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Kinetic Study of Pyrolysis of Toluene- d_5

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Reaction mechanism of pyrolysis of toluene was studied with toluene- d_5 of high isotopic purity. The rate constant of pyrolysis of toluene- d_5 in gas phase was determined to be $k = 10^{11.5 \pm 0.3} \times \exp(-70 \pm 1 \text{ kcal/mol}) (\text{sec}^{-1})$ and compared with that of toluene. Hydrogen isotope mixtures produced in the pyrolysis of toluene- d_5 were collected and analyzed by mass spectrometer. Formation of some amount of D_2 is confirmed, and it is concluded that the fission of ring C-D bond is involved to some extent in the pyrolytic reaction of toluene- d_5 at high reaction temperatures. The ratio of rate constants of abstraction type (k_{D-H}/k_{H-H}) is also determined, and the difference of the activation energies between k_{D-H} and k_{H-H} is found to be approximately 14 kcal/mol.

Since the pioneering work by Szwarc,¹⁾ the mechanism of pyrolysis of toluene has been investigated by several workers,²⁻⁶⁾ and it is now fairly established that the main primary process in this reaction is the

homolytic fission of carbon-hydrogen bond of side chain. In consideration of these experiments, Price proposed the value of 85 kcal/mol for the bond dissociation energy $D(C_6H_5CH_2-H)$.⁶⁾ However, the details of the reaction mechanism, particularly of the

1) H. Szwarc, *J. Chem. Phys.*, **16**, 128 (1948).2) H. Blades, A. T. Blades and E. W. R. Steacie, *Can. J. Chem.*, **32**, 1142 (1954).3) I. V. Berezin, N. F. Kazanskaya and K. Martiner, *Zhur. Obshchei Khim.*, **30**, 4092 (1960).4) J. J. Batten, *Australian J. App. Sci.*, **12**, 11 (1961).5) T. Takeuchi, M. Sakaguchi and Y. Togashi, *This Bulletin*, **39**, 1437 (1966).6) S. J. Price, *Can. J. Chem.*, **40**, 1310 (1962).

other competing primary process or successive secondary processes have been not completely understood yet. Our previous study of the pyrolysis of *m*- and *p*-toluene-*d* has revealed that the mechanism of the reaction above *ca.* 850°C is fairly complicated, and that the ring hydrogen is involved in some way in the course of the reaction.⁷⁾ In the present study we attempted to elucidate the further details of the reaction mechanism, concentrating our concern to the question whether the homolytic fission of the ring hydrogen-carbon bond competes with that of methyl hydrogen-carbon bond as a primary process. This will be confirmed by investigating the extent of the formation of D₂ in the pyrolysis of toluene-*d*₅ of high isotopic purity (all ring hydrogens deuterated).

Experimental

Materials. Toluene-*d*₅ was prepared by the Wurtz-Fittig reaction of bromobenzene-*d*₅ (8 g) and methyl iodide (7 g) with sodium (5 g) in ether solution. Toluene-*d*₅ was separated from the reaction mixture by distillation and purified by the preparative gas chromatography with dioctyl phthalate column. The yield of pure toluene-*d*₅ was approximately 50% for bromobenzene-*d*₅, and its isotopic purity was determined by the reduced ionization voltage technique (at 10 and 12 V) with CEC 103 Mass Spectrometer to be approximately 90%, and only detectable impurity was toluene-*d*₄ (10% to toluene-*d*₅).

Apparatus and Procedure of Pyrolysis. The apparatus and procedures used in the present experiment are similar to those described in the previous paper⁴⁾ with slight modification to secure more complete trapping of unreacted toluene. The contact time in each run of the pyrolysis is nearly 0.1 sec with the reaction tube of the effective volume of 31 cc under the pressure of 4–5 mmHg of toluene.

Analysis. Hydrogen, methane and their isotope mixtures of the reaction products are collected and measured with Toepler-gauge, transferred into the sampling bulb, and the mole ratios of H₂, HD and D₂ are determined by Hitachi RMD-2 Mass Spectrometer at Showa Denko Ltd., which is designed specially for the hydrogen isotope analysis, being furnished with double collectors. It is generally known that the analysis of hydrogen isotopes by mass spectrometer, particularly in the case of high content of deuterium, suffers a relatively large error, but the observed ratio of hydrogen isotopes will be enough to measure the extent of participation of ring hydrogen fission semiquantitatively in the primary process of pyrolysis.

The analysis of the other reaction products was not attempted this time since the total amount of the reaction products was too small.

Results and Discussion

Comparison of the Rate Constants of Pyrolysis of Toluene-*d*₅ with Those of Undeuterated

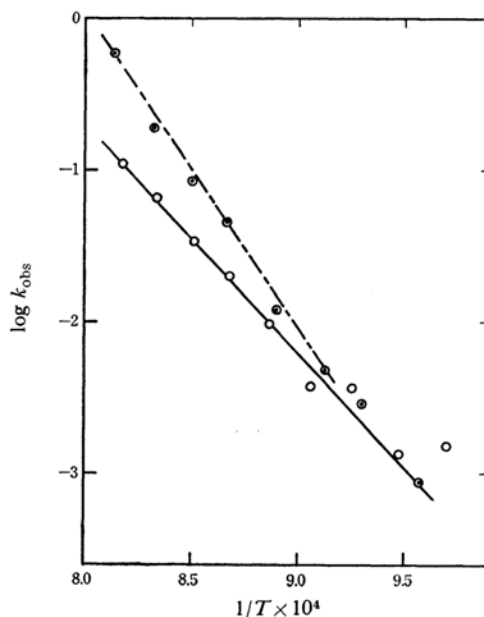


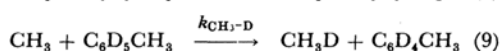
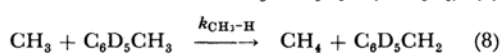
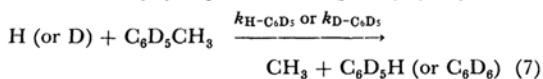
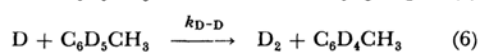
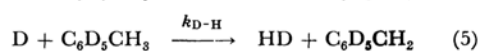
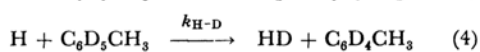
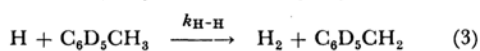
Fig. 1. Arrhenius plot of pyrolysis of toluene and toluene-*d*₅.

●; Toluene

○; Toluene-*d*₅

Toluene. In Fig. 1, the rate constant k_{obs} calculated from the measurements of the combined rate of formation of hydrogen and methane, $(d(\text{H}_2 + \text{HD} + \text{D}_2 + \text{CH}_4 + \text{CH}_3\text{D})/dt)$ in the pyrolysis of toluene-*d*₅ are plotted against $1/T$. For the sake of comparison, the rate constants obtained in the pyrolysis of toluene in the previous paper⁵⁾ are included.

Here we may assume the following reaction mechanism in the pyrolysis of toluene-*d*₅.



Recombination processes between atom and/or radical are not considered, since the concentration of atom or radical is very small compared with that of toluene. This assumption may be justified by the experimental result obtained in the previous work

7) M. Takahasi, This Bulletin, **33**, 801, 808 (1960).

that formation of ethane was negligible in the pyrolysis of toluene.

If the rate of formation of hydrogen atom from toluene is unimolecular and the successive reactions are those shown as above, it is easily shown that the rate of formation of hydrogen and methane is expressed in the following equation, assuming the steady state for hydrogen atom and methyl radical concentrations,

$$\begin{aligned} d(\text{H}_2 + \text{HD} + \text{D}_2 + \text{CH}_4 + \text{CH}_3\text{D})/dt \\ = k_{\text{obs}}(\text{C}_6\text{D}_5\text{CH}_3) = (3k_{\text{H}} + 5k_{\text{D}})(\text{C}_6\text{D}_5\text{CH}_3), \end{aligned} \quad (\text{I})$$

implying that k_{obs} is determined only by the primary processes 1 and 2, being independent of the successive processes.

From the Arrhenius plot of $\log k_{\text{obs}}$ against $1/T$, the apparent activation energy and $\log A$ (A in unit of sec^{-1}) are calculated to be 70 ± 1 kcal/mol and 11.5 respectively. It is interesting that the plot shown in Fig. 1 is almost linear in the temperature range from 781 to 948°C, while in the previous experiment of undeuterated toluene a plot of $\log k_{\text{obs}}$ against $1/T$ shows a concave curvature. Then, k_{obs} in the present case agrees fairly well with k_{obs} in the undeuterated toluene below 900°C, but k_{obs} in the undeuterated toluene deviates upward from the nearly straight line of the plot of toluene- d_5 . The value of 70 kcal/mol for the activation energy seems to be rather too small compared with the value 85 kcal/mol proposed by Price, and further detailed experiments may be required for the complete understanding of this matter, but a possible explanation for the discrepancy between k_{obs} in toluene and that in toluene- d_5 is that above 900°C the participation of the fission of ring carbon-hydrogen bond may contribute to the production of hydrogen atom to larger extent in the pyrolysis of undeuterated toluene compared with the case of deuterated toluene, since the rate constant for the fission of ring carbon-hydrogen bond of the former compound is expected

to be larger than k_{D} due to the primary isotope effect.

Discussion of the Ratio of H_2 to HD and H_2 to D_2 . The observed ratio of H_2 : HD and H_2 : D_2 at various temperatures are given in Table 1. In order to relate the observed isotope ratios to the rate constants defined in the above reaction mechanism, we assumed the steady state condition for the concentration of hydrogen and deuterium atom, resulting the following equations.

$$\begin{aligned} d(\text{H})/dt = & 3(\text{C}_6\text{D}_5\text{CH}_3)k_{\text{H}} \\ & - 3(\text{H})(\text{C}_6\text{D}_5\text{CH}_3)k_{\text{H-H}} \\ & - 5(\text{H})(\text{C}_6\text{D}_5\text{CH}_3)k_{\text{H-D}} \\ & - (\text{H})(\text{C}_6\text{D}_5\text{CH}_3)k_{\text{H-C}_6\text{D}_5}, \end{aligned} \quad (\text{II})$$

$$\begin{aligned} d(\text{D})/dt = & 5(\text{C}_6\text{D}_5\text{CH}_3)k_{\text{D}} \\ & - 3(\text{D})(\text{C}_6\text{D}_5\text{CH}_3)k_{\text{D-H}} \\ & - 5(\text{D})(\text{C}_6\text{D}_5\text{CH}_3)k_{\text{D-D}} \\ & - (\text{D})(\text{C}_6\text{D}_5\text{CH}_3)k_{\text{D-C}_6\text{D}_5}, \end{aligned} \quad (\text{III})$$

$$\frac{(\text{H})}{(\text{D})} = \frac{3k_{\text{H}}(3k_{\text{D-H}} + 5k_{\text{D-D}} + k_{\text{D-C}_6\text{D}_5})}{5k_{\text{D}}(3k_{\text{H-H}} + 5k_{\text{H-D}} + k_{\text{H-C}_6\text{D}_5})} \quad (\text{IV})$$

$$\begin{aligned} \frac{d(\text{H}_2)/dt}{d(\text{D}_2)/dt} &= \frac{3(\text{H})(\text{C}_6\text{D}_5\text{CH}_3)k_{\text{H-H}}}{5(\text{D})(\text{C}_6\text{D}_5\text{CH}_3)k_{\text{D-D}}} \\ &= \frac{9k_{\text{H}}k_{\text{H-H}}(3k_{\text{D-H}} + 5k_{\text{D-D}} + k_{\text{D-C}_6\text{D}_5})}{25k_{\text{D}}k_{\text{D-D}}(3k_{\text{H-H}} + 5k_{\text{H-D}} + k_{\text{H-C}_6\text{D}_5})} \\ &= \frac{9}{25} X \end{aligned} \quad (\text{V})$$

$$\begin{aligned} X &= \frac{k_{\text{H}}k_{\text{H-H}}(3k_{\text{D-H}} + 5k_{\text{D-D}} + k_{\text{D-C}_6\text{D}_5})}{k_{\text{D}}k_{\text{D-D}}(3k_{\text{H-H}} + 5k_{\text{H-D}} + k_{\text{H-C}_6\text{D}_5})} \\ \frac{d(\text{HD})/dt}{d(\text{H}_2)/dt} &= \frac{5(\text{H})(\text{C}_6\text{D}_5\text{CH}_3)k_{\text{H-D}} + 3(\text{D})(\text{C}_6\text{D}_5\text{CH}_3)k_{\text{D-H}}}{3(\text{H})(\text{C}_6\text{D}_5\text{CH}_3)k_{\text{H-H}}} \\ &= \frac{5k_{\text{H-D}}}{3k_{\text{H-H}}} + \frac{5k_{\text{D}}(3k_{\text{H-H}} + 5k_{\text{H-D}} + k_{\text{H-C}_6\text{D}_5})k_{\text{D-H}}}{3k_{\text{H}}(3k_{\text{D-H}} + 5k_{\text{D-D}} + k_{\text{D-C}_6\text{D}_5})k_{\text{H-H}}} \\ &= \frac{5k_{\text{H-D}}}{3k_{\text{H-H}}} + \frac{5}{3} \frac{1}{X} \frac{k_{\text{D-H}}}{k_{\text{D-D}}} \end{aligned} \quad (\text{VI})$$

TABLE 1. RATE CONSTANTS OF PYROLYSIS OF TOLUENE- d_5 AND MOLE RATIOS HD/ H_2 AND H_2 / D_2

Exp. No.	Reaction temp., °K	-log k^*	Mole ratio of products hydrogen isotopes**		$k_{\text{H-D}}/k_{\text{H-H}}$	X
			HD/ H_2	H_2 / D_2		
1	1174.9	1.47	2.30	—***	1.44	
2	1127.4	2.01	2.07	—***	1.20	
3	1079.1	2.44	1.49	—***	0.89	
4	1030.0	2.82	0.86	—***	0.51	
5	1221.8	0.96	2.65	—***	1.59	
6	1103.4	2.43	—	5.7	—	15.8
7	1151.3	1.70	—	3.5	—	9.7
8	1198.4	1.18	—	—***	—	
9	1054.6	2.87	—	—***	—	

* k in unit of sec^{-1} .

** Correction due to the contamination of toluene- d_4 was estimated to be negligible in the present case.

*** —, not determined.

Multiplying the experimental value of $H_2 : D_2$ by a statistical factor 25/9, we obtain the value X which is shown in the sixth column of Table 1. Only knowing the two experimental values, $H_2 : HD$ and $H_2 : D_2$, we are not able to determine the unknown six rate constants. However, in order to obtain a rough idea on the extent of the participation of ring hydrogen in the primary step of pyrolysis of toluene, we may assume that the ratios of rate constants of abstraction type (k_{H-H}/k_{D-D}) and $(3k_{D-H} + 5k_{D-D} + k_{D-C_6D_5}) / (3k_{H-H} + 5k_{H-D} + k_{H-C_6D_5})$ do not differ so much from unity at such high reaction temperatures as in the present experiment. If this is the case, it may be concluded that the value X reflects approximately the magnitude of k_H/k_D , and that the rate constant of homolytic fission of ring carbon-deuterium bond is in the order of one tenth the rate constant of side chain carbon-hydrogen bond in the temperature range of the present experiment. Although the present result is of the semiquantitative nature, it is interesting that at such high reaction temperatures the participation of ring hydrogen (here actually deuterium) in the primary step of pyrolysis is confirmed. A tentative evaluation of the difference of the activation energies for k_D (for ring C-D) and k_H (for methyl C-H) gives about 24 kcal/mol, but this value is rather semiquantitative one, in consideration of the involved experimental errors and assumptions.

Next, we will discuss the interpretation of the ratio of H_2 to HD . In the equation VI, we may assume that the second term $(5k_{D-H}/3k_{D-D})(1/X)$ can be neglected compared with the first term, because X is more than ten as seen above and the value k_{D-H}/k_{D-D} may not exceed unity so much at the reaction temperatures of the present experiment, although it is not true in the exact sense to assume that the second term is independent of the reaction temperature. Plotting $\log(k_{H-D}/k_{H-H})$ against $1/T$ on this basis of the above assumption (Fig. 2), we can calculate the difference of the apparent activation energies and $\log A$ (A in unit of sec^{-1}) between k_{H-D} and k_{H-H} to be 14 kcal/mol and 5.2 respectively. Although these values are of the semiquantitative nature, the result that the activation energy of k_{H-D} is larger than that of k_{H-H} is understandable, since the abstraction of ring hydrogen (actually deuterium in the present case) is expected to be more difficult than that from side chain hydrogen. The isotope effect should necessarily superpose on the structure effect in the present case, but its separation is left for future investigation. The positive difference of $\log A$ between k_{H-D} and k_{H-H} indicates that at sufficiently high reaction temperatures k_{H-D} exceeds k_{H-H} . Al-

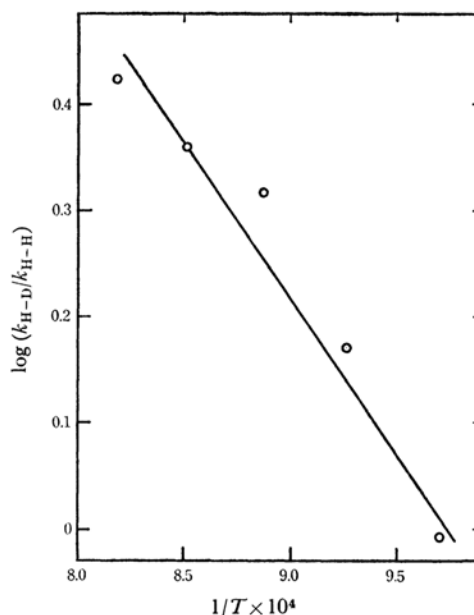


Fig. 2. Plot of $\log(k_{H-D}/k_{H-H})$ against $1/T$.

though further investigation will be required to give a reasonable explanation for this difference of frequency factors, it will be useful to compare the present case with the abstraction reaction of hydrogen in toluene with methyl radical. Cher observed a value of $10^{10.7} \text{ cc mol}^{-1} \text{ sec}^{-1}$ for frequency factor of ring hydrogen and $10^{11.6} \text{ cc mol}^{-1} \text{ sec}^{-1}$ for methyl hydrogen in the abstraction reaction of toluene by methyl radical,⁸⁾ so our result is in an opposite way.

For the mechanism of abstraction of ring hydrogen with methyl radical, Cher proposed two mechanisms (a) a reaction *via* direct abstraction through a three center linear complex, and (b) a reaction *via* a preliminary addition to the ring to form a cyclohexadienyl radical. He presumed that the mechanism (a) is dominant at high temperatures, being characterized by high activation energy (10 cal/mol) and a normal frequency factor. In our case of the abstraction of ring hydrogen with hydrogen, similar two mechanisms are considered to be possible, and the mechanism (a) is probably a more possible one.

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8) M. Cher, C. S. Hollingsworth and F. Scicilio, *J. Phys. Chem.*, **70**, 877 (1966).