The Reaction of Ions in the Radiolysis of *n*-Butane in the Gas Phase

By Tetsuo MIYAZAKI and Shoji SHIDA

(Received May 7, 1965)

The reaction of ions produced in the radiolysis of *n*-butane has been reported in previous papers by the present authors. In the first paper1) it was shown, from a comparison of the results of radiolysis, photolysis and mass spectrum study, that the fragmentation of the excited butane ion is quite different from that of the excited butane molecule. In the second paper2) the deactivation of the excited butane ion was discussed from the point of view of the effect of density in the radiolysis. The present work will concern the role of several ions in the radiolysis of *n*-butane in the gas phase. Since excited molecules and radicals are produced by irradiation in addition to ionic species, the role of ions in radiation chemistry is sometimes obscure. Futrell3) explained the distribution of products in the radiolysis of *n*-hexane by using the mass-spectrometric cracking pattern, working on the assumption that the fragment ions form the products by hydride-ion transfer reactions with *n*-hexane. Ausloos et al.4) studied the radiolysis of a n-C_4H_{10} - n-C_4D_{10} - I_2 mixture and found that C_3H_7D and C_3D_8 were produced in comparable amounts. They concluded that 95% of propane is formed by hydride ion transfer reaction, and they assumed that hot radicals were not produced in the radiolysis.

In the present study ammonia was used as a proton transfer reagent, since ammonia has a high proton affinity (202 kcal./mol.)5) and since products from ammonia by irradiation can be discriminated

---

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

2) T. Miyazaki and S. Shida, This Bulletin, **38**, 716 (1965).

3) J. Futrell, *J. Am. Chem. Soc.*, **81**, 5921 (1959).

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

5) A. P. Altshuller, *J. Am. Chem. Soc.*, **77**, 3480 (1955).

from those from *n*-butane. Ammonia is expected to react with ions to give alkene by the following proton transfer reaction:

$$C_nH_{2n+1}^+ + NH_3 \rightarrow C_nH_{2n} + NH_4^+$$

In the absence of ammonia, an alkyl ion forms alkane by hydride-ion transfer reaction with *n*-butane:

$$C_nH_{2n+1}^+ + n\text{-}C_4H_{10} \rightarrow C_nH_{2n+2} + C_4H_9^+$$

Experimental

The *n*-Butane was the same as that used before.[1] The C_5H_{10}-1 was 99.99% pure. The water and ammonia were also of high purity. The samples were irradiated with γ-rays from Co-60 of 16000 c. at a total dose of 2.5×10^{21} eV. g^{-1}. Most of the analytical procedures were identical with those described before.[1,2] The C_2—C_4 hydrocarbon products were analyzed by gas chromatography (benzyl ether column, 20 m.).

Results and Discussion

The effect of ammonia in the radiolysis of *n*-butane in the gas phase is shown in Table I. The yields given in the table are expressed in moles per 1000 mol. of *n*-butane. This value is proportional to the *G*-value, and for Run 2-1 the yields are given also in *G*-value units. Since iodine has the unfavorable property[6] of reacting with unsaturated products, C_5H_{10}-1 was used as a radical scavenger in spite of its low reactivity to radicals. The yield of C_4H_8-1 was determined in Run 2-1 and Run 4-1 by separating *n*-butane before the analysis, since the peak of C_4H_8-1 in the gas chromatography was not separated from a large peak of *n*-butane. The electron fraction of ammonia in Table I indicates that the direct absorption of radiation energy by ammonia is small compared with that of *n*-butane.

The effect of ammonia is clearly shown in Fig. 1. Each product is affected in quite different ways. The effects may be classified into three types: A) C_2-products and C_3H_8 decrease upon

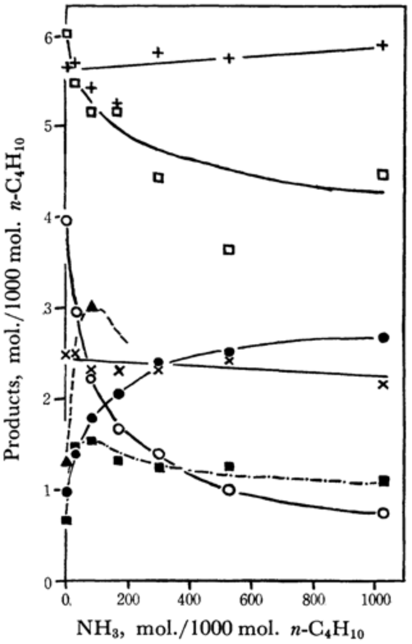

Fig. 1. Effect of ammonia in the radiolysis of *n*-butane at low pressure.
+ H_2 □ C_2 ● C_3H_6 ▲ C_4H_8
× CH_4 ○ C_3H_8 ■ C_4H_8-2

TABLE I. EFFECT OF AMMONIA IN THE RADIOLYSIS OF *n*-BUTANE AT LOW PRESSURE
Yields of Products[a] at 250 mmHg of n-C_4H_{10} and 12.5 mmHg of C_5H_{10}-1

	Run							
	2-1		3-1	4-1	5-1	6-1	8-1	1-1
NH_3, mol.[b]	0		27.4	81.5	167	298	528	1030
Electron fraction	0		0.008	0.023	0.047	0.081	0.13	0.23
Products, mol.[b]		(*G*-value)						
H_2	5.66	(2.33)	5.70	5.43	5.24	5.81	5.75	5.87
CH_4	2.49	(1.03)	2.50	2.31	2.31	2.31	2.41	2.13
C_2	6.02	(2.48)	5.47	5.15	5.16	4.43	3.63	4.46
C_3H_8	3.96	(1.63)	2.95	2.23	1.66	1.39	0.99	0.72
C_3H_6	0.98	(0.40)	1.39	1.78	2.04	2.34	2.42	2.65
C_4H_8-1	0.6	(0.2)		1.5				
trans-C_4H_8-2	0.42	(0.17)	0.88	0.85	0.74	0.75	0.75	0.64
cis-C_4H_8-2	0.26	(0.10)	0.54	0.68	0.57	0.49	0.50	0.43

a) Room temperature. The total dose is 2.5×10^{21} eV. g^{-1} and the dose rate is 1.44×10^{19} eV. g^{-1} hr^{-1}. The volume of reaction cell is about 50 cc.
b) Mol. per 1000 mol. of n-C_4H_{10}.
c) C_2 represents the sum of $C_2H_6+C_2H_4$.

---

[6] T. Kudo and S. Shida, Symposium on Radiation Chemistry, Nagoya (1964).

the addition of ammonia: the latter decreases more markedly.

B) C_3H_6 and C_4H_8 increase upon the addition of ammonia. The latter increases sharply upon the addition of a small amount of ammonia, and then gradually decreases in the high concentrations.

C) H_2 and CH_4 are not significantly affected by ammonia. Although methane and propane are formed by the rupture of the first C–C bond, only propane is affected by ammonia. This shows that the methyl radical produced by the fragmentation of the butane ion does not react with ammonia, while $C_3H_7^+$ does react with it.

The Reaction of $C_3H_7^+$.—The rate of the non-radical formation of C_3H_8 decreases sharply upon the addition of ammonia (Fig. 1). One the contrary, the yield of C_3H_6 increases complementally. This may be due to the high proton affinity of ammonia, which has been described above. Similar phenomena were observed in the radiolysis of mixtures of isobutane and some organic compounds, such as nitromethane, acetone or methyl iodide.[7]

$$n\text{-}C_4H_{10} \xrightarrow{I'(C_3H_7^+)_0} C_3H_7^+ + CH_3 + e \qquad (1)$$

$$C_3H_7^+ + n\text{-}C_4H_{10} \xrightarrow{k_2} C_3H_8 + C_4H_9^+ \qquad (2)$$

$$C_3H_7^+ + NH_3 - \begin{cases} \xrightarrow{k_3} C_3H_6 + NH_4^+ & (3) \\ \xrightarrow{k_4} C_3H_7NH_3^+ & (4) \end{cases}$$

N. B. $I'(C_3H_7^+)_0$: Rate of reaction 1, expressed in moles per 1000 mol. of *n*-butane.
k: Rate constant

$C_3H_7^+$ produced by irradiation forms propane via the hydride-ion transfer reaction with *n*-butane, but in the presence of ammonia it forms propylene via the proton transfer reaction. Since the increment of propylene is smaller than the decrement of propane, the condensation reaction 4 with ammonia may also occur. Though this type of ion-molecule reaction is seldom observed with a low pressure mass spectrometer, it is possible in the present use because of the deactivation of the condensed ion at 250 mmHg. The steady-state treatment leads to Eq. 1 for the decrease in propane and to Eq. 2 for the increase in propylene:

$$\frac{[NH_3]}{-\Delta G'(C_3H_8)} = \frac{k_2[C_4H_{10}]}{(k_3+k_4)I'(C_3H_7^+)_0} + \frac{1}{I'(C_3H_7^+)_0}[NH_3] \qquad \text{(Eq. 1)}$$

$$\frac{[NH_3]}{\Delta G'(C_3H_6)} = \frac{k_2[C_4H_{10}]}{k_3 I'(C_3H_7^+)_0} + \frac{(k_3+k_4)}{k_3 I'(C_3H_7^+)_0}[NH_3] \qquad \text{(Ep. 2)}$$

N. B. G' is expressed in moles per 1000 mol. of *n*-butane: it is proportional to G-value. $\Delta G'$ represents the increment in the product.

Thus, there must be a linear relationship between $[NH_3]/-\Delta G'(C_3H_8)$ and $[NH_3]$, and between $[NH_3]/\Delta G'(C_3H_6)$ and $[NH_3]$. As may be seen in Fig. 2 and Fig. 3, satisfactory straight lines are obtained. From the slopes and the intercepts

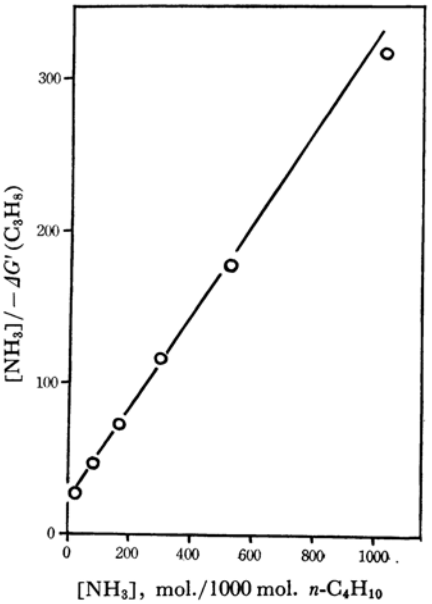

Fig. 2. Relation between $[NH_3]/-\Delta G'(C_3H_8)$ and $[NH_3]$.

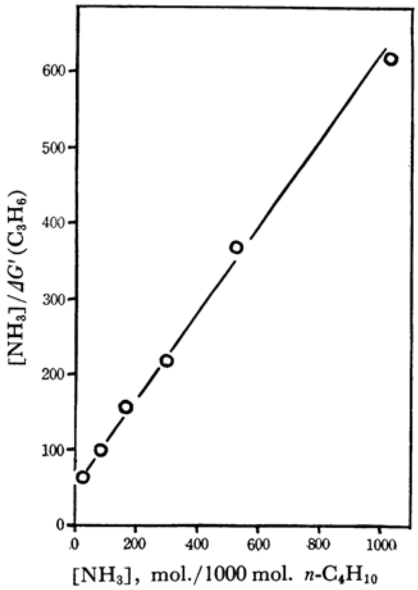

Fig. 3. Relation between $[NH_3]/\Delta G'(C_3H_6)$ and $[NH_3]$.

---

[7] R. P. Borkowski and P. J. Ausloos, *J. Chem. Phys.*, **40**, 1128 (1964).

of Fig. 2 and Fig. 3, the following relationships are obtained:

$$\frac{1}{I'(C_3H_7{}^+)_0}=0.306 \quad 1000\text{ mol. of } n\text{-}C_4H_{10}/\text{mol.} \qquad \text{(Eq. 3)}$$

$$\frac{k_2[C_4H_{10}]}{I'(C_3H_7{}^+)_0(k_3+k_4)}=20 \qquad \text{(Eq. 4)}$$

$$\frac{(k_3+k_4)}{k_3I'(C_3H_7{}^+)_0}=0.574 \quad 1000\text{ mol. of } n\text{-}C_4H_{10}/\text{mol.} \qquad \text{(Eq. 5)}$$

$$\frac{k_2[C_4H_{10}]}{k_3I'(C_3H_7{}^+)_0}=52 \qquad \text{(Eq. 6)}$$

From the above four equations, we get $k_3=6.0k_2$ and $k_4=7.1k_2$ as the average values.

The Reaction of $C_4H_9{}^+$.—As is shown in Fig. 1, C_4H_8 increases sharply upon the addition of a small amount of ammonia, and then it decreases gradually upon any further addition. This increase may be due to the proton transfer reaction between $C_4H_9{}^+$ and NH_3. Since the following fragmentation is not known to occur from the mass spectrum of *n*-butane:

$$C_4H_{10}{}^{+*} \rightarrow C_4H_9{}^+ + H \qquad (5)$$

the $C_4H_9{}^+$ in the radiolysis may be formed by the following secondary reactions:

$$C_4H_{10} \overset{I(Fr^+)_0}{\rightsquigarrow} Fr^+ + N + e \qquad (1)$$

$$Fr^+ + C_4H_{10} \xrightarrow{k_6} FrH + C_4H_9{}^+ \qquad (6)$$

$$C_4H_9{}^+ \rightarrow P \qquad (7)$$

$$C_4H_9{}^+ + NH_3 - \begin{cases} \xrightarrow{k_8} C_4H_8 + NH_4 & (8) \\ \xrightarrow{k_9} C_4H_9NH_3{}^+ & (9) \end{cases}$$

$$Fr^+ + NH_3 \rightarrow \text{Products} \qquad (10)$$

N. B. Fr^+: Fragment ions from the excited butane ion, such as $C_2H_5{}^+$ and $C_3H_7{}^+$.

N: Neutral fragments from the excited butane ion

P: A product

Reaction 10 represents the reaction of fragment ions and ammonia; cf., for example, reactions 3 and 4.

While the yield of C_4H_8 is increased by reaction 8 in a low concentration of ammonia, in a high concentration the reactions of ammonia with fragment ions cause a decrease in $C_4H_9{}^+$ (cf. reactions 10 and 6), that is, a depression of reaction 8.

We are able to estimate the life time of $C_4H_9{}^+$. As seen in Fig. 1, the concentration of ammonia where the rate of reaction 7 is about the same magnitude as that of reaction 8 is 5—10 mol./1000 mol. *n*-C_4H_{10}. Assuming that

$$R(7) \simeq R(8) \text{ at } [NH_3]=7.5\text{ mol.}/1000\text{ mol. } n\text{-}C_4H_{10} = 7.5\text{ mol.}/7.42\times10^4\text{ l.}$$

the life time of $C_4H_9{}^+$ is given as follows;

$$t(C_4H_9{}^+)=\frac{1}{k_8[NH_3]} \qquad \text{(Eq. 7)}$$

If k_8 is assumed to be equal to k_3 and if k_2 is taken as 1.3×10^{-9} cc. molec^{-1} sec^{-1},[8] we get $t(C_4H_9{}^+)=2.1\times10^{-9}$ sec., a value which is much shorter than the time of neutralization (10^{-2}—10^{-3} sec.) in the gas-phase radiolysis.[9] Therefore, it seems that $C_4H_9{}^+$ reacts with *n*-butane or with the unsaturated products, including C_5H_{10}-1, before the neutralization.

The Yields of $C_4H_{10}{}^{+*}$.—One of the most important problems in the radiolysis is how to estimate the relative importance of the excited ion and the molecule. Their importance in the C–C rupture of *n*-butane will, therefore, now be considered in spite of some uncertainty.

We get, from Eq. 3, Eq. 4, Eq. 5 and Eq. 6: $I'(C_3H_7{}^+)_0=3.52$ mol./1000 mol. *n*-C_4H_{10}, which is the initial yield of $C_3H_7{}^+$. Since $-\Delta G'(C_3H_8)=3.24$ at the concentration of 1030 mol./1000 mol. *n*-C_4H_{10} of ammonia, more than 90% of the ions react with ammonia at this concentration. Now we may assume that all of the fragment ions are eliminated by the proton transfer and condensation reactions with ammonia at 1030 mol./1000 mol. *n*-C_4H_{10}, and that the rate constants of the two reactions are the same. Since the total decreases in the C_2 and C_3 products upon the addition of ammonia are due to the condensation reaction, the yields of ions which react with ammonia should be twice the decrement:

$$-\Delta G'(C_3)=1.58 \text{ at } 1030\text{ mol. } NH_3/1000\text{ mol. } n\text{-}C_4H_{10}$$

$$-\Delta G'(C_2)=1.56 \text{ at } 1030\text{ mol. } NH_3/1000\text{ mol. } n\text{-}C_4H_{10}$$

Thus, $G'(C_4H_{10}{}^{+*})_{C_3}=3.2$ and $G'(C_4H_{10}{}^{+*})_{C_2}=3.1$ respectively. Therefore, $G'(C_4H_{10}{}^{+*})=6.3$ or $G(C_4H_{10}{}^{+*})=2.6$, as expressed in usual *G*-value units.

Most of the fragment ions form $C_4H_9{}^+$ via the hydride-ion transfer reaction with *n*-butane (cf. reaction 6); therefore, the yields of $C_4H_9{}^+$ may be considered to be approximately equal to that of $C_4H_{10}{}^{+*}$. The increment in C_4H_8 in Fig. 1 represents that of reaction 8. Assuming that $k_8/k_9 \simeq k_3/k_4 \simeq 1$ as before, the yields of $C_4H_9{}^+$ are twice the increment of C_4H_8 (cf. reactions 8 and 9):

$$G(C_4H_9{}^+)=2\Delta G(C_4H_8)_{\text{at }[NH_3]=81.5}/0.6 \qquad \text{(Eq. 8)}$$

The denominator is the correction factor as calculated from the decrease in C_3H_8 at 81.5 mol. NH_3/

---

[8] F. H. Field and F. W. Lampe, *J. Am. Chem. Soc.*, **80**, 5587 (1958).

[9] D. P. Stevenson, *J. Phys. Chem.*, **61**, 1453 (1957).

1000 mol. n-C_4H_{10}, since some of the fragment ions are lost by the reaction with ammonia at this concentration. Therefore, we get $G(C_4H_9^+)=2.4$. The agreement with $G(C_4H_{10}^{+*})$, as estimated from the decrement of products, is satisfactory.

Since the total G-value of the products from the C–C rupture, that is, $G(\sum C_1—C_3, C_5—C_7)$, is 6.5 (as determined by a previous study by the present authors[1]), the contribution of the excited molecule to the C–C rupture can be estimated by using $G(C_4H_{10}^{+*})$. As may be seen in Table II, the ionic C–C rupture is important in the radiolysis of gaseous n-butane. This result supports the conclusion of previous studies.[1,4]

TABLE II. THE CONTRIBUTION OF EXCITED ION AND MOLECULE IN THE C–C RUPTURE REACTION

	A	B	C
$G(C_4H_{10}^{+*})$	2.6	2.4	2.6
$G(C_4H_{10}^{*})$	0.7	0.9	0.8

A: Estimated from the reaction between fragment ions and NH_3.
B: Estimated from the reaction between $C_4H_9^+$ and NH_3.
C: Estimated from the analysis of products in the radiolysis of n-C_4H_{10} - n-C_4D_{10} - I_2 mixture.[4]

$C_4H_{10}^+$ at High Pressure.—Williams[10] used ND_3 as a proton scavenger in studying the ionic processes in the radiolysis of liquid cyclohexane. Since the saturation solubility of ND_3 in liquid cyclohexane is limited to a small percentage, however, he could not succeed in discussing the mechanism in detail. The present authors reported in a previous paper[2] that the radiolysis of n-butane near the critical state is similar to that in the liquid phase. Since we can get homogeneous mixtures of n-butane and the additive (water or ammonia) at any arbitrary concentration near the critical state, the effect of water or ammonia in high concentrations (up to 20%) has been studied near the critical state. The results in Table III show that all products by the C–C rupture decreases upon the addition of water or ammonia. Methane decreases to 70% upon the addition of 200 mol./1000 mol. n-C_4H_{10} of ammonia though it does not decrease upon the addition of even 500 mol./1000 mol. n-C_4H_{10} in the radiolysis at a low pressure (cf. Fig. 1). This fact suggests that the C–C rupture near the critical state may occur from the $C_4H_{10}^+$ produced by the deactivation of the excited butane ion:

$$C_4H_{10}^{+*} + C_4H_{10} \longrightarrow C_4H_{10}^{+} + C_4H_{10} \qquad (11)$$

$$C_4H_{10}^{+} \xrightarrow[\text{or neutralization}]{\text{Thermal cracking}} CH_4,\ C_2H_6,\ \text{etc.} \qquad (12)$$

$$C_4H_{10}^{+} + NH_3 \longrightarrow Q \qquad (13)$$

A more detailed study will be needed in order to discuss the mechanism of the effect of water or ammonia at high pressures.

TABLE III. EFFECT OF AMMONIA (OR WATER) IN THE RADIOLYSIS OF n-BUTANE AT HIGH PRESSURE

Yields of Products[a] at the density of 0.12 g. cc^{-1} of n-butane

Additive mol.[b]	Product, mol.[b]			
	H_2	CH_4	C_2H_6	C_3H_8
None	11.10	3.71	4.26	0.93
None	11.40	3.82	4.40	1.02
H_2O				
9.8	11.08	3.45	4.13	0.71
49.8	12.52	3.49	3.83	0.55
112	13.21	3.19	3.55	0.42
276	13.60	2.57	2.80	0.28
NH_3				
101	12.65	2.98	3.67	0.47
198	14.30	2.62	2.88	0.24

a) 200°C, The total dose is 2.5×10^{21} eV. g^{-1}.
b) Mol. per 1000 mol. of n-C_4H_{10}.

Summary

The effect of ammonia in the radiolysis of n-butane has been investigated. In low pressure radiolysis, C_3H_8 and C_2-products decrease upon the addition of ammonia while C_3H_6 increases. C_4H_8 increases sharply upon the addition of a small amount of ammonia, but it gradually decreases upon further addition. CH_4 and H_2 are not significantly affected by ammonia. These results have been interpreted in terms of the proton transfer reaction of ammonia with ions, and their rate constants have been estimated. The contribution of the excited ion to the C–C rupture has been concluded to be much more important than that of the excited molecule in low-pressure radiolysis.

In high-pressure radiolysis all the products from the C–C rupture, including CH_4, decrease upon the addition of ammonia (or water).

We appreciate the help of the Japan Atomic Energy Institute in performing the irradiation.

Laboratory of Physical Chemistry
Tokyo Institute of Technology
Ookayama, Tokyo

---

[10] F. Williams, *J. Am. Chem. Soc.*, **86**, 3954 (1964).