BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 2344—2346 (1966)

The Reactions of t-$C_4H_9^+$ in the Radiolysis of Neopentane in the Gas Phase

By Tetsuo MIYAZAKI and Shoji SHIDA

Laboratory of Physical Chemistry, Tokyo Institute of Technology, Ookayama, Tokyo

(Received March 1, 1966)

The yields and reactions of t-$C_4H_9{}^+$ produced in the radiolysis of neopentane in the gas phase have been studied by the use of ammonia. The yields of *iso*-C_4H_8 increase sharply upon the addition of a small amount of ammonia in the radiolysis of neopentane and show a constant value upon the further addition of ammonia (more than 10 mol.%). Since this increase is due to the following reaction:

$$t\text{-}C_4H_9{}^+ + NH_3 \rightarrow iso\text{-}C_4H_8 + NH_4{}^+$$

we get $G(t\text{-}C_4H_9{}^+) = 1.76$ by assuming the increment of *iso*-C_4H_8 to be equal to the yield of t-$C_4H_9{}^+$. This value is consistent with the value expected from the mass spectrum of neopentane. It has, therefore, been concluded that the ammonia method is a very effective general method for studying the reactions of ions. It is applicable to the study of ions under high pressures, ions which can not be studied by a mass spectrometer. It is especially effective in the study of less reactive ions.

In order to study ionic reactions in general, it is desirable to devise a general method which can easily and definitely discriminate the reactions of ions from those of neutral active species. Ausloos(1) studied ionic reactions using deuterated compounds and radical scavengers in the radiolysis of hydrocarbons. However, the application of his method is limited to highly reactive ions.

The present authors showed in a previous

---

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

Table I. Effect of ammonia in the radiolysis of neopentane

Yields of products at 180 mmHg of neopentane

Run	Additive[a]		Product[a]					
	C_5H_{10}-1	NH_3	H_2	CH_4	C_2[b]	C_3H_6	*iso*-C_4H_{10}	*iso*-C_4H_8
6	0	0	2.07	3.43	4.38	0.87	1.65	0.82
28	50	0	2.43	3.42	5.09	0.71	0.40	1.09
8	50	0	2.08	3.04	4.41	0.64	0.32	1.12
11	50	9.21	2.20	3.19	4.11	0.64	0.38	2.14
13	50	18.4	2.11	3.31	3.68	0.46	0.40	3.03
14	50	40.9	2.73	3.43	4.01	0.63	0.34	4.23
15	50	77.4	2.36	3.44	4.21	0.64	0.44	4.59
23	50	151	2.04	3.15	3.30	0.50	0.38	4.82
29	50	246	2.21	3.18	3.40	0.44	0.46	5.28
9	50	487	2.57	3.41	3.60	0.36	0.51	5.16

a) Moles per 1000 mol. of *neo*-C_5H_{12}.

b) C_2 represents the sum of C_2H_6, C_2H_4 and C_2H_2.

paper[2] that ammonia is a very effective reagent for studying the reactions of ions in the radiolysis of *n*-butane and that this method can also be applied to the study of an unreactive ion, such as *sec*-$C_4H_9^+$. Though the *t*-$C_4H_9^+$ ion is the most abundant ion in the mass spectrum of neopentane, the yield and the reaction of this ion in the radiolysis of neopentane have not been decided, since *t*-$C_4H_9^+$ does not produce C_4-products directly because of its low reactivity. Here we have studied the reaction of *t*-$C_4H_9^+$ in the radiolysis of neopentane by the use of the ammonia method.

Experimental

Most of the experimental procedures were identical with those described in the previous study.[2] Neopentane was supplied by the Takachiho Shoji Co.; its gas chromatographic analysis showed the presence of 0.05% *n*-pentane as an impurity. C_5H_{10}-1, used as a radical scavenger, was 99.99% pure. NH_3 was also of a high purity. The samples were irradiated at room temperature with γ-rays from Cs-137 of 5000 c. The total dose was 2.4×10^{21} eV.g^{-1}, and the dose rate was 8.9×10^{18} eV. g^{-1} hr^{-1} The reaction vessel was a glass cylinder (2.0 cm. in external diameter, 15 cm. high, and with a volume of about 50 cc.). The analytical procedures were identical with those described before.[3] C_2–C_4 hydrocarbon products were analysed by gas chromatography (dimethyl sulfolane column, 15 m.).

Results and Discussion

The effect of ammonia on the radiolysis of neopentane in the gas phase is shown in Table I and in Fig. 1. Though H_2, CH_4 and C_2 Products are not significantly affected by ammonia, *iso*-C_4H_8 increases markedly upon the addition of ammonia even only a small percentage, and becomes constant at a high concentration of ammonia. These phenomena are thought to be due to the following reactions, as in the radiolysis of the *n*-C_4H_{10}–NH_3 system[2]:

$$neo\text{-}C_5H_{12} \overset{I}{\rightsquigarrow} t\text{-}C_4H_9^+ + CH_3 \qquad (1)$$

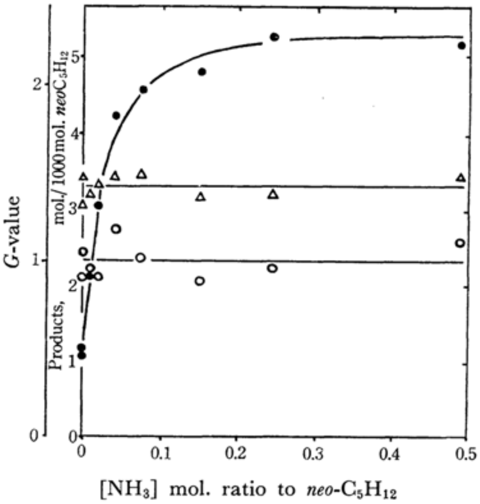

Fig. 1. Effect of ammonia in the radiolysis of *neo*-C_5H_{12}
H_2 ○, CH_4 △, *iso*-C_4H_8 ●

$$t\text{-}C_4H_9^+ \xrightarrow{k_2} P \qquad (2)$$

$$t\text{-}C_4H_9^+ + NH_3 \xrightarrow{k_3} iso\text{-}C_5H_8 + NH_4^+ \qquad (3)$$

(I: Rate of reaction 1; k: Rate constant)

t-$C_4H_9^+$ cannot produce *iso*-C_4H_{10} by the following hydride ion transfer reaction with neopentane, because this reaction is endothermic by about 20 kcal.[4]:

---

[2] T. Miyazaki and S. Shida, This Bulletin, **38**, 2114 (1965).

[3] T. Miyazaki, S. Arai, S. Shida and S. Sunohara, ibid., **37**, 1352 (1964).

[4] S. G. Lias and P. Ausloos, *J. Chem. Phys.*, **43**, 2748 (1965).

$$t\text{-}C_4H_9^+ + neo\text{-}C_5H_{12} \longrightarrow iso\text{-}C_4H_{10} + C_5H_{11}^+ \quad (4)$$

From a kinetic treatment similar to one described before,[2] we get $k_2/k_3 = 11.5$ mol./1000 mol. *neo*-C_5H_{12}. If k_3 is taken as 2×10^{-9} cc.molecule^{-1} sec^{-1},[5] we get $k_2 = 1.38\times10^8$ sec^{-1}. Therefore, the life time of t-$C_4H_9^+$ is about 7×10^{-9} sec., which is the same order of magnitude as the life time of the *sec*-$C_4H_9^+$ produced in the radiolysis of *n*-butane.[2] Since the life time of t-$C_4H_9^+$ is much shorter than the time of neutralization ($10^{-2}-10^{-3}$ sec.),[6] and the time of diffusion to wall of the vessel (about 10^{-1} sec.),[7] t-$C_4H_9^+$ may be consumed by the addition to C_5H_{10}-1;

$$t\text{-}C_4H_9^+ + C_5H_{10}\text{-}1 \longrightarrow C_9H_{19}^+ \quad (5)$$

Then, $k_2 = k_5[C_5H_{10}\text{-}1]$. Therefore, we get $k_5 = 0.45\times10^{-9}$ cc. molecule^{-1} sec^{-1}, which is similar to the ordinary rate constant of ion-molecule reactions. Since the total dose was large in this work and since an unsaturated product, such as *iso*-C_4H_8, may react with radicals, C_5H_{10}-1 was added as a radical scavenger. However, we found that C_5H_{10}-1 may react also as an ion-scavenger. Since *iso*-C_4H_{10} is formed in considerable amounts in the absence of C_5H_{10}-1 in the radiolysis of neopentane (Table I), the neutralization of t-$C_4H_9^+$ may produce the t-C_4H_9 radical as follows:

$$t\text{-}C_4H_9^+ + e \longrightarrow t\text{-}C_4H_9 \quad (6)$$

$$t\text{-}C_4H_9 + neo\text{-}C_5H_{12} \longrightarrow iso\text{-}C_4H_{10} + C_5H_{11} \quad (7)$$

$$t\text{-}C_4H_9 + R \longrightarrow P \quad (8)$$

(R: a radical; P: the products of Reaction 8, a combination- and disproportionation reaction between t-C_4H_9 and a radical of the system.)

In the mass spectrum of neopentane, the fraction of t-$C_4H_9^+$ amounts to 41% of all the ions. Taking $W_{neo\text{-}C_5H_{12}}$ as 24 eV., it may be expected that $G(t\text{-}C_4H_9^+) = 1.7$. Since the increment of *iso*-C_4H_8 is equal to the yield of t-$C_4H_9^+$ in the present work, we get $G(t\text{-}C_4H_9^+) = 1.76$ in the radiolysis of neopentane; this is in good agreement with the mass spectrometric value. Recently Ausloos reported that the $G(iso\text{-}C_4H_8)$ value in the radiolysis of *neo*-C_5H_{12}–NO in a stainless-steel reaction vessel differs from that in a graphite-coated reaction vessel.[4] Assuming this difference to be equal to t-$C_4H_9^+$, he obtained $G(t\text{-}C_4H_9^+) = 1.23$. However, this value seems to be an underestimate.

It can be concluded that ammonia is a very effective reagent for studying the reaction of ions, especially that of the unreactive ions in the radiolysis of hydrocarbon, and that ionic reactions at high pressures, which can not be studied by a mass spectrometer, can be studied easily by the ammonia method.

The authors appreciate the help of Dr. Toshio Sugiura and others of the Japan Atomic Energy Institute in performing the work.

---

[5] M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **87**, 4242 (1965).

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

[7] C. N. Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," Claredon Press, Oxford (1933), p. 29.