Radiolysis of n-Butane in the Gas, Liquid and Solid Phases

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Many investigations have been made of the radiolysis of alkanes in order to elucidate the radiolysis mechanism. Although the phase seems to influence the mechanism of the radiolysis, experimental studies of its effect have been few. A comparison of the gas phase with the liquid phase was made by Dewhurst[1] for the radiolysis of *n*-hexane. He reported that the vapor-phase radiolysis showed a much higher proportions of products which must ultimately result from C–C bond cleavage, while the liquid-phase radiolysis showed a higher proportion of product, which must result from C–H bond cleavage. Hamashima et al.[2] compared the radiolysis of neopentane in the gas and the liquid phases.

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[1] H. A. Dewhurst, *J. Am. Chem. Soc.*, **83**, 1050 (1961).

[2] M. Hamashima, M. P. Reddy and M. Burton, *J. Phys. Chem.*, **62**, 246 (1958).

The present authors have studied the phase effect on the radiolysis of *n*-butane; it is the simplest hydrocarbon which contains two types of C–C bond and is easily liquefied. They found a clear difference between the C–C bond scissions in the gas and the condensed phases.

Experimental

Materials.—A commercial pure-grade *n*-butane, stated to be of 99.7% purity, was used without further purification. The gas chromatographic analysis of this material showed 0.036% isobutane and 0.130% isopentane, but no unsaturated impurities were detected.

Irradiation.—The radiolysis in the gas phase was carried out in a glass cylinder 1 liter in volume. The cell used for the liquid and solid radiolyses was a heavy-walled glass tube 1.5 cm. in diameter and 13 cm. long. The samples were irradiated with 1.5 MeV. electrons from a Van de Graaff accelerator with γ-rays from cobalt-60 of 200 c. and 16000 c. The gas samples were irradiated with electrons at room temperature. The hydrogen yield ($G(H_2)=1.3$) from irradiated ethylene at 100 mmHg was used as the measure of the gas dosimetry.[3] The liquid samples were irradiated with γ-rays and electrons at room temperature. The dose rate of γ-rays was 1.5×10^{19} eV./g. hr. and 3.1×10^{19} eV./g hr. Doses were determined by a Fricke dosimeter, taking $G(Fe^{+3})=15.5$. The solid radiolysis was carried out at $-196°C$.

Product Analysis. — After irradiation, non-condensable gas (a mixture of hydrogen and methane) at $-196°C$ was transferred to a gas burette by a Toepler pump and then analyzed using a copper oxide furnace. Condensable gas was vaporized into a gas holder, an aliquot of which was subjected to gas chromatography. The columns used were of dimethyl sulfolane at room temperature for C_2-C_5 hydrocarbons, of silica gel at 40°C for ethane and ethylene, and of dinonyl phthalate at 80°C for C_6-C_8 hydrocarbons. For runs with iodine added, alkyl iodide products were analyzed by gas chromatography with a dinonyl phthalate column at 80°C.

Results and Discussion

***G*-Value.** — The amounts of the major irradiation products of liquid *n*-butane are plotted against the energy absorbed in Fig. 1 and Fig. 2.

The initial yield was calculated from the initial slopes of these curves, since the amount of olefin did not increase linearly with the energy absorbed.

The radiolytic yields obtained in the gaseous, liquid and solid phases are listed in Table I.

The *G*-values obtained for gaseous and liquid *n*-butane are in good agreement with those reported in the previous works.[4-7]

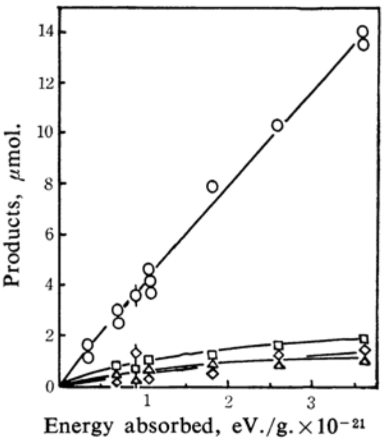

Fig. 1. Product formation in the liquid phase radiolysis as a function of the energy absorbed. Ordinates represent the yield from 1000 μmol. *n*-butane. The hydrogen yield in the electron bombardment was assumed to be equal to that in the γ-rays radiolysis.

	γ-Rays	Electrons
H_2	○	○⃒
C_4H_8-1	□	□⃒
trans C_4H_8-2	◇	◇⃒
cis C_4H_8-2	△	△⃒

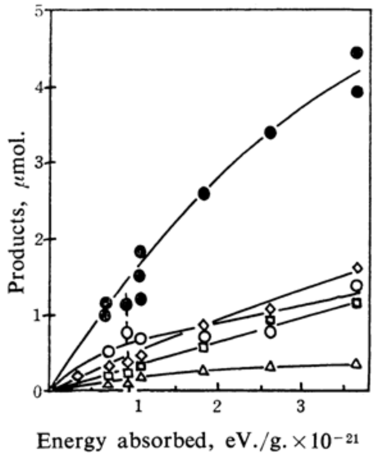

Fig. 2. Product formation in the liquid phase radiolysis as a function of the energy absorbed. Ordinates represent the yield from 1000 μmol. *n*-butane.

	γ-Rays	Electrons
CH_4	◇	△⃒
C_3H_8	□	□⃒
C_3H_6	△	△⃒
C_2H_6	●	●⃒
C_2H_4	○	○⃒

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[3] M. C. Sauer and L. M. Dorfman, ibid., **66**, 322 (1960).

[4] S. C. Lind and D. C. Bardwell, *J. Am. Chem. Soc.*, **48**, 2235 (1926).

[5] A. Kuppermann and M. Burton, *Radiation Research*, **10**, 636 (1959).

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

[7] C. D. Wagner, *J. Phys. Chem.*, **67**, 1793 (1963).

TABLE I. G VALUES OF THE RADIOLYSIS OF n-BUTANE

Product	Gas[a] (room temp.)	Liquid[b] (room temp.)	Solid[c] (−196°C)
H_2	5.06	4.73	2.84
CH_4	0.96	0.50	0.21
C_2H_6	1.89	1.29	0.69
C_2H_4	0.59	0.58	0.23
C_3H_8	2.12	0.29	0.13
C_3H_6	0.18	0.16	0.03
C_4H_8-1	0.23	0.88	0.74
trans-C_4H_8-2	0.64	0.50	0.43
cis-C_4H_8-2	0.18	0.48	0.10
C_5	0.32	0.18	—
C_6	0.38	0.38	—
C_7	0.09	0.05	—
C_{8A}	0.26	0.38	0.20

a) Results are the averages at the pressure of 50 and 100 mmHg. The total dose is 2.5×10^{21} eV./g.

b) The yields of hydrogen and lower hydrocarbons (C_1–C_4) were determined by extrapolation to zero dose. The yields of C_5–C_8 hydrocarbons represent the mean values of two runs at the total dose 3.7×10^{21} eV./g.

c) The mean values of three individual irradiations, that is, two runs at 3.7×10^{21} eV./g. and one run at 2.6×10^{21} eV./g.

Formation of C_2 and C_3 Products.—n-Butane has two types of C–C bonds, and the major products from these C–C bond scissions are C_1, C_2 and C_3 hydrocarbons. It is noted in Table I that the $G(C_2)$ of the liquid phase is approximately the same as that of the gas phase, while for $G(C_3)$ this is not the case.

Since the irradiation with 1.5 MeV. electrons and γ-rays gave the same yield (Fig. 1 and Fig. 2), the different $G(C_3)$ values cannot be ascribed to the different dose rate and, therefore, must be due to the different radiolysis mechanisms in the two phases.

Table II compares the radiolyses in the gas, liquid and solid phases, the vacuum ultraviolet photolysis (1470A and 1236A),[8,9] the mass spectral fragmentation[10] and the appearance potentials of ions from n-butane.[11]

The C_2/C_3 ratios in the radiolyses of liquid and solid butane are 4.2 and 5.7 respectively. These values are similar to the value of the photolysis, where only the cracking of neutral excited butane takes part, but not to that of mass spectral fragmentation. Since the parent ion in the mass spectral fragmentation is highly excited, the fragmentation of low excited ions which may take part in the condensed-phase radiolysis would be different from that in the mass spectroscopy. As may be seen in Table II, the appearance potential of $C_3H_7^+$ is lower than that of $C_2H_5^+$ and, accordingly, the low-excited ion produces C_3 products mainly; the C_2/C_3 in the fragmentation of the low excited ion should be less than 1.43. Therefore, the values of C_2/C_3 in the liquid and solid radiolyses cannot be explained, even by the fragmentation of such a low-excited butane ion.

On the contrary, the C_2/C_3 in the radiolysis of n-butane in the gas phase is analogous to that of mass spectral fragmentation, but not so that of the photolysis.

Bond Dissociation Energy.—In the radiolysis of liquid hydrocarbons, it has been shown that weaker bonds are preferentially broken.[12,13]

Since the difference between the gas and liquid radiolyses of n-butane obviously cannot be explained by the bond strength of the neutral molecule alone, the bond strength of the butane ion is also considered here.

The bond dissociation energies of n-butane and the butane ion are given below.

TABLE II. COMPARISON OF RADIOLYSIS OF n-BUTANE WITH OTHER CRACKING PROCESSES

	Solid	Liquid	Gas	Photolysis (1470A, 1236A)	Mass spectrum[b]	A. P. of ions from n-butane
C_2/C_3[a]	5.7	4.2	1.1	3–4	1.4	$C_4H_{10}^+$ 10.4 eV.
						$C_3H_6^+$ 11.0 eV.
						$C_3H_7^+$ 11.2 eV.
						$C_2H_4^+$ 11.6 eV.
						$C_2H_5^+$ 12.1 eV.

a) C_2 represents the sum of the yields of ethane and ethylene.
C_3 represents the sum of the yields of propane and propylene.

b) The complementarity between ion and radical is assumed to hold in the mass spectral fragmentation.

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8) M. C. Sauer and L. M. Dorfman, *J. Chem. Phys.*, **35**, 497 (1961).

9) H. Okabe and D. A. Becker, ibid., **39**, 2549 (1963).

10) American Petroleum Institute Research Project No. 44, Mass Spectral Data.

11) M. B. Loffel and R. A. Lad, *J. Chem. Phys.*, **16** 420 (1948).

12) H. Yamazaki and S. Shida, ibid., **32**, 950 (1960).

13) K. Fueki and K. Hirota, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 209 (1960).

	n-Butane molecule	ΔH (kcal./mol.)
$CH_3CH_2CH_2CH_3$	$\rightarrow CH_3 + C_3H_7$	84.0
	$\searrow$ 2 C_2H_5	81.0
	Butane ion	
$CH_3CH_2CH_2CH_3{}^+$	$\rightarrow CH_3 + C_3H_7{}^+$	3.5
	$\searrow C_2H_5 + C_2H_5{}^+$	30.2

The bond dissociation energies of the butane ion have been derived by assuming the heats of formation of C_4H_{10}, $C_3H_7{}^+$, $C_2H_5{}^+$, CH_3 and C_2H_5 to be 219, 190, 224, 32.4 and 25.2 kcal./mol. respectively.[14] In the butane molecule, the second bond is weaker than the first bond, while in the butane ion the first bond is much weaker than the second bond. Therefore, one may expect that C_2 products are more readily formed than C_3 products from the fragmentation of the butane molecule, while C_3 products become the major product from that of the butane ion.

Radical Detection by the Scavenger Method.—*n*-Butane saturated with iodine was irradiated with γ-rays in the gaseous and liquid phases. The yields of alkyl iodide, which represent the yields of the radical, and the decrement of each product upon the addition of DPPH are shown in Table III.

TABLE III. *G* VALUES OF RADICALS IN THE RADIOLYSIS OF *n*-BUTANE AND IODINE (or DPPH) MIXTURE[a)]

	Gas[b)] (I_2)	Liquid[c)] (I_2)		Liquid[d)] (DPPH)
CH_3I	1.54	0.29	ΔCH_4	0.22
C_2H_5I	0.69	0.59	ΔC_2	0.83
iso-C_3H_7I	0.33	0.15	ΔC_3	0.16
n-C_3H_7I	—	0.06		

a) Results are the averages of two or more runs at the total dose 3.7×10^{21} eV./g. The dose rate is 8×10^{18} eV./g. hr.
b) The pressure of *n*-butane is 200 mmHg and that of I_2 is 0.3 mmHg.
c) The concentration of I_2 is 0.025 mol./l.
d) The concentration of DPPH is about 0.001 mol./l. ΔCH_4, ΔC_2 and ΔC_3 represent the difference between the initial yield and the molecular yield of methane, C_2-products and C_3-products respectively. This difference can be thought to represent the yield of radical.

The present data on liquid butane are not similar to the reported values.[15] The disagreement seems to be due to the different analytical techniques. McCauley et al. separated the alkyl iodides by fractional distillation, but in the present study iodides were analyzed by gas chromatography.

The yield of the propyl radical is only one-fifth of that of the methyl radical in the gas phase, while in the liquid phase the amounts of methyl and propyl radicals are approximately equal. From this result, it seems that in the liquid phase the homolytic dissociation of the butane molecule into two radicals occurs, while in the gas phase this mode of dissociation is of minor importance. From the mass spectral study, the scission of the first C–C bond of the butane ion is known to produce the propyl ion and the methyl radical, but not the propyl radical or the methyl ion. Since the yield of the methyl radical is extremely high as compared with that of the propyl radical in the gas phase radiolysis, the dissociation of the butane ion seems to occur in the gas phase.

Conclusion

From these discussions it seems that the fragmentation of butane ion is important in the gas phase radiolysis, but that in the condensed phases that of the butane molecule is important. The main reactions are as follows:

Solid and liquid radiolyses

$$n\text{-}C_4H_{10} \rightsquigarrow n\text{-}C_4H_{10}{}' \rightarrow C_3H_7 + CH_3$$
$$\searrow 2\ C_2H_5$$
$$C_3H_7 + n\text{-}C_4H_{10} \xrightarrow[\text{solid, liquid}]{} C_3H_8 + C_4H_9$$
$$C_3H_7 + R \xrightarrow[\text{liquid}]{} C_3H_6,\ \text{Products}$$

Gas radiolysis

$$n\text{-}C_4H_{10} \rightsquigarrow C_4H_{10}{}^+ \rightarrow C_3H_7{}^+ + CH_3$$
$$\searrow C_2H_5{}^+ + C_2H_5$$
$$C_3H_7{}^+ + n\text{-}C_4H_{10} \longrightarrow C_3H_8 + C_4H_9{}^+$$
$$C_4H_9{}^+ + e \longrightarrow C_4H_8,\ \text{Products}$$

N. B. $C_4H_{10}{}'$ represents a neutral precursor of fragmentation.
R represents some radicals.

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[14] F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York (1957).
[15] C. E. McCauley and R. H. Schuler, *J. Am. Chem. Soc.*, 79, 4008 (1957).