Effect of Density in the Radiolysis of *n*-Butane

By Tetsuo MIYAZAKI and Shoji SHIDA

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The radiolysis of *n*-butane has been studied by several investigators. We reported in a previous paper¹⁾ on the difference between the gas-phase and the condensed-phase radiolyses of *n*-butane and concluded that the fragmentation of the butane ion is important in the gas-phase radiolysis, while that of the butane molecule is predominant in the liquid-phase radiolysis. In order to obtain further information on the different mechanisms involved in the two phases, we have now undertaken a study of the radiolysis of *n*-butane near the critical state. Toi et al.²⁾ reported on the effect of the density in the radiolysis of ammonia at the critical temperature and found sharp decreases in $G(H_2)$ and $G(N_2)$ in the density region from 0.05 to 0.15 g. cc^{-1}. Hotta³⁾ reported the radiolysis of ethane at high pressures and found a decrease in $G(H_2)$ in the density region from 0.08 to 0.14 g. cc^{-1}. Recently Ausloos et al.⁴⁾ reported the effect of pressure from 0.05 atm. to 180 atm. in the radiolysis of methane.

In the present work the yields of propane and methane have been found to decrease sharply in the 0—0.1 g. cc^{-1} density region. The results are interpreted in terms of the deactivation of excited ions.

Experimental

The sample and the analytical procedure are similar to those described before.¹⁾ The critical temperature, pressure and density of *n*-butane are 152°C, 37.5 atm. and 0.228 g. cc^{-1} respectively. The samples were irradiated at 170°C with γ-rays from cobalt-60 of 16000 c.

Stainless-steel autoclaves have usually been used in high-pressure experiments, but they have some drawbacks, such as the condensation of *n*-butane in the needle valve, contamination by air during the sampling procedure, etc. Therefore, it is useful to use a glass reaction cell, even in a high-pressure experiment. The authors found that a glass cell with a small diameter can bear a pressure of 40 atm. After pure *n*-butane had been sealed off in a glass cell (0.5 cm. external diameter, 0.3 cm. inner diameter and 6 cm. long), the cell was placed in a stainless steel autoclave (30 cc.; 2 cm. inner diameter); the latter was then surrounded by a heated jacket which permitted the temperature to be controlled within ±2°C at 170°C.

The energy absorbed in *n*-butane was calculated from Fricke dosimetry without using any correction factor,²⁾ on the assumption that the energy input is simply proportional to the electron density. The energy absorbed in the low density is due almost entirely to secondary electrons produced by γ-ray absorption in the glass vessel wall. If the stopping power per electron in *n*-butane is assumed to be the same as that in the wall, the energy absorbed in *n*-butane of a low density can be determined directly from Fricke dosimetry,⁵⁾ as in the liquid. In the intermediate density region, however, it might be necessary to use some correction factor in calculating the energy absorbed.

Results and Discussion

The variation in the major products of the radiolysis of *n*-butane in the density region from the gas phase of 3.8 atm. to the liquid phase is shown in Table I and Fig. 1. The

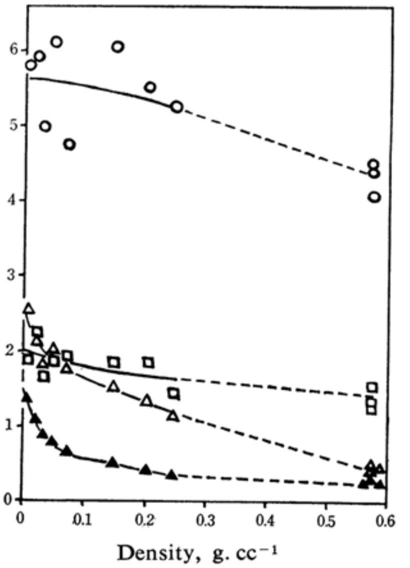

Fig. 1. Variation in $G(H_2)$ (○), $G(C_2H_6)$ (□), $G(CH_4)$ (△) and $G(C_3H_8)$ (▲) with density in the radiolysis of *n*-butane.

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1) T. Miyazaki, S. Arai, S. Shida and S. Sunohara, This Bulletin, 37, 1352 (1964).

2) Y. Toi, D. B. Peterson and M. Burton, *Radiation Research*, 17, 399 (1962).

3) H. Hotta, The 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.

4) P. Ausloos, R. Gordon, Jr., and S. G. Lias, *J. Chem. Phys.*, 40, 1854 (1964).

5) G. R. A. Johnson, *J. Inorg. Nucl. Chem.*, 24, 461 (1962).

TABLE I. *G*-VALUES OF PRODUCTS IN THE γ-RADIOLYSIS OF *n*-BUTANE[a]

Density g. cc^{-1}	Temp. °C	*G*-Value					$G(CH_4)$-$G(C_3H_8)$
		H_2	CH_4	C_2H_6	C_3H_8	C_3H_6	
0.575[b]	20	4.50	0.49	1.55	0.30	0.15	0.19
0.575[b]	20	4.41	0.47	1.31	0.25	0.11	0.22
0.575[b]	20	4.05	0.42	1.25	0.27	0.09	0.15
0.247	170	5.25	1.16	1.43	0.36	trace	0.80
0.204	170	5.52	1.31	1.83	0.41	trace	0.90
0.1479	170	6.05	1.51	1.83	0.50	trace	1.01
0.0722	170	4.75	1.72	1.91	0.66	trace	1.06
0.0485	170	6.12	2.00	1.85	0.79	trace	1.21
0.0309	170	4.98	1.80	1.65	0.88	trace	0.92
0.0205	170	5.92	2.11	2.24	1.09	trace	1.02
0.00604[c]	170	5.80	2.56	1.89	1.37	trace	1.19

a) Total dose is about 1.9×10^{21} eV. g^{-1} and dose rate is 1.9×10^{19} eV. g^{-1} hr^{-1}.
b) Liquid at room temperature.
c) Pressure of the gas is 3.8 atm.

most striking feature of the data is the marked decrease in $G(C_3H_8)$ and $G(CH_4)$ in the density region from 0 to 0.1 g. cc^{-1}. $G(H_2)$ and $G(C_2H_6)$ seem, however, to be practically independent of the variation in density. The yields near the critical density except for $G(CH_4)$ are similar to those of the liquid phase.

It seems impossible to explain the marked decrease in $G(C_3H_8)$ in the density region 0—0.1 g. cc^{-1} by means of the cage effect, which has been thought to be one of the most important causes of the difference between the radiolysis of the gas phase and that of the liquid phase.[6] In the fragmentation of a molecule to radicals, the probability (α) of the recombination of fragments was estimated by Franck and Rabinowitsch[7] as follows:

Pressure	1	10	100 atm.
α	10^{-9}	10^{-6}	10^{-3}

It is clear that there exists no cage effect in the density of 0.1 g. cc^{-1} (i. e., about 20 atm.). Therefore, the steep decrease must be attributed to some other effects.

It is reasonable, on the basis of a previous study by the present authors[1] and of a study by Ausloos et al.,[8] to expect that the butane ion plays an important role in the radiolysis of the gas phase. Since the ion may be formed in highly-excited states, it is probable that the deactivation of an excited ion occurs in the density region from 0 to 0.1 g. cc^{-1}; that is,

$$M \overset{I}{\rightsquigarrow} M^{+*} + e \qquad (1)$$

$$M^{+*}\begin{cases}\xrightarrow{k_2} P & (2)\\ \xrightarrow{k_3} Q & (3)\end{cases}$$

$$M^{+*} + M \xrightarrow{k_4} M^{+} + M \qquad (4)$$

where M : *n*-butane molecule
M^{+*}: excited butane ion
M^{+}: stable butane ion (or perhaps the ion cluster proposed by Funabashi et al.[9])
P: product
Q: products except P
I: rate of reaction 1
k: rate constant

The steady-state treatment leads to Eq. i:

$$G(P)=\frac{Ik_2}{k_2+k_3+k_4[M]} \qquad (i)$$

The decrease in the products with an increase in the density, or an increase in [M], could be explained by Eq. i. However, the constant yield of ethane over the whole density region and that of propane in the high density region cannot be explained by this equation only. Therefore, the production of P by the neutralization of M^{+} should be considered in addition to 1—4.

$$M^{+} + e \xrightarrow{k_5} M^{*} \qquad (5)$$

$$M^{*}\begin{cases}\xrightarrow{k_6} P & (6)\\ \xrightarrow{k_7} R & (7)\end{cases}$$

where M^{*}: excited butane molecule
R: products except P

Then,

$$G(P)=\frac{Ik_2}{k_2+k_3+k_4[M]}+\frac{Ik_4k_6[M]}{(k_6+k_7)(k_2+k_3+k_4[M])} \qquad (ii)$$

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[6] L. Kevan and W. F. Libby, *J. Chem. Phys.*, **39**, 1288 (1963).

[7] J. Franck and E. Rabinowitsch, *Trans. Faraday Soc.*, **30**, 120 (1934).

[8] R. P. Borkowski and P. J. Ausloos, *J. Chem. Phys.*, **39**, 818 (1963).

[9] J. L. Magee and K. Funabashi, *Radiation Research*, **10**, 622 (1959).

The first term in Eq. ii represents the production of P by ionic fragmentation, while the second term represents that by neutralization. The constant yield of C_3H_8 in the high density region can be explained by Eq. ii. Suppose the yield of P from the excited butane ion to be the same as that from the excited butane molecule; that is, if $k_2/(k_2+k_3)=k_6/(k_6+k_7)$, G(P) is $G(\mathrm{P})=Ik_2/(k_2+k_3)$ and independent of [M]. The constant yield of C_2H_6 might be due to this effect.

The Formation of Propane.—Since the decomposition of neutral excited *n*-butane produced by electron bombardment in a mass spectrometer[10] yields mainly ethane and ethylene:

$$C_4H_{10}^* \rightarrow C_2H_4 + C_2H_6 \qquad (8)$$

the formation of propane at 0.00604 g. cc^{-1} (i. e., 3.8 atm.) may be due to the ionic process. From the mass spectrometric study, the main fragmentation processes of butane ion are found to be as follows:[11]

$$C_4H_{10}^{+*} - \left| \begin{array}{lrr} & e_0 & \\ \xrightarrow{k_9} C_2H_5^+ + C_2H_5 & 30\ \text{kcal./mol.} & (9) \\ \xrightarrow{k_{10}} C_2H_4^+ + C_2H_6 & 17\ \text{kcal./mol.} & (10) \\ \xrightarrow{k_{11}} C_3H_7^+ + CH_3 & 4\ \text{kcal./mol.} & (11) \\ \xrightarrow{k_3} Q & & (3) \end{array} \right.$$

where e_0 denotes the heat of the reaction of ionic fragmentation. The propyl ion in reaction 11 reacts very rapidly with *n*-butane to produce propane:

$$C_3H_7^+ + n\text{-}C_4H_{10} \rightarrow C_3H_8 + C_4H_9^+ \qquad (12)$$

Propane might also be formed by the combination of the methyl and ethyl radicals produced in reactions 9 and 11, but $G(C_3H_8)=1.37$ at 170°C at 0.00604 g. cc^{-1} is consistent with $G(CH_3\cdot)=1.54$[1] and with the molecular yield, $G_M(C_3H_8)=1.43$,[8] in the gaseous radiolysis of *n*-butane at ordinary pressure. Therefore, it is reasonable to consider that at 0.00604 g. cc^{-1} propane is formed by the ionic process of Reaction 11, followed by 12. Since the constant yield of propane at a high density is relatively low compared with that at 0.00604 g. cc^{-1}, Eq. i may be used for an analytically convenient treatment in the low density region, neglecting the formation by the neutralization of butane ion. From reactions 1, 9, 11, 3, 12 and 4, we get:

$$\frac{1}{G(C_3H_8)}=\frac{k_9+k_{10}+k_{11}+k_3}{Ik_{11}}+\frac{k_4}{Ik_{11}}[C_4H_{10}] \qquad (iii)$$

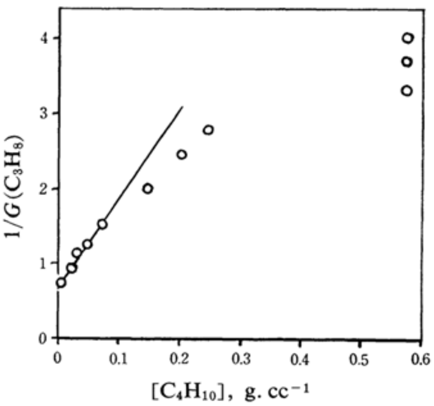

Fig. 2. Relationship between reciprocal of $G(C_3H_8)$ and density of *n*-butane.

Thus, there must be a linear relationship between $1/G(C_3H_8)$ and $[C_4H_{10}]$. As may be seen in Fig. 2, a satisfactory straight line is obtained in the low density region. The discrepancy from the straight line in the high density region may be due to the neglect of the formation by the neutralization of the butane ion. The slope-to-intercept ratio gives: $(k_9+k_{10}+k_{11}+k_3)/k_4=5.7\times10^{20}$ cc^{-1} molecules. Taking $k_4=10^{-9}$ cc. molecules^{-1} sec^{-1}[12], $(k_9+k_{10}+k_{11}+k_3)$ is 5.7×10^{11} sec^{-1}. Since this value is the total rate constant of the fragmentation of the excited butane ion, we have tried to estimate k_{11} and k_9 separately. From the mass spectral pattern of *n*-butane, the ratios of the processes forming $C_3H_7^+$ and $C_2H_5^+$ to the total ionic fragmentation are 0.48 and 0.28 respectively. Therefore, we get $k_{11}=2.7\times10^{11}$ sec^{-1} and $k_9=1.6\times10^{11}$ sec^{-1}.

The Calculation of the Rate Constant.—Rosenstock et al.[13] proposed the quasi-equilibrium rate theory for the fragmentation of polyatomic ions. According to the simplified treatment[14] of this theory, the rate constant of the dissociation of the molecule ion of an excitation energy of e is given by $k(e)$:

$$k(e)=P\nu\left(1-\frac{e_0}{e}\right)^{S-1} \qquad (iv)$$

where P is the steric factor in the range from 1 to 10^{-3}; ν is the reaction frequency; $S=3N-6$ is the number of degrees of the vibrational freedom of the N-atomic molecule ion, and e_0 is the dissociation energy of the ion. $P\nu$ is taken as 10^{14} sec^{-1} for a simple bond dissociation process and as 10^{12} sec^{-1} for a four-center disproportionation process. The molecule ions produced by electron impact have

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[10] D. Beck and A. Niehaus, *J. Chem. Phys.*, **37**, 2705 (1962).

[11] F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York (1957).

[12] The rate constant of binary collision for molecules.

[13] H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig and H. Eyring, *Proc. Natl. Acad. Sci., U. S.*, **38**, 667 (1952).

[14] D. P. Stevenson, *Radiation Research*, **10**, 610 (1959).

different excitation energies. If $D(e)$ is the characteristic distribution function of the excitation energy, the total rate constant is as follows:

$$k=\int_0^{e_{max}} D(e)k(e)\mathrm{d}e \qquad \text{(v)}$$

where $D(e)$ is normalized to the range $0 \leq e \leq e_{max}$ and where e_{max} is the maximum excitation energy of the molecule ion.

We try to calculate k_{11} and k_9 using Eq. v.

$$C_4H_{10}^{+*} \xrightarrow{k_{11}} s\text{-}C_3H_7^{+} + CH_3 \qquad (11)$$

Since the propyl ion produced in reaction 11 is exclusively a secondary ion,[8] this reaction cannot occur by a simple bond dissociation process, but rather only by the dissociation process following rearrangement. Therefore, we take $P\nu = 10^{12}$ sec^{-1}. The maximum excitation energy is assumed to be:

$$e_{max} = 2\bar{e} \qquad \text{(vi)}$$

where $\bar{e}$ is the average excitation energy of the ion. We take the $\bar{e}$ of the propane ion, i. e., 144.3 kcal./mol., as that of the butane ion also. An analytically-convenient distribution function that has been used in the interpretation of the mass spectra of propane[13] is:

$$D(e)=\frac{1}{e_{max}} \qquad \text{(vii)}$$

Using $S-1=35$ and $e_0=4$ kcal./mol., we get from Eq. v $k_{11}=3.2\times10^{11}$ sec^{-1}. In a similar fashion, we get $k_9=3.3\times10^{11}$ sec^{-1} by using $e_0=30$ kcal./mol. and $P\nu=10^{14}$ sec^{-1} for a simple bond dissociation. The agreement between the observed values and the calculated values is satisfactory in spite of the simplified calculation.

Since the total specific rate of the fragmentation of the ion is 5.7×10^{11} sec^{-1} and since the frequency of successive collisions of a molecule in the liquid phase is of the order of 10^{-13} sec^{-1}, the excited ion produced in the liquid-phase radiolysis may be exclusively deactivated before its fragmentation, and, therefore, C–C bond rupture from butane ion may be strongly suppressed. This supports the conclusion of the previous paper by the present authors.[1]

The Formation of Methane.—The material balance between CH_4 and C_3-products does not hold in the radiolysis at 170°C (Table I). Methane is partly formed from the methyl radical produced in reaction 11; the yields of methane due to other processes ($G(CH_4)-G(C_3H_8)$) are shown in the last column of Table I. Though $G(CH_4)$-$G(C_3H_8)$ at 20°C is small, that at 170°C, near the critical state, is about unity, independent of the variation in density. These results seem to be the effect of temperature. No fragmentation products could be observed by the heating of *n*-butane without radiation at 200°C for 80 hr. Since methane is not formed by the thermal cracking of the butyl radical at 170°C,[15] the discrepancy of the material balance might be due to some characteristic reaction near the critical state. The heat of reaction[11] for the formation of methane from the butane ion is very low.

$$C_4H_{10}^{+} \rightarrow C_3H_6^{+} + CH_4 \quad e_0=4 \text{ kcal./mol.} \quad (13)$$

In the fragmentation of the slightly-excited butane ion,[16] a considerable amount of $C_3H_6^{+}$ is formed, though only a small amount is formed in the fragmentation of the highly-excited butane ion. In the radiolysis of neopentane,[17] the inbalance between products has been also observed; i. e., $G(CH_4) \gg G(C_4)$. The abundance of methane might be due to following reactions, as has been suggested by Williams[18]:

$$\begin{tikzcd}
 & \text{Gas (1 atm.)} & & \text{Liquid} \\
n\text{-}C_4H_{10} \arrow[r, squiggly, "\text{main}"] & C_4H_{10}^{+*} \arrow[r, "C_4H_{10}", "\text{deactivation}"'] \arrow[d, "\text{fragmentation}"] & C_4H_{10}^{+} \arrow[r, "e", "\text{neutralization}"'] \arrow[d, "\text{thermal cracking 170°C}"] & C_4H_{10}^{*} \arrow[d, "\text{fragmentation}"] \\
 & \begin{matrix} C_2H_6 \\ C_3H_8 \\ CH_4 \end{matrix} & CH_4 & C_2H_6 \\
n\text{-}C_4H_{10} \arrow[r, squiggly, "\text{minor}"] & C_4H_{10}^{*} \arrow[d, "\text{fragmentation}"] & & \\
 & C_2H_6 & &
\end{tikzcd}$$

Scheme 1

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[15] A. W. Hay and C. A. Winkler, *Can. J. Res.*, **21B**, 149 (1943).

[16] B. Steiner, C. F. Giese and M. G. Inghram, *J. Chem. Phys.*, **34**, 189 (1961).

[17] W. H. Taylor, S. Mori and M. Burton, *J. Am. Chem. Soc.*, **82**, 5817 (1960).

[18] T. F. Williams, *Trans. Faraday Soc.*, **57**, 755 (1961).

$$\textit{neo}\text{-}C_5H_{12}^+ \rightarrow \underset{\searrow\ \text{higher products}}{C_4H_8^+} + CH_4 \quad e_0 = -4\ \text{kcal./mol.} \qquad (14)$$

Therefore, it is probable that in the radiolysis of *n*-butane near the critical state a part of the methane is formed by reaction 13, while $C_3H_6^+$ forms higher products.

From the above results and discussions, the following conclusions may be drawn. It appears difficult to consider the ionic C–C rupture in the liquid-phase radiolysis of *n*-butane at room temperature. It seems proper to consider that the suppression of the ionic C–C rupture in the liquid phase is due to the deactivation of the excited butane ion. The main C–C rupture reactions in the radiolysis of *n*-butane may be depicted as Scheme 1.

Summary

A study has been made of the effect of density on the radiolysis of *n*-butane at 170°C over the density region 0.006—0.575 g. cc^{-1}. While $G(H_2)$ and $G(C_2H_6)$ are not affected by the density change, $G(CH_4)$ and $G(C_3H_8)$ decrease sharply in the density region from 0 to 0.1 g. cc^{-1}. The latter facts may be interpreted in terms of the collisional deactivation of the excited ion. The rate constant of the fragmentation of the butane ion has been estimated from the deactivation-fragmentation competition scheme and compared with the rate constant calculated from the quasi-equilibrium theory. Agreement is satisfactory. The formation of methane by ionic fragmentation near the critical state has also been considered.

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Laboratory of Physical Chemistry
Tokyo Institute of Technology
Ookayama, Tokyo