

## The Kinetics of Thermal Decomposition of Benzene in a Flow System

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Benzene in helium carrier gas has been decomposed at temperatures from 1173 to 1523°K. and at residence times from 20 to 250 msec., using a tubular flow reactor with a well-defined temperature plateau. The kinetics are complex, demonstrating mixed-order behavior with back reactions and wall effects. Sooting also causes enhancement of the rate. In the early stages of reaction, the decomposition kinetics are compatible with a treatment based upon mixed first- and second-order reactions. The first-order contribution appears to be an unusual chain that involves the wall in one chain-carrying step, while the second-order reaction is probably the homogeneous, bimolecular formation of biphenyl and hydrogen. The rate constant for the former is  $k_{\text{I}} = 10^{9.15} \exp(-52 \text{ kcal./RT}) \text{ sec.}^{-1}$  while the latter is estimated to be  $k_{\text{II}} = 10^{14} \exp(-40 \text{ kcal./RT}) \text{ cc./mole sec.}$

### Introduction

As the simplest aromatic hydrocarbon, benzene has provided the point of departure for innumerable studies, theoretical and experimental, of molecular properties and reactions. It should likewise provide the starting point in a systematic understanding of thermal decompositions involving aromatics, and, indeed, it has been studied from time to time, *e.g.*, in connection with formation of surface carbon deposits<sup>1-3</sup> or with soot formation in diffusion flames.<sup>4,5</sup> Kinetic studies have been carried out by Mead and Burk,<sup>6</sup> Kinney and DelBel,<sup>7</sup> Kinney and Slysh,<sup>8</sup> and most recently by Bauer and Aten.<sup>9</sup> Attempts to obtain rate constants were made mainly by the first and last of these. Slysh<sup>8</sup> did obtain a rate constant, but only at one temperature (1473°K.). Mead and Burk studied the decomposition in a flow system over temperatures from 1023 to 1125°K. They treated the kinetics by means of the differential equation,  $dx/dt = k(a - x)^2/x$ , where  $a$  is the starting concentration and  $x/a$  is the fraction decomposed at time  $t$ . They used this equation because it suited the data and because they felt it made sense in terms of a bimolecular surface reaction that was strongly inhibited by products. The equation suffers from the severe defect that it predicts an infinite rate at the start of reaction, and we therefore do not believe that their rate constants are meaningful.

The work of Bauer and Aten was done with a shock

tube in connection with a study of the optical (2537-Å.) absorption coefficient of C<sub>6</sub>H<sub>6</sub> at high temperatures. They measured the initial rate of reaction, and this fact, plus the use of a shock tube, guarantees that they measured a homogeneous reaction rate. Because they did not have information on the extinction coefficients of products, their rate information was confined to *relative* values. However, these covered a wide temperature range and provided, on a first-order treatment, a good estimate of the activation energy, putting it at about 40 kcal.

The present work stems not only from the intrinsic challenge of the problem but also from an interest in the rate of carbon formation and its relationship to the rates of decomposition of starting materials. A study by Murphy, Palmer, and Kinney<sup>10</sup> provided

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precise information on the rate of carbon film deposition from benzene and could be reasonably interpreted in terms of the rate of decomposition of benzene; however, reliable independent information on this rate was not available and was clearly needed, not only for this purpose but also because of a wish to understand the ease with which benzene forms carbon black.

### Experimental

**Apparatus and Procedure.** The pyrolysis chamber for the flow system used in most of the work (reactor A) was a mullite combustion tube of 5-mm. i.d. The furnace had an over-all length of 66 cm. with a 25.4-cm., essentially uniform hot zone. The current input to the furnace was first led through a rheostat into the control circuit consisting of an on-off switch, pilot light, ammeter, and a mercury relay. This was actuated by a Leeds and Northrup Speedomax indicating controller operating from the thermocouple situated in the center of the heating chamber. The temperature so controlled was maintained within  $\pm 1^\circ$ . The apparatus was operated at atmospheric pressure, using helium as a diluent and carrier gas. Its rate of flow was controlled by Sho-Rate flowmeters equipped with differential relays. The purity of helium was ensured by passing the gas first through a copper furnace at  $500^\circ$  to remove oxygen and then through absorption towers filled with Anhydrone and Ascarite to remove water and carbon dioxide.

A spectroscopic grade of benzene was evaporated into the furnace by bubbling a portion of helium through a sample flask, the temperature of which was maintained at  $14.0 \pm 0.1^\circ$  by circulating water from a constant temperature bath through the outer jacket. The benzene vapor was then routed into the main helium stream. After combining the two gases, the mixture was passed through a multiple loop packed with glass wool to ensure homogeneous mixing. The rate of evaporation was controlled by the bath temperature and the helium flow rate. By adjusting the flow rate of the two helium streams, the desired contact time and the concentration of benzene in the reaction zone was obtained. The total pressure in all runs was  $735 \pm 5$  torr. Normally, the temperature profile for each experimental condition was determined by inserting a platinum-platinum-10% rhodium thermocouple into the pyrolysis tube from the downstream side. The thermocouple used in these measurements was calibrated against a certified platinum-platinum-10% rhodium thermocouple purchased from The Thermolectric Co.

To test the heterogeneity of the reaction, a four-hole reactor (B) with 0.24-cm. i.d. per hole was used to

replace the 0.5-cm. tube. This increased the surface-to-volume ratio by a factor of about 2.

**Analysis.** A Perkin-Elmer Model 154-C vapor fractometer was used for identification of products and measurement of the rate of benzene decomposition. The input or effluent gas streams could be directly flushed through a gas-sampling valve. A comparison of the benzene content of two such gas samples provided a direct measure of the extent of decomposition. The exhaust gas was first quenched by cooling water and was passed through a multiple loop installed downstream of the furnace to ensure that it reached room temperature before the sample was taken. Dinonyl phthalate, obtained from Eastman Organic Chemicals, was used as adsorbant in the separating column. A 1-m. column was used for the analysis of benzene at  $45^\circ$  column temperature and 50-cc./min. helium flow. The retention distance of benzene from sample injection was 3 cm.

### Results and Discussion

Typical temperature profiles of the two reactors for the same temperature setting are illustrated in Figure 1. These are measured gas temperatures under flow conditions (with He) comparable to those in the kinetic runs. The complete profiles were determined for most of the temperature settings used in kinetic runs. They possessed well-defined plateaus in all cases and were found to be essentially independent of flow velocity, from which it is inferred that the thermocouple was reading the gas temperature. The plateaus

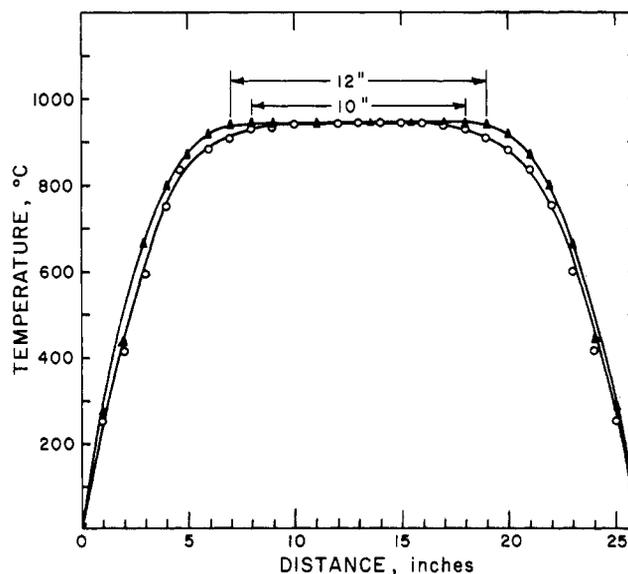


Figure 1. Temperature profiles for a controller setting of  $946^\circ$ : open circles, reactor A (5-mm. i.d.); black triangles, reactor B (4 holes, 2.4-mm. i.d. each).

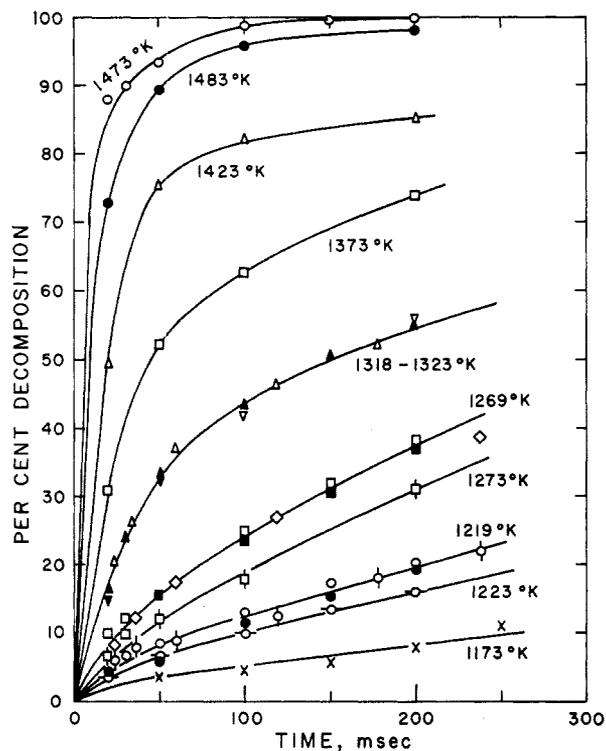


Figure 2. Per cent decomposition as a function of time, at ten temperatures, for a starting concentration of 1 mole % of  $C_6H_6$ . Different symbols are used to distinguish duplicate runs made at the same temperature (1219, 1269, and 1318-1323°K.).

were long enough that the end effect was very small; nevertheless, an allowance was made for this by extending the effective hot zone 2.54 cm. beyond the plateau on both the input end and the output end of the reactor.

Plug flow was assumed; *i.e.*, the reaction time was taken to equal the average residence time of an element of gas in the reactor. Although the flow was laminar, the plug flow assumption was adequate. This can be shown by considering the average diffusion time for a molecule in the tube to reach the wall. With a helium carrier, this time was of the order of  $4 \times 10^{-3}$  sec. for reactor A and  $10^{-3}$  sec. for reactor B. The shortest residence time studied was  $20 \times 10^{-3}$  sec., for which there may have been a moderate nonuniformity of composition in the radial direction for reactor A. However, the agreement in results between reactors A and B supports the conclusion that the nonuniformity was slight.

Plots of the % decomposition as a function of time are shown in Figure 2, for a starting concentration of 1%  $C_6H_6$  in He. Some inconsistency in temperatures is noted. This is probably attributable to placing too much reliance upon the calibration of the temperature

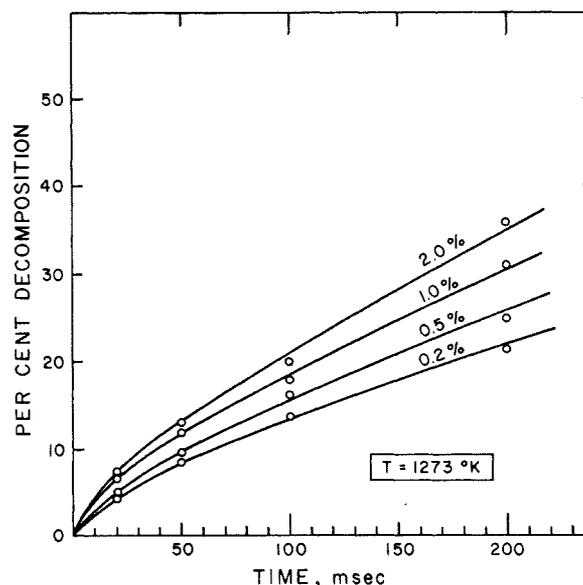


Figure 3. Per cent decomposition as a function of time at 1273°K., showing the effect of variations in the starting concentration.

controller in several of the earlier experiments. In the absence of information on this point, all experiments are included, and an uncertainty of about  $\pm 10^\circ K.$  is assigned to the reported temperatures.

At each temperature, several concentrations were studied. A plot showing the concentration effect at one temperature appears in Figure 3. A somewhat more convenient way of showing concentration effects is to plot the % decomposition at fixed residence time *vs.* the mole % of  $C_6H_6$  at a series of temperatures. Such a plot is given for two temperatures in Figure 4.

Some qualitative conclusions may be drawn from the several plots: (a) the finite intercepts in Figure 4 show that there is a first-order contribution to the rate; (b) the finite slopes in the same figure show that there are higher order reactions occurring; (c) however, the shapes of these plots and also of the plots in Figure 2 show that the order is not simple; (d) in particular, one sees shoulders on the plots in Figure 2 that imply significant contributions from back reactions, but equilibrium is not attained; this suggests that, although there is a *tendency* toward equilibration, decomposition of reaction products prevents it; (e) heterogeneous contributions to the decomposition rate appear to be small; this is implied by the plots for  $T = 1219, 1269, \text{ and } 1318-1323^\circ K.$ , which include points for both reactors A and B.

Because of the complications presented by back-reactions and decomposition of products, quantitative information on rate constants can be obtained most

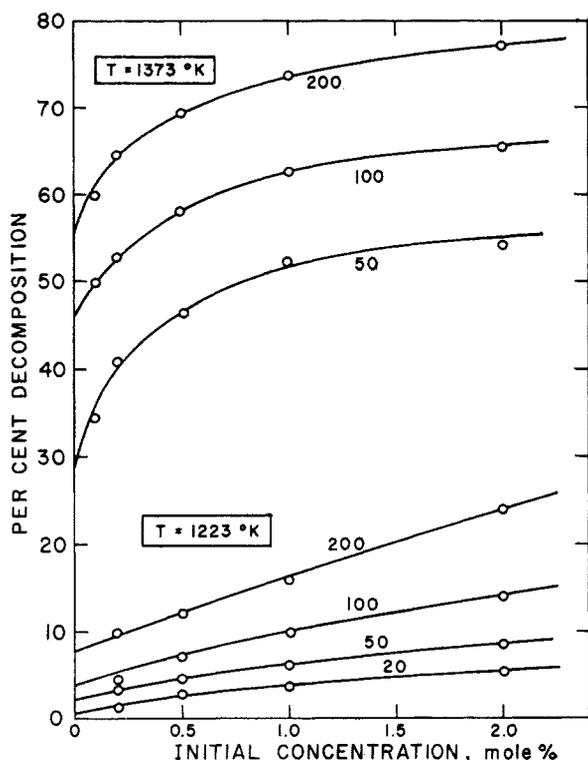


Figure 4. Cross plots of data at 1223 and 1373°K., showing the per cent decomposition as a function of initial concentration, at fixed residence times. The times (in msec.) are indicated on the curves.

readily by using data at short times. Initial slopes could be employed, but better accuracy is available by observing the extent of reaction over short times and comparing this with an integrated expression for a mixed-order reaction. For the latter, we have used an assumed mixture of first- and second-order kinetics. There clearly is a first-order contribution. As for the higher order contribution(s), the data are not sufficiently detailed or sufficiently accurate to permit one to write  $-dC/dt = k_1C + k_nC^n$  and determine  $n$  by curve-fitting. Instead, one hopes to choose the correct  $n$  and justify the choice later by examining the consequences.

Actually, there are some grounds for choice: (a) among homogeneous gaseous reactions of higher order,  $n = 2$  is very frequent,  $n = 3/2$  is fairly common, and other values are rare; (b) dating clear back to the work of Bertholet (as discussed by Mead and Burk<sup>6</sup>), it has been known that the main products of benzene pyrolysis at low temperatures are biphenyl and hydrogen. The first thought that occurs to one is the suitability of the reaction  $2C_6H_6 \rightarrow C_{12}H_{10} + H_2$  as a means of producing biphenyl. If, as seems possible, this is a

straightforward, four-center reaction, it should be second order.

With  $n = 2$ , we have

$$-dC/dt = k_I C \text{ and } k_{II} C^2 \quad (1)$$

as the rate equation. This can be integrated to give

$$-\ln(C/C_0) = k_I t + \ln[(1 + qC_0)/(1 + qC)] \quad (2)$$

where  $q = k_{II}/k_I$ . For convenience, this can be written as

$$-\ln(C/C_0) = k_I t + \ln W \quad (3)$$

where  $W = (1 + qC_0)/(1 + qC)$ . One can now use experimental determinations of  $(C/C_0)$  corresponding to two values of  $C_0$ , at fixed time, and determine both  $k_I$  and the ratio of the  $W$  values. From the latter, one can determine  $q$  and then  $k_{II}$ .

The results of this treatment at  $t = 0.020$  sec. are tabulated in Table I, and an Arrhenius plot of the rate constants appears in Figure 5. The figure includes some additional data from other sources which will be discussed later. The short time, 0.020 sec., was chosen for the calculations in the hope of minimizing the

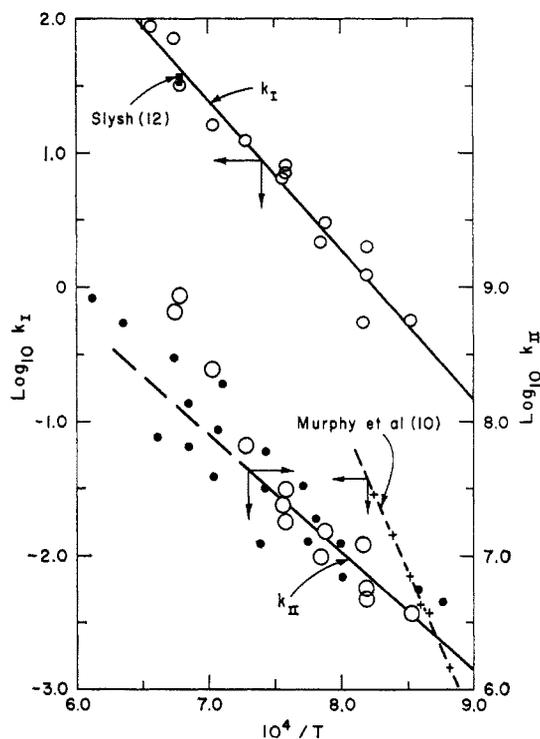


Figure 5. Arrhenius plot of  $k_I$  and  $k_{II}$ , in units of sec.<sup>-1</sup> and cc./mole-sec., respectively. Arrows on the lines indicate the scale to be used: open circles, present results; black circles, normalized data of Bauer and Aten.<sup>9</sup> Results of Murphy, *et al.*,<sup>10</sup> from carbon deposition kinetics are also included, for comparison.

effects of back-reactions. In the absence of knowledge concerning their rates, the success of the treatment can be judged only by the self-consistency of the resulting rate constants. The first-order values, which are the more reliable of the two, seem to behave well. The  $k_{II}$  values at higher temperatures lie above the line that best satisfies the lower temperature results. This divergence is almost certainly due to sooty carbon formation in the gas phase, which was severe at higher temperatures when the concentration exceeded about 0.1%. Because the sooting tendency was a function of concentration, it rendered determination of  $k_{II}$  very unreliable;  $k_I$ , on the other hand, could be calculated quite well under these conditions because it involved essentially the modest correction from 0.1% to infinite dilution.

**Table I:** Rate Constants Computed from the Data at  $t = 0.020$  Sec. by Means of Eq. 3

$T, ^\circ\text{K.}$	$10^4/T$	$k_I, \text{sec.}^{-1a}$	$k_{II}, \text{cc./mole sec.}^a$
1173	8.53	0.56	$3.6 \times 10^6$
1219	8.20	1.23 (A) 2.01 (B)	$4.8 \times 10^6$ (A) $5.5 \times 10^6$ (B)
1223	8.17	0.55	$1.2 \times 10^7$
1269	7.88	3.05	$1.5 \times 10^7$
1273	7.85	2.13	$0.98 \times 10^7$
1318	7.59	7.2 (B) 7.4 (A)	$2.1 \times 10^7$ (B) $1.8 \times 10^7$ (A)
1323	7.56	6.6	$2.4 \times 10^7$
1373	7.28	12.3	$6.6 \times 10^7$
1423	7.03	16.3	$2.46 \times 10^8$
1473	6.79	32.5 35 <sup>b</sup>	$8.7 \times 10^8$
1483	6.74	70.5	$6.45 \times 10^8$
1523	6.56	$88.5 \pm 20$	...

<sup>a</sup> (A) and (B) refer to the two reactors. <sup>b</sup> Corrected to initial rate; from R. S. Slysh, Ph.D. Dissertation, Department of Fuel Technology, The Pennsylvania State University, 1960.

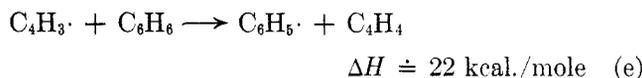
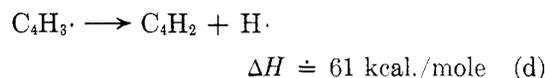
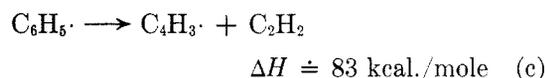
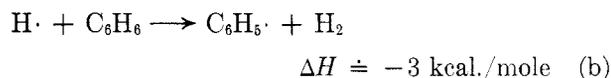
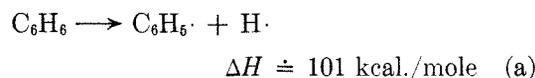
It should be remarked that a mixed first-order-three-halves-order treatment of the data yielded a negative  $k_I$  at 1173°K. and erratic values at higher temperatures [e.g.,  $k_I$  (1373°K.)  $\doteq$   $k_I$  (1483°K.)] without appreciably improving (*i.e.*, straightening) the Arrhenius plot for the higher order contribution.

The Arrhenius expressions for the lines (drawn by eye) in Figure 5 are  $k_I = 10^{9.15} \exp(-51.9 \text{ kcal./RT}) \text{ sec.}^{-1}$  and  $k_{II} = 10^{14.0} \exp(-40.0 \text{ kcal./RT}) \text{ cc./mole sec.}$

The slope of the line for  $k_{II}$  was not determined statistically from the data, but was chosen as a convenient value that was compatible with the lower

temperature results. Its choice was influenced by three considerations: (a) the recent shock tube work by Bauer and Aten<sup>9</sup> yields an activation energy of the order of 40 kcal.; (b) the A-factor that results is typical of four-center reactions, which is the class to which we believe reaction II belongs; (c) the straight line that is most compatible with *all* results for  $k_{II}$  has a slope corresponding to  $E \doteq 60$  kcal. and an A factor of about  $10^{17} \text{ cc./mole sec.}$  This activation energy can be rationalized, but the A factor is impossibly large for a bimolecular reaction. We have not been able to construct a second-order chain reaction that will give an unusually large A factor.

The activation energy of the first-order reaction, 52 kcal., is too low to be reconciled with simple unimolecular decomposition, or even with decomposition in which rate control rests in excitation to the triplet state at 83 kcal. The first-order reaction is almost certainly a chain. Bauer and Aten,<sup>9</sup> reporting first-order decomposition kinetics for benzene in shock waves, have postulated a chain mechanism consisting essentially of the following steps

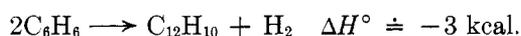


plus terminating radical recombinations. The steps involved all appear quite reasonable. However, while a steady-state treatment of this chain shows that one can obtain first-order kinetics by choosing the terminations properly, one cannot obtain a low activation energy. The main problem is that phenyl radicals are too stable in the gas phase.

The answer to this problem may be that phenyl radicals decompose on the reactor wall. This raises the immediate objection that Bauer and Aten used a shock tube in their study, and, hence, a heterogeneous step involving the wall is ruled out. However, re-examination of their data<sup>11</sup> reveals that the scatter in their rate

(11) We are indebted to Dr. Carl Aten for supplying further information on shock conditions that permitted these calculations to be performed.

constants is appreciably reduced when they are treated as second order rather than first. These second-order values are the black circles in Figure 5, normalized (they reported only *relative* rate constants, not absolute values) so as to provide values comparable to our own values for  $k_{II}$ . Their data seem to support the 40-kcal. Arrhenius slope, with perhaps some tendency to drift above it at higher temperatures. The difference in techniques (they looked at initial reaction rates) lends support to our attribution of high  $k_{II}$  values at high temperatures to sooting in the gas stream. Further support for interpreting their results as simple second order is provided by their failure to observe an induction period. We therefore suggest that  $k_{II}$  is the rate constant for



Biphenyl is, as mentioned earlier, the dominant product of low-temperature pyrolysis, which is consistent with this interpretation.

Now, in the first-order chain, modification of step c in the Bauer and Aten mechanism to provide heterogeneous decomposition of phenyl on the wall can yield an over-all activation energy of the order of 55 kcal., which is well within the uncertainty of our experimental results. The new step c might well be diffusion

controlled and exhibit an effective activation energy of only a few kcal. The products of the heterogeneous decomposition are not known; however, it is only necessary to assume that some radical is returned to the gas phase and participates in further steps of the type represented by reaction e.

There are some difficulties with this scheme: for example, heterogeneity of step c requires that there be an effect of tube diameter upon the rate. Our experimental data concerning this point (Table I) are ambiguous. A second difficulty is that the first-order rate constants do not agree with the first-order results of Murphy, *et al.*,<sup>10</sup> obtained from studies of carbon film deposition. These are included in Figure 5: The discrepancy probably means that the kinetics of carbon deposition are not related in a simple way to the rate of the first step in the pyrolysis. Further shock tube studies of benzene by Aten<sup>12</sup> may help to clear up some of these questions.

*Acknowledgments.* We are very much indebted to the J. M. Huber Corp. for its generous support of this work.

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