Hydrogen Formation in the Radiolysis of Liquid Olefins. The Role of Hot Hydrogen Atoms and Superexcited States

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The γ -radiolysis of liquid olefins was undertaken to obtain reliable evidence for a possible role of hot hydrogen atoms and superexcited states in radiation chemistry. The contribution of thermal hydrogen atoms may reasonably be excluded in this system. The effect of various electron or positive-ion scavengers on hydrogen formation in the radiolyses of liquid propylene and ethylene has been examined. The hydrogen formation is not appreciably affected by these additives, which indicates ionic species may not play an important role in the hydrogen formation. The liquidphase radiolyses of $C_{3}H_{6}-C_{3}D_{6}$ and $C_{2}H_{4}-C_{2}D_{4}$ mixtures have also been investigated and compared with those previously reported of C_4H_8 -1 - C_4D_8 -1 and trans- C_4H_8 - 2-trans- C_4D_8 -2 mixtures. The data indicate that the hydrogen from the olefins except ethylene may be formed for the most part by bimolecular processes. A large part of the hydrogen from liquid ethylene may be interpreted in terms of the molecular detachment of a hydrogen molecule, while from the other olefins it may be interpreted in terms of the hydrogen-atom abstraction reaction of hot hydrogen atoms formed by direct excitation which must at least partially involve superexcitation. To attempt quantitative substantiation of the above viewpoint a simple calculation has been made based on the so-called optical approximation. Calculated yields of the hydrogen formation are apparently in good agreement with observed ones.

The role of a hot hydrogen atom as a reaction intermediate in radiation chemistry has often been indicated complementarily by many authors,1) who have presented little experimental confirmations of its role. Moreover, there have been some criticizing comments²⁾ on the hot-hydrogen-atom process. It has so far been difficult to distinguish the hot-hydrogen-atom process from bimolecular physical interactions or from the hydrogen-atom abstraction reaction by thermal hydrogen atoms. In a previous paper³⁾ on the radiolyses of liquid butene-1 and trans-butene-2, however, these difficulties as described above could appreciably be removed and evidence was presented for a possible role of hot hydrogen atoms in the radiation chemistry of hydrocarbons. Namely, the hydrogen formation was interpreted in

terms of the hydrogen-atom abstraction reaction of hot hydrogen atoms formed by direct excitation which must, at least partially, involve superexcitation. The purpose of the present investigation is twofold: firstly to report new data on liquid propylene and ethylene and to compare these data with those previously reported³⁾ on liquid butene-1 and trans-butene-2, the result for ethylene being in striking contrast to those for the other olefins, and secondly to attempt quantitative substantiation based on the so-called optical approximation of the previous viewpoint.³ Preliminary results of such work have already been reported,⁴⁾ and so the details are presented here.

Experimental

Materials. Research-grade propylene and ethylene from Takachiho Trading Co. were used after the usual degassing and trap-to-trap distillations. Gas-chromatographic analyses of the propylene and the ethylene showed no impurity except for less than 0.1% propane and 0.1%ethane, respectively.

Propylene- d_{δ} was synthesized from methylacetylene- d_{δ} by using a palladium catalyst. The methylacetylene- d_{4} was obtained⁵⁾ from magnesium tricarbide by passing deuterium oxide vapor (99.8 at.% D) in an evacuated system over the carbide at 200°C which was prepared⁶⁾

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by passing n-pentane vapor over a few grams of finely divided magnesium metal in a quartz tube heated to 700°C. The methylacetylene- d_4 was then treated with an equal volume of deuterium over 1 g of palladium catalyst⁷⁾ at 150°C until the calculated pressure fall had taken place. The catalyst was initially placed in an evacuated system at room temperature and reduced for 8 hr with deuterium at 180°C. The deuterium was replaced several times to remove any adsorbed hydrogen. The propylene- d_{θ} produced was used after a gas chromatographic purification and trap-to-trap distillations. No chemical impurity was detected by gas chromatography using dimethylsulfolane, benzyl ether, and AgNO3benzylcyanide columns operated at room temperature. The isotopic purity was determined mass spectrometrically to be 99 at.% D.

Ethylene- d_4 was synthesized from acetylene- d_2 by using a palladium catalyst in a way similar to the case of propylene- d_6 . The acetylene- d_2 was obtained from calcium carbide by passing deuterium oxide vapor in an evacuated system over the purified carbide at room temperature. The ethylene- d_4 produced was used after a gas chromatographic purification and trap-to-trap distillations. No chemical impurity was detected by gas chromatography using squalane and AgNO₃-benzylcyanide columns operated at room temperature. The isotopic purity was determined mass spectrometrically to be again 99 at. % D.

Nitrous oxide (minimum purity: 99.9%), ammonia (>99.5%), and sulfur hexafluoride (>98.0%) were used without further purification. Carbon tetrachloride and methanol (spectral grade) were used after the usual degassing and distillation.

Irradiation. Measured amounts of propylene, ethylene, or the mixtures were sealed *in vacuo* at -196° C in glass ampules 5 mm in diameter and 50 mm long fitted with break-off-tips. The samples were irradiated in the facilities of Tokyo Institute of Technology (6 kCi ⁶⁰Co) at a dose rate of 6.9×10^{19} eV/g hr. Unless otherwise specified, samples were irradiated to a total dose of $4.3 \times$ 10^{20} eV/g at -78° C using dry ice and methanol slushes. The dose rate was determined by Fricke dosimetry using $G(Fe^{3+}) = 15.6$.

Analysis. After irradiations, the sample tubes were attached to a vacuum line and the seals were broken. The products, noncondensable at -210° C, hydrogen and methane, were collected and measured by an analysis device composed of a Toepler pump, a gas burette, a a McLeod gauge, and a copper oxide furnace kept at 250°C. In this furnace, hydrogen was oxidized into water which was then trapped at -196° C.

In the case of isotopic experiments, the relative amounts of H_2 , HD, and D_2 were determined with a Hitachi RMU-5 mass spectrometer.

Results

Figure 1 shows the variation of hydrogen formation as a function of the energy absorbed in the radiolyses of liquid propylene and ethylene at -78° C. The hydrogen formation is directly proportional to the energy absorbed; that is, the G value, the number of molecules formed per 100 eV of the energy





TABLE 1. EFFECT OF VARIOUS ELECTRON OR POSITIVE-ION SCAVENGERS ON HYDROGEN FORMATION IN THE RADIOLYSES OF LIQUID PROPYLENE AND ETHYLENE

System			$G(\mathrm{H}_2)$
C_3H_6			0.82
C_3H_6 +	SF_6	4 тм	0.82
		20 тм	0.82
	N_2O	10 тм	0.78
		60 тм	0.82
	\mathbf{CCl}_{4}	40 тм	0.78
		80 тм	0.86
		120 тм	0.74
	NH_3	0.1 м	0.82
		0.2 м	0.82
	CH ₃ OH	0.5 м	0.86
		1.0 м	0.94
C_2H_4			1.24
C_2H_4 +	SF_6	4 тм	1.30
		20 тм	1.30
	N_2O	10 тм	1.25
		60 тм	1.25
	CCl_4	40 тм	1.24
		80 тм	1.35
		120 тм	1.24
	CH ₃ OH	0.1 м	1.52
		0.2 м	1.42
		0.5 м	1.52
		1.0 м	1.47

absorbed in the system, is independent of the total energy absorbed. The G values of hydrogen formation in the radiolyses of pure liquid propylene and

⁷⁾ T. Kabe and I. Yasumori, Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.), 85, 410 (1964).

ethylene at -78° C have been estimated as 0.82 and 1.24 from Fig. 1, respectively.

Various types of reagents possessing a high reactivity for ionic species, electrons or positive ions, were used. They were also selected on the basis of their ionization potentials being higher than that of propylene or ethylene. Table 1 shows the effect of various electron or positive-ion scavengers, *i.e.*, nitrous oxide, carbon tetrachloride, sulfur hexafluoride, ammonia, and methanol, on the hydrogen formation. The hydrogen formation is scarcely suppressed even at high concentrations above 100 mM of the electron scavengers and above 1 M of the positive-ion scavengers.

These results in Fig. 1 and Table 1 show a marked contrast to those in the radiolysis of saturated hydrocarbons as described in the previous paper,³⁾ in which a detailed comparison was made.

Table 2 shows the relative amounts of H_2 , HD and D_2 evolved from the radiolyses of $C_3H_6 - C_3D_6$ and $C_2H_4 - C_2D_4$ mixtures. From the kinetic analysis as described previously,³⁾ when the value of

Table 2. Isotopic composition of total hydrogen evolved from the liquid-phase radiolyses of $C_3H_6-C_3D_6$ and $C_2H_4-C_2D_4$ mixtures

M-19/	Isotopi	Isotopic composition, %		
1/101%	$\widetilde{\mathbf{H}_2}$	HD	D_2	$D_2/11D$
C_3D_6				
0	100	0	0	
1.40	99.2	0.68	0.14	0.21
1.84	98.6	1.19	0.25	0.21
2.70	98.0	1.63	0.38	0.23
5.50	95.6	3.58	0.87	0.24
11.5	90.5	7.56	2.02	0.27
C_2D_4				
0	100	0	0	
0.96	99.2	0.39	0.47	1.2
1.79	98.6	0.62	0.77	1.2
3.65	96.9	1.25	1.80	1.4
4.03	97.0	1.29	1.84	1.4
5.53	95.6	1.76	2.63	1.5
8.81	92.7	2.92	4.46	1.5
12.9	90.7	3.56	5.70	1.6



Concentration of C_2D_4 , C_3D_6 , C_4D_3 -1, or trans- C_4D_8 -2, mol %

Fig. 2. $D_2/HD vs.$ concentration of the perdeuterated olefins in the liquid-phase radiolyses of C_2H_4 - C_2D_4 , C_8H_6 - C_8D_6 , C_4H_6 -1- C_4D_8 - $1,^{3)}$ and trans- C_4H_8 - trans-2- C_4D_8 - $2^{1)}$ mixtures.

 D_2/HD is extrapolated to zero concentration of C_3D_6 or C_2D_4 , it is found to be one-half of the ratio of unimolecular to bimolecular processes in the hydrogen formation. Values of D₂/HD are listed in the last column of Table 2, and are plotted against the concentration of C₈D₆ or C₂D₄ in Fig. 2. The values of D₂/HD at zero concentration are determined to be, respectively, 0.20 and 1.2 for C₈H₆ - C₈D₆ and C_2H_4 - C_2D_4 mixtures. Thus, 71% and 29% of total hydrogen from propylene and ethylene, respectively, may be formed through bimolecular processes. The results for butene-1 and trans-butene-2, reported previously,⁸⁾ are also plotted in Fig. 2 and listed in Table 3 for ready comparison. Figure 2 or Table 3 shows that the result for ethylene is in striking contrast to those for the other olefins. For ethylene the bimolecular hydrogen formation is less important, while for the other olefins it is most important.

TABLE 3. PERCENTAGES OF UNIMOLECULAR (DENOTED BY I) AND BIMOLECULAR (II) PROCESSES FOR HYDROGEN FORMATION IN THE RADIOLYSIS OF LIQUID OLEFINS

Olefin	$G(\mathrm{H}_2)$	$(D_2/HD)_0^{a}$	I (%)	II (%)	<i>G</i> (H') ^{b)}
trans-C ₄ H ₈ -2°)	1.22	0.11	18	82	1.0
$C_4H_{8}-1^{(2)}$	0.74	0.14	22	78	0.6
C_3H_6	0.82	0.20	29	71	0.6
C_2H_4	1.24	1.2	71	29	0.3

a) $(D_2/HD)_0$ means the value of D_2/HD extrapolated to zero concentration of the perdeuterated olefins.

b) H' means the precursor for bimolecular hydrogen formation in the radiolysis of liquid olefins, probably a hot hydrogen atom.

c) Ref. 3.

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Discussion of the Experimental Results

A fairly large quantity, about one molecule per 100 eV energy absorbed, of hydrogen formation has been observed in the radiolysis of some liquid olefins.⁸⁻¹¹⁾ This cannot be explained by processes involving thermal hydrogen atoms, since for them olefins, RH₂, have a high reactivity; and the addition reaction (1) is dominant compared with the abstraction reaction (2):¹²⁾

$$H + RH_2 \rightarrow RH_3 \tag{1}$$

$$H_2 + RH.$$
 (2)

Thus, Reaction (2) or thermal hydrogen atoms must be unimportant for hydrogen formation in the radiolysis of liquid olefins.

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The hydrogen formation is scarcely suppressed by the addition of an appreciable concentration of various scavengers for ionic species, as shown in Table 1 and in the previous paper.⁸⁾ Consequently, from the discussion similar to that previously reported,³⁾ it seems reasonable to assume that ionic species, electrons and various positive ions, do not play an important role in the formation of observed hydrogen in the radiolysis of liquid olefins. The excited olefin molecule, RH2*, which is formed by recombination of the parent olefin ion and an electron may not be acting as a precursor for the product hydrogen, but rather as a precursor for a thermal hydrogen atom which will eventually be scavenged by olefin itself:

$$\mathbf{RH}_{2^{+}} + \mathbf{e}^{-} \to \mathbf{RH}_{2^{*}} \tag{3}$$

$$RH_2^* \rightarrow H + RH \text{ or } 2H + R \quad (4)$$

$$\mathbf{H} + \mathbf{R}\mathbf{H}_2 \to \mathbf{R}\mathbf{H}_3. \tag{5}$$

The probability of hydrogen formation through various ion-molecule reactions in olefins may also be eliminated.

The most reasonable conclusion to be drawn from available data is that the excited olefin molecules RH₂' formed by direct excitation are essential to the hydrogen formation. Since, as described above, excited states which are formed by recombination of the parent olefin ion and an electron do not play an important role in the hydrogen formation, excited states lying below the ionization potential which are formed by direct excitation may also be of minor importance. Thus, the entities RH2' may be in highly excited states lying above the ionization potential, which are called superexcited states.¹⁸⁾ The importance of direct excitation has never been indicated explicitly in the radiation chemistry. The hydrogen

may be formed by the molecular detachment from RH₂',

$$\mathbf{RH}_2 \rightarrow \mathbf{W} \rightarrow \mathbf{RH}_2'$$
 (6)

$$\mathbf{RH}_{2}' \to \mathbf{H}_{2} + \mathbf{R}, \tag{7}$$

or by the hydrogen-atom abstraction reaction of a hot hydrogen atom H',

$$RH_2' \rightarrow H' + RH$$
 (8)

$$\mathbf{H'} + \mathbf{RH}_2 \rightarrow \mathbf{H}_2 + \mathbf{RH}, \qquad (9)$$

where a part of the highly excited states RH2' may undergo the following autoionization:

$$\mathrm{RH}_{2}' \to \mathrm{RH}_{2}^{+} + \mathrm{e}^{-}. \tag{10}$$

The former is a unimolecular process and the latter bimolecular. Since, for ethylene, a greater part of the total hydrogen is formed by a unimolecular process as shown in Table 3, Reaction (7) is essential to hydrogen formation in the radiolysis of liquid ethylene. For the olefins except ethylene, on the other hand, Reactions (8) and (9) are important for the hydrogen formation as shown in Table 3.

It has well been known¹⁴⁾ from a mass spectrometric investigation that an ion of mono-olefin tends to rupture giving an allyl type ion fragment. Thus, particularly for propylene, the possibility of the following process giving a hot hydrogen atom might be considered :

$$C_{3}H_{6}^{+*} \rightarrow H' + C_{3}H_{5}^{+},$$
 (11)

where $C_3H_6^{+*}$ is an excited ion of propylene. As shown in Table 3, however, it can not be found for propylene to be characteristic of Reaction (11). Thus, the possibility of hot-hydrogen-atom formation through Reaction (11) may be eliminated.

Calculations and Their Discussion

The collisions of electrons, photons, or excited atoms with various molecules have been studied since long ago. Especially in recent years a number of studies have been made on the measurements of electron-energy loss or photoionization spectra providing significant information about the nature of higher excited states of molecules. And, moreover, theory is now able to provide at least an approximative quantitative description of the primary stage of radiolysis. A simple calculation has been made in this paper based on the optical approximation introduced by Platzman.¹⁵⁾

The yield g_s , per 100 eV energy absorbed, of primary decomposition channel s may be estimated by the optical approximation. Thus, g_s can be taken

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$$M_{s^{2}} = \int_{J_{s}}^{\infty} \phi_{s}(E) \frac{R}{E} \frac{\mathrm{d}f}{\mathrm{d}E} \mathrm{d}E, \qquad (12)$$

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where E is the excitation energy in eV, R the Rydberg energy, df/dE the differential oscillator strength, $\phi_s(E)$ the probability of decomposition s upon excitation at E, and J_s the threshold excitation energy for s. Utilizing data on ionization, namely the Wvalue (in eV) and M_i^2 , the dipole matrix-element squared for ionization,16)

$$M_i^2 = \int_I^{\infty} \eta(E) \frac{R}{E} \frac{\mathrm{d}f}{\mathrm{d}E} \mathrm{d}E, \qquad (13)$$

we may write¹⁵⁾

$$g_s = \frac{100}{W} \frac{M_s^2}{M_i^2}.$$
 (14)

In Eq. (13), I is the ionization energy and $\eta(E)$ is the probability of ionization upon excitation at E. Since the G value for hydrogen formation measured in our experiment is considered to represent the combined yield of hot hydrogen atoms and molecularly detached hydrogen:

$$\mathbf{RH}_{2}' \rightarrow \mathbf{H}' + \mathbf{RH}$$
 (15)

$$H_2 + R,$$
 (16)

we can compare $G(H_2)$ with g_s calculated from Eqs. (12), (13), and (14) taking these two decomposition modes as the channel s.

In calculating g_s by numerical integrations in the above equations, we have relied upon the following sources of information. The differential oscillator strength df/dE is deduced from photo-absorption¹⁷) and electron energy loss data.¹⁸⁾ The former has been mainly used and is shown in Fig. 3. The spectrum of butene-1 has not been reported in the region of large E. In the region of small E (<12 eV), however, it has been reported¹⁷) that the spectrum of butene-1 is very similar to that of butene-2. Then, it is supposed that the quantity M_s^2 for butene-1 is nearly equal to that for butene-2. For ethylene, the data of Metzger and Cook somewhat differ from those of Schoen, which we have primarily relied upon.¹⁷⁾ The differential oscillator strength df/dEis proportional to the absorption cross section at E, and $\eta(E)$ is equal to the ratio of the ionization cross section to the total absorption cross section at E. The quantity M_i^2 is taken from ionization cross sections for fast electrons.¹⁹⁾ The W value is quoted



Fig. 3. Exitation spectra of olefins.

from the existing paper,²⁰⁾ with an assumption that no artifacts disturbing total ionization such as the Jesse effect are operative. As to the probability $\phi_s(E)$ for the decomposition into a hot hydrogen atom and into a hydrogen molecule, lack of directly relevant information forces us to consider a reasonable model. Namely, we shall tentatively assume that the above decomposition corresponds to all the pathways, except for ionization, by which superexcited states decay:

$$b_s(E) = 1 - \eta(E), \quad I < E.$$
 (17)

The highly exploratory nature of the model must be

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emphasized. Firstly, contribution of hot hydrogen atoms from excitation in the region $J_s < E < I$ are not included:

$$\phi_s(E) = 0, \quad J_s < E < I. \tag{18}$$

The value of J_s is difficult to be estimated a priori. A reasonable assumption, however, is that J_s is near *I*, because neutralization has been experimentally found not to contribute appreciably to the hydrogen formation as described in the last section. Secondly, other decomposition modes, C-C bond ruptures, have been disregarded. Presently available evidence does not seem to allow a conclusive statement as to this point,²¹⁾ although a recent study indicates the predominance of the C-H bond rupture in photolysis of ethylene at 11.6-11.8 eV.22) Finally, influence of condensed phase on primary activation¹⁵) has been neglected.

The results are listed in Table 4. Apparently g_s is in good agreement with $G(H_2)$. Although these results are still very tentative owing to approximate nature of estimation, they definitely lend some support to a significant role of superexcited states of hydrocarbons in the radiolysis.

In Table 4 the experimentally estimated yields of hot hydrogen atoms, $G(\mathbf{H}')$, in the radiolysis of these olefins are also listed. As indicated in footnote 18 of the previous paper³⁾ it is a question whether the hot hydrogen atom H' is a ground-state atom with appreciable kinetic energy or an electronically excited one. If we assume that H' is electronically excited, its precursor requires at least about 14 eV

TABLE 4. COMPARISON OF CALCULATED AND OBSERVED HYDROGEN YIELDS

	g _s	$G(\mathrm{H}_2)$	<i>G</i> (H')
C ₄ H ₈ -2	0.7	1.2, a) 1.0b)	1.0a)
C₄H₃-1	0.7	0.7ª)	0.6ª)
$C_{3}H_{6}$	0.8	0.8	0.6
C_2H_4	1.0	1.2	0.3
cyclo-C ₆ H ₁₀		1.3c)	_

a) Ref. 3.

b) Ref. 9.

c) Ref. 10.

of the excitation energy that is the sum of the C-H bond dissociation energy, about 4 eV, and the threshold energy, 10.2 eV, for the production of H(2P). Optical data in Fig. 3 show that superexcitation above 14 eV occupies relatively a small fraction of the absorption spectrum except in the case of ethylene. Thus, the majority of the hot hydrogen atoms in the other cases appears to be the ground-state atoms with kinetic energies rather than electronically excited ones.

As described in the last section, the experimental result for ethylene is in striking contrast to those for the other olefins. When, in Fig. 3, it is found for the spectrum of ethylene to be characteristic, it might be considered that the above two facts have some relations with each other.

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