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A Nonchain Process for Formation of Methane and Toluene in the Pyrolytic Hydrogenolysis of Xylenes

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Despite the structural and chemical similarities between xylene and toluene, the pyrolysis of xylene (*o*-, *m*-, *p*-, and the methyl-labeled xylenes- d_6) with a hydrogen or deuterium carrier takes place by a mechanism which is strikingly different from the mechanism of toluene pyrolysis with hydrogen.¹ Methane and toluene are the xylene products, at 700° and low conversion; the tracer experiments show that both the carrier hydrogen and the xylene contribute to formation of the products, but the xylene recovered from the tracer experiments shows very little hydrogen-deuterium exchange. The activation energy for formation of toluene is about 67 kcal./mole, and the pre-exponential factor is 2×10^{12} . The mechanism of xylene pyrolysis is thus a nonchain process of high activation energy and high *A* factor. A probable primary process is a split of xylene into tolyl and methyl radicals, which then attack both the carrier hydrogen and the xylene. Hydrogen atoms are probably formed during the xylene pyrolysis and probably react with the xylene methyl groups, but they do not displace methyl groups or other hydrogen atoms. They must disappear by combination processes. The tracer experiments show that, at 700°, the rate constant for methyl radical attack on xylene is five times that for attack on deuterium; the corresponding rate constant ratio for tolyl radicals is 10.

Introduction

This paper reports the results of pyrolyzing, at about 700°, each of the three xylenes, and the methyl-labeled xylenes- d_6 , with hydrogen or deuterium. These studies were begun in the expectation that the pyrolysis of xylene in the presence of hydrogen would take place by a chain mechanism similar to that proposed for toluene pyrolysis¹ with a hydrogen carrier.

It has turned out, however, that the xylene pyrolysis mechanism is quite different from that of toluene pyrolysis. The differences have been discovered by a combination of tracer techniques and rate measurements which are described in the following sections.

Experimental

Materials.—*o*-, *m*-, and *p*-xylenes (Eastman Kodak) were purified by preparative gas chromatography, using a Ucon 50-HB-2000 packed column at 160°. This was the only method of purification which would give materials with reproducible rates of pyrolysis. The deuterated xylenes (*o*-, *m*-, and *p*-C₈H₈(CD₃)₂) were obtained from Volk Radiochemical Corp. They were purified also by gas chromatography. The deuterium content of the purified materials was determined by low voltage mass spectrometry; each of them contained about 30% of C₈H₈D₆. This is not a satisfactory isotope purity and some features of the results are obscured by the high hydrogen content of these materials.

Procedures and Analyses.—The experimental set-up for the pyrolyses was the same as that used for the toluene pyrolysis,^{1b} and the procedures were the same. Sample sizes and flow rates were closely similar to those used in the toluene experiments. The volatility of xylene is lower than that of toluene and so the fritted sample injection chamber of the apparatus (IC in Fig. 1 of ref. 1b) was warmed to about 40° during each run. The product toluene was separated from unreacted xylene by gas chromatography, using the same column and conditions as were used to separate benzene and toluene. Recovery of xylene was usually better than 90% of the amount charged.

Results

Products and Yields.—The only pyrolysis products detectable under the conditions of temperature and contact time which we used were methane, toluene, and a trace of benzene. No carbonization of the tube took place, and no high boiling products were formed. The yield of methane is consistently higher than the yield of toluene, but no products were found which would account for this difference. A similar difference between the methane and benzene yields was found in the case of the toluene pyrolysis. We are now in-

clined to ascribe these differences to the different methods of analysis for the two products. Since the toluene analysis is the more straightforward, we have placed the greater reliance upon the values for toluene formation and have equated these, in most cases, to the rate of xylene consumption.

Kinetic Data.—The rates of pyrolysis of each of the three xylenes were measured at several temperatures. The data are shown in Table I. The total flow of gas

TABLE I
TEMPERATURE DEPENDENCE OF THE RATE OF XYLENE
PYROLYSIS WITH HYDROGEN CARRIER

Xylene	Temp., °C.	Contact time, sec.	Sample injected, mmoles	Methane, mmole	Toluene, mmole	10 ³ <i>k</i> ; sec. ⁻¹
<i>ortho</i>	644	3.77	1.905	0.0110	0.00743	1.04
<i>ortho</i>	681	3.77	1.947	.0506	.0334	4.53
<i>ortho</i>	705	3.77	1.898	.1080	.0632	8.82
<i>ortho-d₆</i>	707	3.57	1.585	.0963	.0560	9.90
<i>meta</i>	649	3.73	2.235	.0037	.00313	0.376
<i>meta</i>	706	3.73	2.216	.0345	.0244	2.95
<i>meta-d₆</i>	709	3.48	1.817	.0890	.0521	8.25
<i>para</i>	676	3.56	2.195	.0135	.00724	0.926
<i>para</i>	714	3.56	2.199	.0470	.0310	3.96
<i>para</i>	757	3.56	2.194	.1933	.0806	15.63
<i>para-d₆</i>	706	3.43	1.934	.0516	.0242	3.64

in each of these runs was about 2000–2500 ml. From the total flow, the percentage conversion to toluene, and the contact time, the pseudo-unimolecular rate constants were calculated (the reaction is probably actually first order in xylene and half order in hydrogen).² The values of *k* so obtained are shown in Table I. Semilog plots of *k* vs. 1/*T*°K. gave straight lines corresponding to apparent activation energies of 65 kcal./mole for *o*-xylene and 67 kcal./mole for *p*-xylene consumption.³

Using the higher values of ΔE and the observed rate constants for toluene formation, it was calculated that the Arrhenius pre-exponential factor, log *A*, was 12.3 for both *o*-xylene and *p*-xylene. The corresponding data for *m*-xylene is insufficient for similar calcula-

(2) A. Tsuchiya, A. Hashimoto, H. Tominaga, and S. Masamune, *Bull. Japan Petrol. Inst.*, **2**, 85 (1960).

(3) The apparent activation energy for pyrolysis of *o*-xylene which had not been purified by gas chromatography was lower, 60 kcal./mole; ΔE for unpurified *p*-xylene was also lower.

(1) (a) R. A. Meyer and J. G. Burr, *J. Am. Chem. Soc.*, **85**, 478 (1963); (b) J. G. Burr, R. A. Meyer, and J. D. Strong, *ibid.*, **86**, 3846 (1964).

TABLE II
THE ISOTOPIC COMPOSITION OF THE METHANE AND TOLUENE
FROM PYROLYSIS OF XYLENE

Temp., °C. Xylene Carrier Product	690		707		682		709		682		706		682	
	o-Xylene		o-d ₆		o-d ₆		m-d ₆		m-d ₆		p-d ₆		p-d ₆	
	H ₂	D ₂	H ₂	D ₂	H ₂	D ₂	H ₂	D ₂	H ₂	D ₂	H ₂	D ₂	H ₂	D ₂
Methane-d ₀	24.4	1.2	..	2.0
-d ₁	74.4	2.0	3.1	2.7	2.4
-d ₂	1.3	23.4	21.4	0.8	17.0
-d ₃	..	72.7	21.1	72.2	21.0	76.4	15.0
-d ₄	..	1.9	78.9	2.1	73.8	2.2	85.0
Toluene-d ₀	38.0
-d ₁	57.0	1.7	..	3.5	..	2.8
-d ₂	5.0	24.4	6.2	21.7	6.5	19.1	6.1
-d ₃	..	73.9	32.5	71.7	34.0	78.1	31.9
-d ₄	55.1	2.2	53.0	..	58.1
-d ₅	4.9	0.4	5.0	..	2.7

TABLE III
ABUNDANCE OF ISOTOPIC XYLENE SPECIES BEFORE AND AFTER PYROLYSIS

Isotopic species	o-Xylene			m-Xylene			p-Xylene		
	Initial	H ₂ carr.	D ₂ carr.	Init.	H ₂ carr.	D ₂ carr.	Init.	H ₂ carr.	D ₂ carr.
C ₈ H ₁₀	100	..	98	100	100
C ₈ H ₉ D	2
C ₈ H ₈ D ₂	7.5	7.2	7.2	8.4	6.8	8.0	6.6	7.2	6.5
C ₈ H ₇ D ₃	30.6	30	30	30.0	28	29	26.1	27	26
C ₈ H ₆ D ₄	61.2	62	61	59.7	63	58	64.7	64	65

tions (however, the two-point plot of $\log k$ vs. $1/T$ for this substance determined a line parallel to the analogous line for *p*-xylene). These values are substantially higher than the values of ΔE of 55 and 50 kcal./mole, $A = 10^6$, reported by Tsuchiya, *et al.*,² for hydrogenolysis for *o*-xylene and *p*-xylene, respectively, and much higher than the respective values of 47.8 and 34 kcal./mole, $\log A = 10$ and 6, reported by Betts, *et al.*,⁴ for the hydrogenolyses of *o*-xylene and *p*-xylene at 100 atmospheres hydrogen pressure. The reason for the higher values which we observed is probably the much lower contact times and much lower total conversions which we employed; the amount of benzene formed in our experiments was negligible.

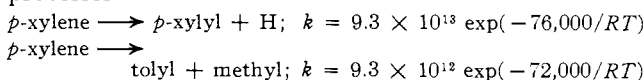
The isotopic composition of the products is shown in Table II for each of the runs with labeled carrier or labeled xylene. It was observed that the recovered xylenes-d₆ had almost exactly the same composition before and after a run, showing that isotopic exchange between the carrier and the xylene was not detectable; a small amount of exchange was observed for xylene-deuterium mixtures. In order to make this feature of the experiments more clear, the data on the recovered xylenes have been collected into Table III.

Discussion

The pyrolysis of *p*-xylene at temperatures of about 1000° and with very short contact times has drawn much recent attention⁵ because under these conditions *p*-xylene is converted in high yield to the very reactive and useful intermediate *p*-xylylene. This substance is not produced when the pyrolysis temperature is below 800°⁶; the principal product at temperatures under

800° and with contact times of 0.5–1.0 sec. is dimethyl-diphenylethane—the coupling product of the *p*-xylyl radical. Analogous coupling products are formed from the other xylenes. The gaseous products are hydrogen and methane in about a 60:40 ratio. A large number of other products are formed in low yield.⁷

Szwarc⁸ equated the rate of hydrogen + methane formation to the rate of xylene consumption, and thus reported that the activation energies for consumption of *o*-, *m*-, or *p*-xylenes were about the same and fell in the range of 74–77.5 kcal./mole, with A factors of about 4×10^{13} . Errede and DeMaria⁷ calculated the rate constants at 1000° for two separate primary processes



These results are very similar to those for the corresponding processes in toluene pyrolysis, and in fact Szwarc⁸ and others have concluded that the principal primary processes in xylene pyrolysis as well as in toluene pyrolysis is the breaking of a methyl group C-H bond to give methylbenzyl or benzyl radicals and possibly the breaking of a ring-methyl C-C bond to give a phenyl or tolyl radical. When toluene is pyrolyzed in a hydrogen atmosphere¹ the exclusive fate of the benzyl radical is reaction with hydrogen to give another hydrogen atom; the hydrogen atoms react with toluene in part by displacing methyl or phenyl radicals. The pyrolysis thus becomes a chain reaction propagated by hydrogen atoms. This has a number of consequences. The activation energy and A factor for the pyrolysis drop to 45 kcal./mole and 10^{8-9} sec.⁻¹, the products formed in the pyrolysis become simply methane and benzene, and when deuterated species are used in the reaction the isotopic composition of both the recovered toluenes and the products show that extensive hydrogen/deuterium exchange has taken place in the toluene ring (but not in the methyl group of the toluene).

Use of a hydrogen atmosphere in the xylene pyrolysis does not have quite the same effect. The products do become simply methane and toluene, rather than methane and dimethylbibenzyls, and no carbonization or formation of other complex products occurs. The hydrogen is thus obviously taking part in the pyrolysis, but the activation energy and the A factor, 65–67 kcal./mole and 2×10^{12} , remain remarkably close to those observed by Errede and DeMaria⁷ for conversion of pure *p*-xylene to toluene. Finally, the *o*-xylene recovered from runs with deuterium carrier is only about 2% exchanged (Table III). Exchange in the xylenes-d₆ is harder to detect, but the compounds recovered from runs with either hydrogen or deuterium carrier have very nearly the same composition as they did before the pyrolysis.

(4) W. D. Betts, F. Popper, and R. I. Silsby, *J. Appl. Chem.*, **7**, 497 (1957).

(5) L. A. Errede and J. P. Cassidy, *J. Phys. Chem.*, **67**, 69, 73 (1963), and earlier papers in this series; also secondary references contained in these papers.

(6) M. Levy, M. Szwarc, and J. Throssell, *J. Chem. Phys.*, **22**, 1904 (1954).

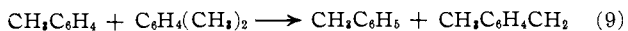
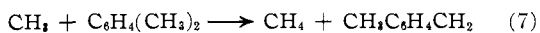
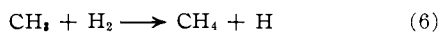
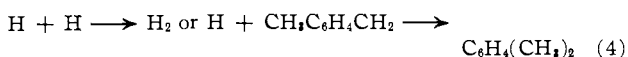
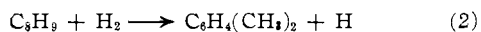
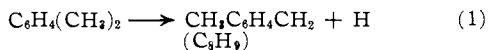
(7) L. A. Errede and F. DeMaria, *J. Phys. Chem.*, **66**, 2664 (1962).

(8) M. Szwarc, *J. Chem. Phys.*, **16**, 134 (1948).

The methanes and toluenes recovered from runs where either the xylene or the carrier was deuterium-labeled contain deuterium (Table II); it is evident that the additional hydrogen is derived both from the carrier and from the xylenes. This is further evidence that the carrier hydrogen (or deuterium) has participated in the formation of these products. The most likely mechanism for this interaction is an attack on the molecular hydrogen by methyl or tolyl radicals. The other product of this interaction would be a hydrogen atom.

However, if hydrogen atoms are intermediates in this pyrolysis they obviously do not react with the xylene ring because there is not the extensive isotopic exchange observed in the toluene-hydrogen pyrolyses. The amount of exchange actually observed in the xylene-deuterium pyrolyses resembles the very slight isotopic exchange on the methyl groups which was observed in the toluene-hydrogen system. The lack of ring hydrogen exchange found in the xylene system suggests strongly that the displacement of methyl or tolyl radicals by hydrogen atoms does not take place either, and thus that methane and toluene are not formed by a chain process with hydrogen atoms as carriers. The absence of such a chain reaction is also confirmed by the high activation energies and high pre-exponential factors found for methane and toluene formation.

The involvement of hydrogen in the xylene pyrolyses, the probable presence of hydrogen atom intermediates during the reactions, and the absence of a hydrogen atom carried chain process for product formation are best explained by eq. 1-9.

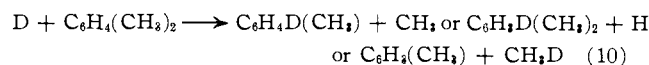


Formation of the products methane and toluene takes place *via* a primary split of xylene into methyl and tolyl radicals (eq. 5)⁹; these radicals become converted to the products by competitive reaction with the carrier (eq. 6) and with xylene (eq. 7). The hydrogen atoms formed in reactions 6 and 8 and those formed in the usual C-H bond split, eq. 1, are consumed by reactions 3 and 4. Reactions 1 + 2 + 3 thus constitute a chain process for exchange of methyl group hydrogen with carrier hydrogen. The actual

(9) A primary split of toluene into phenyl and methyl radicals was originally postulated for the toluene-hydrogen pyrolyses^{1a} but abandoned later^{1b} because of the low activation energy and pre-exponential factor.

amount of such exchange is very small (Table III). This probably means that the chain length is very short and that combination reactions like (4) are the most probable fate of the hydrogen atoms. This inefficient isotopic exchange process also suggests that reaction 1 is not as important as a prior consideration might indicate. If our value of the rate constant for toluene formation is taken as the rate constant for (5) and Errede and DeMaria's value⁷ used for reaction 1, then at 700°, $R_1 = 0.46R_5$; reaction 5 is thus the predominant primary process rather than (1).

The reactions which are excluded in this mechanism—and whose exclusion makes the xylene pyrolysis so strikingly different from the toluene pyrolysis—are any interactions of hydrogen atoms with the xylene ring (eq. 10).



We do not know why such reactions are prominent in the toluene pyrolysis and negligible in the xylene pyrolysis, unless it is simply the greater statistical abundance of methyl group hydrogens in xylene, combined possibly with a greater specific reactivity of these methyl hydrogens.

It should be noted at this point that the pyrolyses of *o*-, *m*-, and *p*-xylenes and of the deuteriomethyl analogs appear to proceed identically. The differences in molecular structure do not appear to be reflected in any of the rate processes or isotopic distributions.

Deductions from the Isotopic Content of the Products.—From the mechanism outlined in eq. 1-9 and the usual steady-state assumption for intermediates, the deuterium content of the methane formed from runs with xylene and deuterium carrier is unambiguously related to the ratio of rate constants, k_7^M/k_6^M , by eq. 11

$$k_7^M/k_6^M = (\text{CH}_4/\text{CH}_3\text{D})(\text{D}_2/\text{Xy}) \quad (11)$$

where D_2/Xy is the mole ratio of deuterium to xylene in the pyrolysis chamber. A similar ratio of rate constants, k_9^T/k_8^T , can be derived for the reactions of the tolyl radicals, $\text{CH}_2\text{C}_6\text{H}_4$, with deuterium and with xylene. The abundance of the methane species, $\text{CH}_4/\text{CH}_3\text{D}$ (run 60, Table II), together with the D_2/Xy mole ratio of 16.1, correspond to $k_7^M/k_6^M = 5.3$. The corresponding ratio for tolyl radicals, k_9^T/k_8^T , is 10.7. Thus at 700° methyl radicals attack xylene five times faster than they attack deuterium, and tolyl radicals are twice as selective as methyl radicals.

If allowance is made for the fact that the xylenes-*d*₅ used contained about 30% xylenes-*d*₆ and thus produced methyl radicals which were 15% CD_2H and tolyl radicals which were 15% $\text{CD}_2\text{HC}_6\text{H}_4$, then the rate constants for radical attack on (1) the carrier hydrogen, (2) the xylene ring, and (3) the xylene side chains can be expressed by an equation similar to (11) in terms of both the ratios $\text{CD}_3\text{H}/\text{CD}_4$ and $\text{CD}_2\text{H}_2/\text{CD}_4$. However, the amount of CD_4 produced in the runs listed in Table II is so small that this expression was not useful.