#### SOME ASPECTS OF THE TOLUENE PYROLYSIS<sup>1</sup>

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The extensive use of the toluene carrier gas technique by Szwarc (7, 8) and co-workers has attracted wide interest (1, 2, 4, 6) in the mechanism of the pyrolysis of toluene in the past few years. The present note is concerned with the reactions of hydrogen atoms with toluene- $d_3$  and of benzyl radicals with p-fluorotoluene.

### REACTION OF HYDROGEN ATOMS WITH TOLUENE

According to Szwarc, radicals in general react with toluene in the following manner:

$$R^{\bullet} + C_{6}H_{5}CH_{3} \rightarrow RH + C_{6}H_{5}CH_{2}^{\bullet}$$

$$[1]$$

$$2C_{6}H_{6}CH_{5}^{\bullet} \rightarrow C_{6}H_{4}$$

$$[2]$$

$$\mathcal{L}_{6}H_{5}CH_{2} \longrightarrow C_{14}H_{14}.$$
<sup>[2]</sup>

He found it necessary, however, to propose an additional mechanism for the reaction of hydrogen atoms with toluene since methane as well as hydrogen is a product of the pyrolysis of toluene. Two radically different mechanisms might be proposed for the production of methane in this instance.

$$\Pi + 0 \subset \Pi \subset \Pi + C \Pi + C \Pi + C \Pi C \Pi + 0 \subset \Pi C \Pi + C$$

$$1 + 2C_6\Pi_5C\Pi_3 \rightarrow C\Pi_4 + C_6\Pi_6 + C_6\Pi_5C\Pi_2 \qquad [5]$$

or II

I

$$C_{6}H_{5}CH_{3} \longrightarrow C_{6}H_{5} + CH_{3}$$
[6]

$$CH_3 + C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2$$
<sup>(7)</sup>

Since the ratio of  $H_2$  to  $CH_4$  in the products is independent of temperature, it follows that either  $E_3 = E_6$  or  $E_4 = E_5$ . Szwarc reasoned that the activation energy for the over-all decomposition (77.5 kcal./mole) was too low for  $E_6$ and hence assumed that mechanism I was responsible for the methane production. Recent studies on the kinetics of the pyrolysis (2) and on the photobromination (1) of toluene suggest that this activation energy may not be reliable and hence that mechanism II cannot be ruled out by this argument.

Szwarc (5) has produced hydrogen atoms by the pyrolysis of n-propyl benzene in the presence of toluene and found both hydrogen and methane in the products in roughly the same proportion as in the toluene pyrolysis.

$$\begin{array}{rcl} C_6H_5C_3H_7 & \rightarrow C_6H_5CH_2 \cdot + C_2H_5 \cdot \\ C_2H_5 \cdot & \rightarrow H \cdot + C_2H_4 \\ H \cdot + C_6H_5CH_3 & \rightarrow H_2 + C_6H_5CH_2 \cdot \\ H \cdot + 2C_6H_5CH_3 \rightarrow CH_4 + C_6H_6 + C_6H_5CH_2 \cdot \end{array}$$

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It is conceivable, however, that propyl benzene, like propane, might decompose by a molecular mechanism into methane and the corresponding olefin.

| C₃H₅           | $\rightarrow CH_4 + C_2H_4$   |
|----------------|---|
| $C_6H_5C_3H_7$ | $\rightarrow$ CH <sub>4</sub> + C <sub>6</sub> H <sub>5</sub> CHCH <sub>2</sub> |

By carrying out the pyrolysis of *n*-propyl benzene in an excess of toluene- $d_3$ , it was hoped that further light might be thrown on the mechanism of the decomposition of propyl benzene and on the reaction of hydrogen atoms with toluene.

The "toluene- $d_3$ " was prepared in these laboratories by Dr. L. C. Leitch and was found to contain  $66\% d_3$ ,  $29\% d_2$ , and  $5\% d_1$  toluene. The propyl benzene was pyrolyzed at 995° K., at a total pressure of 1.7 cm. Hg, a contact time of 0.45 sec., and a toluene to propyl benzene ratio of 40 to 1, in an apparatus similar to that described previously (2). Under these conditions the propyl benzene was about 30% decomposed, the products being hydrogen, methane, ethane, ethylene, benzene, and bibenzyl. Mass spectra of the various fractions indicated:

$$\begin{array}{ll} H_2: HD: D_2 &= 1:1: \sim 0 \\ CD_4: CD_3H: CD_2H_2 &= 1:1.5: \sim 1. \end{array}$$

The benzene was mostly  $\mathrm{C}_6\mathrm{H}_6$  but small percentages of  $\mathrm{C}_6\mathrm{H}_5\mathrm{D}$  may also have been present.

The production of deuterated methanes in this pyrolysis rules out the intramolecular production of methane in the propyl benzene pyrolysis and confirms Szwarc's belief that hydrogen atoms produce methane when reacting with toluene. The fact that he also found roughly the same  $H_2$  to  $CH_4$  ratio in the decompositions of both toluene and *n*-propyl benzene is strong evidence that mechanism II is unimportant in the toluene pyrolysis.

Szwarc has suggested two mechanisms for the production of methane when hydrogen atoms react with toluene. With deuterated toluene these are:

III  $H' + C_6H_5CD_3 \rightarrow C_6H_5' + CD_3H$ 

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

IV  $H^{\bullet} + C_6H_5CD_3 \rightarrow CD_3^{\bullet} + C_6H_6$  $CD_3^{\bullet} + C_6H_5CD_3 \rightarrow CD_4 + C_6H_5CD_2^{\bullet}.$ 

 $CD_3 + C_{6115}CD_3 + CD_4 + C_{6115}CD_2$ 

Thus with the deuterated toluene used here, mechanism III would give  $CD_3H$ ,  $CD_2H_2$  etc.,  $C_6H_5D$ , and  $C_6H_6$  while mechanism IV would give  $CD_4$ ,  $CD_3H$  etc., and  $C_6H_6$ . The production of  $CD_4$ ,  $CD_2H$  etc., and  $C_6H_6$  in the present experiments is then good evidence for mechanism IV but III may contribute to a minor degree.

The ratio of  $H_2$  to HD is surprising in view of the fact that the side chain of the toluene was 87% deuterated. This leads to the suspicion that hydrogen atoms may be abstracting from the ring as well as from the side chain. Trotman-Dickenson and Steacie (9) give data for the relative rates of abstraction from benzene and toluene by methyl radicals at 450° K. On extrapolation to 1000° K. these data suggest that about 10% of radicals will abstract from the ring in normal toluene, and with toluene deuterated on the side chain this percentage would certainly be higher.

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## REACTION OF BENZYL RADICALS WITH *p*-FLUOROTOLUENE

The relative unreactivity of the benzyl radical is the basis of the so-called "toluene carrier gas technique" for studying free radical decomposition reactions. In a high mole ratio of toluene to decomposing compound, a radical will tend to react preferentially with toluene to give RH and a benzyl radical (reaction [1]) thereby converting a reactive radical into a molecule and an inert radical. Under the correct conditions of concentration and temperature. these benzyl radicals will dimerize to bibenzyl. Since the technique has been used at temperatures where bibenzyl would be expected to decompose rapidly however, it would be possible for abstraction reactions of benzyl to compete with the dimerization process. To test this, some studies on the relative rates of the reactions

$$C_6H_5CH_2 + p - C_6H_4FCH_3 \rightarrow C_6H_5CH_3 + C_6H_4FCH_2$$
[8]

 $\rightarrow C_{14}H_{14}$ 

[9]

have been attempted by pyrolyzing bibenzyl in the presence of an excess of *p*-fluorotoluene.

The apparatus for the pyrolysis of bibenzyl was similar to that referred to above. The bibenzyl was introduced by passage of the p-fluorotoluene over it at 110° C. The major products were mixtures of fluorinated bibenzyls which were pumped free of p-fluorotoluene at  $0^{\circ}$  C. Quantities of hydrogen (80%) and methane (20%) were produced varying from 1 to 5% of the bibenzyl passed through the reactor.

Analysis of the bibenzyl fraction was attempted from its infrared absorption spectrum in  $CS_2$  solution. Unfortunately, different absorption bands gave radically different analyses and the conclusion was reached that monofluorobibenzyl was also a product along with the di-p-fluorobibenzyl. Analyses were thereby limited to combustion of the mixture and this is unsatisfactory for kinetic data. A typical run at 994° K., contact time of 0.253 sec., pressure of 1.35 cm. Hg, and mole ratio of p-fluorotoluene to bibenzyl of 50 to 1 yielded the information that the equivalent of 35% of the bibenzyl was converted to di-p-fluorobibenzyl.

The following reaction scheme is consistent with the observations if the small amounts of  $H_2$  and  $CH_4$  are neglected.

> $(C_{6}H_{5}CH_{2})_{2} \rightleftharpoons 2C_{6}H_{5}CH_{2}$   $C_{6}H_{5}CH_{2} + C_{6}H_{4}FCH_{3} \rightarrow C_{6}H_{4}FCH_{2} + C_{6}H_{5}CH_{3}$   $\Rightarrow C_{6}H_{5}CH_{2} + C_{6}H_{5}CH_{3}$ [10]

[11]

$$\begin{array}{ccc} _{6}H_{4}FCH_{2} \end{array} \rightleftharpoons (C_{6}H_{4}FCH_{2})_{2} \end{array}$$
 [12]

 $C_6H_5CH_2 + C_6H_4FCH_2 \rightleftharpoons C_6H_4FCH_2CH_2C_6H_5$ [13]

The production of fluorinated bibenzyls confirms the belief that reaction [11] will compete favorably with the reverse of reaction [10] in the neighborhood of 1000° K. under conditions commonly used in the toluene carrier gas technique.

#### GENERAL CONCLUSIONS

It has been demonstrated that methane is a product of the reaction of hydrogen atoms with toluene thereby confirming the Szwarc mechanism for

and

2C6H5CH2

the decompositions of toluene and *n*-propyl benzene. The evidence is consistent with the following mechanism:

$$\begin{array}{rcl} \mathrm{H}^{\bullet} + \mathrm{C}_{6}\mathrm{H}_{5}\mathrm{C}\mathrm{H}_{3} & \rightarrow \mathrm{C}_{6}\mathrm{H}_{6} + \mathrm{C}\mathrm{H}_{3}^{\bullet} \\ \mathrm{C}\mathrm{H}_{3}^{\bullet} + \mathrm{C}_{6}\mathrm{H}_{5}\mathrm{C}\mathrm{H}_{3} & \rightarrow \mathrm{C}\mathrm{H}_{4} + \mathrm{C}_{6}\mathrm{H}_{5}\mathrm{C}\mathrm{H}_{2}^{\bullet} \end{array}$$

Szwarc used the activation energy for the decomposition of toluene to decide on the mechanism; confirmation of the mechanism does not, however, prove the correctness of this activation energy nor does it cast doubt on the higher value obtained by the photobromination of toluene (1, 3). It is worthy of note, however, that this latter is a maximum value and that the true value is less by the activation energy of the reaction

$$C_6H_5CH_2$$
 +  $Br_2 \rightarrow C_6H_5CH_2Br$  +  $Br$ 

and there is no a priori reason for supposing that this is zero.

Evidence has also been presented suggesting that radicals may abstract hydrogen atoms from the ring as well as the side chain in toluene but there is no indication as to how serious a complication this might be in the toluene carrier gas technique. Presumably the resulting tolyl radicals would disappear rapidly by reaction with toluene.

## $C_6H_4CH_3$ + $C_6H_5CH_3 \rightarrow C_6H_5CH_3 + C_6H_5CH_2$

Under the conditions of the toluene carrier gas technique in the neighborhood of 1000° K., abstraction by benzyl radicals has been shown to compete with combination. This implies that, when this technique is used in this temperature region, complications must be anticipated from reactions of the type

## $C_6H_5CH_2$ + RH $\rightarrow C_6H_5CH_3$ + R.

where RH is the decomposing molecule, especially when the R—H bond is weak.

Horrex and Miles (4) have studied the pyrolysis of bibenzyl and arrived at

the rate expression

# $k = 2 \times 10^9 e^{-48,000/RT} \text{ sec.}^{-1}$

for the decomposition into two benzyl radicals. Under the experimental conditions used in the above experiment this would predict only about 2%decomposition of the bibenzyl. Since a minimum of 35% was decomposed, it is suggested that the above rate expression is in error owing to the neglect of the recombination step in their mechanism.

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