tion given above definitely does not hold for the case of ethane where the methylene-substituent bond involves a 1s orbital. $(\Delta CH_3 - \Delta CH_2)$ for ethane is of course zero rather than 20 cycles as predicted by the equation.

Nevertheless the equation is probably reasonably satisfactory as a guide to interpolating between the electronegativity values of the halogens. All of the substituents, except hydrogen, form bonds to the methylene group using an orbital which is primarily a p orbital and similar in symmetry to that used by the halogens.

Table III seems to indicate that the electron withdrawal power of a substituent group is largely determined by the electronegativity of the first atom in the group. The chief variations are observed in the lowering of the group electronegativity of -SH with respect to -S- and -SCN, of NH_2 and OH by the presence of the hydrogen atoms in the group. The presence of linkages such as -C-, -N- and -S- seems to substantially increase the group electronegativity.



Fig. 3.—-Chemical shift vs. electronegativity for the ethyl halides.

It is interesting to note that while the electronegativities are not simply related, the value of $(\Delta CH_3 - \Delta CH_2)$ for ethyl bromide is exactly the average of the values for ethyl chloride and ethyl iodide.

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γ -Ray-induced Deuterium Gas–Water Exchange¹

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Received February 11, 1955

Deuterium gas dissolved in light water has been found to undergo exchange with the protium of the water when these solutions are exposed to the γ -radiation of Co.⁶⁰ In neutral and acid solutions the major product of the exchange is hydrogen deuteride. Hydrogen is also formed in smaller yields. In alkaline solutions the hydrogen deuteride formation is suppressed whereas the hydrogen formation is unchanged over a wide range of *p*H's. The effects of *p*H, deuterium concentration and dose rate have been determined, and a mechanism is postulated.

Deuterium gas, when dissolved in water and exposed to $\operatorname{Co}^{60} \gamma$ -rays is found to undergo exchange with the protium of the water.² Two independent reactions appear to be occurring, and the stoichiometry can be accounted for by equations 1 and 2

$$D_2 + H_2O = HD + HDO$$
 (1)
 $D_2 + 2H_2O = H_2 + 2HDO$ (2)

Unexposed solutions of the gas do not give evidence of this exchange. The yield of reaction (1) is highly dependent upon pH in the range 0.5 to 13. The effect of pH, dosage rate and concentration of dissolved D₂ upon the yield of the exchange is reported in the present paper. Reaction (2) is independent of pH in the range 0.5 to 13. Evidence is provided for the existence of H atoms in irradiated solutions as well as evidence for the previously postulated ionization of the OH radical.^{2,3} A mechanism is proposed for the exchange and its dependence on pH.

Experimental

Triply distilled water³ was used in these experiments. Deuterium gas supplied by the Stuart Oxygen Co. and assaying >99.5% in deuterium atom content was used with-

out further purification except to pass it through a liquid air Two procedures were used to degas the water, distrap. solve the deuterium gas and fill the cells. The irradiation cells in experiments 1-14, inclusive, were cylindrical Pyrex cells about 2 cm. in diameter previously described.⁴ The method of deaerating, saturating the water with deuterium gas, and filling the cells has been described.⁵ Solutions and cells in experiments 14-23, inclusive, were prepared by using the syringe technique described previously.³ The *p*H of the solutions was adjusted by adding buffers described in Table III. All ρ H's were measured on the stock solutions remaining after filling the cells, using a Leeds and Northrup ρ H meter, model 7663-Al. All solutions prepared by the above two procedures contained no gas phase and were irradiated with $Co^{60} \gamma$ -rays in specially designed chambers.⁶ The dosage rates were measured by use of the ferrous sulfate actinometer, and a value of 15.5 Fe⁺⁺⁺/100 e.v.⁷ was used to convert chemical yield to electron volts/ liter. After irradiation the gas was extracted from solution, and its volume and pressure were measured in a Van Slyke apparatus. The gas was then dried by passing it back and forth several times through a U-type liquid air trap, and mass spectrographic analysis made. The initial concentra-tion of deuterium, $(D_2)_0$, was obtained on each series of runs by extracting and measuring the gas from the blank in the manner described. The spectrometer used for experiments 15–25, inclusive, was a Nier Consolidated in-strument model 21–201 with dual collection. The peaks were measured by scanning magnetically, and single collection was used to measure the mass 4, 3 and 2 peaks sepa-rately. Pure deuterium, hydrogen and hydrogen deuteride were used to calibrate the instrument for peak sensitivity

- (6) R. A. Blomgren, E. J. Hart and L. S. Markheim, Rev. Sci. Instru., 24, 298 (1953).
- (7) E. J. Hart, Ann. Revs. Phys. Chem., 5, 139 (1954).

 $^{(1)\,}$ Based on work performed under the auspices of the U. S. Atomic Energy Commission.

⁽²⁾ S. Gordon, E. J. Hart and P. D. Walsh, Argonne National Laboratory Report No. UAC-406; S. Gordon and E. J. Hart, paper presented at September, 1952, ACS Meeting.

⁽³⁾ E. J. Hart, S. Gordon and D. A. Hutchison, THIS JOURNAL, 74, 5548 (1952); 76, 6165 (1953).

⁽⁴⁾ E. J. Hart, ibid., 73, 68 (1951).

⁽⁵⁾ E. J. Hart, ibid., 74, 4174 (1952).

and fractionation pattern. The hydrogen deuteride was prepared by using lithium aluminum hydride and heavy water.⁸ Blends of these three gases were made up on a gas blending line, and calibration runs were made using the fractionation factors and sensitivities obtained in the pure gas. Results of these are shown in Table I. In experiments 1-14, inclusive, a Nier deuterium isotope ratio spectrometer,⁹ modified for single collection with voltage scan, was used. With the particular source and pumping used in this instrument, appreciable equilibration of deuterium and hydrogen occurred to give hydrogen deuteride. It was found that the amount of hydrogen deuteride by equilibra-tion depended on the hydrogen/deuterium ratio. Known blends of hydrogen and deuterium were made, and the amount of hydrogen deuteride formed at different H_2/D_2 ratios was determined. This amount of hydrogen deuter-ide was plotted as a function of H_2/D_2 and used as a correc-tion factor in the sample analysis. Blends of hydrogen, deuterium and hydrogen deuteride were made and analyzed using the empirical correction for hydrogen deuteride de-scribed above. The results are shown in Table II. The estimated precision in experiments 1–13 is $\pm 10\%$ on points having an excess of 5% hydrogen deuteride, which in most runs includes all the points except the initial one. The initial point is probably good to $\pm 20\%$. In runs 14–23, the estimated maximum error on all points in the run except the first is $\pm 5\%$, and the first point has a somewhat greater maximum error, probably $\pm 10\%$. The percentage compositions of hydrogen, deuterium and hydrogen deuteride obtained by the mass spectrometric analysis together with the micromoles of total gas measured by the Van Slyke were used to calculate the micromoles of hydrogen deuteride and hydrogen produced and of deuterium consumed.

TABLE I

MASS SPECTROMETRIC ANALYSIS OF SYNTHETIC BLENDS OF Hydrogen, Hydrogen Deuteride and Deuterium, Janua Consolidated Spectrometer Model 21 201

USING CONSOLIDATED SPECTROMBTER, MODEL 21-201								
Hydro Exptl.	ogen, % Found	Hydrogen (Exptl.	deuteride, % Found	Deuteri Exptl.	um, % Found			
9.81	9.82	1.16	1.49	89.04	88.68			
5.80	5.56	1.22	1.58	92.97	93.00			
21.19	20.60	1.00	1.87	77.79	77.56			
52.24	51.39	0.67	0.87	47.09	47.73			
88.47	88.08	0.24	0.65	11.30	11,30			
94.35	93.81	0.17	0.40	5.48	5.83			
1.06	0.89	24.03	23.00	74.90	76.09			
0.27	0.22	7.04	7.21	92.70	92.42			
5.75	4.83	14.89	15.16	79.37	80.01			
7.52	7.36	20.34	21.09	72.15	71.56			

TABLE II

MASS SPECTROMETRIC ANALYSIS OF SYNTHETIC BLENDS OF Hydrogen, Hydrogen Deuteride and Deuterium Using Small Nier Hydrogen Isotope Ratio Spectrometer

Hydrogen, %		Hydrogen deuteride, %		Deuterium, %	
Exptl.	Found	Exptl.	Found	Exptl.	Found
45.90	45.17	6.88	5.78	46.90	49.03
48.27	45.90	10.02	9.95	41.43	44.13
35.61	37.74	29.90	26.28	34.25	35.97
38.32	34.63	27.15	29.78	34.29	35.58
9.30	7.87	6.90	8.53	84.24	83.60
9.36	7.71	9.82	11.26	80.27	81.03
10.39	9.28	18.50	19.50	71.39	71.24
8.19	7.33	32.54	33.88	58.34	58.79

Results and Discussion

The formation of hydrogen deuteride and of hydrogen is a non-linear function of the dose. Figure 1 shows the formation of hydrogen deuteride and

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(9) A. O. C. Nier, M. S. Inghram, C. Stevens and B. Rustad, United States Atomic Energy Commission document MDDC-197.

hydrogen as a function of dose. In all these experiments the total amount of gas was found to be unchanged; that is, the amount of deuterium consumed was always equal to the hydrogen deuteride and hydrogen produced. The concave downward character of the hydrogen deuteride curve probably is due to the secondary exchange of the hydrogen deuteride formed as it builds up to form hydrogen. This would also explain the convex upward character of the hydrogen formation curve. Figure 2 illustrates the production of hydrogen deuteride and hydrogen with dose at pH 6. All G values in Table III were obtained by drawing the initial slopes of curves of this type in approximately the same dose range.

TABLE III

Yields of Products in Co^{60} γ -Ray-Induced Reaction in the Aqueous System Deuterium Gas-Light Water Dosage

T1+	rate					
radia-	• (e. v ./l.				**	
tion	$\frac{11111}{10-20}$	6 T T	Curr	Cm	$(1)_{2}$	Thu (Xan
	~ 10	<i>p</i> 11	GHD	OH2	(#341)	Builer
1	0.2	12.02	0.25	•••	770	10 mM NaOH
2	.185	1.3	4.2	0.51	670	$0.1 N H_2 SO_4$
3	.185	10.62	1.4	1.1	67 8	1 mM Borate + NaOH
4	.185	11.42	0.35	0.6	683	1 mM Borate + NaOH
5	.185	13.00	0.20	0.85	649	NaOH
6	.185	9.59	1.88	0.81	686	1 mM Borate $+ NaOH$
7	.185	8.00	2.40	0.27	671	H ₈ BO ₃ , Na ₂ B ₂ O ₇ , 1 mM
8	.182	10.92	0.83	1.1	664	1 mM NaOH
9	,182	12.90	0.17	0.70	645	100 mM NaOH
10	,18	6.10	2.70^{4}		356	Unbuffered
11	.18	6.12	2.2^a		759	Unbuffered
12	.187	6.00	2.87		690	Unbuffered
13	.014	6,00	3.24^a		684	Unbuffered
14	. 20	6.80	12		683 ⁶	Unbuffered
15	2.0	6.0	2.73	0,41	788	Unbuffered
16	2.0	1.2	3.42	.32	785	0.1 N H2SO4
17	2.0	0.47	2.74	.36	749	0.8 N H2SO4
18	2.0	1,99	3.82	.45	791	0.01 N H2SO4
19	2.0	2,88	4.04	. 41	801	0.001 N H2SO4
20	2.0	3,99	3.21	.36	766	0.0001 N H ₂ SO ₄
21	2.0	5.01	2.82	.31	747	Na ₂ HPO ₄ , KH ₂ PO ₄
						(0.067 M)
22	2.0	6.98	2.41	.40	752	Na2HPO4, KH2PO4
						(0.067 M)
23	2.0	0.78	3.31	.36	768	0.3 N H2SO
24	2.0	2.58	4.09	.24	803	0.003 N H2SO4
-						

^a Due to change in instrument calibration these results were normalized by assuming values obtained in experiment 15. b 50-50 deuterium, hydrogen mixture.

Experiments 10 and 11 (Table III) show the independence of yield on initial concentrations of deuterium over a 2-fold range. Study over a wider range of concentration is precluded by the limited solubility of deuterium in water. Comparison of experiments 12 and 13 (Table III) indicated a slight increase of yield at the lower dose rate. However, this increase is uncertain because of the change in calibration of the mass spectrometer (see footnote a, Table III). Table III summarizes the G values for hydrogen deuteride and hydrogen formation over the range of pH 0.47 to 13.00 studied. Figure 3 shows the dependence of yield of hydrogen deuteride and hydrogen production on pH. The yield of hydrogen is constant over the pH range studied. The increase in the alkaline range is not considered significant and is thought to be due to impurities introduced by the large amount of buffer used in this pH region. The erratic behavior of the results in this pH range would be in line with this conclu-



Fig. 1.—Co⁶⁰ γ -ray-induced exchange of D₂ in H₂O at pH 6.0; \triangle , HD; \Box , H₂.



Fig. 2.—Initial yields of products in Co⁶⁰ γ -ray-induced exchange of D₂ in H₂O at pH 6.0: O, D₂; Δ , HD; \Box , H₂.

sion. The yield of hydrogen deuteride is fairly constant between pH 5 and 8, varying in value between 2.6 and 2.8. This is close to the radical pair yield in water. At lower pH's there is a gradual rise in yield to a maximum of about 4.1 at pH 2.5 and a decrease at still lower pH's to a value of 2.8 at pH 0.5. At alkalinities greater than pH 8 there is a steady drop in yield with increasing pH until at pH 13 the G value is about 0.2. The G value for consumption of deuterium is of course equal to the sum of the G values for hydrogen and hydrogen deuteride production. In experiment no. 14 the composition of the initially dissolved gas was 50% deuterium and 50% hydrogen. The initial G value observed in this run was about 12.

Mechanism

The appearance of hydrogen deuteride in this exchange reaction seems to be rather clear evidence that hydrogen atoms do exist in these irradiated aqueous solutions. The fact that the yield of hydrogen deuteride in aqueous solutions is equal to the yield of free radical formation¹⁰ suggests that the rate-determining step in the exchange is the rate of production of hydrogen atoms. The constancy of

(10) E. J. Hart, Radiation Research, 1, 53 (1954).



Fig. 3.—Effect of pH on yields in γ -ray-induced exchange of D_2 and $H_2O: \bigcirc$, HD; \triangle , H₂.

the hydrogen yield and its magnitude suggests that it arises from the same source as the "molecular yield."¹¹

On the basis of the most recent picture of the primary processes in the radiolysis of aqueous solutions, a possible mechanism for the exchange in neutral solutions consistent with the facts is

$$\begin{array}{cccc} H_2O & \xrightarrow{} H + OH & k_1 & (3) \\ H_2O & \xrightarrow{} \frac{1}{2}H_2 + \frac{1}{2}H_2O_2 & k_2 & (4) \\ H + D_2 & \longrightarrow HD + D & k_1 & (5) \\ OH + D_2 & \longrightarrow HOD + D & k_4 & (6) \\ D + D & \longrightarrow D_2 & k_5 & (7) \end{array}$$

At the steady state in neutral solutions this would lead to a yield of hydrogen deuteride equal to the yield of hydrogen atoms in neutral solutions; namely

$$G_{\rm HD} = G_1 \tag{8}$$

The yield of hydrogen atoms per 100 e.v., G_1 , has been shown¹⁰ to be approximately 2.7 in neutral solutions in good agreement with the yield of hydrogen deuteride observed in this study. Further, it has been shown¹¹ that a radiation-induced chain recombination of hydrogen and hydrogen peroxide occurs in the radiolysis of water. In solutions of deuterium this would involve the dissolved deuterium and the hydrogen peroxide formed in reaction (4) through eqs. 9 and 10

$$OH + D_2 \longrightarrow HOD + D \tag{9}$$

 $D + H_2O_2 \longrightarrow HOD + OH$ (10)

Therefore an amount of deuterium would be consumed in the recombination reaction equivalent to the amount of hydrogen produced in reaction (4). It follows from this that the amount of deuterium consumed would be equal to the sum of the hydrogen deuteride and hydrogen produced in reactions (1) and (2), respectively, in agreement with the stoichiometry observed.

After the initial production of hydrogen deuteride, the rate of its formation drops off owing to its reaction with hydrogen atoms, resulting in an additional formation of hydrogen (reaction 11)

$$H + HD \longrightarrow H_2 + D \qquad k_6 \qquad (11)$$

The rates of formation of hydrogen deuteride, hydrogen and deuterium should then follow the expressions

(11) A. O. Allen, J. Phys. Colloid Chem., 52, 479 (1948).

$$\frac{d(HD)}{dt} = k_1 \frac{(D_2)}{(H_2) + (HD) + (D_2)} - \frac{k_6 \frac{(HD)}{(H_2) + (HD) + (D_2)}}{\frac{d(H_2)}{dt} = k_2 + k_6 \frac{(HD)}{(H_2) + (HD) + (D_2)}} - \frac{d(D_2)}{dt} = \frac{d(HD)}{dt} + \frac{d(H_2)}{dt} = k_1 \frac{(D_2)}{(H_2) + (HD) + (D_2)} + k_1 \frac{(D_2)}{(H_2) + (HD) + (D_2)} + k_1 \frac{(D_2)}{(H_2) + (HD) + (D_2)} + k_2 \frac{(D_2)}{dt} + k_2 \frac{(D_2)}{dt} + k_1 \frac{(D_2)}{(H_2) + (HD) + (D_2)} + k_2 \frac{(D_2)}{dt} + k_2 \frac{(D_2)}{dt} + k_1 \frac{(D_2)}{(H_2) + (HD) + (D_2)} + k_2 \frac{(D_2)}{dt} + k_2 \frac{(D_2)}{dt} + k_1 \frac{(D_2)}{(H_2) + (HD) + (D_2)} + k_2 \frac{(D_2)}{dt} + k_2 \frac{(D_2)}{dt} + k_1 \frac{(D_2)}{dt} + k_2 \frac{(D_2)}{dt} + k_2 \frac{(D_2)}{dt} + k_2 \frac{(D_2)}{dt} + k_2 \frac{(D_2)}{dt} + k_1 \frac{(D_2)}{(D_2) + (D_2)} + k_2 \frac{(D_2)}{dt} + k_1 \frac{(D_2)}{dt} + k_2 \frac{(D_2)}{dt} + k_2 \frac{(D_2)}{dt} + k_1 \frac{(D_2)}{dt} + k_2 \frac{(D_2)}{dt} + k$$

This integrates to

$$\frac{k_1}{(D_2)_0} t = -\ln \frac{(D_2) + (D_2)_0 k_2/k_1}{(D_2)_0 + (D_2)_0 k_2/k_1}$$

and

$$Ct = -\ln \frac{(D_2) + k_2/C}{(D_2)_0 + k_2/C}$$
(12)

where $C = k_1/(D_2)_0$. Plots of $\ln D_2/(D_2)_0 vs$. energy absorbed per liter (which is directly proportional to t), were made for all the runs. Straight lines were obtained. From the slope of these lines values of $C = k_1/(D_2)_0$ were found. These were fed back into eq. 12 together with values of k_2 resulting from the plots of the hydrogen yield vs. energy input such as is shown in Fig. 2 and replotted. Straight lines were again obtained with slightly different values of $k_1/(D_2)_0$. A third trial did not perceptibly change the values of $k_1/(D_2)_0$. The k_1 values derived in this manner were in agreement with those obtained from the initial slopes of the yield vs. dose curves plotted for the various runs as illustrated by Fig. 2.



Fig. 4.—Determination of rate constants of reactions induced by $\operatorname{Co}^{60} \gamma$ -rays in the system D_2 -H₂O.

The drop in hydrogen deuteride yield with increasing alkalinity has led us to postulate the ionization of the OH radical.^{2,3} Using this postulate and the assumption that the ionization of the hydroxyl radical is a rapid equilibrium process, one can construct the following possible mechanism in alkaline solutions. In addition to reactions (3) through (7), inclusive, the following reactions are assumed

$$OH \xrightarrow{\bullet} O^- + H^+ \qquad K$$

$$O^- + H \xrightarrow{\bullet} OH^- \qquad k_6$$

$$O^- + D \xrightarrow{\bullet} OD^- \qquad k_7$$

In this scheme the O^- ions compete with deuterium for the hydrogen atoms, the rate-determining step in hydrogen deuteride production, thereby lowering the yield. A steady-state treatment of this series of reactions leads to the following kinetic expression for hydrogen deuteride production

$$d(HD)/dt = \frac{k_1}{1 + k_1 K k_6 / k_3 k_4 (H^+) (D_2)^2}$$

Since the value for k_1 obtained in neutral solution had been used to calculate k_1Kk_6/k_3k_4 at ρ H 6, the values of d(HD)dt at other ρ H's were calculated and plotted on Fig. 3 (dotted line). Assuming a value of $K \approx 10^{-9}$,³ from the ρ H dependence curve one calculates for k_6/k_3k_4 a value of *ca*. 1.1 × 10⁻⁸.

An explanation for the rise in yield at lower pH's can be found if one considers the primary reaction (15) postulated by Dainton and Sutton¹² and by Allen.¹³

$$2H_2O = 2H + H_2O_2$$
 (15)

Hart¹⁴ has shown from work on formic acid that this reaction becomes more important at lower pH's. This has also been demonstrated by Hart and coworkers¹⁵ by their study of the γ -ray-induced hydrogen peroxide formation in O¹⁶O¹⁸-H₂O¹⁸ aqueous solutions, and by Sworski¹⁶ in his work on the effect of bromide ion on the formation of hydrogen peroxide in water decomposed by $Co^{60} \gamma$ -irradiation. If this is accepted, then one can understand the rise in yield of hydrogen deuteride with increasing acidity since the steady-state concentration of hydrogen atoms would increase at the lower pH's. To explain the maximum at pH 2, it may be possible that the H_2^+ postulated by Weiss¹⁷ becomes an important entity at this pH. The H_2^+ would decrease the steady state of free hydrogen atoms thereby decreasing the rate of hydrogen deuteride production, and this effect would become more important with increasing acidity.

The higher yield of hydrogen deuteride obtained when starting with a mixture of 50% deuterium and 50% hydrogen (experiment no. 14) is probably due to a short chain reaction, the chain propagation steps being reactions (5) and (16).

$$D + H_2 \longrightarrow HD + H$$
 (16)

This chain reaction has been observed by Mund and co-workers¹⁸ by α -irradiation of mixtures of deuterium and hydrogen in the gas phase with and without the presence of water vapor. Short chains are found in the presence of water vapor.

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