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Pyrolysis of Ethylbenzene

BY C. TERENCE BROOKS† AND STANLEY J. PEACOCK
British Gas Corporation, London Research Station, Michael Road,
London SW6 2AD

AND BRYAN G. REUBEN*
Department of Chemical Engineering, Polytechnic of the South Bank,
Borough Road, London SE1 0AA

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The pyrolysis of ethylbenzene has been studied using a static reactor. At low conversion hydrogen and styrene are the major products together with methane, toluene, ethylene, ethane and benzene plus traces of higher molecular-weight hydrocarbons. The pyrolysis is a chain reaction with a chain length of the order of 10 initiated by

$$PhC_2H_5 \rightarrow PhCH_2 + CH_3$$

for which $k/s^{-1} = 10^{14.4 \pm 1.1} \exp(-293 \pm 18 \text{ kJ mol}^{-1}/RT)$ based on an average of toluene and methane yields. This agrees well with previous work involving toluene and aniline carriers. The results may be explained by a complex mechanism involving free radicals, CH_3, $PhCH_2$, $PhCHCH_3$, $PhCH_2CH_2$, C_2H_5, Ph and H.

Termination appears to occur mainly by the reaction

$$2PhCHCH_3 \rightarrow PhCH{:}CH_2 + PhC_2H_5.$$

For the reaction

$$PhCHCH_3 \rightarrow PhCH{:}CH_2 + H$$

a rate constant $k/s^{-1} = 10^{15.9} \exp(-217 \text{ kJ mol}^{-1}/RT)$ was deduced.

The hydrogenation of coal and oil is a potentially important route to substitute natural gas. In these processes the cracking and subsequent hydrogenation of aromatic compounds, such as ethylbenzene, play a part. Although there have been many studies of the pyrolyses of aromatic hydrocarbons, their mechanism is still uncertain.

Studies of the pyrolysis of ethylbenzene date back to Szwarc's work[1] in 1949. Szwarc suggested that the reaction be described by a free-radical chain mechanism. Initiation occurs by fission of the aliphatic C—C bond to yield benzyl and methyl radicals.

$$PhCH_2CH_3 \rightarrow PhCH_2 + CH_3. \tag{1}$$

This was followed by the propagation reactions

$$CH_3 + PhCH_2CH_3 \rightarrow CH_4 + PhCHCH_3 \tag{2a}$$

$$CH_3 + PhCH_2CH_3 \rightarrow CH_4 + PhCH_2CH_2 \tag{2}$$

$$PhCHCH_3 \rightarrow H + PhCHCH_2 \tag{5}$$

$$H + PhCH_2CH_3 \rightarrow H_2 + PhCH_2CH_2 \tag{6}$$

$$H + PhCH_2CH_3 \rightarrow H_2 + PhCHCH_3 \tag{6a}$$

$$H + PhCH_2CH_3 \rightarrow PhH + C_2H_5 \tag{6b}$$

$$H + PhCH_2CH_3 \rightarrow CH_4 + PhCH_2 \tag{6c}$$

† Present Address: British Gas Corporation, Westfield Development Centre, Cardenden, Fife.

$$C_2H_5+PhCH_2CH_3 \rightarrow C_2H_6+PhCH_2CH_2 \qquad (8)$$

$$C_2H_5+PhCH_2CH_3 \rightarrow C_2H_6+PhCHCH_3. \qquad (8a)$$

Possible chain-termination processes were

$$H+PhCH_2 \rightarrow PhCH_3 \qquad (10e)$$

$$2C_2H_5 \rightarrow C_2H_4+C_2H_6 \qquad (10d)$$

$$H+H+M \rightarrow H_2+M. \qquad (10a)$$

Szwarc suggested that the reaction was too complicated to be suitable for a conventional study and proposed a technique employing an excess of toluene as a carrier. Thus the reaction was modified to

$$PhCH_2CH_3 \rightarrow PhCH_2+CH_3 \qquad (1)$$

$$PhCH_3+CH_3 \rightarrow PhCH_2+CH_4 \qquad (11)$$

$$2\ PhCH_2 \rightarrow (PhCH_2)_2. \qquad (12)$$

Szwarc obtained a rate constant for reaction (1)

$$k/\mathrm{s^{-1}} = 10^{13} \exp(-263.3\ \mathrm{kJ\ mol^{-1}}/\boldsymbol{R}T).$$

The carrier method has been widely used in one form or another in subsequent investigations.[2-4] Estban *et al.*[2] used aniline as a carrier in a plug flow apparatus. They obtained the rate constant for reaction (1)

$$k/\mathrm{s^{-1}} = 10^{14.6} \exp(-292.6\ \mathrm{kJ\ mol^{-1}}/\boldsymbol{R}T)$$

from the methane yield.

Crown *et al.*[3] used a stirred flow reactor to study the pyrolysis in the presence of an excess of toluene. Their findings show that the experimental first-order rate constant is dependent on the pressure of toluene and that the rate of methane production falls with a reduction in carrier pressure for a given partial pressure of reactant.

The rate constant for reaction (1) was

$$k/\mathrm{s^{-1}} = 10^{14.7} \exp(-289.2\ \mathrm{kJ\ mol^{-1}}/\boldsymbol{R}T).$$

Clarke and Price[4] have carried out a detailed investigation using a toluene carrier and have suggested that the pyrolysis occurs between 910 and 1089 K by 3 main reactions

$$PhCH_2CH_3 \rightarrow PhCH_2+CH_3 \qquad (1)$$

$$PhCH_2CH_3 \rightarrow PhH+C_2H_4 \qquad (13)$$

$$PhCH_2CH_3 \rightarrow PhC_2H_3+H_2. \qquad (14)$$

For the initiation reaction (1) a rate constant of

$$k/\mathrm{s^{-1}} = 10^{14.7} \exp(-293\ \mathrm{kJ\ mol^{-1}}/\boldsymbol{R}T)$$

was obtained.

Experiments showed ethylene yield to be surface-dependent but in a conditioned quartz vessel a rate constant of

$$k/\mathrm{s^{-1}} = 10^{9.06} \exp(-216.1\ \mathrm{kJ\ mol^{-1}}/\boldsymbol{R}T)$$

for reaction (13) was obtained.

A rate constant for reaction (14) of

$$k/\mathrm{s}^{-1} = 10^{12.7} \exp(-267.5\ \mathrm{kJ\ mol^{-1}}/\boldsymbol{R}T)$$

was obtained from styrene yield.

Experiments without a carrier gas have been performed by Lee and Oliver[5] and Hausmann and King[6] who found the order of reaction for styrene formation to be one-half. A rate expression

$$\mathrm{d[styrene]/d}t = k_{\frac{1}{2}}[\mathrm{PhCH_2CH_3}]^{\frac{1}{2}} \qquad \text{(i)}$$

where

$$k_{\frac{1}{2}}/\mathrm{mol}^{\frac{1}{2}}\ \mathrm{dm}^{-\frac{3}{2}}\ \mathrm{s}^{-1} = 10^{15} \exp(-292.6\ \mathrm{kJ\ mol^{-1}}\boldsymbol{R}T)$$

was proposed. Considerable scatter on the Arrhenius plot makes the value unreliable. The following chain mechanism was proposed

$$\mathrm{PhCH_2CH_3 \rightarrow PhCH_2 + CH_3} \qquad (1)$$

$$\mathrm{CH_3 + PhCH_2CH_3 \rightarrow PhCHCH_3 + CH_4} \qquad (2a)$$

$$\mathrm{PhCHCH_3 \rightarrow PhCHCH_2 + H} \qquad (5)$$

$$\mathrm{H + PhCH_2CH_3 \rightarrow PhCHCH_3 + H_2} \qquad (6a)$$

$$2\ \mathrm{PhCHCH_3} \rightarrow \text{various products.} \qquad (10c)$$

For long chains the expression

$$\mathrm{d[styrene]/d}t = (k_1 k_5^2/2k_{10c})^{\frac{1}{2}}[\mathrm{PhCH_2CH_3}]^{\frac{1}{2}} \qquad \text{(ii)}$$

was found to be consistent with the experimental results.

Thus the bulk of the kinetic studies have been carried out with carriers in flow systems. As better experimental techniques became available the limitations of these techniques became apparent.

For a more complete investigation from which a reaction mechanism can be proposed it is desirable that the pyrolysis be carried out in the absence of carriers.

Modern methods enable accurate results to be obtained for vapours in a static system.[7]

This paper sets out (*a*) to confirm that the rate data obtained for the initiation reaction by carrier techniques also apply to the system in the absence of a carrier and (*b*) to obtain a satisfactory reaction mechanism.

EXPERIMENTAL

A conventional static system described previously was used.[7]

RESULTS

PRELIMINARY EXPERIMENTS

The major reaction products are hydrogen and styrene. To minimise side reactions and secondary product formation, the reaction was studied at low conversions. A typical experiment at 783 K with 4 min residence time gave *ca.* 3% conversion. Thus *ca.* 0.55 Torr† of hydrogen and styrene were produced from an initial concentration of 30 Torr of ethylbenzene. The other products are methane and toluene formed in

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† 1 Torr = 101 325/760 Pa.

approximately an order of magnitude lower concentration together with ethylene, ethane and benzene.

At these low conversions no other gaseous or liquid products were seen. After evaporating a sample of the condensate only trace quantities of solid products were identified by mass spectrometry. Hence we assume that only the primary pyrolysis reactions are taking place and accordingly for most of the kinetic experiments conversions were kept at these low levels.

Reaction (12) giving bibenzyl is an attractive chain termination step but repeated attempts to detect it in the reaction products were unsuccessful. This was surprising but it is significant that the most recent study of the pyrolysis in the absence of carrier gas also failed to detect bibenzyl.[8] It is possible that it is unstable at the temperatures of these experiments.

Oxygen impurity has a profound effect on hydrocarbon pyrolysis. Rates of pyrolysis were measured from samples of ethylbenzene which had been degassed a different number of times. The rate was independent of the number of degassing cycles which suggests that the ethylbenzene is oxygen-free.

The variation of gaseous product yield with time is shown in fig. 1. For all products a linear relationship is obtained and hence initial rate was taken as the yield after 4 min divided by time.

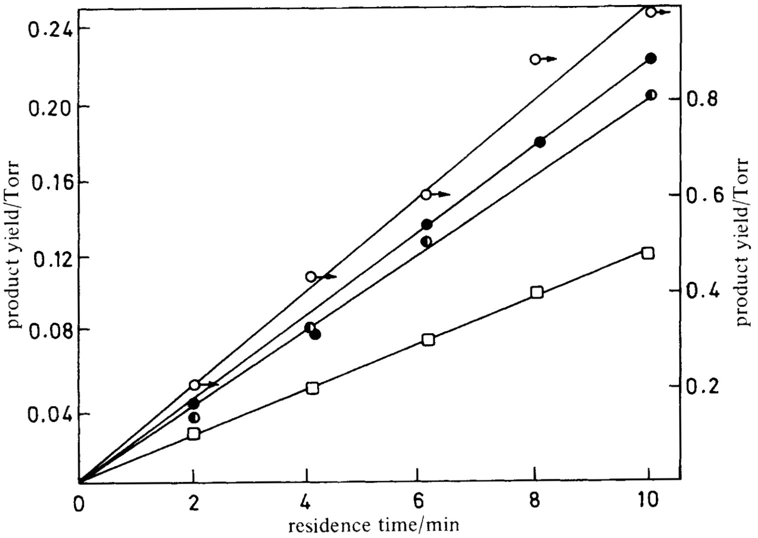

FIG. 1.—Progress of reaction with time. Hydrogen ○, methane □, ethane ● and ethylene ◐ yield at 788 K for a mixture of 30 Torr of ethylbenzene and 300 Torr of nitrogen.

Most experiments were carried out with a 6 cm diameter, 20 cm long silica reaction vessel with a surface-to-volume ratio of 0.077 mm^{-1}. Initial rates were methane 2.5×10^{-4} Torr s^{-1}, hydrogen 2.29×10^{-3} Torr s^{-1}, ethylene 3.54×10^{-4} Torr s^{-1} and ethane 3.75×10^{-4} Torr s^{-1} for a reaction temperature of 792 K and ethylbenzene concentration of 34 Torr. Under similar conditions in a reaction vessel packed with silica tubes (1.105 mm^{-1} surface-to-volume ratio) initial rates were methane 3.12×10^{-4} Torr s^{-1}, hydrogen 2.17×10^{-3} Torr s^{-1}, ethylene 3.96×10^{-4} Torr s^{-1} and ethane 3.12×10^{-4} Torr s^{-1}.

Therefore under the conditions of our experiments the effects of surface were assumed to be insignificant.

Fig. 2 shows the effect of added nitrogen on reaction rate. Varying amounts of nitrogen were added to 30 Torr of ethylbenzene with a reaction temperature of 788 K and residence time of 4 min. Nitrogen increases ethylene yield and may decrease the benzene yield slightly but the other products are apparently unaffected.

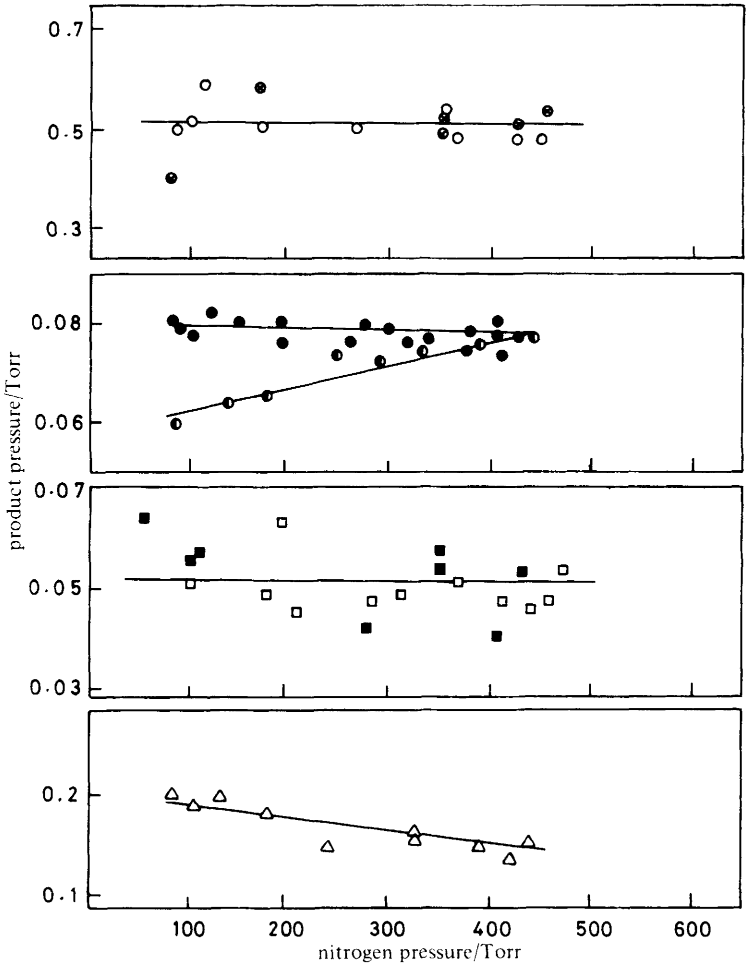

FIG. 2.—Effect of added nitrogen on rate. Hydrogen ○, methane □, ethane ●, styrene ⊗, toluene ■, ethylene ◐ and benzene △ yields after 4 min.

FORMATION OF METHANE AND TOLUENE

If methane and toluene are formed only in an initiation reaction then their yields should be equal and the rate constant derived from both products should be the same. The rates of formation of these products showed a first-order dependence on ethylbenzene concentration (fig. 3). The temperature dependences for methane and toluene formation are shown in fig. 4. The slopes of the lines yield values of

$$k/\mathrm{s}^{-1} = 10^{14.48\pm1.1} \exp(-293.8\pm18\ \mathrm{kJ\ mol^{-1}}/\boldsymbol{R}T)$$

and

$$k/\mathrm{s}^{-1} = 10^{14.35\pm1.2} \exp(-291.8\pm19\ \mathrm{kJ\ mol^{-1}}/\boldsymbol{R}T)$$

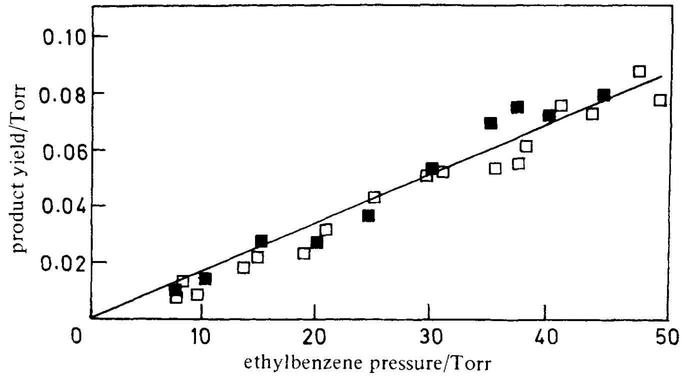

FIG. 3.—Dependence of methane □ and toluene ■ yield on ethylbenzene pressure. Reaction temperature = 719 K, residence time = 4 min.

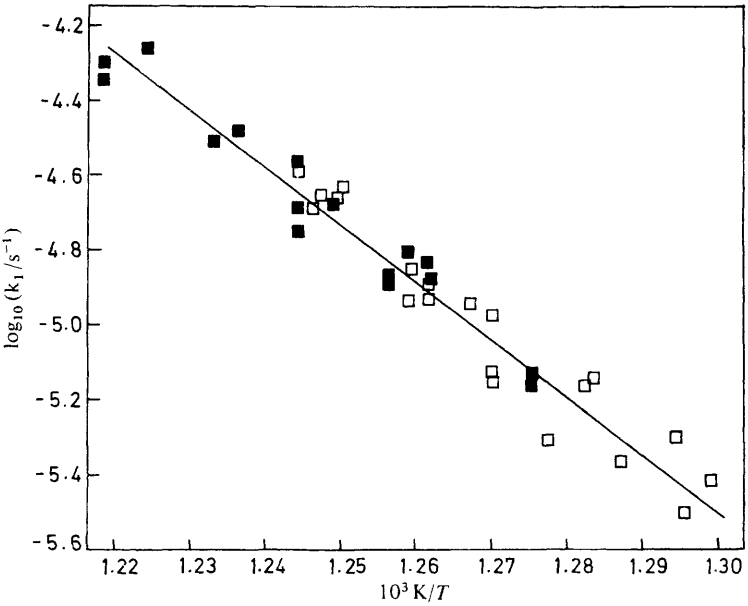

FIG. 4.—Temperature dependence of methane □ and toluene ■ yield.

respectively, which are identical within experimental error. These rate data agree well with those obtained by carrier techniques and we conclude that methane and toluene are indeed produced only in an initiation stage.

FORMATION OF HYDROGEN AND STYRENE

Hydrogen and styrene account for 90% of the total reaction products. Fig. 5 shows the dependence of these products on ethylbenzene pressure and a least-squares analysis of a log–log line yields 0.6 reaction order for both products. The temperature dependence plot (fig. 6) yields a rate expression (in mol dm^{-3} s^{-1}) of

$$d[H_2]/dt = 10^{19.8\pm0.5} \exp(-377.4\pm16.8 \text{ kJ mol}^{-1}/RT)[PhC_2H_5]^{0.6}$$

$$d[\text{styrene}]/dt = 10^{18.2\pm0.3} \exp(-359.5\pm16.0 \text{ kJ mol}^{-1}/RT)[PhC_2H_5]^{0.6}.$$

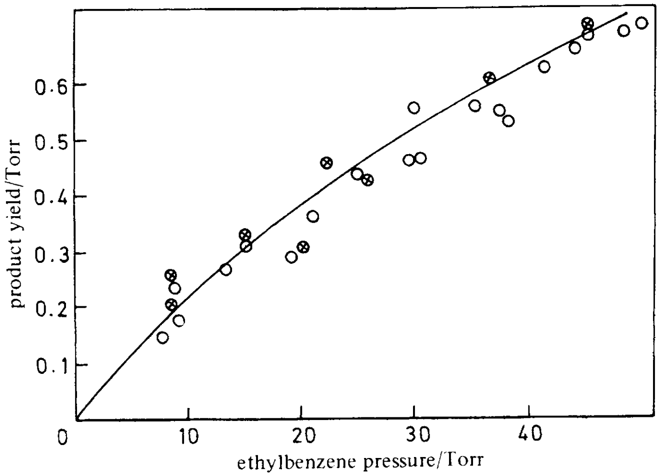

FIG. 5.—Dependence of hydrogen ○ and styrene ⊗ yield on ethylbenzene pressure. Reaction temperature = 719 K, residence time = 4 min.

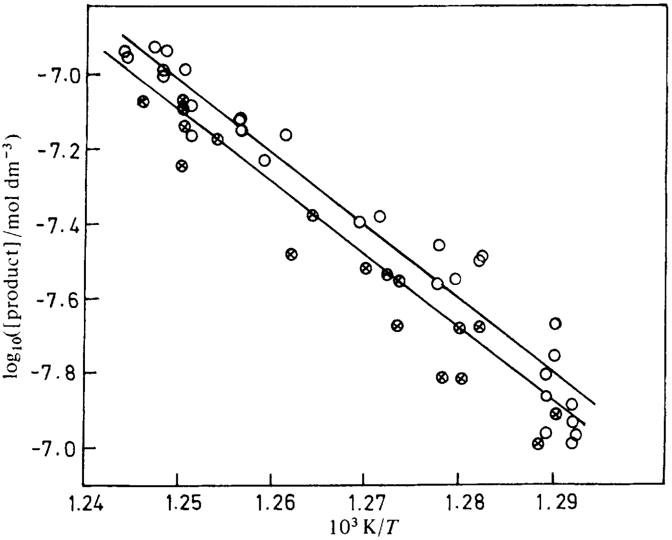

FIG. 6.—Temperature dependence of hydrogen ○ and styrene ⊗ yield. Ethylbenzene concentration = 6.05 × 10^{-4} mol dm^{-3}, residence time = 4 min.

FORMATION OF ETHANE, ETHYLENE AND BENZENE

Fig. 7 shows the effect of ethylbenzene pressure on the yields of ethane, ethylene and benzene and reaction orders of 1.1, 0.9 and 1.0, respectively, are obtained. The temperature dependences (fig. 8) give rise to the rate expressions (all in mol dm^{-3} s^{-1})

$$d[C_2H_6]/dt = 10^{21.08\pm0.4} \exp(-389.9\pm16.4 \text{ kJ mol}^{-1})/\boldsymbol{R}T[PhC_2H_5]^{1.1}$$

$$d[C_2H_4]/dt = 10^{21.48\pm0.2} \exp(-405.5\pm6.0 \text{ kJ mol}^{-1})/\boldsymbol{R}T[PhC_2H_5]^{0.9}$$

$$d[PhH]/dt = 10^{16.59\pm0.2} \exp(-321.4\pm18.0 \text{ kJ mol}^{-1})/\boldsymbol{R}T[PhC_2H_5].$$

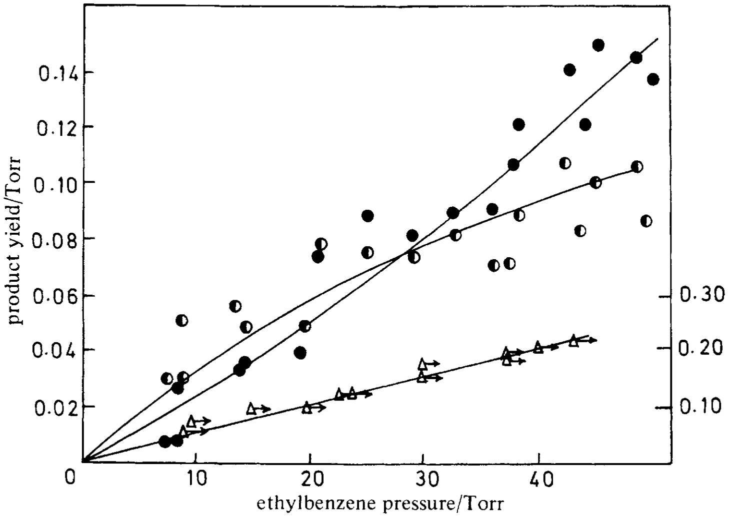

FIG. 7.—Dependence of ethane ●, ethylene ◐ and benzene △ yield on ethylbenzene pressure. Reaction temperature = 719 K, residence time = 4 min.

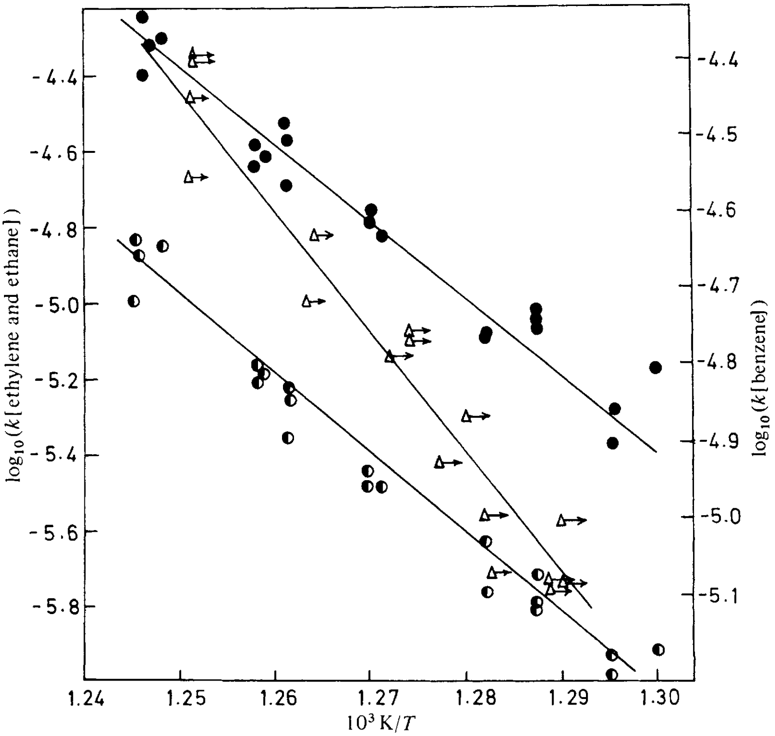

FIG. 8.—Temperature dependence of ethane ● ethylene ◐ and benzene △ yield. Ethylbenzene concentration = 6.05×10^{-4} mol dm^{-3}, residence time = 4 min.

TABLE 1.—SOLID COMPOUNDS FOUND BY MASS SPECTROMETRIC ANALYSIS OF THE RESIDUE FROM THE PYROLYSIS OF ETHYLBENZENE AT HIGH CONVERSIONS

molecular weight	accurate mass (measured) molecular formula	relative intensity (%)	compound[a]
128	—	5	naphthalene
142	142.0770 ($C_{11}H_{10}$)	trace	methylnaphthalene
152	—	11	biphenylene
154	154.0793 ($C_{12}H_{10}$)	4	biphenyl
166	166.0782 ($C_{13}H_{10}$)	5	fluorene
168	168.0939 ($C_{13}H_{12}$)	2	biphenylmethane
178	178.0782 ($C_{14}H_{10}$)	100	anthracene
180	180.0939 ($C_{14}H_{12}$)	20	stilbene
192	192.0939 ($C_{15}H_{12}$)	14	methylanthracene
194	194.1095 ($C_{15}H_{14}$)	2	ethylfluorene
202	202.0783 ($C_{16}H_{10}$)	26	pyrene
204	204.0939 ($C_{16}H_{12}$)	29	dihydropyrene
206	206.1096 ($C_{16}H_{14}$)	5	ethylanthracene
216	216.0938 ($C_{17}H_{12}$)	4	methylpyrene
228	—	4	chrysene
230	—	5	*p*-terphenyl
252	—	10	benzopyrene
254	—	17	dihydrobenzopyrene
278	—	9	benzochrysenes
280	—	6	dihydrobenzochrysenes
300	—	trace	coronene
302	—	2	benzoperylenes
304	—	2	dihydrobenzoperylenes
330	—	3	methylbenzonaphthoperinaphthenes
342	—	trace	methyldibenzochrysene
350	—	trace	pyrenopyrene
378	—	trace	dibenzopicenes
380	—	trace	dihydrobenzopicenes
402	—	trace	tetrabenzopyrene
502	—	trace	benzanthracenopyrene

[a] Other isomeric forms are possible.

FORMATION OF HIGHER MOLECULAR WEIGHT PRODUCTS

Samples of the solid products of reaction in the condensate were prepared in a simple flow apparatus operating at 778 K and 833 K with 2 min residence time. The electron impact mass spectrum of the volatile matter in the sample was obtained using a Varian MAT 311 A mass spectrometer linked to an on-line data system.

At low conversions obtained from the experiment carried out at 778 K, very few products other than styrene, toluene and benzene are observed. However, at higher conversions a range of polynuclear aromatic hydrocarbons was found. The m/z values for the parent peaks together with relative abundance and possible structures are shown in table 1. It also shows examples of some of the components of the solid products identified by accurate mass measurements.

DISCUSSION

STOICHIOMETRY AND ANALYTICAL ERROR

The reaction products obtained by all workers suggest that the integrity of the benzene ring is retained in all reactions in this system at temperatures up to *ca.* 800 K. If multi-ring products are discounted, then stoichiometry demands that styrene yield must equal hydrogen + methane + ethane yields, methane yield must equal toluene yield and benzene yield must equal ethane + ethylene yields. Previous workers, for example Shirazi,[8] have not concentrated on this point, presumably because of analytical difficulties that were also observed in this work.

Toluene and methane yields were found to be identical within experimental error, as mentioned earlier and shown in fig. 4.

Hydrogen yields typically appeared 15% higher than styrene yields as illustrated in fig. 6, though at the low temperature used for the run shown in fig. 5 they appear equal as would be expected in view of the methane and ethane yields being small compared with the styrene yield. The styrene peak on the gas chromatograph trace occurred on the side of a very large ethylbenzene peak and though its size was estimated by a consistent technique, we are inclined to attribute the discrepancy largely to a systematic error in this measurement. Nonetheless, note that formation of coking precursors such as polynuclear aromatic hydrocarbons would lead to an excess of hydrogen over styrene and that this would increase with temperature.

Yields of benzene were approximately in balance with ethane + ethylene (fig. 7) considering the errors involved in measurement of such small concentrations. The activation energy for benzene production (fig. 8) is slightly less than for ethane and ethylene which would be consistent with a loss of benzene at higher temperatures to give polynuclear aromatic hydrocarbons. The effect of added nitrogen is most difficult to explain (fig. 2) in that benzene yields drop while ethane remains constant and ethylene increases. This would also be consistent with the formation of polynuclear aromatic hydrocarbons and the amounts that would need to be formed are very small. There is no obvious reason, however, why added nitrogen should have this effect.

POSSIBLE REACTION MECHANISMS

To account for all the products, any reaction mechanism is necessarily complicated. Initiation is *via* reaction (1) followed in Szwarc's scheme by reactions (2) and (2*a*) which give rise to $PhCH_2CH_2$ and $PhCHCH_3$. Whether both these radicals are involved in the mechanism is open to discussion. On the one hand, abstraction reactions between free radicals and olefins containing allylic hydrogen atoms are generally accepted to involve only the latter. Reaction (2*a*) might thus be expected to be at least an order of magnitude faster than reaction (2) and subsequent reactions of $PhCH_2CH_2$ might reasonably be ignored. On the other hand, the added stability of the $PhCHCH_3$ radical which makes it the preferred product also leads to its being less reactive. Shirazi[8] has calculated that in certain cases $PhCH_2CH_2$ reacts 10^7 times as fast as $PhCHCH_3$ and we have consequently felt it justifiable to retain both species in our mechanism.

Formation of toluene and methane in equal amounts suggests that the benzyl radical is more reactive than originally proposed by Szwarc and suggests the need for reactions (3) and (3*a*):

$$PhCH_2 + PhCH_2CH_3 \rightarrow PhCH_2CH_2 + PhCH_3 \qquad (3)$$

$$PhCH_2 + PhCH_2CH_3 \rightarrow PhCHCH_3 + PhCH_3. \qquad (3a)$$

Szwarc suggested that toluene might also be formed by the reaction

$$CH_3 + PhC_2H_5 \rightarrow C_2H_5 + PhCH_3. \qquad (15)$$

We have not felt it necessary to include it because our rate constants for toluene formation agree with those involving carriers where reaction (15) is not thought to take place.

Decomposition of $PhCHCH_3$ was proposed to account for styrene formation in reaction (5). The radical $PhCH_2CH_2$ might similarly react as in reaction (4) to give ethylene

$$PhCH_2CH_2 \rightarrow Ph + C_2H_4. \qquad (4)$$

The phenyl radical can then react as in reactions (7) and (7*a*) to yield benzene

$$Ph + PhC_2H_5 \rightarrow PhH + PhCH_2CH_2 \qquad (7)$$

$$Ph + PhC_2H_5 \rightarrow PhH + PhCHCH_3. \qquad (7a)$$

Ethane, the remaining product, can be formed by attack of an ethyl radical on ethylbenzene

$$C_2H_5 + PhC_2H_5 \rightarrow PhCH_2CH_2 + C_2H_6 \qquad (8)$$

$$C_2H_5 + PhC_2H_5 \rightarrow PhCHCH_3 + C_2H_6. \qquad (8a)$$

Ethylene formation is dependent on nitrogen concentration and under the conditions of this work the reaction

$$C_2H_5 + M \rightarrow C_2H_4 + H + M \qquad (9)$$

is in its pressure-dependent region and hence it probably also occurs. The mechanism is therefore made up of a number of cycles. The major cycle yields hydrogen and styrene and this accounts for 90% of the reaction product.

Benzene and ethylene are formed in another cycle whilst ethane is formed in the third cycle. In addition some ethylene is formed separately by the decomposition of ethyl radicals. Fig. 9 represents the scheme diagrammatically. It illustrates the interlocking cyclic nature of the reactions. The solid circles represent reactions and reactants are shown as entering and products as emerging from them. Free radicals are shown as molecular formulae and neutral molecules as names. The 'crossroads' at the open circle reflect the fact that reactions generating $PhCH_2CH_2$ might also generate $PhCHCH_3$.

To summarise, the propagation reactions considered are reactions (2)-(9) below:

$$PhCH_2CH_3 \rightarrow PhCH_2 + CH_3 \qquad (1)$$

$$CH_3 + PhCH_2CH_3 \rightarrow PhCH_2CH_2 + CH_4 \qquad (2)$$

$$CH_3 + PhCH_2CH_3 \rightarrow PhCHCH_3 + CH_4 \qquad (2a)$$

$$PhCH_2 + PhCH_2CH_3 \rightarrow PhCH_2CH_2 + PhCH_3 \qquad (3)$$

$$PhCH_2 + PhCH_2CH_3 \rightarrow PhCHCH_3 + PhCH_3 \qquad (3a)$$

$$PhCH_2CH_2 \rightarrow Ph + C_2H_4 \qquad (4)$$

$$PhCHCH_3 \rightarrow H + PhCH{:}CH_2 \qquad (5)$$

$$H + PhCH_2CH_3 \rightarrow PhCH_2CH_2 + H_2 \qquad (6)$$

$$H + PhCH_2CH_3 \rightarrow PhCHCH_3 + H_2 \qquad (6a)$$

$$H + PhCH_2CH_3 \rightarrow C_2H_5 + PhH \qquad (6b)$$

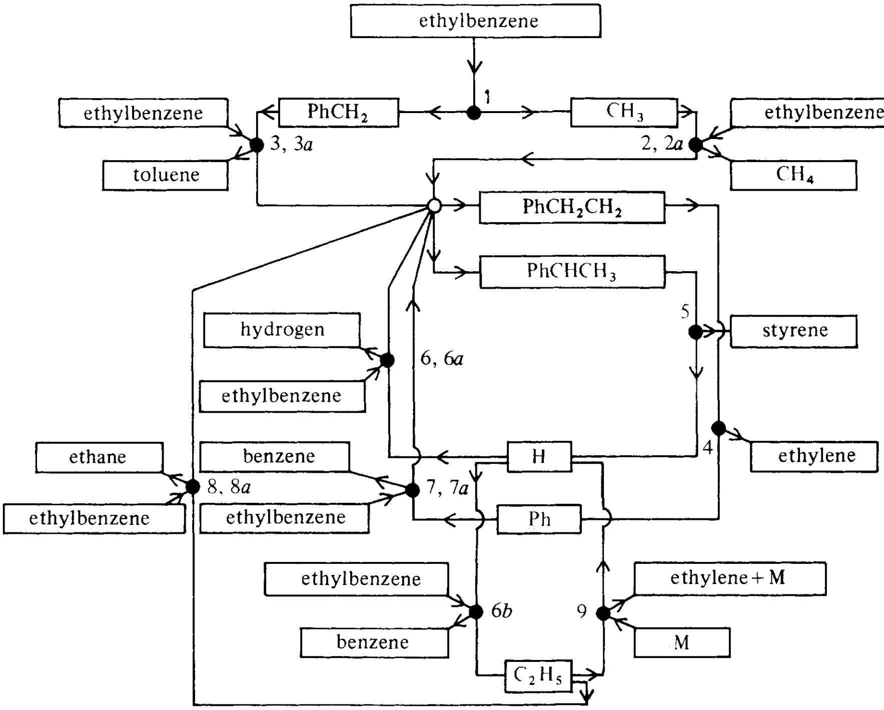

FIG. 9.—Diagrammatic representation of the proposed ethylbenzene pyrolysis mechanism.

$$\mathrm{Ph + PhCH_2CH_3 \rightarrow PhCH_2CH_2 + PhH} \qquad (7)$$

$$\mathrm{Ph + PhCH_2CH_3 \rightarrow PhCHCH_3 + PhH} \qquad (7a)$$

$$\mathrm{C_2H_5 + PhCH_2CH_3 \rightarrow PhCH_2CH_2 + C_2H_6} \qquad (8)$$

$$\mathrm{C_2H_5 + PhC_2H_3 \rightarrow PhCHCH_3 + C_2H_6} \qquad (8a)$$

$$\mathrm{C_2H_5 + (M) \rightarrow H + C_2H_4 + (M)} \qquad (9)$$

$$\mathrm{2\ PhC_2H_4 \rightarrow PhCH_2CH_3 + PhCH{:}CH_2.} \qquad (10)$$

Szwarc reported a chain length of *ca.* 15. The ratio initiation/overall rate in this work suggests a chain length of just over 10.

No single high-molecular-weight product predominates in the mass spectrometric analysis of the solid products and hence we assume that the major termination reaction is *via* disproportionation

$$\mathrm{2\ PhCHCH_3 \rightarrow PhCH_2CH_3 + PhCHCH_2.} \qquad (10)$$

The rate expression for styrene is

$$\mathrm{d[PhCH{:}CH_2]}/\mathrm{d}t = 2k_1[\mathrm{PhC_2H_5}] + k_5(k_1/k_{10})^{\frac{1}{2}}[\mathrm{PhC_2H_5}]^{\frac{1}{2}}. \qquad \text{(iii)}$$

Hence a plot of rate of styrene formation/[ethylbenzene] against [ethylbenzene]$^{\frac{1}{2}}$ should be a straight line with the intercept equal to k_1. Fig. 10 shows that this is approximately true. From the methane and toluene yield $2k_1 = 19.42 \times 10^{-8}\ \mathrm{s^{-1}}$. The least-squares intercept is $2.5 \times 10^{-5}\ \mathrm{s^{-1}}$ but there is considerable scatter and the line in effect goes through the origin. If $2k_1$ $[PhC_2H_5]$ is assumed to be small compared with $k_5(k_1/k_{10})^{\frac{1}{2}}[PhC_2H_5]^{\frac{1}{2}}$ then

$$d[PhCH\!:\!CH_2]/dt = k_5(k_1/k_{10})^{\frac{1}{2}}[PhC_2H_5]^{\frac{1}{2}} \qquad \text{(iv)}$$

and half-order kinetics are predicted. In fact the chain length is *ca.* 10; so the first term cannot be neglected and hence an order slightly greater than 0.5 is predicted by the mechanism. Experiment gives a value of *ca.* 0.6.

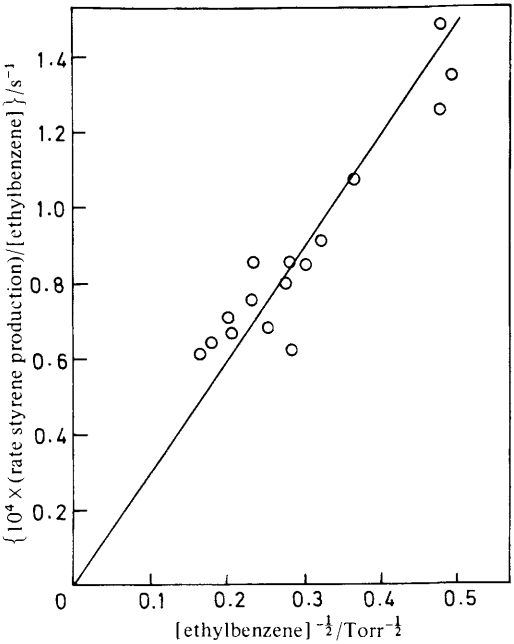

FIG. 10.—Function plot to test the proposed mechanism.

If a value for the rate constant of the termination reaction (10) is assumed, then it is possible to estimate a value for the rate constant for reaction (5)

$$PhCHCH_3 \rightarrow H + PhCH\!:\!CH_2. \qquad (5)$$

$$\text{Now } k_{\text{styrene}} = k_5(k_1/k_{10})^{\frac{1}{2}} \qquad \text{(v)}$$

$$k_5/s^{-1} = (A_{\text{styrene}})\,(A_{10}/A_1)^{\frac{1}{2}}\exp[(-E_{\text{styrene}}+\tfrac{1}{2}E_1)/\boldsymbol{R}T] \qquad \text{(vi)}$$

where k_{styrene} and A_{styrene} are the experimentally measured rate constants and Arrhenius parameters.

Substituting for k_1 and k_{styrene} and assuming a value for k_{10} allows k_5 to be estimated. Benson[9] suggests that termination reactions involving large radicals have a rate constant of *ca.* $10^{9.8}$ dm^3 mol^{-1} s^{-1}. Hence using this figure

$$k_5/s^{-1} \simeq 10^{15.9}\exp(-217\text{ kJ mol}^{-1}/\boldsymbol{R}T).$$

The high value for the activation energy is a result of the resonance stabilisation of the radical $PhCHCH_3$. Thermochemical calculation suggests a value of *ca.* 205 kJ mol^{-1} for the activation energy.

The rate expression for hydrogen yield is more complicated as hydrogen is produced in reactions (6) and (6*a*) and hydrogen atoms are consumed in reactions (6), (6*a*) and (6*b*).

Eqn (vii) describes hydrogen yield

$$d[H_2]/dt = \frac{k_5(k_6+k_{6a})[PhC_2H_5]^{\frac{1}{2}}(k_1/k_{10})^{\frac{1}{2}}\theta}{(k_6+k_{6a}+k_{6b})\theta+k_9k_{6b}} \tag{vii}$$

where $\theta = (k_8+k_{8a})[PhC_2H_5]+k_9$.

If $k_{6b} \ll (k_6+k_{6a})$ then an expression identical to that for styrene yield is obtained.

$$d[H_2]/dt = k_5(k_1/k_{10})^{\frac{1}{2}}[PhC_2H_5]^{\frac{1}{2}}. \tag{viii}$$

By carrying out an analysis as described earlier a further check of the rate constant for reaction (5) can be obtained. This yields

$$k_5/s^{-1} = 10^{16.5} \exp(-229.9 \text{ kJ mol}^{-1}/\boldsymbol{RT}).$$

This value is less accurate than that obtained from styrene yield because in addition to the assumptions made there it also assumes that k_{6b} is very small compared with (k_6+k_{6a}).

A comparison of hydrogen yield with ethane yield gives the rate expression

$$\frac{d[H_2]/dt}{d[C_2H_6]/dt} = \frac{(k_6+k_{6a})}{k_{6b}} + \frac{(k_6+k_{6a})k_9}{(k_8+k_{8a})k_{6b}}[PhC_2H_5]^{-1}. \tag{ix}$$

A plot of $(d[H_2]/dt)/(d[C_2H_6]/dt)$ against $[PhC_2H_5]^{-1}$ should yield a straight line with an intercept of $(k_6+k_{6a})/k_{6b}$ and a gradient of $(k_6+k_{6a})\,k_9/(k_8+k_{8a})\,k_{8b}$. Fig. 11 shows that this holds true for a number of temperatures between 758 and 945 K.

The ratio of gradient to intercept gives a value of $k_9/(k_8+k_{8a})$. Thus an Arrhenius plot of log(gradient/intercept) against inverse temperature will yield an activation energy and pre-exponential factor for this ratio of rate constants. However a small

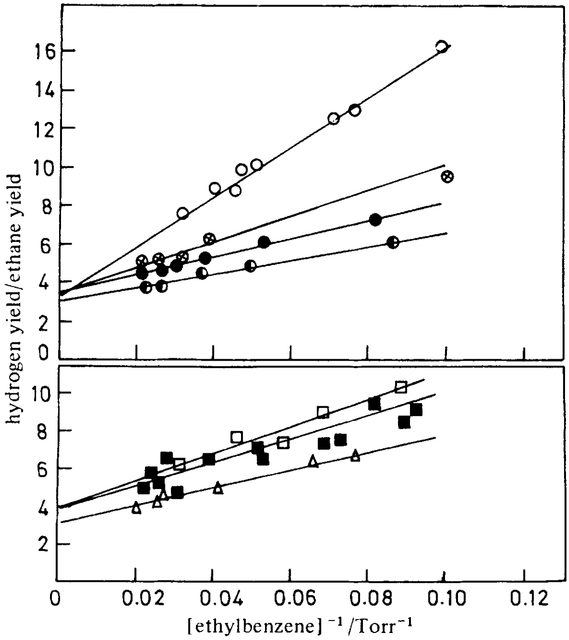

FIG. 11.—Comparison of hydrogen and ethane yields with [ethylbenzene]$^{-1}$ at 845 K ○, 815 K ⊗, 791 K ●, 764 K ◐, 825 K □, 798.5 K ■ and 758 K △.

error in the value of the intercept has a large effect on the function (gradient/intercept) and leads to a meaningless plot. A more productive approach is to plot log(gradient) against inverse temperature to yield Arrhenius parameters for the function $(k_6+k_{6a})k_9/(k_8+k_{8a})k_{6b}$. The plot is shown in fig. 12. It yields a value of 47.2 ± 11.7 kJ mol^{-1} for the activation energy. This is equal to $E_{6,6a}+E_9-E_{8,8a}-E_{6b}$ where $E_{6,6a}$ and $E_{8,8a}$ are approximate activation energies applicable to reactions (6) and (6*a*) and (8) and (8*a*), respectively. The scattered intercepts in fig. 11 suggest that $E_{6,6a}-E_{6b}$ is *ca.* 0. If so $E_9-E_{8,8a} = 47.2$ kJ mol^{-1}.

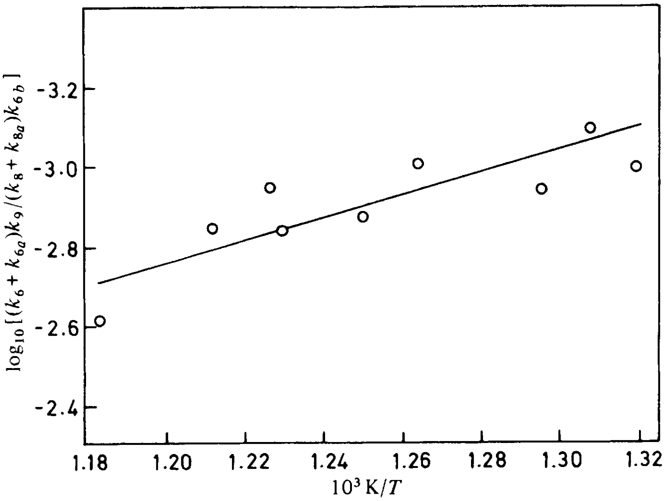

FIG. 12.—Arrhenius plot for the function (k_6+k_{6a}) $k_9/(k_8+k_{8a})$ k_{6b} derived from the pyrolysis reaction scheme.

Arrhenius parameters for reaction (9) are well documented. Lin and Back[10] suggest

$$k_\infty/\text{s}^{-1} = 10^{13.6} \exp(-158.8 \text{ kJ mol}^{-1}/\boldsymbol{R}T).$$

Arrhenius parameters for the ethane-forming reactions (8) and (8*a*) are more difficult to obtain. However, by analogy with ethyl radical reactions an activation energy of 58.5 kJ mol^{-1} seems reasonable. This means that $E_9-E_{8,8a}$ is *ca.* 100 kJ mol^{-1} compared with the experimental value of 47 ± 11 kJ mol^{-1}.

Reaction (9) is, however, in its pressure-dependent region and Lin and Back report the activation energy for the bimolecular limit to be 135.4 kJ mol^{-1}. Using this value $E_9-E_{8,8a}$ becomes 76.1 kJ mol^{-1} giving better but still only moderate agreement with experiment

$$\frac{d[C_2H_6]}{dt} = \frac{(k_8+k_{8a})[PhC_2H_5]^{\frac{3}{2}}k_{6b}k_5(k_1/k_{10})^{\frac{1}{2}}}{(k_6+k_{6a}+k_{6b})\theta+k_9k_{6b}} \qquad \text{(x)}$$

where $\theta = (k_8+k_{8a})[PhC_2H_5]+k_9$.

If $k_9 \gg (k_8+k_{8a})[PhC_2H_5]$ then an order of $\frac{3}{2}$ is predicted if reaction (9) is taken as second order. In this pressure region its order will be 2 so an order of $\frac{3}{2}$ is predicted. If the reverse is true and k_9 is small then

$$\frac{d[C_2H_6]}{dt} = \frac{k_{6b}k_5(k_1/k_{10})^{\frac{1}{2}}[PhC_2H_5]^{\frac{1}{2}}}{(k_6+k_{6a}+k_{6b})} \qquad \text{(xi)}$$

and an order of ½ is predicted. This does not agree with the experimental value of 1.1 and suggests that the two terms are of similar value, and if anything reaction (9) is the more important. If so, a considerable quantity of ethylene is produced *via* reaction (9) and its inclusion in the mechanism is justified.

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