Pyrolysis of Organic Compounds. II. Pyrolysis of Toluene-3-d and Toluene-4-d

By Makoto TAKAHASI

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In recent years the bond dissociation energy of toluene, $D(C_6H_5CH_2{-}H)$, has become a topic of considerable dispute, and various attempts to determine the bond dissociation energy were reviewed by Benson & Buss[1] and by the present author[2]. Szwarc[3] estimated the activation energy of the pyrolytic reaction of toluene by the flow method to be 77.5 kcal./mol., and the frequency factor to be 2×10^{13} in the reaction temperature range 738~864°C. H. Blades, A. Blades and Steacie[4] repeated the study of the pyrolysis of toluene by the same method, and they observed that the first order rate constant increases, as the contact time is increased. They calculated the apparent activation energy of the pyrolytic reaction to be 90 kcal./mol., keeping the contact time constant at 0.068 sec. in the reaction temperature range 860~940°C, but they concluded that it is premature to assign any definite value to the bond dissociation energy of toluene. At first, in order to explain the higher activation energy and the occurrence of methane, they suggested reaction 2, which proceeds concurrently with the main reaction 1.

$$C_6H_5CH_3 \rightarrow C_6H_5CH_2\cdot + H\cdot \qquad (1)$$

$$C_6H_5CH_3 \rightarrow C_6H_5\cdot + CH_3\cdot \qquad (2)$$

Later, however, they[5] approved of Szwarc's view that the contribution of reaction 2 to the apparent activation energy of pyrolysis of toluene is of a minor degree, for they considered the facts that the ratio of hydrogen to methane in the reaction product of pyrolysis of toluene is constant over the reaction temperature range, and that the ratio does not vary even in the decomposition of *n*-propylbenzene in the presence of excessive toluene[6].

The present author[2] carried out the pyrolysis of toluene in both of the temperature ranges, 738~864 and 860~940°C, to elucidate the cause of the discrepancy of the bond dissociation energies of toluene obtained by the two groups, and it was found that the apparent activation energy for the first order rate expression of pyrolysis of toluene increases, as the reaction

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[1] S. W. Benson and J. H. Buss, *J. Phys. & Colloid Chem.*, **61**, 104 (1957).

[2] M. Takahasi, This Bulletin, **33**, 801 (1960).

[3] M. Szwarc, *J. Chem. Phys.*, **16**, 128 (1948).

[4] H. Blades, A. T. Blades and E. W. R. Steacie. *Can. J. Chem.*, **32**, 298 (1954).

[5] A. Blades and E. W. R. Steacie, ibid., **32**, 1142 (1954).

[6] C. H. Leigh and M. Szwarc, *J. Chem. Phys.*, **20**, 403 (1952).

temperature was extended to a higher range. The author discussed the possible causes of the nonlinearity of the relation of log k versus $1/T$, and suggested complication by the involvement of some competitive reaction. Blades and Steacie[5] suggested the same possibility in the reaction, and carried out the pyrolysis of n-propylbenzene in an excess of deuterated toluenes (mixture of toluene-α-d_3: 66%, toluene-α-d_2: 29%, and toluene-α-d: 5%) at 722°C at contact time 0.45 sec. They found the products were composed of hydrogen, methane, ethane, ethylene, benzene and bibenzyl, and the ratios of the gaseous products were:

$$H_2 : HD : D_2 = 1 : 1 : 0$$

and

$$CD_4 : CD_3H : CD_2H_2 = 1 : 1.5 : 1$$

respectively.

The large ratio of H_2 to HD suggested that hydrogen atoms may be abstracted from the ring as well as from the side chain. In addition, they concluded that concerning two mechanisms 3 and 4 suggested by Szwarc,

$$H\cdot + C_6H_5CD_3 \text{ (or } C_6H_5CD_2H) \rightarrow C_6H_5\cdot + CD_3H \text{ (or } CD_2H_2) \quad (3)$$

$$C_6H_5\cdot + C_6H_5CD_3 \rightarrow C_6H_5D + C_6H_5CD_2\cdot$$

$$H\cdot + C_6H_5CD_3 \text{ (or } C_6H_5CD_2H) \rightarrow CD_3\cdot \text{ (or } CD_2H\cdot) + C_6H_6$$

$$CD_3\cdot \text{ (or } CD_2H\cdot) + C_6H_5CD_3 \text{ (or } C_6H_5CD_2H) \rightarrow CD_4 + C_6H_5CD_2\cdot \text{ (or } CD_3H,\ CD_2H_2) \quad (4)$$

mechanism 3 would give CD_3H and CD_2H_2, while mechanism 4 would give CD_4, CD_3H and CD_2H_2. They considered that the production of CD_4 in their experiment is a good evidence for mechanism 4, and that mechanism 3 contributes to a minor degree. As the pyrolysis of toluene itself was not carried out in their experiment, it was not clear whether the initiations reaction of pyrolysis of toluene involves the ring-hydrogen or not. The present author attempted to study the pyrolysis of toluene-3-d and toluene-4-d in the temperature range 830~955°C, and investigated the reactivities of the meta and para positions of toluene.

Experimental

Materials.—Toluene-3-d and -4-d were prepared by the reaction of m- and p-tolylmagnesium bromide with deuterium hydroxide according to Gold[7] with some modifications. The Grignard reagent was prepared from 50 g. of m- or p-bromotoluene, 7 g. of magnesium and 120 ml. of ethyl ether; and 6 ml. of deuterium hydroxide (99.78 g. D_2O/100 g.) was added to the reaction mixture. In adding deuterium hydroxide, care should be taken to continue vigorous stirring to secure the contact of deuterium hydroxide with the Grignard reagent. The reaction mixture was refluxed for about ten minutes, and left to stand overnight. In order to decompose the remaining Grignard reagent, dry carbon dioxide was passed through for some time, and then 7 g. of ammonium chloride solution in 25 ml. of water was added, a solid material being formed. Then 20 ml. of concentrated hydrochloric acid was added to dissolve the solid. Ether layer was separated, and the aqueous layer was extracted with 100 ml. of ether. The combined ether solution was washed with a dilute sodium hydroxide solution and with distilled water successively, and dried with calcium chloride. Ether was removed by distillation with Vigreux's columm, and toluene fraction boiling at 111~112°C was collected, weighing about 15 g. The toluene fraction was then shaken with about 15% hydrochloric acid to remove a trace of ether which interferes with pyrolysis of toluene, and distilled through a spinning band column of 150 cm. in length. Although the deuterated toluenes thus obtained contained about 22% of undeuterated toluene (see the next section), some improvements of isotopic purity may be obtained by the more elaborated method proposed by Weldon[8].

Determination of Isotopic Purity of Deuterated Toluenes. — For the determination of the isotopic purity of the deuterated organic compounds, mass spectrometry under reduced ionization voltage[9] is recommended, but the available mass spectrometer of CEC 103 A type operated at ionizing voltage 70 V. was unsuitable for the present purpose. So the present author was obliged to apply the infrared spectra for the determination of the isotopic purity of synthesized deuterated toluenes, in spite of less accuracy of the method. Infrared spectra of toluene, toluene-3-d and toluene-4-d were already given by Tiers[10] in the region of 693~835 cm^{-1}. Comparison of their spectral data of toluene with those of the present author gave good agreement in the wave numbers of the absorption maxima, but not in the intensity, their absorption coefficients at characteristic absorption maxima being larger by about twice than the present author's. While standard toluene-3-d and -4-d of isotopic purity of more than 99% were not available to us, Tier's data were not proper to be applied to the present analysis, so that the present author adopted the method to determine the content of undeuterated toluene in the synthesized mixture. The infrared spectral data obtained by a Perkin Elmer 112 infrared spectrometer are shown in Table I. The absorption band of toluene at 730 cm^{-1} is too strong to determine the absorption coefficient in liquid state. Therefore, the absorption band at 695 cm^{-1} was used in the analysis of the mixture of toluene and toluene-4-d, the latter of which has no characteristic absorption at the wave number. The extinction coefficient of standard

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[7] V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, **1951**, 2743.

[8] L. H. P. Weldon and C. L. Wilson, *J. Chem. Soc.*, **1946**, 235.

[9] The Institute of Petroleum, "Applied Mass Spectrometry", London, (1954), p. 91.

[10] G. V. D. Tiers and J. H. Tiers, *J. Chem. Phys.*, **20**, 761 (1953).

TABLE I. EXTINCTION COEFFICIENTS OF STANDARD TOLUENE, AND OF MIXTURES OF TOLUENE-3-*d* OR -4-*d* AND TOLUENE

Wave numbers, cm^{-1}	3030	835	798	730	710	695
Standard toluene	430	0	0	1470	0	840
Sample I (toluene+toluene-3-*d*)	260	0	540	480	0	800
Sample II (toluene+toluene-4-*d*)	260	640	0	490	200	190

Extinction coefficient $K_\nu = \log(I_0/I)/d$.
Cell thickness $d = 0.00087$ cm.

TABLE II. COMPARISON OF MASS SPECTRA OF STANDARD TOLUENE, SAMPLES I AND II, WITH API DATA

m/e	Standard toluene	Sample I	Sample II	Toluene*	Toluene-3-*d**	Toluene-4-*d**
95	—	0.21	0.26	—	—	—
94	0.16	5.38	5.49	0.16	—	—
93	6.00	69.09	70.39	5.60	72.5	71.6
92	78.37	100	100	78.5	100	100
91	100	35.15	37.07	100	8.51	8.53
90	7.70	4.50	4.57	9.08	2.53	3.66
89	3.72	2.14	2.09	4.13	1.00	0.93
88	0.27	0.45	0.42	0.36	0.32	0.33
87	0.58	0.80	0.75	0.60	0.61	0.61
86	0.99	0.98	0.99	0.94	0.69	0.67
85	0.78	0.71	0.73	0.66	0.48	0.48
84	0.33	0.35	0.35	0.22	0.23	0.21

Ionization voltage : 70 V.
Ionizing current : 10.5 μA.
* From API Spectral Data, Serial No. 418, 687 and 688.
Components containing ^{13}C have been removed in the API Data.

toluene at 695 cm^{-1} being 840, the content of toluene in Sample II (mixture of toluene and toluene-4-*d*) was ascertained as 22%. In the analysis of Sample I (mixture of toluene and toluene-3-*d*) the band at 695 cm^{-1} is unsuitable, for toluene-3-*d* has the absorption band of nearly the same strength as toluene at the position. However, as the extinction coefficient of Sample I at 730 cm^{-1} is accidentally almost the same as that of Sample II, the content of toluene in Sample I was presumed to be nearly the same as that of Sample II, that is, 22%. Mass spectrometric data which are shown in Table II may support the above conclusion, although they are not sufficient for determining the precise isotopic purity.

Apparatus and Procedure of Pyrolysis. — They were previously described in Part I. Experiments in the temperature range lower than 830°C and at a contact time less than 0.1 sec. were not carried out, for a sufficient amount of gas for the mass spectrometric analysis was not produced under these conditions.

Analysis of Gaseous Products and Experimental Results

The gas products of pyrolysis of the mixture of toluene and toluene-3-*d* or -4-*d* consisted of H_2, HD, a trace of D_2, CH_4 and CH_3D. No complete method of determination of the ratio of HD to H_2 appeared to be established until most recently[11], in the case where the relative abundance of HD to H_2 is more than 10% and the total amount of hydrogen is small. Recent development of gas chromatography has made it possible to separate HD from H_2, using a very small amount of a sample[12], and this method may be applied to the analysis. In the present experiment, the author was satisfied with determining the ratio approximately. As pure HD for a standard was not available, its mass spectrometric sensitivity at *m/e* 3, was assumed to be equal to that of H_2 at *m/e* 2. It has been pointed out that the peak at *m/e* 3 contains the component of H_3^+, in addition to that of HD^+, but its contribution was not appreciable in the present case, using ionizing current of 10.5 μA. The contribution of D^+ to *m/e* 2 is not known, but it may be neglected,

TABLE III

m/e	18	17	16	15	14	13
			CH_4^+	CH_3^+	CH_2^+	CH^+
		$^{13}CH_4^+$	$^{13}CH_3^+$	$^{13}CH_2^+$	$^{13}CH^+$	$^{13}C^+$
		CH_3D^+	CH_2D^+	CHD^+	CD^+	CH^+
	$^{13}CH_3D^+$	$^{13}CH_2D^+$	$^{13}CHD^+$	$^{13}CD^+$	$^{13}CH^+$	$^{13}C^+$
	P_{18}	P_{17}	P_{16}	P_{15}	P_{14}	P_{13}

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11) The Institute of Petroleum, " Applied Mass Spectrometry ", London (1954) p. 81.

12) S. Ohkoshi, Y. Fujita and T. Kwan, This Bulletin, 31, 771 (1958).

considering that the relative abundance of H^+ produced from H_2 is 2.1% to that of H_2^+ [13].

The ratio CH_3D/CH_4 was determined according to the following procedure. As each peak of the mixture of CH_4 and CH_3D at m/e 18∼13 is composed of the following several components as shown in Table III, Eqs. 5 and 6

$$P_{17}=\frac{1}{100}\{S_{CH_4}(a_{^{13}CH_4^+}\times 0.0101)X$$
$$+S_{CH_3D}(b_{CH_3D^+}\times 0.9896+b_{^{13}CH_2D^+}\times 0.0101)Y\} \tag{5}$$

$$P_{16}=\frac{1}{100}[S_{CH_4}(a_{CH_4^+}\times 0.9896+a_{^{13}CH_3^+}\times 0.0101)X$$
$$+S_{CH_3D}\{b_{CH_2D^+}\times 0.9896+(b_{^{13}CHD^+}+b_{^{13}CH_3^+})$$
$$\times 0.0101\}Y] \tag{6}$$

are derived, where P_{17} and P_{16} are observed peak heights at m/c 17 and 16, S_{CH_4} and S_{CH_3D} are sensitivities of CH_4 and CH_3D at their parent peaks, a_{R^+} and b_{R^+} are relative abundances of ions produced from CH_4 and CH_3D, and X and Y are pressures of ($CH_4+{}^{13}CH_4$) and ($CH_3D+{}^{13}CH_3D$), respectively.

TABLE VI. MASS SPECTRA OF CH_4 AND CH_3D

m/e	CH_4 (a)	CH_3D (b)	CH_4 (a')
17		100	
16	100	79.8	100
15	89.3	23.7	88.1
14	19.4	10.5	19.8
	Mohler's data, $^{13}CH_4$ component has been removed.		this work

For the measurement of standard CH_4 by the present author gave nearly the same cracking pattern a' as a of Mohler[14] (Table IV), the author applied his data a and b to the present analysis. From Eqs. 5 and 6, Eq. 7 is derived assuming $S_{CH_4}=S_{CH_3D}$, and using Mohler's data,

$$Y/X=99.052\frac{(1.00808\,P_{17}-0.0101\,P_{16})}{(98.96\,P_{16}-79.207\,P_{17})} \tag{7}$$

The data of mole ratios HD/H_2 and CH_3D/CH_4 obtained in the pyrolysis of Samples I and II under various conditions are shown in Table V, where Eq. 7 was applied to the determination of CH_3D/CH_4. The determination of the mole ratio (H_2+HD)/(CH_4+CH_3D) was not performed, for sufficient accuracy was not expected for the determination by the mass spectrometric analysis, and from the previous data it may be presumed that the ratio is about 2[2].

Analyses of liquid products were carried out by both infrared and mass spectrometric methods. Toluene recovered from the reaction products of Samples I and II gave nearly the same infrared spectra as the original ones. Therefore, it may be concluded that any transfer of deuterium from the initial position did not occur in the pyrolysis. Mass spectra of the recovered toluene were also nearly the same in the mass range of C_7 groups, but some differences were observed in the range of C_6 groups as shown in Table VI.

Table VI shows that the peak at m/e 78 includes $C_6H_6^+$, $C_6H_4D^+$ and $C_5{}^{13}CH_5^+$, and the peak at m/e 79 does $C_6H_5D^+$, $C_6H_3D_2^+$ and $C_5{}^{13}CH_6^+$, but it was not carried out to determine the ratio $C_6H_6:C_6H_5D:C_6H_4D_2$ from these data. It is to be noted that the increase of benzene content due to the rise of the reaction temperature is rather small compared

TABLE V. MOLE RATIOS HD/H_2, D_2/H_2 AND CH_3D/CH_4 IN THE PYROLYSIS OF SAMPLES I AND II

Expt. No.	Reaction temp., °C	Vapor pressure, mmHg	k, sec^{-1}	HD/H_2	D_2/H_2	CH_3D/CH_4
Sample I (mixture of 22% toluene and 78% toluene-3-*d*)						
I-4	830.3	8.92	(1.0×10^{-2})	—	—	0.060*
I-3	832.0	7.36	1.0×10^{-2}	0.11	0.000	0.052
I-1	876.6	8.80	4.2×10^{-2}	0.14	0.004	0.077
I-5	902.6	8.46	1.2×10^{-1}	—	—	0.091*
I-2	908.1	8.82	1.3×10^{-1}	0.13	0.004	0.075
Sample I′ (toluene recovered from the reaction mixture of Sample I after pyrolysis)						
I′-1	850.3	3.66	—	0.17	0.006	0.058
I′-2	852.0	10.62	2.8×10^{-2}	0.19	0.007	0.082
I′-3	919.0	8.96	2.9×10^{-1}	0.18	0.007	0.085
Sample II (mixture of 22% of toluene and 78% of toluene-4-*d*)						
II-3	834.3	7.86	1.2×10^{-2}	—	—	0.053*
II-1	876.5	5.42	7.8×10^{-2}	0.15	0.005	0.074
II-4	907.3	5.60	1.9×10^{-1}	—	—	0.098*
II-2	955.6	3.90	1.1	0.19	0.004	0.079

* In these cases, sensitivity of mass spectrometer was low and unstable particularly for hydrogen.

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[13] API Mass Spectral Data. No. 452.

[14] F. L. Mohler, V. H. Dibeler and E. Quinn, *J. Research Natl. Bur. Standards*, 61, 171 (1958).

TABLE VI. MASS SPECTRA OF UNPYROLYZED AND PYROLYZED TOLUENES

Sample No.	Reaction temp. °C	m/e 72	78	Δ 78*	79	Δ 79*	80	84	93	94
Sample I	(before pyrolysis)	0.09	1.30	—	0.16	—	0.00	0.35	69.1	100
I-4	830.0	0.08	1.42	0.12	0.21	0.05	0.00	0.35	68.2	〃
I-3	832.0	0.10	1.39	0.09	0.25	0.09	0.00	0.35	70.2	〃
I-1	876.6	0.09	1.43	0.17	0.33	0.17	0.05	0.31	71.6	〃
I-5	902.6	0.08	1.66	0.36	0.72	0.56	0.11	0.31	69.3	〃
I-2	908.1	0.09	1.48	0.18	0.56	0.40	0.08	0.34	71.1	〃
Sample II	(before pyrolysis)	0.09	11.30	—	0.17	—	0.00	0.35	70.4	〃
II-3	834.3	0.09	1.47	0.17	0.25	0.08	0.00	0.35	69.4	〃
II-4	907.3	0.09	1.52	0.22	0.93	0.76	0.16	0.36	68.8	〃

* Δ means increment of relative abundance by pyrolysis.

with the increase of velocity constant in the same reaction temperature range (cf. Table V).

These experimental results are summarized as follows:

1) Toluene-3-*d* and -4-*d* (isotopic purity: 78%) gave H_2, HD, a trace of D_2, CH_4 and CH_3D by pyrolysis, and their mole ratios were determined by mass spectrometric analysis.

2) There was not any distinct difference in the mole ratios of HD/H_2 and CH_3D/CH_4 in the reaction of either toluene-3-*d* or -4-*d*, and it may be concluded that the reactivities of *m*- and *p*-hydrogen of toluene are of the same order.

3) As the pyrolyzed toluene gave a nearly similar infrared spectra as those of unpyrolyzed one, exchange reaction of hydrogen between toluenes did not occur to an appreciable extent in the temperature range 830～900°C.

The following reaction mechanism may be presented to explain the formation of HD and CH_3D.

In the above schemes, statistical weight shows numbers of reacting hydrogens in each set of elementary processes. The production of HD may be explained by one or more of reactions 5′—7, and that of CH_3D by 10 and/or 13. If it is assumed that eight hydrogens of toluene

(toluene-3-*d* or -4-*d* containing 22% toluene)

					Statistical weight on the assumption of equal reactivity	
$C_6H_4D\text{-}CH_3$	⟶	$C_6H_4D\text{-}CH_2\cdot + H\cdot$	………	(1)	3	Initiation
〃 〃	⟶	$\cdot C_6H_3D\text{-}CH_3 + H\cdot$	………	(2)	4	
〃 〃	⟶	$\cdot C_6H_4\text{-}CH_3 + H\cdot$	………	(2′)	1	
〃 〃	⟶	$\cdot C_6H_4D + CH_3\cdot$	………	(3)		
$H\cdot + C_6H_4D\text{-}CH_3$	⟶	$C_6H_4D\text{-}CH_2\cdot + H_2$	………	(4)	3	Abstraction by H atom
〃 〃	⟶	$\cdot C_6H_3D\text{-}CH_3 + H_2$	………	(5)	4	
〃 〃	⟶	$\cdot C_6H_4\text{-}CH_3 + HD$	………	(5′)	1	
$D\cdot + C_6H_4D\text{-}CH_3$	⟶	$C_6H_4D\text{-}CH_2\cdot + HD$	………	(6)	3	Abstraction by D atom
〃 〃	⟶	$\cdot C_6H_3D\text{-}CH_3 + HD$	………	(7)	4	
〃 〃	⟶	$\cdot C_6H_4\text{-}CH_3 + D_2$	………	(7′)	1	
$H\cdot + C_6H_4D\text{-}CH_3$	⟶	$\cdot C_6H_4D + CH_4$	………	(8)		Metathesis by H atom
〃 〃	⟶	$C_6H_5D + CH_3\cdot$	………	(9)		
$D\cdot + C_6H_4D\text{-}CH_3$	⟶	$\cdot C_6H_4D + CH_3D$	………	(10)		Metathesis by D atom
〃 〃	⟶	$C_6H_4D_2 + CH_3\cdot$	………	(11)		
$CH_3\cdot + C_6H_4D\text{-}CH_3$	⟶	$C_6H_4D\text{-}CH_2\cdot + CH_4$	………	(12)	3	Abstraction by CH_3 radical
〃 〃	⟶	$\cdot C_6H_3D\text{-}CH_3 + CH_4$	………	(13)	4	
〃 〃	⟶	$\cdot C_6H_4\text{-}CH_3 + CH_3D$	………	(13′)	1	
$2\cdot C_6H_3D\text{-}CH_3$ (or $\cdot C_6H_4\text{-}CH_3$)	⟶	Deuterated and undeuterated dimethylbiphenyls	………	(14)		Termination
$C_6H_4D\text{-}CH_2\cdot$ (or $C_6H_5\text{-}CH_2\cdot$)	⟶	Deuterated and undeuterated bibenzyls	………	(15)		

(The reactions of undeuterated toluene omitted.)

had the reactivities of the same order both in the initiations and propagations, (that is, here both isotope effect and structure effect are neglected), the expected ratio $H_2:HD:D_2$ in the pyrolysis of toluene-*d* of 100% of isotopic purity might be $7/8\times7/8+7/8\times1/8:1/8\times7/8:1/8\times1/8=1:0.29:0.02$. On the other hand, if it is assumed that HD was produced only by the abstraction of D atom from benzene ring by hydrogen atom (reaction 5′), not by reactions 6 and 7, the ratio $H_2:HD:D_2$ might be $7/8:1/8:0=1:0.14:0$ (natural abundance 0.02% of D is neglected). As the experimental results (Table V) show the ratio, $1:0.10\sim0.19:0.000\sim0.007$, it is indicated that the ratio is in the middle of the two assumed ratios, and it may be expected that HD/H_2 is augmented, if 22% of undeuterated toluene is removed from Samples I and II. Although these results do not suffice to establish the initiation reactions 2 and 2′, they may not be a negative evidence for such processes. A more direct evidence supporting the existence of process 2′ may be obtained by pyrolyzing $C_6D_5CH_3$, for $C_6D_5CH_3$ would give D_2 by the successive reactions 2′, 6 and 7 in a high yield.

The ratio $CH_3D:CH_4$ is relatively low compared with that of $HD:H_2$ in the whole reaction temperature range. The possible processes to produce CH_3D may be 10 and/or 13′, and if it is assumed that processes 2 and 2′ gave H and D atoms in the ratio 7 : 1, and that processes 12—13′ proceeded with statistical weights (3 : 4 : 1), the ratio of CH_3D to CH_4 obtained by reactions 8 and 10 might be 1/7, and the ratio of CH_3D to CH_4 obtained by reactions 12—13′ might be also 1/7. On the other hand, if it is assumed that D atom was not produced by the initiation reaction 2′, CH_3D might be produced only by reaction 13. In this case, the ratio $CH_3D:CH_4$ depends on the relative velocity rate of reactions 8 and 9. If it is assumed that the relative rate ratio is $\alpha:1$, the ratio CH_3D/CH_4 should be $1/(7+8\alpha)$, and less than 1/7.

These experimental results are rather unexpected, considering the generally accepted fact that $D(C_6H_5\text{-}H)$ is larger than $D(C_6H_5CH_2\text{-}H)$. Dr. Kobayashi[15] suggested that the benzyl radical would rearrange to cycloheptatrienyl radical, considering the mass spectrometric evidence of the rearrangement of benzyl cation to cycloheptatrienium cation[16]. If such a rearrangement took place, transfer of deuterium atom in the aromatic ring would be observed. Unfortunately the amount of aromatic products produced by pyrolysis was not sufficient to be analyzed. On the other hand, it has been known that CH_3 radical abstracts hydrogen from the benzene ring[17,18], and this fact may explain the production of CH_3D. As may be described in the succeeding paper, pyrolysis of benzene proceeds in the relatively low temperature range, and its apparent activation energy is unexpectedly low. Although the reaction mechanism of pyrolysis of benzene is not yet completely established, it may be compatible with the present results.

Summary

In order to elucidate the mechanism of the pyrolysis of toluene, pyrolysis of toluene-3-*d* and -4-*d* was carried out by the flow method in the temperature range 830～955°C, and the mole ratios $D_2:HD:H_2$ and $CH_3D:CH_4$ were determined by mass spectrometry. The involvement of the reaction of ring-hydrogen in the pyrolysis has been confirmed from the formation of HD and CH_3D. As there was not any distinct difference in the mole ratios between the reactions of toluene-3-*d* nor -4-*d*, it is concluded that the reactivities of *m*- and *p*-hydrogens of toluene are of the same order. Considering these results, the possible elementary processes involving ring-hydrogen are discussed.

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Department pf Chemistry
College of General Education
The University of Tokyo
Meguro-ku, Tokyo

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