the rate of exchange of D-atoms with water vapor in a flow system at vapor pressures of 0.05 mm. These authors attribute part of the exchange yield at this low pressure to wall reaction and estimate a more probable higher value (10.5 to 12 kcal.) for the homogeneous reaction. Farkas and Melville[18] obtained an apparent activation energy of 7 kcal./mole for reaction 4 from measurements of the mercury-sensitized exchange between deuterium and water vapor exposed to 2537 Å. light. Water vapor pressures were limited to 11–12 mm. Their value is probably low, because, as they suggest, their water may have been decomposed by excited mercury atoms. Both cited investigations suggest that the activation energy for the homogeneous exchange of D-atoms with water must be greater than 7 kcal./mole and at least as great as 12 kcal./mole. It is, therefore, reasonable and consistent to assign the apparent activation energy of 18 ± 1 kcal./mole to reaction 4. The large pressures of water vapor employed in this work give strong support to the conclusion that reaction 4 is homogeneous.

Chain termination appears to be predominantly first order. Absence of a change in yield with fivefold variation in dosage rate in the chain region (samples 11, 12, 13, 14) indicates that reaction 7 cannot play a major role.

It is interesting to compare the value obtained in this work for $G(-H_2O)$ in water vapor (11.7 ± 0.6 molecules/100 e.v.) with Hart's value of 3.8, measured in liquid tritium–water using formic acid and oxygen as free radical scavengers.[20] One may conclude from this comparison that about 70% of those water molecules which dissociate in the vapor would fail to do so in the liquid, or, that having dissociated, the resulting intermediates merely react to re-form water. In the gas phase one would expect reaction of the intermediates with an efficient scavenger to be favored over recombination, as indicated by the results of this investigation.

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Ion-deficient Phases in Titanium and Vanadium Compounds of the Perovskite Type[1,2]

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Cation deficiency, represented by $M_{1-x}BO_3$, has been observed in lanthanum vanadium oxide. Anion deficiency, represented by $MBO_{(3-x)}$, has been investigated in strontium titanium oxide, lanthanum titanium oxide, lanthanum zirconium oxide, lanthanum vanadium oxide and strontium vanadium oxide.

Departures from stoichiometry in compounds with the perovskite structure have been demonstrated in many instances. Cation deficiency, represented by $M_{1-x}BO_3$, appears to have the widest range in the sodium tungsten bronzes, where x may vary from 0.05 to 0.7.[3] The range narrows considerably in the strontium niobium oxide to 0.05 to 0.3,[4] and in the lanthanum titanium oxide to 0 to 0.3.[5] Part of the work described here is an extension of this phenomenon to lanthanum vanadium oxide.

Anion deficiency, represented by MBO_{3-x}, has been reported for several compounds with structures closely related to the perovskite type. In barium iron oxide, x is about 0.28[6] while for barium cobalt oxide three phases were reported with values of x = 0.28, 0.69 and 0.77.[7] Other oxygen deficient phases such as $SrFeO_{3-x}$,[8–10] $BaNiO_{2.75}$ and $BaNiO_2$[11] also have been described. All of these phases were produced by heating under oxidizing conditions at various temperatures and there was no strict control over the composition of the final phase. With similar systems involving titanium and vanadium, however, precise control of the composition of mixtures is possible because of the availability of thermally stable higher oxides of these elements. This paper describes some oxygen deficient phases of titanium and vanadium.

Experimental

The general technique used for the preparation of samples was to mix intimately finely divided powders of the reactants by grinding in an agate mortar. The samples were pelleted in a hydraulic press and placed in clear silica glass tubes which were sealed under vacuum at elevated temperatures. The sample was heated at an appropriate temperature for a specified period (usually about 24 hours). The sample was then reground and the process repeated until a homogeneous product was obtained. Because of the inevitable losses on handling and the tendency of strontium oxide to volatilize under conditions used, the composition of the final products was checked by chemical analysis. X-Ray diffraction pow-

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(2) The part of this work dealing with vanadium was abstracted from the Master's Thesis of John G. Dickinson, University of Connecticut, 1957.

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