Pyrolysis of Organic Compounds. I. Kinetic Study of the Pyrolysis of Toluene

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(Received October 16, 1959)

In 1948 Szwarc[1] measured the reaction velocities of the pyrolysis of toluene by the flow technique in the temperature range 738∼864°C. He assumed that the reaction is homogeneous, and proposed the following reaction scheme:

$$C_6H_5CH_3 \longrightarrow C_6H_5CH_2\cdot + H\cdot \qquad (1)$$
initiation

$$H\cdot + C_6H_5CH_3 \longrightarrow H_2 + C_6H_5CH_2\cdot \qquad (2)$$
abstraction by H atom

$$H\cdot + C_6H_5CH_3 \longrightarrow C_6H_6 + CH_3\cdot \qquad (3)$$
metathesis

$$CH_3\cdot + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2\cdot \qquad (4)$$
abstraction by CH_3 radical

$$2C_6H_5CH_2\cdot \longrightarrow C_6H_5CH_2CH_2C_6H_5 \qquad (5)$$
termination by recombination

He considered that the rate determining step

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[1] H. Szwarc, *J. Chem. Phys.*, 16, 128 (1948).

is the unimolecular reaction 1, and assumed that the velocity constant k observed by the flow method corresponds to that of the reaction 1. The activation energy and the temperature independent factor of the reaction 1 obtained by plotting $\log k$ versus $1/T$ are 77.5 kcal./mol. and 2×10^{13} respectively, and he assumed that the activation energy corresponds to the bond dissociation energy, $D(C_6H_5CH_2\text{-}H)$. H. R. Anderson Jr., H. A. Scheraga, and E. R. Van Artsdalen²⁾ studied the thermal bromination of toluene, and they derived 89.5 kcal./mol. for the upper limit of the bond dissociation energy of toluene. H. Blades, A. T. Blades and E. W. R. Steacie³⁾ repeated the study of the pyrolysis of toluene in a flow system, and they carried out a more elaborate analysis of the reaction products. Styrene, dimethylbiphenyls and anthracene were obtained in addition to bibenzyl which was reported by Szwarc to be the sole nonvolatile product in the reaction. Steacie and Blades ascribed the origin of the dimethylbiphenyls to the secondary decomposition of bibenzyl. They observed that the first order rate constant increases, as the contact time is increased, and that the rate of the reaction depends upon the condition of the surface of the reaction vessel. They calculated the apparent activation energy to be 90 kcal./mol., keeping the contact time constant at 0.068 sec., although they did not assert that the value corresponds to the true bond dissociation energy of toluene $D(C_6H_5CH_2\text{-}H)$.

Most recently, S. W. Benson and J. H. Buss⁴⁾ reviewed various attempts to determine the bond dissociation energy of toluene, and they attempted a measurement of the equilibrium constant for the reaction:

$$C_6H_5CH_3(g)+Br_2(g) \rightleftarrows C_6H_5CH_2Br(g)+HBr(g)$$

at 150°C, and they estimated the bond dissociation energy of toluene to be 84 kcal./mol., together with the known thermal data.

The bond dissociation energy was also obtained by electron impact measurement by D. O. Schissler and D. P. Stevenson⁵⁾ as 77.3 kcal./mol., and J. B. Farmer, I. H. S. Henderson, C. A. McDowell and F. P. Lossing⁶⁾ criticized the value, and they presumed that the bond dissociation energy is possibly higher by about 20 kcal./mol.

From the theoretical point of view, the present author considers that Szwarc's value of the bond dissociation energy of toluene is somewhat too low, for the difference:

$$D(CH_3-H)-D(C_6H_5CH_2-H)$$
$$=103-77.5=22.5 \text{ kcal./mol.}$$

is too large compared with the extra resonance energy of the benzyl radical which was calculated as about 14 kcal./mol.⁷⁾ If such an abnormal weakening of toluene bond were assured by experiments, the fact might be an interesting theoretical problem, but at present it seems to be premature to discuss this point, for there remain many points which should be made clear in the experiments.

It is to be noted that the value obtained by Steacie and his collaborators for the activation energy of the pyrolysis of toluene is different from that by Szwarc, although the method was the same. A. F. Trotman-Dickenson⁸⁾ pointed out that Steacie and his collaborators measured the rate constant, keeping the contact time far less than in the experiments by Szwarc.

However, the present author considers that it is very unfortunate that the two groups made experiments in the different ranges of the reaction temperatures; that is, Szwarc in the range between 738~864°C, and Steacie and his collaborators between 860~940°C. Therefore, the present experiment was carried out to cover the whole temperature range 737~953°C, and efforts were made to elucidate the cause of the discrepancy of the bond dissociation energies of toluene obtained by the two groups.

Experimental Procedure

Materials.—Both Szwarc's and Steacies groups used toluene prepyrolyzed to remove interfering impurities which would give extra hydrogen and light hydrocarbons by pyrolysis. The present author attempted to obtain toluene of higher purity which is usable without prepyrolysis. Toluene from two sources were examined, the one of which was obtained by the usual purification process combined with azeotropic distillation with acetonitrile to remove interfering impurities which were presumed to be cycloalkanes. This toluene was conceived to be of very high purity, but nevertheless it gave some amount of ethylene and propylene in addition to hydrogen and methane by pyrolysis, if it was subjected to prepyrolysis.

In order to obtain toluene of higher purity which contains no alkanes nor cycloalkanes, the author prepared toluene from toluidine by applying the method described in Organic Syntheses⁹⁾. A cold diazonium solution was prepared from 105 g. of toluidine, 190 ml. of concentrated hydrochloric acid,

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2) H. R. Anderson Jr., H. A. Scheraga and E. R. Van Artsdalen, ibid., **21**, 1258 (1953).

3) H. Blades, A. T. Blades and E. W. R. Steacie, *Can. J. Chem.*, **32**, 1142 (1954).

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

5) D. O. Schissler and D. P. Stevenson, *J. Chem. Phys.*, **22**, 151 (1954).

6) J. B. Farmer, I. H. S. Henderson, C. A. McDowell and F. P. Lossing, ibid., **22**, 1948 (1954).

7) M. Takahasi, This Bulletin, **29**, 625 (1956).

8) A. F. Trotman-Dickenson, "Gas Kinetics", Butterworths Scientific Publications, London (1955), p. 108.

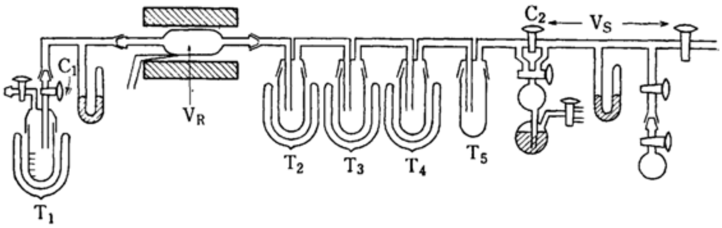

Fig. 1. Apparatus for Pyrolysis.

TABLE I. VELOCITY CONSTANTS IN THE CASE OF THE REACTION VESSEL I

Exp. No.	Vap. pressure mmHg	Reaction temp., °C	$-\log k$	Mole ratio of H_2 to CH_4	Contact time, sec.
95	7.24	763.5	3.24		
94	8.38	787.2	2.95		
93	9.60	819.0	2.52		
40	4.98	856.5	1.81		0.26
41	4.94	863.9	1.71		
42	5.24	866.3	1.65		
90	8.00	879.8	1.54		
89	7.54	880.6	1.58		
91	7.00	894.0	1.34		
47	5.04	912.0	1.11	2.0	
48	5.15	933.1	0.78		
49	5.98	936.9	0.72		
50	5.34	939.3	0.69		

and 69 g. of sodium nitrite in 200 ml. of water, and it was poured into a flask containing 520 g. of sodium hypophosphorite, $NaH_2PO_2 \cdot H_2O$, 256 g. of concentrated hydrochloric acid and 40 g. of water. Evolution of nitrogen was controlled, keeping the solution at 5°C. The flask was placed in a refrigerator overnight, and the reaction product was transfered to a separating funnel, and the upper oil was separated from the aqueous phase. Ether extraction should be avoided, for it causes the contamination of toluene with ether. A fraction boiling at 110°C. was gathered by simple distillation which weighed about 55 g., and then it was distilled through a spinning band fractionating column of 150 cm. in length. This toluene did not give any appreciable amount of ethylene and higher hydrocarbons in the pyrolysis, even if prepyrolysis was not carried out, and therefore the latter toluene was used in the present kinetic study.

Apparatus and Procedure—The general arrangement of apparatus for pyrolysis shown in Fig. 1 is similar to that used by Szwarc but with a small modification to improve experimental accuracy. Toluene which had been refluxed with sodium for about one hour was distilled under reduced pressure into the storage vessel T_1. This vessel was weighed before and after each run of experiment, to measure the amount of toluene passed in each run, if it was necessary to calculate accurate contact time. In the usual runs, the amount of toluene was determined by volume in the storage flask. During runs, the vessel was kept in a Dewar vessel contaning water maintained at a temperature constant to 0.1°C. Toluene was evaporated from T_1 through cock C_1 to maintain its vapor pressure 4~10 mmHg, and led into a silica reaction vessel heated by an electric furnace. Contact time was controlled by replacing silica reaction vessels which were designated as I, II, and III. (Table V). The electrical furnace was about 70 cm. long, and the variation of temperature along the reaction vessel was ±2°C. The temperature of the reaction vessel was measured by a calibrated Pt-Rh thermocouple with a potentiometer. It was checked to discover whether temperature difference inside and outside the reaction vessel might be caused by passing toluene, but the difference did not exceed 2°C.

The reaction system was evacuated to 10^{-6}mmHg before the experiment, and pressure increase in the reaction system in the course of about 20 min. was checked without passing toluene. The increase of pressure was caused mainly by evaporation of toluene previously dissolved in grease of cocks but not by leakage of air, being suppressed to about 10^{-3} mmHg in the course of about 20 minutes, a time comparable to that of one usual run of pyrolysis.

The vapor leaving the reaction vessel passed through traps T_2 and T_3 which were cooled with a mixture of ether and solid carbon dioxide. Toluene and the less volatile products such as bibenzyl and dimethylbiphenyls were almost completely condensed in trap T_2. The noncondensable gas passed through trap T_4 which was cooled by liquid nitrogen or oxygen. Trap T_5 was reserved for distillation, and

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9) "Organic Syntheses", Collective Vol. II. John & Willey Sons, Inc., New York, p. 1039.

TABLE II. VELOCITY CONSTANTS IN THE CASE OF THE REACTION VESSEL II

Exp. No.	Vap. pressure mmHg	Reaction temp., °C	$-\log k$	Mole ratio of H_2 to CH_4	Contact time, sec.
13	5.02	737.8	3.43		
80	8.39	741.1	3.11		
81	9.62	749.0	3.34		
88	8.14	755.2	3.24		
87	8.47	763.6	3.13		
82	9.22	770.8	3.05		
12	5.76	779.0	2.91		
86	8.64	791.3	2.71		
18	6.64	801.9	2.57		
19	5.88	801.9	2.54	2.1	
20	5.66	803.5	2.50	2.3	
85	9.20	814.1	2.38		
83	8.64	814.9	2.31		
11	7.14	821.4	2.32		
84	9.06	828.7	2.15		
77	9.26	837.5	1.98		
78	9.10	837.5	1.90		
10	7.04	839.1	2.06		
76	9.66	848.7	1.78		
79	9.10	850.3	1.92		
75	9.58	851.1	1.78		
21	6.12	855.1	1.79	2.1	
8	6.34	859.1	1.67		0.11
35	6.40	860.7	1.67		
74	9.76	860.7	1.65		
9	6.28	863.9	1.62		0.10
5	5.68	863.9	1.70		0.09
72	9.00	875.0	1.48		
73	10.02	875.8	1.42		
10	9.64	880.6	1.34		0.24
71	9.49	890.1	1.22		
17	6.50	897.9	1.14	2.3	0.11*
69	9.35	902.6	1.07		
6	5.40	908.1	0.94		0.14
68	10.14	908.9	0.93		
64	9.28	916.7	0.85		
27	6.58	918.3	0.89	2.2	
38	5.80	928.4	0.72	1.8	
65	9.94	932.3	0.60		0.14
16	6.50	937.0	0.52		
14	6.24	938.6	0.52	2.3	0.13
15	7.19	940.1	0.60		0.15
66	9.70	944.0	0.40		
67	10.60	953.3	0.26		
24	4.34	953.7	0.25	1.9	
7	6.49	955.6	0.23		0.16

* Condensable gas at liquid nitrogen temperature amounted to 2% of total gas product.

kept at room temperature. Noncondensable gas in trap T_4 was composed of hydrogen and methane, and it was pumped out by a Toepler pump and collected in a storage vessel of about 100 ml. The quantity of hydrogen and methane produced was given by reading the pressure in the storage vessel with a McLeod gauge or a U tube manometer according to the pressure. The reaction time extended from 3 to 30 minutes, according to the quantity of gas produced. After the flow of toluene vapor was stopped, the trap T_2 was warmed to room temperature to distil toluene from trap T_2 to T_3. All the produced gas, remaining in the reaction system and dissolved in toluene of trap T_2, was pumped out by a Toepler pump to the storage vessel. Hydrogen and methane expelled from trap T_2 amounted to about 10% of the total gas produced. Operation of Toepler pump was continued for 15 min. after flow of toluene was stopped. After the pressure of a mixture of hydrogen and methane was read, trap T_4 was warmed to $-70°C$ by changing the cooling material to a mixture of ether and carbon dioxide. The amount of gas condensable in trap T_4 at liquid nitrogen temperature was at most a few per cent of that of condensable gas, if toluene which was synthesized from toluidine as described above was pyrolyzed.

As the experimental conditions were so chosen that the decomposition ranged from 0.001 percent to 0.6 percent of total toluene, the reaction rate constant for the unimolecular reaction was calculated by the equation,

$$k=\frac{P_s\times V_s\times T_R}{P_t\times t\times T_r\times V_R} \tag{6}$$

where P_t is vapor pressure of toluene (mmHg), T_R is reaction temperature (°K), V_R is volume of reaction vessel (l.), t is time of flow (sec.), and P_s is pressure of product gas (H_2+CH_4) (mmHg) at T_r °K in a storage vessel of V_s. The contact time was calculated according to Eq. 7,

$$\tau=V_R/v=\frac{V_R\times P_t\times t}{m\times 0.082\times T_R\times 760} \tag{7}$$

$$k=\text{fractional decomposition}/\tau \tag{8}$$

where m is moles of toluene passed, and v (l.) is volume of toluene which passed through the reaction vessel per second at T °K. Contact time was calculated in several runs, but not in all runs, because it depends mainly on the value of reaction vessel and vapor pressure of toluene, the latter being varied over a small range.

TABLE III. VELOCITY CONSTANTS IN THE CASE OF THE REACTION VESSEL III

Exp. No.	Vap. pressure mmHg	Reaction temp., °C	$-\log k$	Contact time, sec.
101	9.88	811.7	2.34	
100	10.78	836.7	2.01	
99	10.80	868.8	1.58	
98	10.95	888.8	1.30	
97	10.60	908.1	0.99	
54	7.28	925.3	0.66	0.03
55	6.48	925.3	0.67	
56	6.36	939.3	0.61	
96	11.10	948.7	0.44	
57	6.51	958.7	0.38	
61	7.22	960.3	0.33	

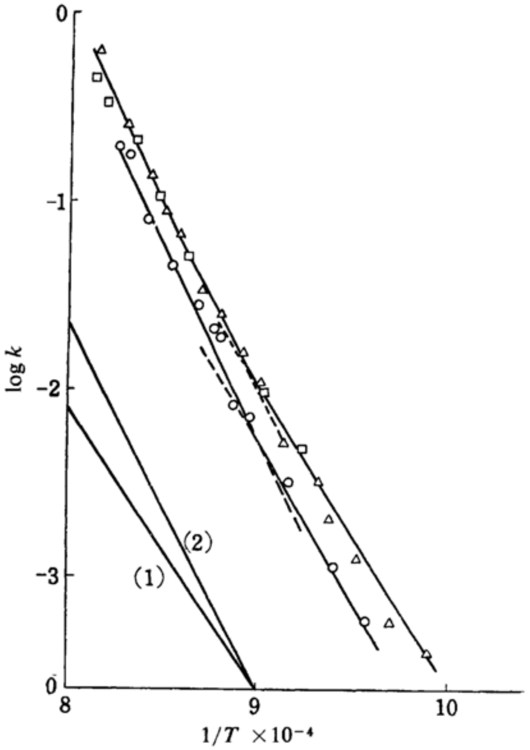

Fig. 2. Relation of $\log k$ versus $1/T$

△ Reaction Vessel I
○ 〃 II
□ 〃 III

(1) gradient corresponding to the activation energy of 70 kcal./mol.
(2) 〃 of 90 kcal./mol.

Experimental Results

The results are shown in Tables I, II and III, and the relation of $\log k$ versus $1/T$ is shown in Fig. 2. From the figure it may be apparently concluded that the relation was linear, but the more precise analysis makes clear the curve is slightly concave. Therefore, the temperature range was rather arbitrarily divided into three parts, that is, higher, medium, and lower temperature ranges, and a linear relation of $\log k$ versus $1/T$ was assumed in each range, and experimental activation energies and temperature independent factors were calculated by the least square method. The results are summarized in Table IV. Different gradients were obtained in each temperature range, corresponding to different activation energies and different frequency factors. The probable cause of deviation of the relation of

TABLE IV. EXPERIMENTAL ACTIVATION ENERGIES AND log *A* OF PYROLYSIS OF TOLUENE UNDER VARIOUS CONDITIONS

Temp. range °C	Number of experiments	Volume of reaction vessel, ml.	Contact time, sec.	*E* kcal./mol.	log *A*
764∼843	4	53.7	0.3	81.3	13.7
857∼894	6	〃	〃	69.2	11.5
912∼933	4	〃	〃	104.9	18.1
738∼849	19	31.0	0.1∼0.2	73.7	12.4
850∼898	13	〃	〃	93.3	16.2
903∼956	14	〃	〃	103.5	18.0
812∼889	4	6.4	0.02∼0.04	78.0	13.3
908∼960	7	〃	〃	76.2	13.1
Szwarc1)					
738∼850	27	not described	0.2∼0.9	77.5	13.1
Steacie and his collaborators8)					
850∼940	9	not described	0.068	90	not described

log *K* versus 1/*T* from linearity is discussed below.

Identification and Analysis of Products.—The mole ratio of hydrogen to methane was determined by a mass spectrometer of CEC 21-103A type by using peaks of *m*/*e* 2 and 16, although quantitative analysis of hydrogen by the mass spectrometer did not give sufficient accuracy. Complete analysis of solid and oily matters which were obtained in trap T_2 was not carried out, but the ultraviolet absorption spectrum (Fig. 3) showed that the main products were composed of bibenzyl and dimethylbiphenyls, and this result agrees with that of Steacie and his collaborators.

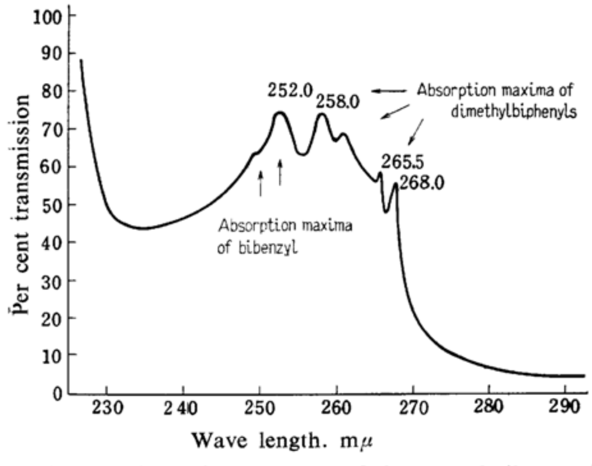

Fig. 3. Absorption spectrum of the nonvolatile reaction products of pyrolysis of toluene in ethanol.

Discussions

As described above, the present experimental results show that the relation of log *k* versus 1/*T* in the temperature range 737∼953°C is not strictly linear and that high activation energies and high frequency factors are obtained in the higher temperature range in the series of the experiments which were carried out at contact time of 0.1∼0.3 sec. In the case of shorter contact time, 0.02∼0.04 sec., (Table IV), the activation energy is obtained only in the higher temperature range 812∼960°C, because the experiment in the lower temperature range should give a smaller amount of gas product and involve larger experimental error, compared with the experiments of longer contact time. It is to be noted that the lower activation energy is obtained even in the higher temperature range, compared with the experiment of longer contact time in the same temperature range.

Now the author will discuss the probable cause of systematic deviation of the relation of log*k* versus 1/*T* from linearity.

1) Experimental errors: It may be possible that *k* at lower temperatures involves relatively large error, because the amount of the product gas at lower reaction temperature is very small, even if the reaction time is lengthened. As was described in the experimental part, the pressure increase in the storage vessel in the blank test amounted to about 10^{-3} mmHg in the course of about 15 min. Total pressure of product gas which was given by pyrolysis of toluene for ten minutes at the lowest reaction temperature, 738°C, amounted to about 0.06 mmHg (cf. Exp. No. 13). This may mean that the observed velocity constants at lower reaction temperatures should be reduced by some percentage, but such correction seems not to increase so much the activation energy obtained at the lower temperature range.

Alkanes and cycloalkanes which may supposedly exist in commercial toluene may be decomposed more rapidly than toluene, and such toluene may increase the apparent k at lower reaction temperatures, but the toluene which was synthesized from toluidine may be free from such impurities.

2) Correction by using the more elaborate Arrhenius equation: As was pointed out by many authors[10], under some conditions the frequency factor is a function of the temperature and a more accurate equation 10 than the usual Arrhenius equation 9 should be used.

$$k=A\exp(-E_a/\boldsymbol{R}T) \tag{9}$$

$$k=AT^n\exp(-E/\boldsymbol{R}T) \tag{10}$$

or $$\ln k=-E/\boldsymbol{R}T+n\ln T+\ln A$$

and the difference of the two activation energies is

$$E=E_a-n\boldsymbol{R}T. \tag{11}$$

In the present case, n is not known, but if n is assumed to be 1/2 as in the usual collision theory, $n(\ln T_1-\ln T_2)$ amounts to 0.042, when T_1 and T_2 are assumed 953°C and 737°C respectively. This may reduce activation energies in the higher temperature range to some extent, but the correction seems not to contribute so much to reducing the concave nature of the relation of $\log k$ versus $1/T$.

3) Complications due to competitive reactions: H. Blades, A, T. Blades and E. W. R. Steacie[3] pointed out that the first order rate constants for the pyrolysis of toluene depends on the condition of the surface of the reactor, and the contact time, and on the pressure. A. Frost and R. G. Pearson[10] pointed out that a plot of $\log k$ versus $1/T$ shows a curvature if there are two competing reactions with different activation energies.

One case is that where the same reaction occurs both homogeneously and heterogeneously. The homogeneous reaction usually has a higher activation energy, and it is favored at high temperatures whereas the heterogeneous reaction predominates at lower temperatures. In the present experiment, it is shown that k at the same temperature varies slightly as shown in Fig. 2, when the reaction vessel is replaced (I, II, and III). Contact time, volume and surface area of reaction vessel are varied as shown in Table V by replacing the reaction vessel, but it is not yet elucidated how these conditions affect the velocity constant and activation energy of pyrolysis of toluene. The present author presumed that any unfavorable secondary reaction may be suppressed, if the experiment is carried out under a smaller contact time, but such a presumption could not be confirmed in the present experiment.

TABLE V

Reaction vessel	Volume ml.	Contact time, sec.	Surface area, cm^2
I	53.7	0.3	113
II	31.0	0.2—0.1	94
III	6.4	0.03	44

Thus, the author's efforts to obtain a value as much smaller than k as possible especially in the lower temperature range appeared not to modify the concave nature of $\log k$ versus $1/T$, and another source of complications of the present reaction is now considered in the following. At the higher temperature range between 900～950°C, it may be possible that the observed k becomes rather increased, as the reaction temperature is increased, because some competitive side reaction takes place, giving hydrogen and methane. Already both Szwarc[1] and Steacie[3] considered the following reaction,

$$C_6H_5CH_3 \longrightarrow C_6H_5\cdot + CH_3\cdot$$

as one of possible side reactions, but they considered that such a reaction is less probable, because the ratio of hydrogen to methane does not vary over the whole temperature range. The present experimental results of the ratio of hydrogen to methane appear to support their conclusion. Another possible reaction is one involving the participation of ring-hydrogen in initiation and/or propagation reaction as follows:

$$C_6H_5CH_3 \longrightarrow \cdot C_6H_4CH_3 + H\cdot \quad \text{initiation}$$

$$C_6H_5CH_3 + H\cdot \longrightarrow \cdot C_6H_4CH_3 + H_2$$
abstraction by hydrogen atom

$$C_6H_5CH_3 + CH_3\cdot \longrightarrow \cdot C_6H_4CH_3 + CH_4$$
abstraction by methyl radical

Blades and Steacie[11] pointed out such a possibility in the experiment of pyrolysis of n-propylbenzene in the presence of toluene-$\alpha-d_3$ at 722°C. They found that the amount of methane in the reaction product is unexpectedly large compared with the amount of methane-d. Recently S. H. Wilen and E. L. Eliel[12] assumed abstraction of ring-hydrogen by methyl radicals in the reaction of acetyl peroxide with ring-deuterated toluene at 131～147°C. which gave rise to some methane-d. The present author's experiment of toluene-3-d and toluene-4-d which confirms the involvement of ring-hydrogen in the pyrolytic reaction of toluene itself will be reported in the succeeding paper, although it remains unsolved whether the involvement of ring-hydrogen modifies the overall activation energy or not.

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[10] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", John Wiley Sons, Inc., New York (1953), p. 24.

[11] A. T. Blades and E. W. R. Steacie, *Can. J. Chem.*, 32, 1142 (1954).

[12] S. H. Wilen and E. L. Eliel, *J. Am. Chem. Soc.*, 80, 3309 (1958).

Summary

Pyrolysis of toluene by the flow technique was carried out under various conditions, and the velocity was measured over the wide temperature range 737∼953°C at contact time 0.02∼0.3 sec. The relation of $\log k$ versus $1/T$ appears to be linear, but the more precise analysis shows a slight concave nature, and therefore activation energy tends to increase, as the reaction temperature is raised. Detailed investigation on its cause was made, and it is presumed that such an increase of activation energy with rise of temperature is mainly brought about by some competitive reaction, but not by experimental conditions. The present author considers that the involvement of ring-hydrogen reaction may compete with the reaction of fission of C-H bond of the methyl group, and such competitive reaction may modify the activation energy of the fission of the methyl bond of toluene, if the experiment is carried out over the wide reaction temperature range.

The author wishes to express his hearty thanks to Professor Y. Urushibara and Professor O. Simamura for their kind guidance and encouragement of the present work. The author is grateful to Dr. M. Kobayashi for experimental help and for stimulating discussions, and to Dr. T. Tamura and Mr. H. Saito for fractional distillation of toluene.

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