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The Addition Reactions of Ethanol to Ethylene Induced by Gamma-ray Irradiation in the Gaseous Phase. I. Results and the Reaction Mechanisms

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In the reaction named in the title, the major products of the reactions in the gaseous phase were 2-alkanols, 3-methyl-3-alkanols and 2-ketones, while low hydrocarbons were found only at temperatures higher than about 150°C. The reactions in the liquid phase, carried out at 100°C, did not give 2-ketones. The following conclusions were obtained by the analysis of the results. The major primary precursor is 1-hydroxyethyl radical. The radicals produced by its addition to ethylene, $CH_3\text{-}CH(OH)\text{-}(CH_2)_{2n}\cdot$, give not only 2-alkanols but also radicals, $CH_3\text{-}\dot{C}(OH)\text{-}(CH_2)_{2n-1}\text{-}CH_3$, as a result of rearrangement by the intramolecular hydrogen transfer. Some of the latter radicals act as precursors of 3-methyl-3-alkanols by their addition to ethylene, while the rest of the radicals give 2-ketones by hydrogen abstraction by ethylene. The latter reaction gives the ethyl radical, which is the precursor of various hydrocarbons. The intramolecular hydrogen transfer occurs even in the liquid phase to give 3-methyl-3-alkanols, but the rearranged radicals can give 2-ketones only in the gaseous phase.

The addition reaction of 2-propanol to ethylene, induced by gamma-ray irradiation in the gaseous phase, was studied in a previous paper[1] in order to compare the reactions in the gaseous phase with those in the liquid phases, since the latter reactions had been already reported by Hirota and Hatada.[2] However, in the previous paper,[1] most of the products could not be identified by gas chromatography, as the standard reagents corresponding to the expected compounds were not available. Therefore, ethanol was used instead of 2-propanol in the present study, because the addition products of ethanol to ethylene were expected to be simpler than those of 2-propanol, furthermore, ethanol might give some more information about the dependence of the reactions on the chemical structure in comparison with the results of 2-propanol.

The whole reaction scheme for the present system is discussed in the present paper, while the results will be analyzed kinetically on the basis of the present scheme in the following paper, where the chain transfer constants will also be estimated as a result of the analysis.

Experimental

The experimental procedures were the same as in the previous paper.[1] The samples, collected in a hard-glass tube (about 50 cc), were irradiated at 1.0×10^5 R/hr of cobalt-60 gamma rays for five hours. The composition of the samples and the irradiation temperature are listed in Table 1. Two or three runs were carried out for each conditions. The amounts of the products were almost proportional to the irradiation time.

After irradiation, the gases non-condensable at −196°C were analyzed by mass-spectrometry in order to determine the amounts of hydrogen and methane produced. Then, the amount of ethylene consumed was determined by measuring the decrease in the gases non-condensable at −94°C (frozen methanol). The condensable liquid was analyzed as soon as possible, after opening the sample tube; it was analyzed by gas chromatography, using a column of PEG 6000, at 70, 115 and 150°C. The products were identified from their retention time by adding the standard reagent to the sample.

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[1] T. Kurihara and H. Hotta, This Bulletin, **37**, 1448 (1964).

[2] K. Hirota and M. Hatada, *ibid.*, **34**, 1644 (1961).

TABLE 1. EXPERIMENTAL CONDITIONS

No.	Composition, 10^{-3} mol		Temp. °C
	Ethanol	Ethylene	
1	3.5	2.1	198
2	3.5	2.1	175
3	3.5	2.1	171
4	3.5	2.1	150
5	3.5	2.1	125
6	3.5	2.1	100
7	5.52	0.0	175
8	5.04	0.59	175
9	4.20	1.34	175
10	3.93	1.70	175
11	3.68	1.92	175
12	2.38	2.38	175
13*	855	3	100

* No. 13 was irradiated at liquid phase.

TABLE 2. RELATIVE MOLAR SENSITIVITY OF GAS CHROMATOGRAPHY

Compound	Molecular weight	Relative molar sensitivity	
		This work	Messner *et al.*'s value[3]
n-Pentane	72.15	1.36	1.46
n-Hexane	86.18	1.39	1.71
n-Heptane	100.21	1.76	1.99
n-Octane	114.23	2.01	2.22
Methanol	32.04	0.74	0.76
Ethanol	46.07	1.00	1.00
n-Pentanol	88.15	1.50	1.49
2-Butanol	74.12	1.34	1.35
2-Hexanol	102.18	1.70	—
2-Octanol	130.23	1.95	—
2-Butanone	72.11	1.40	1.36
2-Hexanone	100.16	1.51	—
2-Octanone	128.22	1.71	—

The relative molar sensitivities of gas chromatography, α, for the identified products were determined experimentally and compared with the reported values,[3] as is shown in Table 2. They were linear to their molecular weight in the homolog.

Estimation of *G*-Values from the Gas Chromatography. The *G*-value of the *j*th product, G_j, is estimated by the equation;

$$G_j = 1.10\times 10^{12}\left(\frac{M_p \alpha_j A_j}{tD(\sum \rho_i m_i)A_p}\right) \qquad \text{(i)}$$

where

M_p=amount of the parent reactant (ethanol) in mol,

α_j=relative sensitivity of gas chromatography for the *j*th product to that of the parent reactant,

A_j=peak area of the *j*th product in the gas chromatogram,

t=irradiation time in hr,

D=dose rate measured by the Fricke dosimeter in R/hr,

ρ_i=relative electron density of the *i*th reactant to air,

m_i=mass of the *i*th reactant in g,

A_p=peak area of the parent reactant in the gas chromatogram.

The W_{air} is assumed to be 34.0 eV/ionpair in Eq. (i). The initial amount of the reactants can be used in Eq. (i) for the low conversion, which was less than 3 per cent in the present experiments. The relative electron densities are 1.14 and 1.13 for ethylene and ethanol respectively.

Results

Non-condensable Gases. The *G*-values of hydrogen, methane, and the consumed ethylene for experiments 7—12, as estimated for the total absorption energy in the mixture, are plotted in Fig. 1 against the mole fraction of ethylene in the mixture. The $G(-C_2H_4)$ value is proportional to the mole fraction of ethylene.

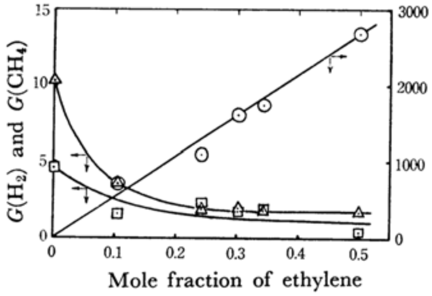

Fig. 1. $G(H_2)$ (△), $G(CH_4)$ (⊡) and $G(-C_2H_4)$ (⊙) at 175°C as the function of the mole fraction of ethylene.

As may be seen in Table 3, the present *G*-values of hydrogen and methane for gaseous pure ethanol (experiment 7) are relatively large as compared to the various reported values in the gaseous phase[4-6] as well as in the liquid phase.[6,7] On comparing the irradiation conditions with each other, the *G*-value is found to be large at the conditions under which the combination of primary species is prevented, that is, for the lower LET radiation, at a higher temperature and at a lower pressure. The possibility of an LET effect in the gaseous phase had usually been ignored, but Myron and Freeman recently suggested such an effect.[6] The $G(H_2)$

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[3] A. E. Messner, D. M. Rosie and P. A. Argabright, *Anal. Chem.*, **31**, 230 (1959).

[4] L. W. Sieck and R. H. Johnson, *J. Phys. Chem.*, **69**, 1699 (1965).

[5] J. M. Ramaradhya and G. R. Freeman, *Can. J. Chem.*, **39**, 1836 (1961).

[6] J. J. J. Myron and G. R. Freeman, *ibid.*, **43**, 1484 (1965)

[7] G. E. Adams, J. H. Baxendale and R. D. Sedgwick, *J. Phys. Chem.*, **63**, 854 (1959).

TABLE 3. RADIOLYSIS OF ETHANOL AND ETHYLENE

Run	Reactant	Radiation	Temp. °C	Phase (pressure)	$G(H_2)$	$G(CH_4)$	$G(H_2)_M$	$G(CH_4)_M$	Reference
a	Ethanol	^{60}Co γ-rays	175	Gas (4 atm)	10.29	4.63	1.66	0.42	This work
b	Ethanol	2MeV electron	25	Gas (42 torr)	11.0	0.90	3.50	0.32	4
c	Ethanol	^{210}Po α-rays	108	Gas (?)	7.6	1.66	—	—	5
d	Ethanol	^{60}Co γ-rays	105	Gas (800 torr)	7.5	2.3	1.8	0.82	6
e	Ethanol	^{60}Co γ-rays	25	Liquid	4.2	0.5	1.1	0.10	6
f	Ethanol	^{60}Co γ-rays	25	Liquid	4.35	0.60	1.65	0.16	7
g	Ethylene	^{60}Co γ-rays	25	Gas (400 torr)	2.0	0.10	—	—	8
h	Ethylene	1MeV electron	25	Gas (100 torr)	1.2	0.22	—	—	9
i	Ethylene	2MeV electron	25	Gas (150 torr)	1.28	0.12	—	—	10

of ethylene is also larger for gamma-rays[8] than for fast electrons[9,10] (Table 3).

The *G*-values of hydrogen and methane for experiment 12, at which the mole fraction of ethylene is the highest (0.5), are shown as $G(H_2)_M$ and $G(CH_4)_M$ in line a of Table 3. They are nearly equal to the unscavengable $G(H_2)$ of runs d, e and f, shown in the columns of $G(H_2)_M$ and $G(CH_4)_M$. They are assumed to be the molecular yield. As seen in Fig. 1, the *G*-values of hydrogen and methane do not increase with an increase in the mole fraction of ethylene, that is, they are independent of the chain addition reactions. This means that the hydrogen abstraction reactions by hydrogen atoms or methyl radicals do not occur in the present system.

Condensable Products. As compared with the retention time of methanol, the gas chromatogram of the condensable liquid gave nineteen peaks of a shorter retention time between butane and octane, and fifteen peaks of a longer retention time between 2-butanone and 2-octanone, however, no distinct peak could be detected after the peak of 2-octanol. Among these, the identified products are five *n*-hydrocarbons, three 2-alkanols, two *t*-alcohols, and three 2-ketones. Unidentified products are denoted by the peak number in the present paper. Their *G*-values for experiment 11 are shown in Table 4 in the order of the retention time. The dependence of their *G*-values on the ethylene mole fraction is shown in Figs. 2, 3 and 4 respectively from the results of experiments 8—12.

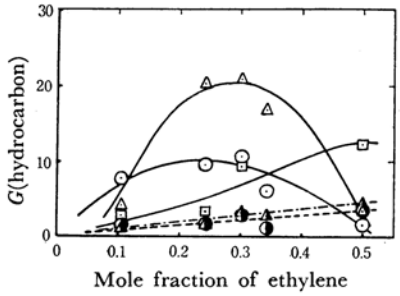

Fig. 2. The *G*-values of hydrocarbons at 175°C as the function of ethylene mole fraction: butane (⊙), hexane (△), octane (⊡), pentane (◑) and heptane (▲).

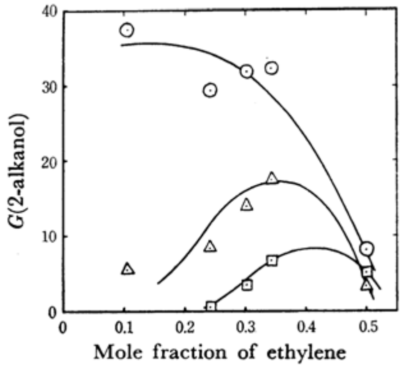

Fig. 3. The *G*-values of 2-alkanols at 175°C as the function of ethylene mole fraction: 2-butanol (⊙), 2-hexanol (△), and 2-octanol (⊡).

Furthermore, peaks having retention times corresponding to methanol and *n*-pentanol were observed. Their *G*-values for experiment 11 are shown in parentheses in Table 4. Since the peak of *n*-propanol overlapped with that of water, its *G*-value could not be determined quantitatively. However, as will be discussed later, there is some doubt concerning these identifications.

There were no distinct peaks in the gas chromatogram which correspond to diethyl ether, ethyl *n*-butyl ether, di-*n*-butyl ether, *n*-butanol, *n*-hexanol, acetaldehyde, *n*-propylaldehyde, and paraldehyde. Since ethers and aldehydes, which would have shorter retention times, were not detected in any samples, all the products with shorter retention times than that of methanol are considered to be hydrocarbons. Such products were not formed at lower temperatures (experiments 5 and 6).

Diols, namely, ethylene glycols, 1, 3- and 2, 3-butanediols, give no distinct peak under the present conditions of gas chromatography. Therefore, diols could not be detected even if they were produced.

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[8] F. W. Lampe, *Radiation Res.*, **10**, 691 (1959).
[9] G. G. Meisels, *J. Am. Chem. Soc.*, **87**, 950 (1965).
[10] K. Yang and P. J. Manno, *J. Phys. Chem.*, **63**, 752 (1959).

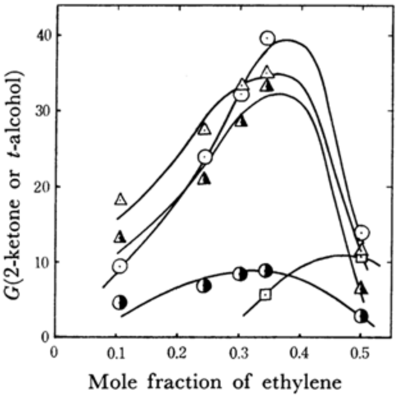


Fig. 4. The G-values of 2-ketones and t-alcohols at 175°C as the function of ethylene mole fraction: 2-butanone (⊙), 2-hexanone (△), 2-octanone (⊡), 3-methyl-3-pentanol (◑), and 3-methyl-3-heptanol (▲).

TABLE 4. G-VALUES FOR EXPERIMENT 11

−Ethylene		1740	
Total detected products		302.0	
Hydrogen	1.8	Methanol	(13.4)
Methane	1.9	2-Butanone	39.7
n-Butane	6.1	2-Butanol	32.3
1	6.3	16	1.5
n-Pentane	1.1	3-Methyl-3-pentanol	8.8
3	1.2		
4	3.0	2-Hexanone	35.1
n-Hexane	16.8	2-Hexanol	17.4
6	9.3	n-Pentanol	(16.0)
n-Heptane	2.8	3-Methyl-3-heptanol	33.3
10	22.5		
n-Octane	6.0	2-Octanone	5.7
13	10.6	2-Octanol	6.7
14	2.7		

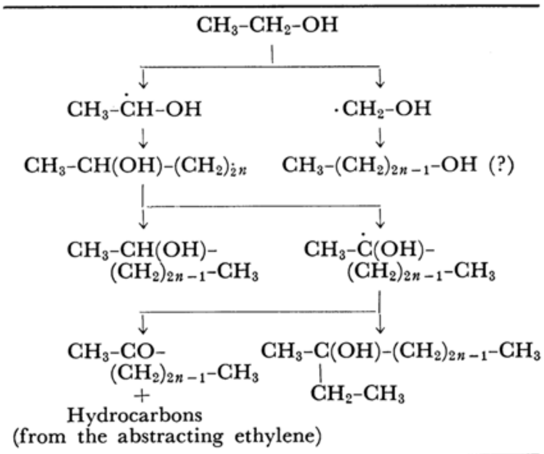
Discussion

Since ethylene is relatively stable for radiation due to the double bond, the absorbed energy is dissipated chemically after being transferred to ethanol in the mixture of ethanol and ethylene. Therefore, most of the primary species of the radiolysis are given from ethanol. Then, the G-values estimated for the total absorbed energy in the mixture by Eq. (i) may be correct. The result can be interpreted on this assumption by the reaction scheme shown in Table 5 as follows.

Radicals from Ethanol. The major primary radical formed from ethanol is 1-hydroxyethyl radical, $CH_3-\dot{C}H-OH$, which is the precursor of 2-alkanols.

Although hydroxymethyl radical, $\cdot CH_2-OH$, seems to be formed to some extent from the production of odd n-alkanols, for example, n-pentanol, it is not sure whether or not their identification only from the retention time of gas chromatography is correct. This is because the chain process containing the methyl abstraction reaction from ethanol is not so expected, as this gives a high G-value, as seen in Table 4.

TABLE 5. THE WHOLE REACTION SCHEME



It may be concluded that 2-hydroxyethyl radical, $\cdot CH_2-CH_2-OH$, and ethoxy radical, $CH_3-CH_2-O\cdot$, are not formed, because not even n-alkanols and ethers were detected. Myron and Freeman concluded, for the radiolysis of ethanol, that ethoxy radical is formed to a significant extent in the liquid phase, but not in the gaseous phase.[6] The results of the ion-molecule reaction of ethanol and methanol in a mass spectrometer indicate that the hydrogen in the hydroxy group is less reactive than in the methylene and methyl groups.[11,12] They also concluded that the relative contributions of three different groups in the ethanol molecule to hydrogen production are in the order $CH_2 > OH \gg CH_3$.[6] According to them, the reactions are ionic. On the other hand, as has been seen above, the major primary radical for the radical chain reaction with ethanol is 1-hydroxyethyl radical.

Precursor of 2-Ketones. As seen in Table 4, 2-ketones are produced, while no acetaldehyde is found. The latter fact suggests that the precursor of 2-ketones is not acetyl radical, $CH_3-\dot{C}=O$. If 1-hydroxy-1-methyl alkyl radical, $CH_3-\dot{C}(OH)-(CH_2)_{2n-1}-CH_3$, is formed by the intramolecular hydrogen transfer from an α-position to an ω-position in the precursor radical of 2-alkanols, $CH_3-CH(OH)-(CH_2)_{2n-1}-\dot{C}H_2$, this radical might give 2-ketones as well at t-alcohols. In fact, t-alcohols are detected, as seen in Table 4. Such an isomerization is assumed for the production of s-alcohols in the liquid mixture of methanol and

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[11] K. R. Ryan, L. W. Sieck and J. H. Futrell, *J. Chem. Phys.*, **41**, 111 (1964).

[12] T. Yamamoto, Y. Shinozaki and G. Meshitsuka, *Shitsuryobunseki*, **12**, No. 26, 93 (1964).

ethylene by cobalt-60 gamma-ray irradiation.[13] A similar intramolecular rearrangement is suggested for the isomerization of hydrocarbons, as will be discussed later.[14,15]

It has been reported in the previous paper[1] that acetone is produced in a high yield from the gaseous mixture of 2-propanol and ethylene. This high yield is attributed to the hydrogen abstraction reaction of ethylene from the hydroxyl group;

$$CH_3\text{-}\dot{C}(OH)\text{-}CH_3 + C_2H_4 \rightarrow CH_3\text{-}CO\text{-}CH_3 + \cdot C_2H_5 \quad (1)$$

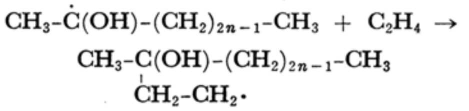
rather than to the disproportionation reaction;

$$2\ CH_3\text{-}\dot{C}(OH)\text{-}CH_3 \rightarrow CH_3\text{-}CH(OH)\text{-}CH_3 + CH_3\text{-}CO\text{-}CH_3 \quad (2)$$

Similarly, it is assumed in the present system that the intramolecularly-rearranged radicals react subsequently with ethylene to form 2-ketones;

$$CH_3\text{-}\dot{C}(OH)\text{-}(CH_2)_{2n-1}\text{-}CH_3 + C_2H_4 \rightarrow CH_3\text{-}CO\text{-}(CH_2)_{2n-1}\text{-}CH_3 + \cdot C_2H_5 \quad (3)$$

On the other hand, a part of the rearranged radicals give *t*-alcohols as a result of the addition to ethylene;



$$CH_3\text{-}\dot{C}(OH)\text{-}(CH_2)_{2n-1}\text{-}CH_3 + C_2H_4 \rightarrow CH_3\text{-}\underset{\substack{|\\ CH_2\text{-}CH_2\cdot}}{C}(OH)\text{-}(CH_2)_{2n-1}\text{-}CH_3 \quad (4)$$

In Fig. 4, the yields of 2-butanone and 2-hexanone show a dependence on the mole fraction of ethylene similar to those of 3-methyl-3-pentanol and 3-methyl-3-heptanol, as suggesting that they are formed through the competitive reactions of the same reactants, shown as reactions (3) and (4). The G(2-butanone)/G(3-methyl-3-pentanol) ratio is much different from the G(2-hexanone)/G-(3-methyl-3-heptanol) ratio. This shows that the rate of reaction (3) is very dependent on the chain length of the transient radical.

TABLE 6. APPEARENT ACTIVATION ENERGY kcal/mol

−Ethylene	5	*n*-Pentanol*	(10)
n-Butane	17	2-Butanol	12
n-Pentane	19	2-Butanone	16
n-Hexane	23	2-Hexanone	8
n-Heptane	22	2-Octanone	10
n-Octane	21	3-Methyl-3-pentanol	11
6	12	3-Methyl-3-heptanol	6
13	7		

* See text.

Furthermore, when the yields of 2-ketones in Fig. 4 are compared with those of the corresponding 2-alkanols in Fig. 3, the G(2-ketone)/G(2-alkanol) ratio is in the order of 2-hexanone>2-octanone>2-butanone. The apparent activation energy of the product formation is given in Table 6, estimated from the temperature dependence of the yields for experiments 1—6. The value of 2-ketones is also in the order of 2-hexanone<2-octanone<2-butanone. This shows that there is an optimum chain length for the intramolecular rearrangement to the transient radical.

Precursor of Low Hydrocarbons. The formation of hydrocarbons is initiated not by the primary species from the radiolysis of ethylene, but by ethyl radicals formed by reaction (3). This assumption is supported by the fact that most of the *n*-hydrocarbons have an even number of carbon atom, as seen in Fig. 2. Although ethyl radical is also formed by the addition of hydrogen atom to ethylene, the G(H) value from ethanol and ethylene is much lower than the total G-value of even *n*-hydrocarbons, as seen in Tables 2 and 3.

The unidentified products 1—14 in Table 4 are supposed to be hydrocarbons as has been mentioned already. Furthermore, they must be branched hydrocarbons. This isomerization by the intramolecular hydrogen tranfer has been assumed for *n*-alkyl radicals at higher temperaure,[14] and also for the chain branching in polyethylene during polymerization.[15]

Reactions in the Liquid Phase. Experiment 13 in Table 1, carried out in the liquid phase, gave only five condensable products, as seen in Table 7.

TABLE 7. G-VALUES FOR EXPERIMENT 13 (LIQUID PHASE)

13	9.6
14	6.4
2-Butanol	253.5
2-Hexanol	56.2
3-Methyl-3-heptanol	51.2

Two unidentified products had retention times between *n*-octane and methanol. They are the major products even if there are some products undetected at the present condition of gas chromatography.[13] It is interesting that no 2-ketones and low hydrocarbons are produced in the liquid phase. This is consistent with the assumption that both the products are formed by the same reaction, namely, reaction (3) in the gaseous phase. This difference may be due not only to the phase, but also to either the low mole fraction of ethylene or the lower reaction temperature (100°C).

The authors wish to express their appreciation to Dr. Hiroshi Itatani, Ube Industries, for his preliminary experiment.

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[13] M. Takehisa, M. Yasumoto and Y. Urano, private communication.

[14] A. S. Gordon and J. M. McNesby, *J. Chem. Phys.*, **31**, 853 (1959).

[15] M. J. Roedel, *J. Am. Chem. Soc.*, **75**, 6110 (1953).