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**SOME KINETIC STUDIES
OF THE BENZENE-HYDROGEN
AND BENZENE-METHANE SYSTEMS
IN THE TEMPERATURE RANGE 600° TO 800°C**

D.R. MacKenzie and F.B. Growcock

February 1977

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ABSTRACT

Benzene pyrolysis experiments were carried out in a stainless steel flow system at temperatures between 600° and 790°C, with hydrogen or argon used as carrier. Rate constants for benzene loss were calculated at 600°C and in the range 760° to 790°C. The results obtained compare reasonably well with extrapolations of higher temperature results of Hou and Palmer, but not with the extrapolation of Asaba and Fujii's results. The pyrolysis rate constant determined from a static experiment in a quartz reactor was considerably lower than those determined with the stainless steel system, so that the metal appears to have had a significant catalytic effect. Static experiments in quartz with the benzene-methane system at 720°C yielded reasonably reproducible values of the rate constant for benzene loss. The rate of toluene formation was approximately linear with methane concentration for constant initial benzene concentration. From the product distributions obtained in the experiments, some inferences regarding the mechanism of toluene formation can be drawn.

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INTRODUCTION

This kinetic study was suggested by the results of our work in 1974-75¹ on rapid hydrogenation (or flash hydropyrolysis as it is usually called now) of coal. These results showed that liquid yields increase with temperature up to 750°C, and at temperatures $\geq 750^\circ\text{C}$ benzene constitutes almost the sole liquid product. Also the gaseous products at these temperatures consist mostly of methane and a small amount of ethane.

We felt it would be useful to examine the reactions of benzene and methane in the temperature range used in the coal study. Our experimental procedure in that study had involved rapid product removal from the hot reaction zone (~ 0.5 sec product residence time as a rule), but in an industrial process such short residence times might not be feasible. They also might not be desirable. For example, if one wanted to increase liquid yields, formation of toluene and xylenes from CH_4 and benzene might be brought about to a useful extent by proper control of the temperature downstream from a reactor. There appeared to be no published work on the homogeneous gas phase reaction of methane and benzene, so we proposed to study its kinetics in the temperature range 600° to 800°C.

In this range, benzene is the reactive species, since methane is quite stable to even higher temperatures. Thus it is helpful to know what happens to benzene itself when it undergoes thermal decomposition at these temperatures. Kinetic studies had not been done in the region below 900°C, although considerable work has been done with shock tubes in the region 900° to 1700°C, particularly by Palmer and co-workers at Penn State,^{2,3} and by Asaba and Fujii at University of Tokyo.⁴ We therefore decided to investigate the thermal decomposition of benzene as an adjunct to our kinetic study of the methane-benzene system.

EXPERIMENTAL

1. Benzene Pyrolysis

A stainless steel flow system was used for this study. Benzene vapor was introduced into the reaction zone in a stream of hydrogen or argon. The carrier gas was saturated by bubbling it through liquid benzene in a reservoir kept at a temperature controlled to $\pm 0.05^\circ\text{C}$ by a CRC Circutemp thermoregulator.

The reactor consisted of a 12-cm length of $\frac{1}{8}$ -in.-o.d. 316 stainless steel tubing. It was heated resistively and the temperature measured by three thermocouples of 31 gauge wire spot-welded to the wall at intervals along the length of the heated zone. Flow rate was measured with a Matheson mass flowmeter, and the time at re-

Figure 1. Top: longitudinal cross section of quartz reactor. Bottom: temperature profiles along the length of the reactor; points taken every 5 mm. ΔT is the maximum spread in temperature except for 1 cm at each end.

action temperature was determined from the flow rate and the length of the heated zone. The concentration of benzene entering the reactor section could be calculated from the measured carrier gas flow rate and the vapor pressure of benzene at the temperature of the bubbler. This value was checked by collecting samples of the effluent stream for known lengths of time before heating the reactor. The reactor was then quickly brought to reaction temperature, and after flow rate and temperature had stabilized samples of the effluent gas stream were again collected.

Samples were analyzed for unreacted benzene and reaction products by gas-liquid chromatography (GLC). However, the major products were polyphenyls, which were partially held up in the metal lines ahead of the sample collectors. Because of this the reaction products were measured only in a semiquantitative manner, and the main emphasis was placed on analysis of benzene for determination of overall rate constants.

2. Benzene-Methane Reaction

In order to avoid possible catalytic effects of a metal surface, a quartz reaction vessel was used to study the benzene-methane reaction. The vessel, shown in Figure 1, was attached to a 1/4-in. Nupro valve by a Swagelok fitting with Teflon ferrules. Reactants were admitted to the reactor through this valve, and volatile products were removed through it to a sampling system after an experiment. Products were analyzed by GLC.

The quartz reaction vessel was heated by placing it in an inductively heated metal tube at a much higher temperature than desired for the experiment, then dropping the temperature of the metal tube as the reactor approached the required experimental temperature. In this way, the quartz tube could be brought up to temperature in 40 to 45 sec, and the time during which it was within 50° of the final temperature could be kept to ≤ 10 sec.

Temperature uniformity inside the reactor was checked with an argon filling and an internal thermocouple. Two equilibrium temperature profiles are shown at the bottom of Figure 1 for two slightly different induction coil configurations. At 700° to 750°C, maximum temperature variations along the length of the reactor, except for 1 cm at each end, was 6° in one case and 7° in the other. Radial variation was barely detectable.

RESULTS AND DISCUSSION

1. Benzene Pyrolysis

According to Asaba and Fujii,⁴ benzene decomposition in the temperature range 1100° to 1700°C proceeds by a chain reaction. They list the following reactions as contributing to the overall mechanism, forward reactions (2) and (3) being the chain propagating steps.

In the temperature range of our work (600° to 790°C) this same general mechanism applies, as can be seen from the major products formed in the seventh and ninth experiments listed in Table 2 (similar to those formed in the flow experiments). These experiments and the flow experiments also show that methane and ethylene are significant products. Ethane is formed in trace amounts, and free carbon is also formed. No acetylene could be detected in any of the experiments, so possibly reaction (4) does not occur at these lower temperatures. However, one or more ring-opening reactions similar to (4) must occur to account for methane and ethylene formation and, of course, free carbon.*

Asaba and Fujii's experimental conditions were such that a reasonable simplification of their scheme led to the expression

$$-\frac{d[\text{C}_6\text{H}_6]}{dt} = 2k_1[\text{C}_6\text{H}_6] + \frac{4k_1k_3}{k_4}[\text{C}_6\text{H}_6]^2,$$

*Reaction (4) may occur under our conditions, but the resulting acetylene, although stable with respect to thermal decomposition, may be removed by radical initiated polymer formation.

Figure 2. Plots of benzene pyrolysis first- and second-order rate constants, k_I and k_{II} , respectively, taken from the literature. Open circles represent data taken from Murphy, Palmer, and Kinney² and from Hou and Palmer.³ Filled circles represent data taken from Asaba and Fujii.⁴

Figure 3. Plots of benzene pyrolysis first- and second-order rate constants from this work. $\circ$, First-order constants, metal flow system; $\square$, first-order constant, static quartz reactor; $\bullet$, second-order constants, metal flow system; $\blacksquare$, second-order constant, static quartz reactor. Solid lines are extrapolations of first-order results, and dashed lines of second-order results, taken from the literature and plotted in Figure 2.

with both a first-order and a second-order term in benzene concentration. Their experimental results, shown in Figure 2, were obtained under conditions such that the first-order term contributed very little. The temperature dependence of their second-order rate constant thus determined is claimed to be consistent with that calculated from values of the Arrhenius parameters for elementary reactions (1), (3), and (4) given by Benson⁵ and Franklin.⁶ However, a sizable extrapolation in temperature is involved and agreement may be fortuitous.

Agreement with Hou and Palmer's experimental second-order rate constants³ (see Figure 2) is dubious. Although Asaba and Fujii's lowest temperature data agree with some of Hou and Palmer's points, the temperature dependence is markedly different. Data of Hou and Palmer for the first-order rate constant are also shown in the figure. These are seen to be at considerable variance with those obtained earlier by Murphy, Palmer, and Kinney. Thus the kinetics of benzene de-

composition in the high-temperature region cannot yet be considered completely understood.

In Figure 3 our results are plotted for two sets of experiments, one at 600°C and the other in the range 760° to 790°C. Also plotted is the result of the single static experiment in a silica vessel without added CH₄ and hydrogen reported in Tables 1 and 2. The results at the higher temperatures are plotted as both first-order and second-order rate constants. The lines are extrapolations of the published results given in Figure 2. The scatter in our results is considerable even at 760° to 790°C, and at 600°C it is so great as to make detailed comparison of dubious value. However, it is prob-

Table 1

Rate Constants for Benzene Loss in Static Methane-Benzene Experiments
in Quartz Reactor at 720°C

Initial pressure, mm				Rate constants	
C ₆ H ₆	CH ₄	Xe	H ₂	1st-order, sec ⁻¹ × 10 ⁴	2nd-order, liter mole ⁻¹ sec ⁻¹
137	166			10.3	0.55
137	166			7.9	0.42
137	164			9.9	0.55
137	187	453		9.9	0.56
140	223			12.5	0.68
137	278			9.5	0.53
137	619			11.2	0.65
137		619		9.6	0.54
137	163		551	6.2	0.24
137			627	4.8	0.19

Table 2

Products in Static Pyrolysis Experiments for 1.8×10^{-4} Moles Benzene
at 720°C and a 7-min Reaction Time

Initial pressure, mm				Product, * μmoles				
C ₆ H ₆	CH ₄	Xe	H ₂	CH ₄	C ₂ H ₄	Toluene	C ₁₂ H ₁₀	C ₁₈ H ₁₄ **
137	166				0.016	2.33	4.17	0.20
137	166				0.014	2.73	3.33	0.42
137	164				0.017	2.93	4.73	—
137	187	453			0.037	3.13	7.26	0.95
140	223				0.042	4.75	7.70	0.17
137	278				0.032	4.49	2.67	0.13
137	619				0.009	8.04	4.72	0.39
137		619		0.27	0.037	0	8.57	0.68
137	163		551		0.007	3.4	1.07	0.0004
137			627	0.13	0.005	0.0003	0.88	0

*C₂H₆ was in the range 10⁻³ to 10⁻⁴ μmoles. **In general, *m*-C₁₈H₁₄ > *o*-C₁₈H₁₄ > *p*-C₁₈H₁₄.

ably worth noting that both sets of data for the first-order rate constants fall only a little above the extrapolation of Hou and Palmer's results and have essentially the same temperature dependence. These are roughly four orders of magnitude above values to be expected from the results of Murphy, Palmer, and Kinney. The rough agreement of our result with those of Hou and Palmer would indicate that the earlier results from Penn State are incorrect.

Our second-order results agree reasonably well with the extrapolation from Hou and Palmer's data, lending further support to this contention. Also our results are very much lower than would be expected on the basis of the extrapolation from Asaba and Fujii's results. This is particularly true of the single result of the static experiment in quartz at 720°C. This value is probably more accurate than those from the flow experiments, considering the relatively small spread in rate constant values for the static experiments (Table 1). It probably indicates that there is an enhancement of the rate by the metal surfaces in the flow runs, but, even with this enhancement, the results are decisively lower than Asaba and Fujii's extrapolation.

There is certainly a change in the detailed mechanism of the benzene decomposition in going to the higher temperatures of Asaba and Fujii's experiments, as shown by the change in product distribution (e.g., we saw no acetylene, whereas it was a major product for them). Thus the temperature dependence of the overall rate constant could well change appreciably between these temperature ranges, and Asaba and Fujii's results would be consistent both with those of Hou and Palmer and with our own. That would require only that, when k_4 in Asaba and Fujii's rate expression is replaced by a rate constant for a new reaction (or reactions) using up C_6H_5 , this new rate constant change less rapidly with temperature in comparison with k_1 and k_3 than does k_4 .

This is an interesting problem, obviously quite complex, requiring much more effort for a full understanding than we were able to give. The precision of our rate constant measurements even at the higher temperatures was only fair because of the difficulty in measuring accurately the small amounts of benzene decomposing. This was still more of a problem at the lower temperature, where slowing the flow rates (allowing longer reaction times) could not easily be done to an extent sufficient to compensate for the very much smaller decomposition rate. Even greater experimental difficulties would undoubtedly be met in measuring products quantitatively – e.g., carbon and polycyclics – for determination of rate constants of elementary reactions. There is also the previously mentioned problem of catalytic effects of the stainless steel. Such surface effects were probably not large, but appear to be real.

2. Benzene-Methane Reaction

Results of a series of experiments at 720°C with the same initial benzene concentration are given in Tables 1 and 2. Reaction time was usually 7 min, although in several experiments it was 5 to 6 min. Amounts of products in Table 2 are adjusted to a reaction time of 7 min by assuming that change in product concentration was linear with time in this range.

In Table 1 rate constants for disappearance of benzene are given for both first-order and second-order treatment of the data. The scatter is much less than in the

flow experiments, and the values are essentially constant for both first- and second-order treatment, which indicates that addition of methane has little effect on overall benzene loss. This is in contrast to Asaba and Fujii's results at much higher temperatures (1200° to 1500°C), which showed a 30 to 70% increase in benzene pyrolysis rate with addition of an equimolar amount of methane. With or without methane, addition of hydrogen causes a marked decrease in the rate constants (last two experiments), as predicted by the greatly increased importance of Asaba's reaction (-2)

and as observed by Asaba and Fujii.⁴

From the product yields given in Table 2, one can draw several conclusions regarding the kinetics of the benzene-methane reaction. Within the precision of the experiments, the rate of toluene formation is approximately linear with initial CH_4 concentration. If it is assumed that the rate also shows a first-power dependence on benzene concentration, a second-order rate constant of $\sim 2 \times 10^{-3}$ liter mole⁻¹ sec⁻¹ is obtained for the overall reaction of benzene and methane to form toluene at 720°C.

This tells us nothing about the way in which toluene is formed. Since benzene is the unstable component at this temperature, its decomposition products, $\text{C}_6\text{H}_5\cdot$ and $\text{H}\cdot$, must be responsible for initiating reaction with CH_4 . $\text{H}\cdot$ will abstract $\text{H}\cdot$ from CH_4 (as well as from C_6H_6) yielding $\text{CH}_3\cdot$ radical. $\text{C}_6\text{H}_5\cdot$ will also abstract $\text{H}\cdot$ from CH_4 :

It conceivably could also react directly with CH_4 to form toluene:

This reaction is quite endothermic so its rate would be expected to be rather low at 720°C. There is good evidence that it is not occurring to a significant extent in these experiments. One sees in the experiment using both hydrogen and methane that the rate of toluene formation is at least as great as and possibly greater than the rate obtained with only methane present at the same concentration. If reaction (11) were contributing appreciably to the rate of toluene formation, that rate should decrease rather than increase, since $\text{C}_6\text{H}_5\cdot$ with excess hydrogen present is removed to a great extent via reaction (-2)

and to that extent is not available for reaction (11). This leads to less overall benzene consumption, as shown by the much decreased pyrolysis rate (Table 1) and biphenyl formation (Table 2). $\text{CH}_3\cdot$ formation under these conditions should not be appreciably affected, since $\text{C}_6\text{H}_5\cdot$ not available for reaction (10) because of competition by reaction (-2) is simply replaced by the $\text{H}\cdot$ formed in (-2). This $\text{H}\cdot$ then is available to form $\text{CH}_3\cdot$ according to reaction (9).

Thus formation of toluene at this temperature occurs largely if not entirely from reaction of methyl radicals with benzene. Direct formation by the reaction

is, like reaction (11), not likely to have an appreciable rate, although it is less endothermic than (11) and its rate is, therefore, estimated to be higher than that of (11).^{5,6} Addition of $\text{CH}_3\cdot$ to the benzene ring seems to be the most likely route leading to toluene, but no information about the detailed mechanism can be deduced from the present experiments.

REFERENCES

1. GROWCOCK, F.B. AND MACKENZIE, D.R., *Fuel* **56**, 349 (1976).
2. MURPHY, D.B., PALMER, H.B., AND KINNEY, C.R., *Ind. Carbon Graphite, Pap. Conf.*, p. 77, London, 1958.
3. HOU, K.C. AND PALMER, H.B., *J. Phys. Chem.* **69**, 863 (1965).
4. ASABA, T. AND FUJII, N., *13th Symp. (Int.) Combust. (Proc.)*, p. 155, Pittsburgh, 1971.
5. FRANKLIN, J.L., *Brit. Chem. Eng.* **7**, 340 (1962).
6. BENSON, S.W., *Thermochemical Kinetics*, Wiley, New York, 1967.