The Radiolysis of Liquid cis-2-Butene

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Previous investigations of the radiation chemistry of unsaturated hydrocarbons have dealt almost exclusively with radiation-induced polymerization; little attention has been paid to the minor low-molecular-weight products. It therefore appeared of interest to investigate the low-molecular-weight products in the expectation that they might be produced through the non-free radical mechanism. This was of interest because it has been known that olefins (e. g., *cis*-2-butene in this investigation) and other unsaturated compounds behave as effective scavengers for hydrogen and free radicals.(1) Thus, almost all free radicals from the radiolysis of unsaturated compounds may easily react to form dimers and higher polymers, and may not contribute to the formation of the low-molecular-weight products (e. g., hydrogen and $C_1 \sim C_4$ products from C_4 hydrocarbons). Detailed studies of such systems might assist the understanding of the essential features of the molecular mechanism in the radiation chemistry. With these prospects, the radiolysis of liquid *cis*-2-butene at room temperature was undertaken in this investigation. *cis*-2-Butene is simple in chemical structure, although it is readily liquefied.

There has been, to the authors' knowledge, only one paper(2) dealing with the radiolysis of *cis*-2-butene. Kaufman(2) carried out the irradiation of butenes in gas and liquid phases and suggested that the ion-molecule processes are applicable to the dimer formation. On the other hand, Cundall(3,4) carried out radiolysis on particular systems (butenes in hydrocarbon solvents) and explained the cis-trans isomerization of 2-butene by means of the energy transfer mechanism from solvents. In this case the isomerization of 2-butene is not due to the direct effect of radiation.

Experimental

Materials.—Matheson pure-grade *cis*-2-butene was used after the usual degassing and bulb-to-bulb distillations. It was found by gas chromatography to contain less than 0.4% *trans*-2-butene. Commercial reagents of chemically-pure-grade benzene,

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1) K. Kikuchi, S. Sato and S. Shida, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **84**, 561 (1963).

2) P. C. Kaufman, *J. Phys. Chem.*, **67**, 1671 (1963).

3) R. B. Cundall and P. A. Griffiths, *J. Am. Chem. Soc.*, **85**, 1211 (1963).

4) R. B. Cundall and P. A. Griffiths, *Discussions Faraday Soc.*, **36**, 111 (1963).

naphthalene, anthracene, iodine, and *p*-benzoquinone were used as additives without further purification.

Irradiation.—The radiation employed in the radiolysis of liquid *cis*-2-butene was γ-rays from 16000 c. ^{60}Co. Measured amounts of *cis*-2-butene were sealed in vacuo at -196°C in glass ampoules 10 mm. in diameter and of a 10 ml. capacity fitted with breaker seals. Irradiations were made at room temperature. The total doses were 0.30×10^{21} to 3.59×10^{21} eV./g. for examining the dose dependence of products and 2.90×10^{21} eV./g. throughout the experiments to which additive materials were applied. The dose rate was 2.21×10^{19} eV./g. hr.

Analysis. — After irradiations the sample tubes were attached to the vacuum line and the seals were broken. The gases non-condensable at -196°C (hydrogen and methane) were collected and measured by an analysis device composed of a Toepler pump, a McLeod gauge, and a copper oxide furnace. Products condensable at -196°C were expanded into a reservior of a sufficiently large volume to maintain hydrocarbons up to C_8 in the gas phase. Aliquots of the gaseous mixture were then analyzed by a home-made reduced-pressure-type gas chromatograph. For the separation of $C_1\sim C_4$ hydrocarbons, a benzyl ether column was mainly used at room temperature, but a squalane-alumina column and a dimethylsulfolane column were also used. For the separation of $C_5\sim C_8$ hydrocarbons, a dioctylphthalate column was used at 80°C. After distillation of the volatile products in vacuo at room temperature, a viscous residue was found on the wall of the glass ampoules. This substance was readily soluble in acetone and was determined gravimetrically as a polymer of the butene.

Results and Dicussion

The major products in the radiolysis of liquid *cis*-2-butene at room temperature are hydrogen, *n*-butane, 1-butene, *trans*-2-butene, C_8 hydrocarbons, and higher polymers. Small amounts of $C_1\sim C_3$ and $C_5\sim C_7$ hydrocarbons are also formed. The formation of each product was estimated as a function of the energy absorbed in the liquid *cis*-2-butene (Fig. 1). The data in Fig. 1 show that each product formation is directly proportional to the energy absorbed; that is, the radiation chemical yield, *G*, the number of molecules formed per 100 eV. of energy absorbed in the system, is independent of the total energy absorbed. In view of the fact that *cis*-2-butene itself is an effective radical scavenger,*1 this result can be readily understood.

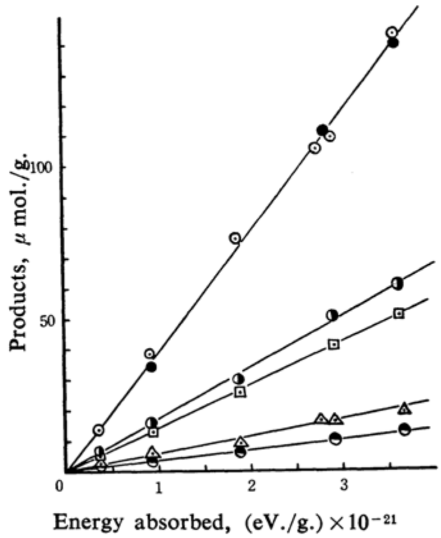

Fig. 1. Variation of products formation as a function of the energy absorbed, in the radiolysis of liquid *cis*-2-butene at room temperature. Dose rate: 2.21×10^{19} eV./g. hr.

⊙ *trans*-2-C_4H_8 △ 1-C_4H_8
⊡ *n*-C_4H_{10} ◑ H_2
◓ CH_4 ● C_8

The *G*-values of products in the radiolysis of liquid *cis*-2-butene at room temperature have been determined from Fig. 1 and are shown in Table I. The sum of *G*-values for hydrogen and $C_1\sim C_4$ hydrocarbons in Table I is 5.20, whereas it is 9.41 in the radiolysis of liquid *n*-butane at room temperature;$^{7)}$ these results indicate that a smaller amount of gaseous products (55% of the latter) is formed from an unsaturated hydrocarbon than from a saturated one. Further, the ratio $\{G(C_1\sim C_3)+G(C_5\sim C_7)\}/\{G(C_4)+G(C_8)\}$ is 0.098 for *cis*-2-butene and 1.53 for *n*-butane$^{7)}$ respectively, where $\{G(C_1\sim C_3)+G(C_5\sim C_7)\}$ represents the yield for the C–C bond rupture. These results indicate that in the butene radiolysis the reactive species formed by the C–C bond rupture (e. g., C_1, C_2, and C_3 radicals) do not make an important contribution to the formation of

TABLE I. THE *G*-VALUE OF THE PRODUCTS IN THE RADIOLYSIS OF LIQUID *cis*-2-BUTENE

Irradiation was made at room temperature. Dose rate was 2.21×10^{19} eV./g. hr.

H_2	1.02	1-C_4H_8	0.40
CH_4	0.21	*trans*-2-C_4H_8	2.29
C_2H_6	0.03	1,3-C_4H_6	0.10
C_2H_4	0.08	C_5	<0.01
C_2H_2	0.11	C_6	trace
C_3H_6	0.13	C_7	<0.01
n-C_4H_{10}	0.83	C_8	2.30

[*1] The gradual decrease in the *G*-values at higher doses has often been observed in the radiolysis of saturated hydrocarbons and explained by the scavenging effect of olefin products.$^{5,6)}$

5) H. A. Dewhurst, *J. Phys. Chem.*, **62**, 15 (1958).

6) S. Sato and S. Shida, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 435 (1961).

7) T. Miyazaki, S. Arai and S. Shida, This Bulletin, **37**, 1352 (1964).

low-molecular-weight products, but that the greater part of these reactive species may be converted to dimers or higher polymers.

Iodine and *p*-benzoquinone (BQ) were used as radical scavengers more effective than olefins. Table II lists several molecular and radical yields obtained with a *cis*-2-butene/BQ solution. The concentration range of BQ used here is 40 to 180 mM. With a *cis*-2-butene/I_2 solution (although we shall omit detailed information here), the same additive effect on the products formation except for the isomerization were observed as in the *cis*-2-butene/BQ system. The marked increase in the rate of cis-trans isomerization observed with the *cis*-2-butene/I_2 solution ($G=5.5$ at 10 mM) might be due to the catalytic action of iodine atoms and/or the electron-capture effect of iodine molecules. It seems that the effect of added iodine on the reaction mechanism is complicated and presents some difficulty.[8] As is shown in Table II, the free radical mechanism is not important for the formation of any low-molecular-weight products except methane and *n*-butane. Since 95% of *n*-butane is produced through the free radical mechanism, it is proposed that *n*-butane formation occurs by the disproportionation of *s*-butyl radicals: $2C_4H_9 \rightarrow C_4H_8 + C_4H_{10}$. Assuming that *cis*- and *trans*-2-butene are produced simultaneously with *n*-butane in the ratio of 1 : 1 in the disproportionation reaction, then one obtains the expected radical yield of *trans*-2-butene as 0.32, $\{G_R(n\text{-}C_4H_{10})-G_R(1\text{-}C_4H_8)\}/2$, which is in good agreement with the observed value, i. e., 0.29.[*2] Thus, at least 80% of the *trans*-2-butene is formed through the molecular mechanism.

Since the greater part of the low-molecular-weight products are formed through the molecular mechanism described above, such aromatic hydrocarbons as benzene, naphthalene, and anthracene were used as additives; they were expected to exert remarkable effects on the molecular mechanism. The variation in product yields with the concentration of the additives is given in Fig. 2. The rate of cis-trans isomerization is markedly affected by the sort of additives and their concentrations, whereas the rate of the formation of other products is not so much affected as in the case of isomerization. The increase in G(*trans*-2-butene) at lower concentrations and the decrease at higher concentrations are obvious. On the other hand, the dependence of G(*n*-butane) on additive concentrations is much less than that of G(*trans*-2-butene). Therefore, the decrease in G(*trans*-2-butene) at higher concentrations is not due to the radical-scavenging effect by additives.

TABLE II. THE MOLECULAR AND RADICAL YIELD OF THE PRODUCTS IN THE RADIOLYSIS OF LIQUID *cis*-2-BUTENE

Irradiation was made at room temperature.
p-Benzoquinone was used as a radical scavenger.
Total dose: 2.90×10^{21} eV./g.
Dose rate: 2.21×10^{19} eV./g. hr.

Product	Radical yield		Molecular yield	
	G_R	$(\%)_R$	G_M	$(\%)_M$
H_2	0.00	0	1.02	100
CH_4	0.12	57	0.09	43
C_2H_2	0.00	0	0.11	100
C_3H_6	0.00	0	0.13	100
n-C_4H_{10}	0.79	95	0.04	5
1-C_4H_8	0.16	40	0.24	60
trans-2-C_4H_8	0.29	13	2.00	87

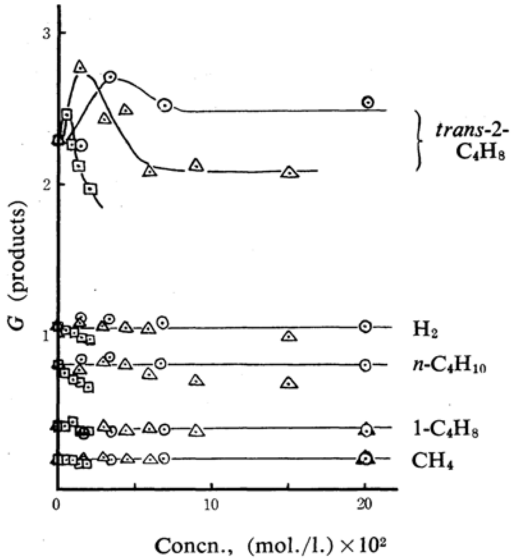

Fig. 2. Additive effects of benzene, nahthalene and anthracene on products formation in the radiolysis of liquid *cis*-2-butene at room temperature. Total dose: 2.90×10^{21} eV./g., Dose rate: 2.21×10^{19} eV./g. hr.
⊙ Benzene △ Naphthalene ⊡ Anthracene

The rate of cis-trans isomerization in pure liquid *cis*-2-butene is independent of the total doses, as is shown in Fig. 1. Therefore, the

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[8] T. Kudo and S. Shida, to be published.

[*2] On the other hand, if an assumption is made that in the disproportionation reaction of *s*-butyl radicals 1-butene, *trans*-2-butene, and *cis*-2-butene are produced with the ratio of 2 : 1 : 1, respectively,[9] as found in the corresponding gas-phase reaction, then the radical yield of *trans*-2-butene might be $0.79\times1/4=0.2$ and that of 1-butene $0.79\times1/2=0.4$. The former is again in agreement with the observed value, but not the latter. It is probable that the ratio of 1-butene to *cis*- or *trans*-2-butene is not the same as the ratio in the gas phase.

[9] B. S. Radinovitch and R. W. Diesen, *J. Chem. Phys.*, **30**, 735 (1959).

increase in *G*(*trans*-2-butene) at a lower concentration of additives is not due to the protection by aromatics of the initially-formed *trans*-2-butene from radical attack, a protection which was observed with olefin formation in the radiolysis of a cyclohexane/benzene mixture.[10]

The ionization potentials of benzene, naphthalene, and anthracene have been offered as 9.52, 8.12 and 7.23 eV., and their electron affinities as 2.19, 2.59, and 3.11 eV. respectively.[11] For *cis*-2-butene, the ionization potential is 9.34 eV.,[12] and the electron affinity is less than the values for the aromatics.[13] On the other hand, it may be considered that in the lower concentration of additives the interaction between additives and electrons prevails over the interaction between additives and positive butene ions in a spur, and that with an increasing concentration of additives the latter interaction cannot be set aside. Thus, comparing the results in Fig. 2 with the values listed above one may conclude that the increase in *G*(*trans*-2-butene) at a lower concentration of additives corresponds to the electron affinities of additives and the decrease at higher concentrations, to the ionization potentials of additives.

In view of the above discussion, the most reasonable conclusion to be drawn from the available data is as follows: The increase in *G*(*trans*-2-butene) at a lower concentration of additives may be due to the electron-capture effect of additives, which prolongs the lifetime of positive butene ions. As a result, the recombination process of electrons will be altered:

a) $\mathrm{Cis} \rightarrow \mathrm{Cis}^+ + e$ (Cis ; *cis*-2-butene)

b) $e + \mathrm{M} \rightarrow \mathrm{M}^-$ (M ; additives)

c) $\mathrm{Cis}^+ \rightarrow \mathrm{Trans}^+$ (Trans ; *trans*-2-butene)

d) $\mathrm{Cis}^+ + e$

$\rightarrow \mathrm{Cis}^* \rightarrow 1/4$; Cis (singlet)

$\searrow 3/4$; Cis (triplet) $\rightarrow 3/8$; Trans

$\searrow 3/8$; Cis

e) $\mathrm{Trans}^+ + e$

$\rightarrow \mathrm{Trans}^* \rightarrow 1/4$; Trans (singlet)

$\searrow 3/4$; Trans (triplet) $\rightarrow 3/8$; Trans

$\searrow 3/8$; Cis

where asterisks indicate excited states involving high levels of the different state manifolds, and " singlet " and " triplet " indicate the ground state and the first excited triplet state respectively. The additional processes b, c and e may occur beside the processes a and d if the additives are used. From the processes d and e, the net value, 1/4 of the primary ionization of *cis*-2-butene, additionally contributes to the cis-trans isomerization in the presence of sufficient amounts of the additives, since it might be considered that singlet and triplet states are formed by the recombination of electrons and positive butene ions in the ratio of 1 : 3. When the concentration of additives is increased however, the isomerization due to the process $\mathrm{Cis}^+ + \mathrm{M}^-$ cannot be set aside in comparison with the processes d and e. When the concentration is increased further, $\mathrm{Cis}^+ + \mathrm{M}^-$ prevails over $\mathrm{Trans}^+ + \mathrm{M}^-$, and finally the contribution, the above " 1/4," may be ignored. Since butene has a lower ionization potential than benzene, the charge transfer from butene to benzene will be impossible. Although the electronic energy levels of 2-butene are not known with any accuracy, the electronic excitation transfer from butene to benzene may also be impossible. This is supported by theoretical considerations[14-16] and by experimental results from the studies of the benzene-photosensitzed isomerization of 2-butene.[17],*3 When benzene is used as an additive, therefore, no further decrease in *G*(*trans*-2-butene) is observed with an increase in the concentration. Since butene has a higher triplet energy and a higher ionization potential than naphthalene and anthracene, both electronic excitation transfer and charge transfer are possible as follows:

$$\mathrm{Cis}^*\ (\mathrm{triplet}) + \mathrm{M}\ (\mathrm{singlet}) \rightarrow \mathrm{Cis}\ (\mathrm{singlet}) + \mathrm{M}^*\ (\mathrm{triplet})$$

$$\mathrm{Cis}^+ + \mathrm{M} \rightarrow \mathrm{Cis} + \mathrm{M}^+$$

When naphthalene and anthracene are used as additives, therefore, a steeper decrease in *G*(*trans*-2-butene) at higher concentrations is observed. From investigations of the sensitized fluorescence,[19] however, an electronic excitation transfer is possible only when two atoms or molecules have energy levels lying near enough together to raise a quantum mechanical resonance effect between them.

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[10] K. Kikuchi, S. Sato and S. Shida, The 17th Annual Meeting of the Chemical Society of Japan, Tokyo (1964).

[11] F. A. Matsen, *J. Chem. Phys.*, **24**, 602 (1956).

[12] J. Collins and F. P. Lossing, *J. Am. Chem. Soc.*, **81**, 2064 (1959).

[13] P. C. Chang, N. C. Yang and C. D. Wagner, ibid., **81**, 2060 (1959).

[14] D. F. Evans, *J. Chem. Soc.*, **1960**, 1735.

[15] V. A. Crawford, *Quart. Rev.*, **3**, 226 (1949).

[16] J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).

[17] S. Sato, K. Kikuchi and M. Tanaka, ibid., **39**, 239 (1963).

*3 Furthermore, the experiment on the naphthalene-photosensitized reaction of 2-butene was undertaken in this Institute. However, the reaction products were scarcely observed.[18]

[18] T. Terao and S. Sato, private communications (1964).

[19] A. C. G. Mitchell and M. W. Zemansky, " Resonance Radiation and Excited Atoms, " Cambridge University Press, London (1934), p. 62.

Consequently, it may be considered that only the charge transfer process plays a leading role in this case, since the difference between the lowest triplet energy levels of 2-butene and that of naphthalene (2.6 eV.)[20] or that of anthracene (1.9 eV.)[20] is too large compared with that of benzene (3.6 eV).[20,21]

Summary

The radiolysis of *cis*-2-butene has been studied in the liquid phase at room temperature.

(1) The major products (and their *G*-values) were hydrogen (1.02), *n*-butane (0.83), 1-butene (0.40), *trans*-2-butene (2.29), C_8 hydrocarbons (2.30), and higher polymers, the *G*-values being independent of the total dose. Small amounts of $C_1 \sim C_3$ and $C_5 \sim C_7$ hydrocarbons were also formed. The hydrogen and the lower hydrocarbons except for *n*-butane were found, by using *p*-benzoquinone as a radical scavenger, to be produced for the most part through the molecular mechanism.

(2) The addition of benzene, naphthalene, and anthracene to liquid *cis*-butene have remarkable effects on the formation of *trans*-2-butene; thus, the cis-trans isomerization increases at a lower concentration of additives, while it decreases at a higher concentration of additives. The radical scavenging effect cannot explain these results. From a comparison of the experimental results with the ionization potentials and electron affinities of aromatics, it has been concluded that the increase in the isomerization at lower concentrations is due to the electron capture effect of additives, while the decrease at higher concentrations is due to the charge transfer from the butene to the additives.

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[20] R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

[21] H. B. Klevans and J. R. Platt, ibid., **17**, 470 (1949).