718. *Isotope Effects in the Abstraction of Hydrogen from Ethanol by Hydrogen Atoms in Irradiated Aqueous Solutions.*

By Chava Lifshitz and Gabriel Stein.

The reaction, $RH + H \longrightarrow H_2 + R$, has been investigated in aqueous ethanol and t-butyl alcohol at a low pH. By isotopic labelling of the water and/or the ethanol the sites of attack on the ethanol molecule were determined and the degree of selectivity in abstraction was found. The attack on the hydrogen atoms of the ethanol is in the order, α-H > β-H > OH $\approx$ 0. The isotope effect in the abstraction from an α-C–H bond compared with an α-C–D bond is calculated. The results for ethanol and t-butyl alcohol are correlated. The results are discussed in the light of previous information concerning the radiation chemistry of alcohols.

The radiation chemistry of pure alcohols [1-5] and aqueous alcohols [6,7] has been widely investigated, by using radical scavengers [2a,3b,5] as well as isotopic labelling.[2b,4] There is, however, disagreement between the different authors. The points under discussion are (*a*) the relative contributions of truly "molecular" processes and radical abstraction, in the formation of hydrogen, (*b*) in the case of pure alcohols the site of origin of the primarily formed hydrogen atoms, and (*c*) the sites of attack by atomic hydrogen in the abstraction. In the radiation chemistry of dilute aqueous solutions of the alcohols all the results may be explained as consequences of the primary act: [6,7]

$$(1)\ H_2O \rightsquigarrow H, OH, H_2\ H_2O_2$$

where H_2 and H_2O_2 are the "molecular" products, and H and OH the radical products, or their precursors.

The part of radical and molecular products in act (1) for ^{60}Co γ-rays or 200 kv *X*-rays is reasonably certain, at least for 0·8—0·1N-sulphuric acid solutions.[8] Further, in such dilute alcohol solutions the origin of the hydrogen atoms is certainly from the water alone by reaction (1). In acid solutions the electrons primarily formed yield hydrogen atoms.[8] These systems may, therefore, help in the study of selectivity effects in the abstraction:

$$(2)\ RH + H \longrightarrow R + H_2$$

If the attacking species in reaction (2) is assumed to be the same in irradiation of the pure alcohol and in its aqueous solution, some interesting conclusions can be drawn for the unsolved points (*a*) and (*b*) above.

We have applied an extension of the isotopic labelling method used for methanol in water [7] to the case of ethanol in water.

Some results have recently been obtained on the selectivity of abstracting radicals.[9,10] Further, the dependence of reaction (2) on the position of the hydrogen atoms and their replacement by deuterium, which was found in the radiation chemical results for deuterated ethanol,[4] was again studied in a more quantitative way.[11] Our results furnish further information about this matter.

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[1] McDonell and Newton, *J. Amer. Chem. Soc.*, 1954, **76**, 4651; McDonell and Newton, *ibid.*, 1956, **78**, 4554.

[2] (*a*) Meshitzuka and Burton, *Radiation Res.*, 1958, **8**, 285; (*b*) Meshitzuka, Ouchi, Hirota, and Kusomoto, *J. Chem. Soc., Japan*, 1957, **78**, 129.

[3] (*a*) Adams and Baxendale, *J. Amer. Chem. Soc.*, 1958, **80**, 4215; (*b*) Adams, Baxendale, and Sedgwick, *J. Phys. Chem.*, 1959, **63**, 854.

[4] Burr, *J. Phys. Chem.*, 1957, **61**, 1477, 1483; *J. Amer. Chem. Soc.*, 1957, **79**, 651.

[5] Bakh and Sorokin, Symposium on Radiation Chem. Akad. Sci. U.S.S.R., Moscow, 1955, p. 135.

[6] Jayson, Scholes, and Weiss, *J.*, 1957, 258, 1358; Allan, Hayon, and Weiss, *J.*, 1959, 3913.

[7] Baxendale and Hughes, *Z. phys. Chem. (Frankfurt)*, 1958, **14**, 306.

[8] Allan and Scholes, *Nature*, 1960, **187**, 218; Czapski and Allen, *J. Phys. Chem.*, 1962, **66**, 262.

[9] Herk and Szwarc, *J. Amer. Chem. Soc.*, 1960, **82**, 3558.

[10] McNesby, Scheer, and Klein, *J. Chem. Phys.*, 1960, **32**, 1814.

[11] Burr and Scarborough, *J. Phys. Chem.*, 1960, **64**, 1372.

EXPERIMENTAL

Irradiations were carried out with an *X*-ray machine operated at 200 kv and 15 mA. The vessels were cylindrical Pyrex tubes with about 200 c.c. free volume above the 10 or 100 c.c. of liquid phase. Dose rates were measured by the Fricke dosimeter (10^{-3}M-ferrous sulphate in 0·1N-sulphuric acid), $G(Fe^{3+})$ being taken as 15·5, and were usually 6500 r./min. ($\sim 4 \times 10^{17}$ ev ml.$^{-1}$ min.$^{-1}$) and 2000 r./min. ($\sim 1{\cdot}2 \times 10^{17}$ ev ml.$^{-1}$ min.$^{-1}$) for 10 and 100 c.c. of solutions, respectively. The value chosen for $G(Fe^{3+})$ is higher than that given by Hardwick.[12b] If Hardwick's value were to be used, all *G* values given in this paper would have to be multiplied by 0·93.

Solutions were prepared from triply distilled water (ordinary distilled water, further distilled from alkaline permanganate and then from phosphoric acid). Heavy water (obtained from Norsk Hydro; 99·76—99·8% deuterium) was used without purification. B.D.H. "AnalaR" ethanol was used without purification. Low pH values were obtained by means of "AnalaR" sulphuric acid. Deuteroethanol, $CH_3{\cdot}CD_2{\cdot}OH$ was synthesized from lithium aluminium tetradeuteride and acetic anhydride.[13] The deuteride (Metal Hydrides Inc.) contained not more than a few thousandths of a percent of active light hydrogen. After final distillation of the ethanol *in vacuo*, it had n_D^{23} 1·36022 and b. p. 76°/690 mm. Gas-chromatography showed it to contain less than 1% of impurities.

The irradiation vessels were cleaned with concentrated nitric acid, washed several times with ordinary and then triply distilled water, and thoroughly dried by evacuation.

Evacuation was through a liquid-air trap by an oil-pump and a mercury-pump in series, with repeated shaking of the solution and opening to the vacuum-line. The ultimate air pressure was always less than 10^{-4} mm. Hg and the loss of liquid was negligible.

After irradiation *in vacuo* the hydrogen gas evolved was pumped by a Toepler pump through a liquid-air trap into a known volume and its pressure was measured by a McLeod gauge.

Isotopic determination of the hydrogen was by mass-spectroscopy at the Isotope Department of the Weizmann Institute, Rehovoth. The mass-spectrometer was a Consolidated Engineering Corp. model 21–401 adjusted to hydrogen–deuterium measurements. The mass-spectrometer was calibrated with zinc-decomposed water mixtures of known isotopic composition. The masses were always determined in the order: 2, 3, 4, 3, 2 to take into account pressure changes in the mass spectrometer, and the H : D ratio was determined as the mean of two values.

RESULTS

The yield of hydrogen evolved, *G*(hydrogen), and the isotopic composition of the evolved gas from 1,1-dideuteroethanol in light water, are given in Table 1. The ethanol concentration given is the initial one. *G*(hydrogen) is the total hydrogen yield (light and heavy) evolved per 100 ev absorbed radiation. (D/H)exp is the isotopic composition of this gas, and (D/H)eth is the isotopic composition of the hydrogen atoms abstracted from the ethanol. (D/H)eth was calculated as follows from (D/H)exp., *G*(hydrogen), and $G(H_2)$ [where $G(H_2)$ is the molecular

TABLE 1.

[EtOH] (10^{-2}M)	Dose rate (r./min.)	Dose (10^{19} ev)	*G*(hydrogen)	pH adjustment	(D/H)exp.	$G(H_2)$	(D/H)eth.
			$CH_3{\cdot}CD_2{\cdot}OH$ in H_2O.				
1·75	2100	6·4	4·5	0·8N-H_2SO_4	0·15	0·5	0·41
3·50	6370	9·7	4·7	0·8N- ,,	0·17	0·5	0·47
3·50	6370	11·9	4·1	0·1N- ,,	0·17	0·5	0·50
5·85	6370	11·9	4·5	0·8N- ,,	0·18	0·5	0·53
10·5	6370	3·4	4·9	0·8N- ,,	0·16	0·4	0·45
0·87	6370	11·9	1·9	Phosphate, pH 7·25	0·12	0·65	0·49

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[12] (*a*) Farmer, Rigg, and Weiss, *J.*, 1955, 582; (*b*) Hardwick, *J. Chem. Phys.*, 1959, **31**, 226.

[13] Shiner, *J. Amer. Chem. Soc.*, 1953, **75**, 2929.

hydrogen yield in reaction (1)]: from the experimental D/H value {D/(H + D)}exp was calculated. Then

$$\{D/(H + D)\}\text{exp} \,.\, G(\text{hydrogen}) = X\{G(\text{hydrogen}) - G(H_2)\},$$

where $X = \frac{1}{2}\{D/(H + D)\}\text{eth}$, the factor $\frac{1}{2}$ arising from the fact that one hydrogen atom in the abstraction reaction originates always in the light water. We chose the value of $G(H_2) = 0{\cdot}5$ for the yield of " molecular " hydrogen for these experiments in light water.

In Tables 2 and 3 results are given for $CH_3{\cdot}CH_2{\cdot}OD$ in D_2O and $CH_3{\cdot}CD_2{\cdot}OD$ in D_2O, respectively. By dissolving $CH_3{\cdot}CH_2{\cdot}OH$ or $CH_3{\cdot}CD_2{\cdot}OH$ in D_2O, isotopic labelling of the OH is obtained by rapid hydrogen exchange with the water.[7] G(HD) and $G(D_2)$ given in Table 2 were calculated from G(hydrogen) and the experimental isotopic composition of the gas. However, when $CH_3{\cdot}CD_2{\cdot}OD$ is used in D_2O (Table 3), part of the yield of deuterium gas originates from an abstraction process. Therefore (as in Table 1) $G(D_2)$ is the value of a " molecular " yield originating from the water, for which we assume a mean value of 0·5. (D/H)eth is then calculated by the same method as for Table 1. It has recently become clear that the so-called " molecular " yield has no constant value but depends on experimental conditions such as scavenger concentration and pH. Therefore, the choice of the values in Tables 1—4 is somewhat arbitrary and may be varied by probably ±0·1 G unit. This, of course, introduces a corresponding uncertainty into our results. For high scavenger concentrations and pH values other than acid some allowance was made for this in Table 1.

TABLE 2.

[EtOH] (10^{-2}M)	Dose rate (r./min.)	Dose (10^{19} ev)	D in solution (%)	G(hydrogen)	(D/H)exp	G(HD)	$G(D_2)$
			$CH_3{\cdot}CH_2{\cdot}OD$ in D_2O; 0·8N-H_2SO_4.				
0·175	6680	2·0	96	4·5	1·08	4·35	0·18
0·320	6680	6·1	99	4·9	1·16	4·54	0·36
0·870	6680	6·1	99	4·5	1·18	4·16	0·38
10·5	6370	3·9	99	5·5	1·06	5·34	0·16
			$CH_3{\cdot}CH_2{\cdot}OD$ in D_2O; 0·1N-H_2SO_4.				
0·140	6370	5·5	99·7	4·3	1·32	3·70	0·60
0·350	6370	7·5	99·7	4·5	1·32	3·88	0·62
10·4	6370	7·5	99·55	5·0	1·15	4·66	0·34
			Bu^{t}OH in D_2O; 0·8N-H_2SO_4.				
1·55	6370	9·7	99	2·7	2·02	1·78	0·92

TABLE 3.

EtOH (10^{-2}M)	Dose rate (r./min.)	Dose (10^{19} ev)	D in solution (%)	G(hydrogen)	(D/H)exp	$G(D_2)$	(D/H)eth.
			$CH_3{\cdot}CD_2{\cdot}OD$ in D_2O; 0·8N-H_2SO_4.				
2·60	6370	19·4	99	4·4	2·53	0·5	0·51

TABLE 4.

$CH_3{\cdot}CH_2{\cdot}OH$–$CH_3{\cdot}CD_2{\cdot}OH$ mixtures in H_2O; dose rate, 6650 r./min.; dose $1{\cdot}24 \times 10^{20}$ ev.

[$CH_3{\cdot}CH_2{\cdot}OH$] (10^{-3}M)	[$CH_3{\cdot}CD_2{\cdot}OH$] (10^{-3}M)	Buffer concn.	G(hydrogen)	(D/H)exp	$G(H_2)$	(D/H)eth.
1·75	1·75	0·8N-H_2SO_4	5·0	0·021	0·5	0·047
4·35	4·35	Phosphate, pH 7·3	2·0	0·015	0·65	0·047

In order to obtain relative rate constants for the reaction of hydrogen atoms with $CH_3{\cdot}CH_2{\cdot}OH$ and $CH_3{\cdot}CD_2{\cdot}OH$, the alcohols were used separately in competition reactions with ferricyanide. The reactions of potassium ferricyanide itself have been investigated before.[14] The results are given in Table 5 with k_{F+H} and k_{A+H} as the velocity constants

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[14] Rabani and Stein, *Trans. Faraday Soc.*, 1962, in the press.

TABLE 5.

Ethanol–$K_3Fe(CN)_6$ and 1,1-dideuteroethanol–$K_3Fe(CN)_6$ in aqueous 0·1N-H_2SO_4.

$[CH_3{\cdot}CH_2{\cdot}OH]$ (10^{-2}M)	$[CH_3{\cdot}CD_2{\cdot}OH]$ (10^{-2}M)	Average $[K_3Fe(CN)_6]$ (10^{-4}M)	Dose rate (r./min.)	Dose (10^{19} ev)	*G*(hydrogen)	k_{F+H}/k_{A+H}
5·13	—	1·46	1990	10·9	3·32	172
1·3	—	1·82	1990	3·62	1·68	153
11·0	—	12·9	6370	1·94	1·63	176
11·0	—	1·02	1990	3·62	1·98	153
—	5·15	1·27	1990	7·24	1·53	1010
—	5·19	1·02	1990	3·62	1·53	1100
—	34·0	4·5	6370	2·73	1·85	1040

of the reaction of hydrogen atoms with ferricyanide and alcohol, respectively, the values $k_{F+H}/k_{A+H} = 165$ and 1050 are the best for ethanol and 1,1-dideuteroethanol, respectively. They represent average results from experiments where the hydrogen atoms are almost equally divided between potassium ferricyanide and the alcohol. We can write:

$$k_a/k_b = k(\text{for } CH_3{\cdot}CH_2{\cdot}OH + H)/k(\text{for } CH_3{\cdot}CO_2{\cdot}OH + H) = 6{\cdot}3$$

The ratio of the reaction velocities of hydrogen atoms with hydrogen or deuterium in the α-position may be calculated from k_a/k_b as follows:

We assume that (i) all three types of H atom of the alcohol are attacked, and (ii) the reaction rates of a β-C–H bond and an O–H bond with hydrogen atoms are independent of deuteration at the α-position of the alcohol; then, if (D/H)eth = 0·48 (average value from Table 1), we have:

$$k_a = 3k_{\beta CH} + 2k_{\alpha CH} + k_{OH}; \qquad \text{(I)}$$

$$k_b = 3k_{\beta CH} + 2k_{\alpha CD} + k_{OH}; \qquad \text{(II)}$$

$$2k_{\alpha CD}/(3k_{\beta CH} + k_{OH}) = 0{\cdot}49; \qquad \text{(III)}$$

$$k_a/k_b = 6{\cdot}3. \qquad \text{(IV)}$$

Hence

$$k_{\alpha CH}/k_{\alpha CD} = 17{\cdot}5. \qquad \text{(V)}$$

Further

$$2k_{\alpha CH}/(3k_{\beta CH} + k_{OH}) = 8{\cdot}4. \qquad \text{(VI)}$$

The same value would have been calculated for $k_{\alpha CH}/k_{\alpha CD}$ if it had been assumed that the hydroxyl group is not attacked by hydrogen atoms. In this case the value of $k_{\alpha CH}/k_{\beta CH} = 12{\cdot}6$ would result.

If a similar calculation is used for the equimolar mixture (Table 4) of $CH_3{\cdot}CH_2{\cdot}OH$ and $CH_3{\cdot}CD_2{\cdot}OH$ in water it is found that $k_{\alpha CH}/k_{\alpha CD} = 17{\cdot}2$. In view of the assumptions made about the molecular yields, $k_{\alpha CH}/k_{\alpha CD} = 17 \pm 1$.

If the frequency factor for reactions,

$$\text{(a) } CH_3{\cdot}CH_2{\cdot}OH + \dot{H} \longrightarrow CH_3{\cdot}CH(OH){\cdot} + H_2$$

$$\text{(b) } CH_3{\cdot}CD_2{\cdot}OH + H \longrightarrow CH_3{\cdot}CD(OH){\cdot} + HD$$

is assumed to be the same,[10] the activation-energy difference between (a) and (b) is calculated to be:

$$\Delta E = E_B - E_A = 1{\cdot}7 \text{ kcal./mole at } 298^\circ \text{ K}.$$

The ratio k(for $CH_3{\cdot}CH_2{\cdot}OH + H$) : k(for $CH_3{\cdot}OH + H$) has been found [15] to be 9·3 : 1. If we again use the assumption made above, we have:

$$(3k_{\beta CH} + 2k_{\alpha CH} + k_{OH})\text{eth}/(3k_{CH} + k_{OH})\text{meth} = 9{\cdot}3,$$

then, from (VI) it is found that:

$$(3k_{\beta CH} + k_{OH})\text{eth}/(3k_{CH} + k_{OH})\text{meth} = 1, \qquad \text{(VII)}$$

which is plausible and shows inner consistency.

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[15] Baxendale and Smithies, *Z. phys. Chem.* (*Frankfurt*), 1956, **7**, 242.

DISCUSSION

Selectivity in the Abstraction Reaction.—Our isotopic results show that the α-position in ethanol is attacked by hydrogen atoms because the hydrogen gas from $CH_3{\cdot}CD_2{\cdot}OH$ in water contains deuterium. That the β-position is attacked as well is seen from the protium content of the gas from $CH_3{\cdot}CD_2{\cdot}OD$ in deuterium oxide. So far as concerns the possibility of attack upon the hydroxyl, the value of (D/H)eth is nearly the same for $CH_3{\cdot}CD_2{\cdot}OH$ in water and in deuterium oxide (in the latter case the alcohol is converted into $CH_3{\cdot}CD_2{\cdot}OD$) (Table 1 and 3). Similarly the results for $CH_3{\cdot}CH_2{\cdot}OD$ in D_2O (Table 2) are in agreement with the assumption that all deuterium gas is due to the " molecular " yield and orginates from the deuterium oxide. Thus our results show no attack on the hydroxylic hydrogen by H atoms, within the limits of our experimental accuracy. They agree in this respect with the results of Baxendale and Hughes for methanol.[7]

These results show that the selectivity of abstraction is in the order of the bond strengths. Generally, when there are different positions for attack, there is selectivity when a saturated hydrocarbon chain is attacked by a radical: [16] the α-hydrogen is preferentially lost when ethanol is attacked by hydroxyl.[16] But the selectivity depends upon the reactivity of the attacking radical—the bond rupture in the transition state and the selectivity of abstraction become smaller the more reactive the attacking radical is. This is also true, of course, for the deuterium isotope effect [17] and in the limit no difference between abstraction of D and H is to be expected if the attacking species has a large energy excess (" hot " radicals).[9] In the present case the selectivity and the isotope effect found are high and are compatible with recent results of isotope effects in hydrogen abstraction.[18] It is thus evident that hydrogen atoms reacting in the irradiated water are not " hot," and that the isotopic bonds undergoing reactions (a) and (b) are broken in the activated complex.[9]

ΔE_a for the isotopic abstraction reactions from a carbon–hydrogen bond varies from 1·1 to 1·67 kcal./mole,[9] while the difference in zero-point energies of a C–H and a C–D bond is 1·25 kcal./mole. For α-deuterated ethylbenzene a value of $\Delta E = 1{\cdot}56 \pm 0{\cdot}1$ kcal./mole [9] was found for the isotopic reactions of methyl radicals and the frequency factor ratio $\nu_D : \nu_H$ was found to be 1·24. As the temperature range available for aqueous solutions is limited the temperature-dependence was not investigated in our experiments. There is thus an uncertainty in the value of ΔE. It seems nevertheless from our results that k_D/k_H for radical abstraction is similar in the gas phase,[9] in a liquid non-polar solvent,[9] and in a polar solvent, as in our case. High isotope effects ($k_H/k_D \approx 16$) similar to ours have been found recently [18] for aqueous solutions and were attributed to tunnelling [18,19] during hydrogen transfer reactions.

t-Butyl Alcohol.—For t-butyl alcohol the total hydrogen yield was much lower than for ethanol. Deuterium atoms formed from the water disappear without the formation of hydrogen gas. As the carbon–oxygen bond in t-butyl alcohol is much weaker than in ethanol the reaction

$$(3)\ ROH + H \longrightarrow R + H_2O$$

will be important in this case, as also when t-butyl alcohol is attacked by hydrogen atoms formed in the photochemistry of chromous ions.[20] If we assume that for ethanol removal of hydrogen from the hydroxyl group [reaction (3)] may be neglected, but that for t-butyl alcohol both reaction (3) and reaction (2) (removal of hydrogenation from C–H bonds) must be taken into account, then $k_3/k_2 = 1{\cdot}64$ results for the latter. This value agrees

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[16] Lewis and Symons, *Quart. Rev.*, 1958, **12**, 230.

[17] Wiberg, *Chem. Rev.*, 1955, **55**, 713.

[18] Stewart and Van der Linden, *Discuss. Faraday Soc.*, 1960, **29**, 211.

[19] Bell, *Discuss. Faraday Soc.*, 1960, **29**, 253.

[20] Collinson, Dainton, and Malati, *Trans. Faraday Soc.*, 1959, **55**, 2096.

quite well with the value of 1·5 ± 0·5 found in photochemistry.[20] (D/H)Bu^t is calculated from Table 2 to be 0·25, which is more than twice the ratio of deuterium atoms to hydrogen atoms in $(CH_3)_3C\cdot OD$ (D/H = 0·11).

The yield of atomic hydrogen, G(H), calculated for the radiation chemistry of the *pure* alcohols[3b] should thus be modified in such a way as to take into account reaction (3), *i.e.*, it should be multiplied by $(k_2 + k_3)/k_2$. This may explain some of the discrepancies found.[3b]

Correlation with Other Systems.—The hydrogen yields recorded in the Tables are somewhat higher than corresponding figures of other authors. As pointed out, the G value may be ~7% high if the $G(Fe^{3+})$ value to be used in the dosimetry is the lower one.[12b] Even so, the hydrogen yields found for 0·1M-alcohol in 0·8N-sulphuric acid are significantly higher than those found for ferrous sulphate solutions.[7,8] At this concentration of ethanol direct excitation by electrons is not likely. On the other hand, the reaction of ethanol with hydroxyl radicals and hydrogen atoms[21] (or their precursors) may prevent some recombination of these radicals.

This view is consistent with the fact that the yield of hydrogen peroxide is much decreased when the ethanol concentration is increased from 10^{-2}M to 1M.[6] In D_2O, if instead of deuterium gas being formed by recombination, the atoms react with ethanol, two HD molecules should be formed by abstraction from the ethanol by reaction (2). Elimination of the back-reaction, $D + OD \longrightarrow D_2O$, leads to further production of HD. In agreement with these views the D/H values for high ethanol concentrations (Table 2) are indeed lowered towards unity. For methanol[7] the situation might be somewhat different because of a smaller scavenging power (absence of α-hydrogen).

We must note the discrepancy (Table 2) between the $G(D_2)$ values in 0·1N- and 0·8N-sulphuric acid. Our results agree with those of Baxendale and Hughes[3b] for 0·1N-, and of Coatsworth, Collinson, and Dainton[22] for 0·8N-acid. The difference thus appears to be real.

For pure organic liquids, Adams, Baxendale, and Sedgwick[3b] found $G(H) = 2{\cdot}7$ for the hydrogen-atom yield and $G_m(H_2) = 1{\cdot}65$ for the molecular-hydrogen yield (not influenced by the presence of benzoquinone, a good scavenger for hydrogen atoms). The known relation[23] between radical and molecule yields in various solvents makes it likely that the high $G_m(H_2)$ found for ethanol is not due to recombination of hydrogen atoms. Burr[4] suggested that with pure ethanol all the hydrogen evolved is due to abstraction by atomic hydrogen, which should therefore be available. The position may be reconciled if we assume that, because of the weakness of the α-C–H bond in ethanol, hydrogen atoms once formed may abstract hydrogen readily from the original or neighbour molecule without benzoquinone's being able to intervene. Burr found[4] that 42% of deuterium was contained in the gas evolved from irradiated pure $CH_3\cdot CD_2\cdot OH$. If we assume with Burr that the contribution of " molecular " hydrogen is small, and that dehydrogenation of ethanol by hydrogen atoms is comparable for aqueous and pure ethanol, our value of (D/H)eth (0·47) leads to the value D/H = 1·08 for hydrogen atoms formed from $CH_3\cdot CD_2\cdot OH$ in the reaction

$$(4)\quad RH \rightsquigarrow R + H$$

For pure $CH_3\cdot CH_2\cdot OD$ Burr[4] found that the deuterium percentage was 34·2. From our values for $CH_3\cdot CH_2\cdot OD$ in D_2O it seems that attack by H or OD is negligible and for pure $CH_3\cdot CH_2\cdot OD$ we obtain D/H = 2·15 for hydrogen atoms formed in reaction (4).

Thus, with these assumptions, the results do not agree with a mechanism where the

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[21] Riesz and Hart, *J. Phys. Chem.*, 1959, **63**, 858.

[22] Coatsworth, Collinson, and Dainton, *Trans. Faraday Soc.*, 1960, **56**, 1008.

[23] Armstrong, Collinson, and Dainton, *Trans. Faraday Soc.*, 1959, **55**, 1384; Cleaver, Collinson, and Dainton, *ibid.*, 1960, **56**, 1640.

hydrogen atoms originate from the α-position. They agree, however, with the assumption[3b] that electron capture may cause reaction 5:

$$(5)\ ROH + e \longrightarrow RO^- + H$$

giving hydrogen atoms in liquid ethanol originating from the hydroxyl group. These may then dehydrogenate the α-position of the same or a neighbouring molecule.

If we assume that part of $G_m(H_2)$ originates in a true " molecular " process, in which one excited ethanol molecule loses one molecule of hydrogen from the α-position, the calculated contribution of reaction (5) will be even higher.

Reaction (5) is contrary to the evidence from mass-spectroscopy,[4] where the ethanols give mainly hydrogen atoms from the α-position. For that in liquid ethanol, however, the situation appears to be different.

A molecular process *via* excitation which would give hydrogen gas originating from α- and OH-positions of the same molecule is not likely,[24] but it would be indistinguishable from reaction (5) followed by intramolecular dehydrogenation.

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[24] Okabe and McNesby, *J. Chem. Phys.*, 1961, **34**, 668.