

[CONTRIBUTION FROM THE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

## The Radiolysis Products from Ethyl Alcohol; Effect of Total Energy Input on the Radiolysis Products

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Data are presented on the effect of increasing bombardment on yields of some products formed in the helium ion irradiation of liquid ethyl alcohol. The energy input was varied from 0.029 to  $2.7 \times 10^{22}$  e.v./ml. Hydrogen, total carbonyl products and vicinal glycol yields decrease markedly with increasing bombardment. The addition of acetaldehyde or hexene-1 causes a marked decrease in the yield of hydrogen but smaller changes in other products. The results are discussed in terms of mechanisms involving charge or excitation exchange and radical traps.

The radiolysis products resulting from the bombardment of various alcohols with high-energy helium ions have been described by McDonnell and Newton.<sup>2</sup> These data were taken at a total energy input of about  $0.6 \times 10^{22}$  e.v./ml. A recent check on ethyl alcohol by one of the authors (ASN) at lower levels of energy input has shown a marked change in radiolysis product yield with total energy input. Combining these new points with some very old data<sup>3</sup> run with a small volume target chamber, the yields of most products are shown to decrease with an increase in total bombardment.

Though few studies have been made on the radiation chemistry of pure organic materials in which the total energy input has been varied, the effects reported here are not an isolated phenomenon. Patrick and Burton<sup>4</sup> showed that the polymers from benzene increase in average molecular weight while the yield of double bonds in such polymers decreases with increasing total energy input. Virginia Burton<sup>5</sup> found a marked change in the composition of gas produced in the deuteron bombardment of oleic acid with the increasing bombardment.

### Experimental

The ethyl alcohol used in these bombardments was purified as described previously.<sup>2</sup> No difference in properties between batches purified was found:  $n_D^{25}$  1.3591,  $d_4^{25}$  0.7851; literature values, 1.35956, 0.78506.<sup>6</sup> The technique for bombarding the samples receiving  $0.4 \times 10^{22}$  e.v./ml. and higher total energy input was essentially that described previously. For the low total energy input bombardments, glass cells of the type described by Garrison, Haymond and Weeks<sup>7</sup> were used. All bombardments were made with about 100 ml. of alcohol except those at energy inputs of  $2 \times 10^{22}$  e.v./ml. and above where the volume of alcohol was 40 ml. The liquid temperature varied from 16 to 25° in the various bombardments.

For bombardments of energy input  $0.9 \times 10^{22}$  e.v./ml. and higher, an average beam current of 2  $\mu$ amp. was maintained though considerable fluctuation occurred due to unsteadiness in operation of the cyclotron. The points at low energy input were made with an average beam current of about 0.1  $\mu$ amp. It is not clear whether reducing the average beam current actually reduces the number of particles

in each pulse (repetition rate =  $10^7$  cycles/second) or whether the number of pulses is reduced by operation on a low frequency ripple on the oscillator as the beam current is reduced.<sup>8</sup> All experiments were not carried out under identical conditions of volume of liquid or volume available for gas expansion. Control of these factors might have led to more self-consistent results and less spread in the points.

In Fig. 1 the observed yields from a total energy input,  $E$ , have been plotted against the total energy input. This yield has been designated as  $\bar{G}$  as it is an average yield over the whole energy input from  $E = 0$  to  $E = E$ . Another type yield which might be calculated is the differential yield, that is the yield of a product formed in any energy interval between  $E$  and  $E + \Delta E$ . The data here are not sufficiently self-consistent for differential yields to be significant. The effect of increasing energy input is to cause a marked decrease in the yields of the principal reduced and oxidized products as well as the total reduction observed in the system. Especially marked are the changes in yields of hydrogen, total carbonyl products and vicinal glycols. It appears that the carbonyl and glycol products are acting as "protective" agents for the alcohol.

In Table I are presented the results of adding acetaldehyde and hexene-1 to ethyl alcohol prior to bombardment. It is seen that there is a considerable effect on the yield of hydrogen and less effect on the yields of heavier products. The yield of hydrogen in the acetaldehyde-containing sample is less than in a bombardment of pure alcohol where the same amount of acetaldehyde is produced because in pure alcohol the yield of hydrogen is decreasing as acetaldehyde is formed and the recorded value is the average yield over the whole bombardment rather than the differential yield at the end of the bombardment.

### Discussion

There are at least two possible mechanisms by which these products could act as protective agents. First is the exchange of excitation energy from the alcohol to a molecule with lower energy states. After transfer this energy may then be dissipated by collisional deactivation, by light emission, or by undergoing chemical changes which do not lead to any of the measured product types. This is the type of process Manion and Burton<sup>9</sup> postulated for the "protection" of cyclohexane by benzene and Burton and Patrick<sup>10</sup> for the "protection" of cyclohexane by benzene- $d_6$ . The mechanism was supported by the results of Patrick and Burton<sup>11</sup> who found propionaldehyde not to be protected by benzene- $d_6$ , consistent with the fact that propionaldehyde has lower energy states than benzene- $d_6$ , while cyclohexane has no such lower states.

The second possible mechanism is the action of aldehydes, glycols and unsaturated compounds as

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(9) J. P. Manion and M. Burton, *J. Phys. Chem.*, **56**, 560 (1952).

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(11) W. N. Patrick and M. Burton, *ibid.*, **58**, 424 (1954).

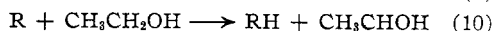
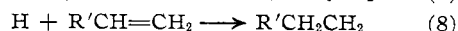
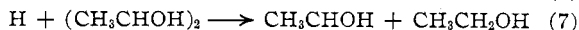
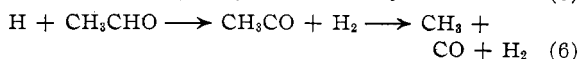
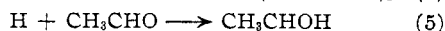
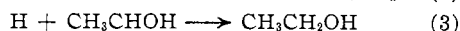
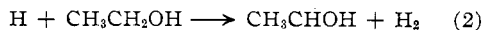
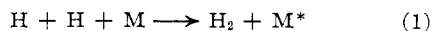
TABLE I  
EFFECT OF ADDED IMPURITIES ON THE YIELDS OF PRODUCTS  
FROM THE HELIUM ION RADIOLYSIS OF ETHYL ALCOHOL

System energy input, e.v. $\times 10^{22}$ /ml. Product	Yields G of product specified in system				
	Pure $C_2H_5OH$ 0.029	$C_2H_5OH$ +0.72% $CH_3CHO$ 0.028	Pure $C_2H_5OH^a$ 0.3	$C_2H_5OH$ +1% hexene-1 0.59	Pure $C_2H_5OH$ 0.60
$H_2$	4.10	3.52	3.8	2.83	3.46
CO	0.093	0.090	0.097	0.10	0.11
$CH_4$	.43	.40	.43	.40	.43
$C_2H_4$	.22	.20	.20	.20	.17
$C_2H_6$	.18	.16	.18	.17	.17
Total carbonyl	3.00	..	2.6	2.26	2.2
vic-Glycol	1.40 $\pm$	1.33 $\pm$	1.3	1.07	1.05
	0.05	0.05			
Total reduction	9.3	8.18	8.8	7.67 <sup>b</sup>	8.19

<sup>a</sup> Read from curves in Fig. 1. The amount of acetaldehyde added corresponds to that found in a bombardment of this energy input. <sup>b</sup> Figure does not include *n*-hexane which was identified as a product but not quantitatively measured.

radical traps. Such action in the bulk of the solution will result in the capture of hydrogen radicals which have escaped from the site of the initial excitation; the larger radicals are more efficiently trapped in the liquid cage at the initial site so they can be expected to be less affected by the presence or absence of aldehyde or other molecules in the bulk solution.

McDonell<sup>12</sup> has shown the yield of glycol in water solutions of methanol to be almost independent of the methanol concentration over a wide concentration range. His postulated reactions are analogous to reactions 1 to 4 below. In order to explain the effect of added aldehyde and unsaturated compounds as well as the effect of product buildup on the observed yields of products other radical reactions are necessary. Reactions 1 to 12 cover most of the possibilities.



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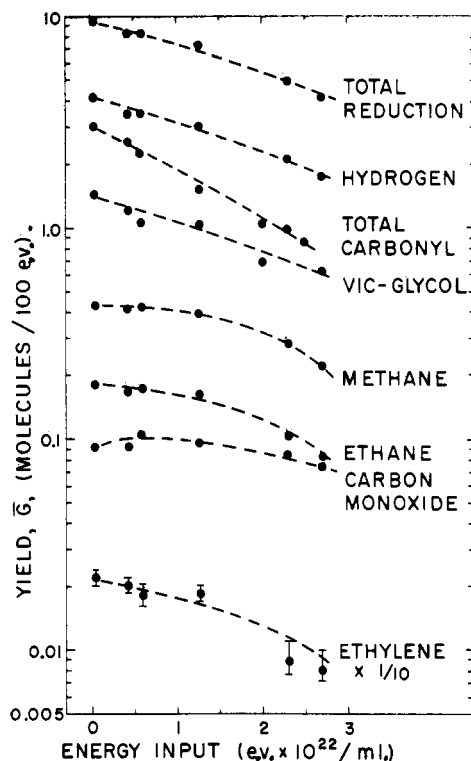
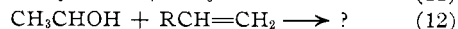
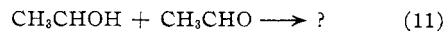


Fig. 1.—Effect of total energy input on the apparent yield of various products formed in the helium ion irradiation of liquid ethyl alcohol.



Reactions 5, 7, 8 and 9 lead to the disappearance of hydrogen radicals without formation of hydrogen as a product. Reactions 5 and 10 lead to the formation of  $1/2$  a glycol molecule, while reactions 3 and 7 lead to the disappearance of  $1/2$  a glycol molecule. Therefore, addition of aldehyde or an unsaturated compound would reduce the hydrogen yield but have little effect on the yield of glycol provided the activation energies of reactions 11 and 12 are high.

It is probable that both the mechanisms involving charge excitation transfer and radical traps are involved in the change in yield of products with increasing bombardment. With the limited data on hand one cannot now estimate the relative importance of the two effects.

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