

730. *On the Mechanism of Hydrogen Evolution from Irradiated Solutions of Ethanol and Formate in Water and Heavy Water.*

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Aqueous solutions of ethanol and formate were irradiated with 200 kvp X-rays. The water and/or the organic solute were isotopically labelled. The dependence of the yield and isotopic composition of the hydrogen evolved on the concentration of added hydrogen and phosphate ions was investigated. The results indicate that the solvated electrons, $e_{aq.}^-$, formed in irradiated water are converted to H atoms by $e_{aq.}^- + H_3O^+ \longrightarrow H + H_2O$ and $e_{aq.}^- + H_2PO_4^- \longrightarrow H + HPO_4^{2-}$. There was no evidence for the reaction $RH_2 + H_2^+ \longrightarrow RH_2^+ + H_2$ in H_2SO_4 solutions of concentration $< 0.8N$.

THE effect of pH on the hydrogen yield from irradiated aqueous solutions of different solutes has been investigated¹⁻⁶ and interpreted in terms of conversion into the reactive forms $e_{aq.}^- \xrightarrow{H^+} H \xrightarrow{H^+} H_2^+$. The results include^{2b,6} work on solutions of methanol and ethanol in D_2O . We have previously investigated⁷ the isotopic composition of hydrogen evolved from irradiated solutions of isotopically-labelled ethanol at a constant low pH. We have now extended the work to aqueous solutions of ethanol and formate in which the water, or the organic molecule, or both, were labelled with deuterium. The variation of yield and composition of hydrogen gas with change of pH was investigated, together with the effect of changes in the concentration of phosphate ions at constant pH.

EXPERIMENTAL

The methods and materials were as previously described.⁷ Some experiments were done in vessels having no free volume above the liquid phase, as in the experiments of Allen and Johnson.⁸ Additional materials were all of AnalaR quality. Intermediate pH values were obtained with phosphate buffers. Isotopic determination of the hydrogen was carried out by mass spectroscopy according to the procedure described in ref. 7. Analyses were performed at the Isotope Department of the Weizmann Institute, Rehovoth. We thank Professor M. Anbar for these.

RESULTS AND DISCUSSION

Solutions of $CH_3 \cdot CD_2 \cdot OH$ in H_2O (pH range 0.4—4.0).—The pH-dependence of the total experimental hydrogen yield, denoted $G(\text{hydrogen})$, and the isotopic composition of the gas evolved in acid conditions were investigated. In Table 1 some representative detailed calculations are given, carried out as described previously⁷: $(D/H)_{exp.}$ is the experimentally obtained ratio of D/H in the evolved gas, and $(D/H)_{eth.}$ is the ratio D/H

¹ Alland and Scholes, *Nature*, 1960, **187**, 218.

² (a) Baxendale and Smithies, *Z. phys. Chem. (Frankfurt)*, 1956, **7**, 242; (b) Baxendale and Hughes, *ibid.*, 1958, **14**, 306.

³ (a) Fricke and Hart, *J. Chem. Phys.*, 1934, **2**, 824; (b) Fricke, Hart, and Smith, *ibid.*, 1938, **6**, 229; (c) Hart, *J. Phys. Chem.*, 1952, **56**, 594; (d) Smithies and Hart, *J. Amer. Chem. Soc.*, 1960, **82**, 4775.

⁴ (a) Barr and Allen, *J. Phys. Chem.*, 1959, **63**, 928; (b) Hayon and Weiss, Proc. 2nd Geneva Conf. Peaceful Uses Atomic Energy, 1958, P/1571.

⁵ (a) Weiss, *Nature*, 1950, **165**, 728; (b) Rigg, Stein, and Weiss, *Proc. Roy. Soc.*, 1952, *A*, **211**, 375.

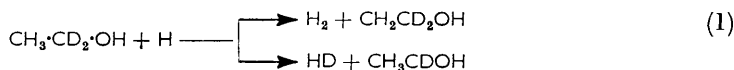
⁶ (a) Riesz and Burr, *Radiation Res.*, 1962, **16**, 661; (b) Taub and Dorfman, *J. Amer. Chem. Soc.*, 1962, **84**, 4053; (c) Lifshitz, Ph.D. Thesis, Jerusalem, 1961.

⁷ (a) Lifshitz and Stein, *J.*, 1962, 3706; (b) Lifshitz, *Canad. J. Chem.*, 1962, **40**, 1903.

⁸ Allen and Johnson, *J. Amer. Chem. Soc.*, 1952, **74**, 4147.

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in the part of the hydrogen that originated from the ethanol. Assuming dehydrogenation by H atoms according to the scheme:



(D/H)eth. is calculated⁷ from (D/H)exp., assuming that $G(\text{H}_2)$, the yield of "molecular" hydrogen originating from H_2O , is $\simeq 0.5$, and using the equation:

$$[\text{D}/(\text{H} + \text{D})] \text{exp.} \times G(\text{hydrogen}) = X \times [G(\text{hydrogen}) - G(\text{H}_2)],$$

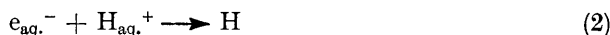
where $X = \frac{1}{2}[\text{D}/(\text{H} + \text{D})]_{\text{eth.}}$

TABLE I.

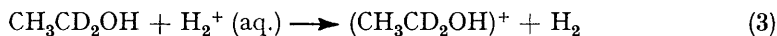
$\text{CH}_3\cdot\text{CD}_2\cdot\text{OH}$ in H_2O . $G(\text{H}_2)$ assumed to be = 0.5. Series A: $1.75 \times 10^{-2}\text{M}$ ethanol, volume irradiated 100 ml., dose rate 2100 rad. min^{-1} . Series B: $3.5 \times 10^{-2}\text{M}$ ethanol, volume irradiated 10 ml., dose rate 6370 rad. min^{-1} . Series C: $3.5 \times 10^{-2}\text{M}$ ethanol, volume irradiated 5 ml., dose rate 5900 rad. min^{-1} .

	Dose (eV)	$G(\text{hydrogen})$	pH adjustment	pH	(D/H)exp.	(D/H)eth.
A	6.4×10^{19}	4.50	0.8N- H_2SO_4	0.45	0.155	0.435
	1.28×10^{20}	4.05	0.1N- H_2SO_4	1.3	0.155	0.44
	1.28×10^{20}	3.55	0.01N- H_2SO_4	2.0	0.150	0.44
B	1.19×10^{20}	4.30	0.8N- H_2SO_4	0.45	0.165	0.475
	1.19×10^{20}	4.10	0.1N- H_2SO_4	1.3	0.165	0.480
	1.19×10^{20}	2.80	0.01N- H_2SO_4	2.0	0.150	0.470
C	4.3×10^{19}	4.50	0.8N- H_2SO_4	0.45	0.165	0.47
	4.3×10^{19}	3.50	10^{-3}N - H_2SO_4	3	0.165	0.47
	8.6×10^{19}	2.90	10^{-3}N - H_2SO_4	3	0.160	0.50
	4.3×10^{19}	2.50	10^{-4}N - H_2SO_4	4	0.165	0.55
	1.3×10^{20}	2.85	10^{-4}N - H_2SO_4	4	0.150	0.46

In the pH range employed hydrogen atoms are available from two sources: H atoms as such reaching the bulk of the solution^{1,9} with $G(\text{H}) \simeq 0.5$, and H atoms formed from the solvated electrons, $e_{\text{aq.}}^-$, according to



(To produce sufficient gas for isotopic analysis comparatively high doses were employed so that secondary back-reactions with reaction products cannot be disregarded in these experiments.) The aldehyde present in the solution will compete⁹ with reaction (2) for $e_{\text{aq.}}^-$. We attribute the pH-dependent decrease in $G(\text{hydrogen})$ observed even at $\text{pH} < 4$ to this competition. On the other hand (D/H)eth. remains essentially constant over this pH range, showing that the mechanism of hydrogen formation by dehydrogenation of ethanol remains unchanged and can be described by reaction (1). In particular there is no evidence in favour of the possibility that in the more acid solutions hydrogen evolution would occur via electron transfer to H_2^+ , according to



since this would produce more hydrogen from the water, thus reducing D/H. Under our experimental conditions, H_2^+ may not even be formed in the presence of ethanol, which reacts directly with H atoms.

Solutions of $\text{CH}_3\text{CD}_2\text{OH}$ in H_2O , $\text{CH}_3\text{CH}_2\text{OD}$ in D_2O , and $\text{CH}_3\text{CH}_2\text{OH}$ in H_2O (pH range 4—10).—Unbuffered solutions of labelled ethanol in H_2O gave erratic hydrogen yields and hydrogen which originated from the water found in the gas. This comes from the relatively

⁹ Rabani and Stein, *J. Chem. Phys.*, 1962, **37**, 1865.

slow reaction of $e_{aq.}^-$ with water, and the amount is greatly influenced by small amounts of impurity.⁹ Reproducible results are obtained in the presence of phosphate buffers. Some of these are given in Table 2. They are treated in the reverse way to those in Table 1,

TABLE 2.

Solutions of $CH_3\cdot CD_2\cdot OH$ in H_2O . Series A: $1.75 \times 10^{-2}M$ ethanol, volume irradiated 100 ml., dose rate 2100 rad. min^{-1} . Series B: $1.75 \times 10^{-3}M$ ethanol, volume irradiated 10 ml., dose rate 6370 rad. min^{-1} .

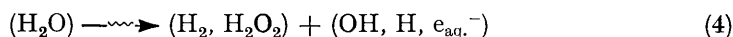
Dose (eV)	G(hydrogen)	pH adjustment, phosphate buffer	pH	G(H ₂)	(D/H)exp.	(D/H)eth.
A { 1.28×10^{20}	1.40	$6.7 \times 10^{-3}M$	5.2	0.70	0.082	0.44
1.28×10^{20}	1.15	„	8.1	0.75	0.057	0.44
2.56×10^{20}	1.10	„	8.1	0.75	0.049	0.44
B { 5.8×10^{19}	1.60	„	7.4	0.90	0.078	0.48
5.8×10^{19}	2.05	$6.7 \times 10^{-2}M$	7.1	0.85	0.106	0.48
1.19×10^{20}	2.20	„	7.2	0.95	0.103	0.48

i.e., $G(H_2)$, the molecular yield, is calculated from the (D/H)eth. value of Table 2. Higher $G(H_2)$ values are obtained for neutral than for acid solutions.

The results also show that up to pH 7, when $H_2PO_4^-$ ions predominate, addition of buffer results in increased $G(\text{hydrogen})$. Thus added phosphate appears to aid the conversion of $e_{aq.}^-$, which does not dehydrogenate ethanol, into H atoms, which do. Above pH 8 where HPO_4^{2-} ions predominate, the effect disappears, and the hydrogen yield approaches the limiting value of $G(\text{hydrogen}) = 1.05$. The electrons react without the formation of H atoms with the electron acceptors, *e.g.*, aldehyde present. Related experiments using CH_3CH_2OD in D_2O and CH_3CH_2OH in H_2O are reported in Table 3. In the presence of added phosphate ion, $G(\text{hydrogen})$ is higher in D_2O than in H_2O solutions.

Solutions of HCOO⁻.—In the case of ethanol the hydrogen of the OH group receives the same labelling as the solvent. This introduces some uncertainty since as the pH changes we cannot ascertain the contribution, if any, of hydrogen evolved as the result of dehydrogenation of this group. We have therefore extended our experiments to solutions of formate. At neutral and alkaline pH this is present as the $HCOO^-$ anion in which the H does not exchange appreciably with the medium. The reactions of formate in irradiated solutions were investigated previously^{3,10,11} and the velocity constants of its various reactions determined. The results in light and in heavy water are shown in Table 3. The effect of $H_2PO_4^-$ in enhancing dehydrogenation is also indicated by the isotopic composition of the gas evolved.^{7b} Therefore we investigated this point separately. At a constant $[HCOONa] = 10^{-1}M$, and varying low $[KH_2PO_4]$, solutions in H_2O were irradiated and the hydrogen yield determined. The results are shown in the Figure.

To interpret these results we denote the overall reaction by:



where the products within the first brackets denote the formation of “molecular” hydrogen and hydrogen peroxide. Low concentrations of added scavengers do not affect the yields of these. Within the second brackets we denote the reactive intermediates in the bulk of the solution which may react there with substrates. For the purpose of the present paper the reaction of the hydroxyl radicals, which dehydrogenate the organic substrate to yield H_2O and an organic radical, need not be considered in detail.

The intermediates reacting in the bulk of the solution and capable of leading to hydrogen evolution are, as mentioned above, the hydrogen atoms, with $^{1,9} G(H) \simeq 0.5$ and solvated electrons with $^9 G(e_{aq.}^-) = 2.7$.

¹⁰ Hardwick, *Radiation Res.*, 1960, **12**, 5.

¹¹ Rabani and Stein, *Trans. Faraday Soc.*, 1962, **58**, 2150.

TABLE 3.

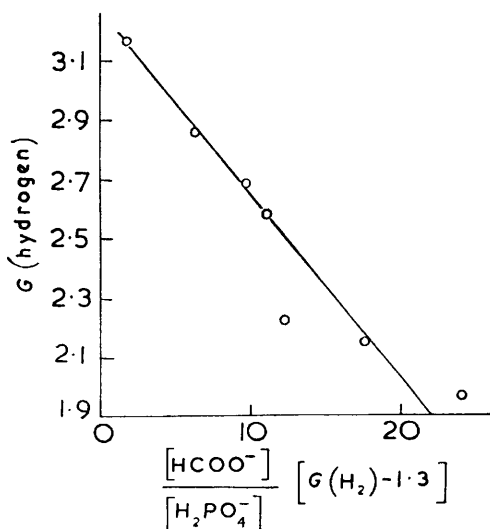
Volume irradiated 10 ml., dose rate 6370 rad. min⁻¹.A. Solutions in D₂O.

Solute and concentration	Dose (eV)	pH adjustment	pH *	% D in solution	G(hydrogen)	G(HD)	G(D ₂)
CH ₃ ·CH ₂ ·OD, 8 × 10 ⁻⁴ M	9.7 × 10 ¹⁹	10 ⁻³ M phosphate buffer	7.4	97	3.6	2.26	1.34
CH ₃ ·CH ₂ ·OD, 1.75 × 10 ⁻¹ M	1.94 × 10 ²⁰	7 × 10 ⁻² M phosphate buffer	7.2	99	3.4	2.56	0.83
HCO ₂ K, 3 × 10 ⁻³ M	5.8 × 10 ¹⁹	HCOOH + KOH	4.3	97	3.43	1.24	2.19
HCO ₂ K, 3 × 10 ⁻² M	1.94 × 10 ²⁰	"	4.3	97	1.82	1.53	0.29
HCO ₂ Na, 9.5 × 10 ⁻³ M	1.94 × 10 ²⁰	nil	*	97	2.3	0.64	1.66
HCO ₂ Na, 9.5 × 10 ⁻² M	1.94 × 10 ²⁰	"	*	97	1.3	0.94	0.36
HCO ₂ Na, 7 × 10 ⁻³ M	9.7 × 10 ¹⁹	"	*	99.8	1.84	0.24	1.6
HCO ₂ Na, 1 × 10 ⁻¹ M	9.7 × 10 ¹⁹	"	*	99.8	1.14	0.63	0.51

* pH values were not measured in the D₂O solutions. Values given are those obtained in equivalent H₂O solutions. In unbuffered solutions the initial pH was 7—8, rising slightly during irradiation.

B. Solutions in H₂O.

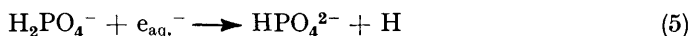
Solute and concentration	Dose (ev)	pH adjustment	pH	G(hydrogen)
CH ₃ ·CH ₂ ·OH, 1.75 × 10 ⁻² M	1.55 × 10 ²⁰	Phosphate buffer, 3.3 × 10 ⁻² M	7.3	2.1
CH ₃ ·CH ₂ ·OH, 3.5 × 10 ⁻² M		HCOOH + KOH	4.3	3.8
HCO ₂ K, 3 × 10 ⁻³ M	5.8 × 10 ¹⁹	"	4.3	2.35
HCO ₂ K, 3 × 10 ⁻² M	1.94 × 10 ²⁰	"	4.3	2.6
HCO ₂ K, 1 × 10 ⁻¹ M	1.94 × 10 ²⁰	"	4.3	3.15
HCO ₂ H, 1 × 10 ⁻¹ M	1.94 × 10 ²⁰	Na ₂ HPO ₄ , 1.5 × 10 ⁻¹ M	6.05	3.35
HCO ₂ H, 1 × 10 ⁻¹ M	1.94 × 10 ²⁰	Na ₂ HPO ₄ , 3 × 10 ⁻¹ M	7.3	3.35
HCO ₂ Na, 10 ⁻² M	5.8 × 10 ¹⁹	nil	*	2.25
" 10 ⁻¹ M	"	"	*	1.45
" "	7.5 × 10 ¹⁹	"	*	1.3



The dependence of the hydrogen yield in irradiated solutions on the ratio of concentrations of formate and dihydrogenphosphate ions.

Consider systems where ferricyanide¹¹ or acetone^{1,9}, *i.e.*, a good electron scavenger, is present at a concentration high enough so that it reacts with $e_{aq.}^-$ without hydrogen-atom formation, but does not yet compete for the hydrogen atoms with the added hydrogen-atom scavenger, *e.g.*, ethanol or formate. Under such conditions⁹ the observed hydrogen yield will approach the limiting sum of the molecular hydrogen yield plus the yield of atomic hydrogen, $G(\text{hydrogen}) = G(\text{H}_2) + G(\text{H}) = 1.1$. In the absence of a good electron scavenger the hydrogen yield observed will be higher than this limit, since some of the $e_{aq.}^-$ will disappear through reacting with water, leading to the formation of hydrogen. The results in the presence of ethanol agree with this mechanism. At lower pH values $\text{H}_{aq.}^+$ scavenges $e_{aq.}^-$ (reaction 2), hydrogen atoms result, and—as the present isotope experiments confirm—these dehydrogenate ethanol. In the presence of formate alone we note that these hydrogen yields are decreased by increasing the formate concentration. We attribute this to a reaction of formate ion with $e_{aq.}^-$ which decomposes formate without evolution of hydrogen. From the isotopic composition of the higher hydrogen yields in the absence of formate one sees that it originates from water.

To explain the role of the phosphate ion we assume that^{6,12} it is capable of converting $e_{aq.}^-$ to H according to:



It is, in this context, of particular interest to compare hydrogen yields and their isotopic composition from neutral ethanol— D_2O solutions not containing added phosphate^{6a,b} with our results in Table 3.

When solutions containing a constant (10^{-4}M) concentration of sodium formate and varying concentrations of potassium dihydrogen phosphate are irradiated, hydrogen atoms formed in the system will dehydrogenate formate and yield hydrogen gas. In the absence of phosphate, $G(\text{hydrogen}) \longrightarrow 1.1$, the sum of $G(\text{H}_2)$ and $G(\text{H})$, the electrons being scavenged by formate. In the presence of phosphate

$$G(\text{hydrogen}) = G(\text{H}_2) + G(\text{H}) + \frac{G(e_{aq.}^-)}{1 + (K[\text{HCOO}^-]/[\text{H}_2\text{PO}_4^-])} \quad (6)$$

where $K = k(\text{for } e^- + \text{HCOO}^-)/k(\text{for } e^- + \text{H}_2\text{PO}_4^-)$. Hence the experimental hydrogen yield, $G(\text{hydrogen})$, should depend on the concentration ratio $[\text{HCOO}^-]/[\text{H}_2\text{PO}_4^-]$ according to:

$$G(\text{hydrogen}) = A - K[G(\text{hydrogen}) - B] \times ([\text{HCOO}^-]/[\text{H}_2\text{PO}_4^-]) \quad (7)$$

where $A = G(\text{H}_2) + G(\text{H}) + G(e_{aq.}^-)$ and $B = A - G(e_{aq.}^-)$. The results in the Figure confirm this dependence on $[\text{H}_2\text{PO}_4^-]$ at a constant formate concentration. Using for B the value 1.3, which is the lowest experimental value in this series, the intercept gives $A = 3.3$ compared to the limiting value of 3.7 obtained at low doses in systems where competition for the electrons by other than the designed acceptor may be fully neglected.⁹

This research was supported by the Israeli Atomic Energy Commission. We thank Professor E. D. Bergman for his constant interest.

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[Received, September 23rd, 1963.]

¹² Jortner, Ottolenghi, Rabani, and Stein, *J. Chem. Phys.*, 1962, **37**, 2488.