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A Study of the Pyrolysis of Toluene Using ^{14}C as a Tracer

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The pyrolysis of toluene-1-^{14}C was carried out by means of the semi-flow method at 800 and at 1000°C in the presence of the registers of porcelain, and the distributions of the radioactive carbon in gaseous products and that of the deposited carbon were determined. The molar c.p.m. of methane and that of a mixture of C_2-compounds were about 1/20 of and twice the molar c.p.m. of the original toluene respectively, while the c.p.m. per gram-atom of the deposited carbon was about twice that of toluene, when the temperature of reaction was 800°C. In the case of the reaction at 1000°C, the c.p.m. per gram-atom of carbon of each product was found to be practically equal to that of the original toluene. It was proposed that methane is formed by the removal of the methyl group of toluene, and that the main source of the carbon of C_2-compounds and the deposited carbon is the 1-carbon of toluene. The equalization of the radioactive carbon in every product at a high temperature was interpreted by assuming that the tropyl radical is formed as an intermediate after the formation of the phenyl radical in the initial stage of the reaction.

The decomposition of toluene by heat, γ-ray irradiation or electron impact has been studied by many investigators.[1-8] These studies have concentrated on measurements of the reaction products, the reaction velocity and the behavior of hydrogen atoms using deuterium as a tracer; the behavior of carbon atoms in the reaction and the influence of the reaction temperature upon the mechanism remain unexplored. It is evident, however, that tracer study using ^{14}C would make the mechanism clearer. This paper is concerned with the pyrolysis of toluene by using toluene-1-^{14}C. The change in the distribution of ^{14}C in the reaction products by the change in reaction temperature from 800 to 1000°C was investigated in order to clarify the mechanism.

Experimental

The toluene-1-^{14}C used was provided by the New England Nuclear Co. Its specific activity was 1.23 mc./mmol. It was diluted to 2.63 mc./mol. with extra pure toluene before use. No impurity was detected in the sample by gas chromatography. The apparatus for the reaction is shown in Fig. 1, where A is a sample reservoir and B is the reaction tube of quartz, whose diameter and length were 2.0 cm. and 50cm. respectively. The tube was fixed in the furnace together with a thermojunction of Pt-Pt·Rh. The registers of porcelain were packed in the tube in order to decompose the reactant readily. U_1 and U_2 are traps for the gaseous products, such as acetylene, ethylene and benzene, and U_3 is for carbon dioxide converted by the combustion of the deposited carbon to assay the ^{14}C. These traps were cooled by liquid nitrogen baths. C is a combustion tube filled with copper oxide. N and M_1 are a McLeod gauge and the manometers respectively. G is a gas-counting tube (about 50cc.), which is connected with an amplifier and a scaler. D is a safety bottle which contains mercury and is used for the admission of oxygen.

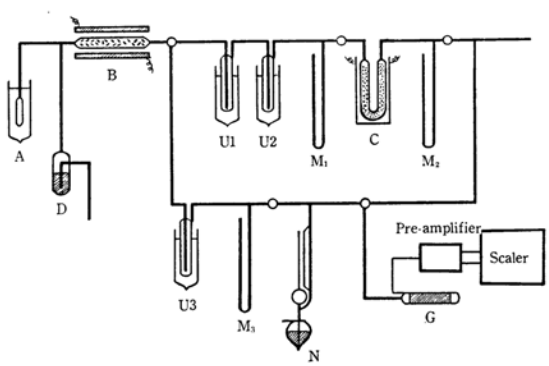

Fig. 1. Apparatus for reaction and assay of ^{14}C.

For each run of experiments, 0.2 cc. of toluene was taken in the sample reservoir. After the air dissolved in the sample had been removed by repeatedly freezing and evacuating the sample, the reaction tube was evacuated up to the pressure of 10^{-3} mmHg, keeping the reservoir at the temperature of liquid nitrogen; then the temperature of the reaction tube was raised to

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1000°C. The reaction was started by replacing the bath of the sample reservoir with a water bath kept at 45°C. The vapor pressure of toluene at this temperature is 75 mmHg. When the sample in the reservoir had run out, the uncondensable gas produced, a mixture of hydrogen and methane, was passed over copper oxide in order to convert the hydrogen into water; then this water was condensed in trap U_3. The amounts of hydrogen and methane were determined by the measurement of pressures before and after the combustion by oxygen. Acetylene and ethylene were separated from benzene and toluene by replacing the liquid nitrogen baths of traps U_1 and U_2 with dry ice baths; they were collected in U_3 by cooling the trap with liquid nitrogen. The combined amount of ethylene and acetylene was determined from the pressure difference produced when the liquid nitrogen baths were replaced with the dry ice baths. The gas was then drawn off until the pressure in the reaction tube showed less than 1 mmHg; the dry ice baths were then replaced by ice baths in order to measure the amount of the mixture of benzene and toluene remaining in the traps. The deposited carbon on porcelain was oxidized to carbon dioxide by passing oxygen through the reaction tube at the temperature of 800°C.

The applied potential of the cathode of the counting tube was 2200V. PR gas, a mixture of argon and methane, was used for a filling gas. The details of the procedure of the assay of ^{14}C were the same as that adopted for tritium, which has been described elsewhere.[9]

Results and Discussion

A large amount of nonvolatile tar was found at the outlet of the reaction tube. The assay of ^{14}C in the substances was not attempted, however, because of the difficulty of collecting them completely. The amounts of gaseous products and the respective counting values are summarized in Tables I and II. The 4th column in each table indicates the molar c. p. m. of the products, while the 5th column indicates the c. p. m. per gram-atom of carbon in each molecule. In order to confirm the reliability of the results of analysis by the method mentioned above, the results were compared with those obtained by a mass spectrometer on the same sample. Nonradioactive toluene was used for this purpose. It was found that the results agree approximately with each other.

The molar c. p. m. of C_2-compounds was about twice, while that of methane was only 1/20 of, the molar c. p. m. of the original toluene in the reaction at 800°C. The small counting value of methane suggests that the carbon comes mainly from the methyl group of toluene. The conspicuously great counting value of C_2-compounds can not be explained in terms of reaction kinetics or mass effect. This point must be left for future investigation. The fact, however, would suggest that the carbon atoms of the C_2-compound come mainly from the 1-carbon atom of toluene. A similar result was reported recently by White et al.[10] Their study of the oxidation of propylene-1-^{14}C indicated that some of the reaction products must be formed from the combination of two or more radioactive fragments.

The c. p. m. per gram-atom of carbon of graphite was about twice that of toluene. This suggests that the graphite might be produced mainly from the carbon atoms of C_2-compounds.

In the case of 1000°C, the c. p. m. per gram-atom of carbon in each product was practically equal to that of toluene. This fact would suggest that each carbon atom of toluene, including that of methyl group, became equivalene in relation to each hydrogen atom at the elevated temperature. Consequently, the seven-membered ring structure of the tropyl radical can be considered, at a high temperature, as an intermediate which is produced by the rearrangement of the benzyl radical first formed. A plausible mechanism of the reaction in the initial stage may be represented as follows:

TABLE I. RESULT OF THE REACTION AT 800°C

Exp. No.	Product	Amount mol.	c.p.m./mol $\times 10^{-7}$	c.p.m./g. atom of C $\times 10^{-7}$
1	Hydrogen	0.486		
2		0.363		
1	Methane	0.224	1.51	1.51
2		0.164	2.20	2.20
1	C_2 compds.	0.011	90.0	45.0
2		0.015	88.1	44.1
1	*Mixture of	0.998	32.1	4.87
2	benzene and toluene	0.591	39.2	5.94
1	Carbon	0.331	13.7	13.7
2	(as CO_2)	0.342	13.2	13.2

The c.p.m. of the original toluene was 46.0/mol. $\times 10^{-7}$.

* The mol. ratio, (benzene)/(toluene), obtained by mass spectrometer after the reaction was 0.63.

TABLE II. RESULT OF THE REACTION AT 1000°C

Exp. No.	Product	Amount mol.	c.p.m./mol. $\times 10^{-7}$	c.p.m./g. atom of C $\times 10^{-7}$
1	Hydrogen	2.21		
2		1.11		
1	Methane	0.52	6.0	6.0
2		0.26	6.1	6.1
1	C_2 compds.	0.30	11.0	5.5
2		0.26	12.6	6.3
1	*Mixture of	0.33	38.4	6.4
2	benzene and toluene	0.19	34.1	5.7
1	Carbon	0.11	5.4	5.4
2	(as CO_2)	0.67	5.5	5.5

The c.p.m. of the original toluene was 45.0/mol. $\times 10^{-7}$.

* The mole ratio, (benzene)/(toluene), obtained by mass spectrometer after the reaction was 80.

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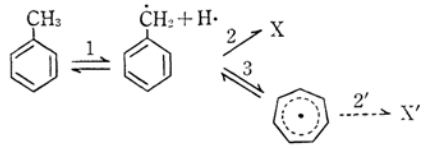

where X and X' denote the products produced successively from the benzyl radical and the tropyl radical respectively. If the velocity of step 2 is greater than that of step 3, it will be difficult for the redistribution of ^{14}C to occur. If step 2' is included in the reaction paths of the decomposition, it seems, from a study of the configuration of carbon atoms, that benzene is not formed as the product. The experimental results suggests that the velocity of step 2 would be greater than that of step 3 at 800°C, but would be smaller at 1000°C, as is diagrammatically represented in Fig. 2. The velocity of the reverse reaction of step 3 would predominate if the reaction temperature were raised to 1000°C. If the velocity of the reverse reaction of step 3 is fairly great even at 800°C, ^{14}C should be detected more or less in methane. In addition to this, the c. p. m. per mol. of benzene would be smaller than that of the original toluene. The results of the reaction at 800°C (Table I) can be interpreted in such a way.

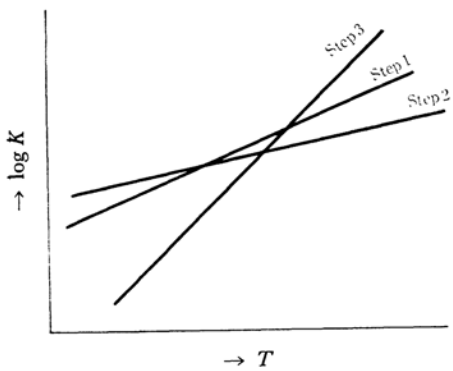

Fig. 2. Approximate representation of dependency of rate constant K in each reaction path on temperature.

Rylander et al.[6], who had found the mass number corresponding to C_7H_7 in the decomposition reaction of deuterated toluene by electron impact, proposed that the principal intermediate of the reaction is the tropylium ion. Recently, however, Gale et al.[7] have proposed, from a study by electron impact using toluene-α-^{14}C, that the tropylium ion should be excluded from the paths of the reaction. Our results would indicate that the reaction mechanisms in electron impact and thermal decomposition are substantially different from one another.

Summary

The pyrolysis of toluene at 800 and 1000°C has been made using toluene-1-^{14}C, and the ^{14}C in the reaction products of the gaseous state, such as methane, acetylene, ethylene and benzene, and the deposited carbon has been assayed.

The molar c. p. m. of methane and that of the mixture of C_2-compounds were about 1/20 of and twice that of the original toluene respectively, when the reaction was carried out at 800°C. The c. p. m. per gram-atom of the carbon in each product was practically equal to that of the original toluene when the reaction was carried out at 1000°C. It has been proposed that methane is formed by the removal of the methyl group and that the deposited carbon is formed mainly by the decomposition of C_2-compounds produced by the reaction. The formation of the tropyl radical has also been proposed as an intermediate in the reaction at a high temperature, through the formation of the benzyl radical.

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