

719. Pyrolysis of Ethyl-, n-Propyl-, and n-Butyl-benzene and the Heats of Formation of the Benzyl and n-Propyl Radicals.

By G. L. ESTEBAN, J. A. KERR, and A. F. TROTMAN-DICKENSON.

Pyrolyses of ethyl-, n-propyl-, and n-butyl-benzene, studied by an aniline-carrier technique, have been shown to be unimolecular, homogeneous decompositions into alkyl and benzyl radicals and to have the following rate constants: ethylbenzene (603—727°), $\log k$ (sec.⁻¹) = 14.6 - (70,100/2.3RT); n-propylbenzene (587—735°), $\log k$ (sec.⁻¹) = 14.9 - (68,600/2.3RT); and n-butylbenzene (590—735°) $\log k$ (sec.⁻¹) = 14.5 - (67,200/2.3RT). From the first two results, $D(\text{C}_6\text{H}_5\text{CH}_2\text{-H}) = 84.6$; and from the third, $D(\text{n-C}_3\text{H}_7\text{-H}) = 96.2$ kcal. mole⁻¹.

MANY workers have attempted to determine the heat of formation of the benzyl radical. It is important because the weakening of the C-H bond in toluene is a classic example of the effect of resonance, for, as a result of following Szwarc's work,¹ toluene has been widely used as a carrier gas in pyrolytic studies, and because benzyl derivatives are frequently pyrolysed in order to determine heats of formation of radicals. Most determinations have been based on the assumption that, when a small radical is eliminated in a unimolecular reaction, the activation energy is equal to the thermochemical strength of the bond broken. Szwarc's determination² was the first to be widely accepted. He found that the rate of the unimolecular reaction $\text{C}_6\text{H}_5\cdot\text{CH}_3 = \text{C}_6\text{H}_5\cdot\text{CH}_2\cdot + \text{H}\cdot$, was given by

$$\log k \text{ (sec.}^{-1}\text{)} = 13.3 - (77,500/2.3RT).$$

Blades, Blades, and Steacie³ showed that this value could not be relied upon without further evidence. Under some conditions, the mechanism was complex and rate constants were dependent on contact time, pressure, and surface : volume ratio. Takahasi⁴ found similar variations. Price⁵ recently selected the optimum conditions and found that

$$\log k \text{ (sec.}^{-1}\text{)} = 14.8 - (85,000/2.3RT)$$

between 640° and 870°. The heat of formation of benzyl can be readily derived from this work since the heats of formation of toluene and the hydrogen atom are well known. Unfortunately the reaction mechanism is so complex that the value cannot be unreservedly accepted.

The interpretation of electron-impact studies on benzyl derivatives is uncertain because the benzyl positive ion isomerises. The spread of reported values is sufficient to cover all determinations by other methods.

Studies of photobromination have yielded some of the best values for bond-dissociation

¹ Szwarc, *J. Chem. Phys.*, 1949, **17**, 431.

² Szwarc, *J. Chem. Phys.*, 1948, **16**, 128.

³ Blades, Blades, and Steacie, *Canad. J. Chem.*, 1954, **32**, 298.

⁴ Takahasi, *Bull. Chem. Soc. Japan*, 1960, **33**, 801.

⁵ Price, *Canad. J. Chem.*, 1962, **40**, 1310.

energies. The study of toluene by Anderson, Scheraga, and Van Artsdalen⁶ was careful and the value of 7.2 kcal. mole⁻¹ for the activation energy of the reaction $\text{Br}\cdot + \text{C}_6\text{H}_5\cdot\text{CH}_3 = \text{C}_6\text{H}_5\cdot\text{CH}_2\cdot + \text{HBr}$ can be accepted. The activation energy for the reverse reaction must also be known. The value reported⁷ of 5.0 kcal. mole⁻¹ is based on the assumption that reaction of the benzyl radical with bromine molecules has no activation energy. In fact, the activation energy for the reaction of benzyl with bromine is likely to be similar to that of trichloromethyl with bromine (say 5 kcal. mole⁻¹).⁷ If this amendment is accepted, $D(\text{C}_6\text{H}_5\cdot\text{CH}_2\text{-H}) = 85$ kcal. mole⁻¹.

The pyrolysis of benzyl bromide has several times been studied by the toluene-carrier technique, and the following values for the rate constant have been obtained:

$$\begin{aligned}\log k \text{ (sec.}^{-1}\text{)} &= 13.0 - (50,500/2.3RT)^8 \\ &= 13.3 - (50,500/2.3RT)^9 \\ &= 13.6 - (51,000/2.3RT)^{10}\end{aligned}$$

No reliable value for the heat of formation of benzyl bromide has been obtained from combustion studies. The best value of 20 kcal. mole⁻¹ for the vapour was obtained by Benson and Buss¹¹ from a consideration of the equilibrium between bromine, toluene, benzyl bromide, and hydrogen bromide. The entropy change for this system could be accurately calculated. The value of $D(\text{C}_6\text{H}_5\cdot\text{CH}_2\text{-H})$ is found to be 83 kcal. mole⁻¹.

A value can also be deduced from the activation energies for the decomposition of dimethyl (60.6) and benzyl methyl sulphone (51.3 kcal. mole⁻¹) found by toluene-carrier pyrolyses.¹² If the heat of formation of the methyl radical¹³ is 33.9 kcal. mole⁻¹ and the radicals are assumed to combine with zero energy of activation, then, from the known heats of formation of the sulphones,¹⁴ $D(\text{C}_6\text{H}_5\cdot\text{CH}_2\text{-H})$ is 86.5 kcal. mole⁻¹. The probable error is large because the result is obtained from a series of determinations each of which may be in error by about 1 kcal. mole⁻¹.

Potentially, the best determinations are those based on the pyrolyses of ethyl- and n-propyl-benzene. The heats of formation of these compounds are very accurately known and the errors in the heats of formation of methyl and ethyl radicals are small. Szwarc¹ found

$$\log k \text{ (sec.}^{-1}\text{)} = 13 - 63,200/2.3RT$$

for ethylbenzene, and Leigh and Szwarc¹⁵ found

$$\log k \text{ (sec.}^{-1}\text{)} = 12.5 - 57,500/2.3RT$$

for n-propylbenzene. The best heats of formation of methyl and ethyl¹³ yield a difference between the C-C bonds in ethyl- and n-propyl-benzene of 2.65 kcal. mole⁻¹. The difference of 5.7 kcal. mole⁻¹ found from the pyrolyses indicates that there is an error in one or both of the activation energies. Errors may have arisen because of the difficulty of estimating the amounts of products that came from ethyl- and n-propyl-benzene directly. The formation of methyl radicals by reaction of hydrogen atoms with toluene probably caused most trouble.

In the present work aniline was the carrier gas because it was unlikely to yield hydrocarbon side-products. Aniline is stable at the temperature of the pyrolyses and there is

⁶ Anderson, Scheraga, and Van Artsdalen, *J. Chem. Phys.*, 1953, **21**, 1258.

⁷ Sullivan and Davidson, *J. Chem. Phys.*, 1951, **19**, 143.

⁸ Szwarc, Ghosh, and Sehon, *J. Chem. Phys.*, 1950, **18**, 1142.

⁹ Leigh, Sehon, and Szwarc, *Proc. Roy. Soc.*, 1951, *A*, **209**, 97.

¹⁰ Levy, Szwarc, and Throssell, *J. Chem. Phys.*, 1954, **22**, 1904.

¹¹ Benson and Buss, *J. Phys. Chem.*, 1957, **61**, 104.

¹² Busfield and Ivin, *Trans. Faraday Soc.*, 1961, **57**, 1044.

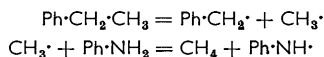
¹³ Fettes and Trotman-Dickenson, *J.*, 1961, 3037.

¹⁴ Busfield, Ivin, Mackle, and O'Hare, *Trans. Faraday Soc.*, 1961, **57**, 1064.

¹⁵ Leigh and Szwarc, *J. Chem. Phys.*, 1952, **20**, 403.

no sign of an induced decomposition. Its principle disadvantages as a carrier gas are its high boiling point and the related difficulty of freeing it from dissolved gases.

The results obtained with ethyl-, n-propyl-, and n-butyl-benzene are summarised in Tables 1—3. The first-order rate constants for ethylbenzene were calculated from the methane formed, which was assumed to come from the following sequence of reactions:



It is supposed that the anilino-radical dimerises or polymerises. The amounts of ethane in the condensable fraction were so small that combination of methyl radicals can be disregarded. Rough calculations of the concentration of methyl radicals indicate that

TABLE 1.
Pyrolysis of ethylbenzene.

| Temp. (°K) | Contact time (sec.) | PhEt (10 ⁻⁵ mole) | CH ₄ (10 ⁻⁵ mole) | H ₂ (10 ⁻⁵ mole) | Condensables (10 ⁻⁵ mole) | 10 ² k (sec. ⁻¹) |
|---------------|---------------------------|---------------------------------|--|---|---|--|
| 876.2 | 3.32 | 55.2 | 0.253 | 0.224 | 0.126 | 0.138 |
| 900.7 T | 1.26 | 150.0 | 0.797 | 0.016 | 0.017 | 0.430 |
| 908.7 | 2.95 | 39.0 | 0.677 | 0.477 | 0.152 | 0.592 |
| 921.3 | 1.23 | 46.0 | 0.612 | 0.487 | lost | 1.076 |
| 921.7 | 1.25 | 118.8 | 1.480 | 1.110 | 0.100 | 0.988 |
| 925.3 | 1.21 | 35.47 | 0.423 | 0.404 | — | 0.990 |
| 931.8 | 0.97 | 47.6 | 0.715 | 0.445 | 0.090 | 1.56 |
| 932.7 | 2.74 | 39.2 | 1.511 | 1.500 | 0.300 | 1.37 |
| 933.2 | 0.58 | 59.4 | 0.543 | 0.447 | 0.047 | 1.59 |
| 938.9 T | 1.08 | 27.2 | 0.633 | 0.102 | 0.078 | 2.19 |
| 941.6 | 0.95 | 48.5 | 1.084 | 0.463 | 0.118 | 2.37 |
| 942.7 T | 1.09 | 37.9 | 1.080 | 0.170 | 0.219 | 2.64 |
| 938.8 P | 0.41 | 56.9 | 0.650 | 0.097 | 0.049 | 2.71 |
| 941.9 P | 0.41 | 46.2 | 0.535 | — | — | 2.79 |
| 942.9 P | 0.41 | 60.2 | 0.787 | 0.182 | 0.029 | 3.21 |
| 955.2 | 1.17 | 49.2 | 2.045 | 1.051 | 0.416 | 3.63 |
| 964.7 | 2.63 | 27.2 | 3.170 | 2.937 | 0.631 | 4.70 |
| 968.5 | 0.95 | 44.7 | 2.801 | 1.053 | 0.350 | 6.76 |
| 972.7 P | 0.39 | 47.7 | 1.552 | 0.610 | 0.050 | 8.31 |
| 972.9 P | 0.39 | 46.2 | 1.544 | — | — | 8.53 |
| 979.4 T | 1.20 | 139.0 | 16.000 | 2.190 | 2.050 | 10.20 |
| 979.9 T | 1.03 | 26.6 | 2.610 | 0.560 | 0.241 | 10.02 |
| 983.3 | 0.94 | 37.9 | 3.572 | 1.930 | 0.198 | 10.53 |
| 994.6 T | 0.10 | 25.6 | 4.150 | 1.157 | — | 17.70 |
| 1000.7 | 0.96 | 40.9 | 7.235 | 4.345 | 0.926 | 20.24 |

Total pressure was between 9.4 and 13.4 mm. T, Runs with toluene as carrier gas. P, Packed runs.

little ethane should be formed. The proposed mechanism is strongly supported by the fact that runs in which toluene was the carrier gas gave results in accord with those in the aniline system. The origin of the hydrogen is uncertain. Much probably comes from the molecular decomposition of ethylbenzene into hydrogen and styrene. That the anilino-radical yields hydrogen cannot be eliminated but seems unlikely because no volatile nitrogenous products were detected. The condensable materials were mainly ethylene, which may also be formed by a molecular decomposition of ethylbenzene, with benzene as the other product. Hereafter, the reaction yielding methane will be regarded as the significant process. The rate constant is independent of the surface area of the reaction vessel and does not vary with the pressure of ethylbenzene. A least-mean-squares treatment of the results yields:

$$\log k \text{ (sec.}^{-1}\text{)} = (14.6 \pm 0.1) - (70,100 \pm 500/2.3RT).$$

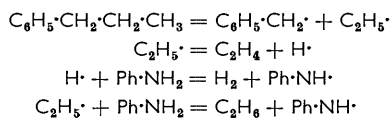
Although the Arrhenius parameters differ considerably from those found by Szwarc,¹ the rate constants for the middle of the temperature range are the same.

TABLE 2.
 Pyrolysis of n-propylbenzene.

| Temp. (°K) | Contact time (sec.) | PhPr ^a (10 ⁻⁵ mole) | H ₂ (10 ⁻⁵ mole) | Condensables (10 ⁻⁵ mole) | 10% (sec. ⁻¹) |
|---------------|---------------------------|--|---|---|------------------------------|
| 860.5 | 1.05 | 78.3 | 0.19 | 0.283 | 0.28 |
| 867.7 | 1.04 | 81.0 | 0.30 | 0.301 | 0.35 |
| 875.9 | 0.61 | 49.6 | 0.10 | 0.203 | 0.67 |
| 887.9 | 0.60 | 49.3 | 0.25 | 0.336 | 1.14 |
| 897.2 | 3.00 | 40.0 | 1.30 | 1.840 | 1.58 |
| 909.2 | 0.60 | 57.0 | 0.58 | 0.812 | 2.38 |
| 911.2 | 0.59 | 45.2 | 0.62 | 0.799 | 3.02 |
| 911.4 | 0.61 | 63.1 | 0.65 | 0.918 | 2.42 |
| 912.2 | 3.12 | 40.8 | — | 3.82 | 3.15 |
| 912.7 M | 0.61 | 49.0 | — | 0.92 | 3.14 |
| 920.0 | 1.14 | 48.4 | 2.51 | 2.58 | 4.78 |
| 920.2 | 1.24 | 55.0 | 2.90 | 2.96 | 4.43 |
| 921.9 | 1.23 | 47.8 | 2.38 | 2.59 | 4.65 |
| 924.8 M | 0.60 | 55.3 | 2.38 | 1.64 | 5.03 |
| 925.2 M | 0.61 | 56.1 | — | 1.69 | 4.99 |
| 927.9 | 0.96 | 51.3 | — | 2.87 | 5.96 |
| 931.8 | 0.59 | 51.2 | 1.42 | 2.02 | 6.79 |
| 934.7 M | 0.59 | 42.3 | 1.20 | 1.98 | 8.13 |
| 939.2 | 0.96 | 42.0 | 3.03 | 3.54 | 9.14 |
| 943.4 M | 0.58 | 53.1 | — | 3.48 | 11.70 |
| 943.7 M | 0.58 | 55.3 | — | 3.96 | 12.70 |
| 943.7 | 0.58 | 48.0 | — | 3.38 | 12.49 |
| 946.5 P | 0.40 | 32.6 | — | 1.51 | 11.70 |
| 948.2 M | 1.18 | 53.3 | 5.10 | 8.40 | 14.30 |
| 955.2 | 0.90 | 37.6 | — | 5.56 | 17.70 |
| 961.2 P | 0.39 | 41.5 | — | 3.59 | 22.9 |
| 963.1 M | 0.57 | 48.6 | — | 6.40 | 24.7 |
| 963.2 M | 0.57 | 46.6 | 5.54 | 5.60 | 22.5 |
| 963.4 | 0.55 | 43.8 | 4.09 | 5.59 | 24.9 |
| 965.7 | 0.56 | 56.4 | 5.64 | 7.60 | 25.4 |
| 971.2 P | 0.39 | 45.5 | — | 5.40 | 31.8 |
| 971.3 M | 0.57 | 48.5 | — | 8.58 | 33.8 |
| 972.5 | 1.14 | 46.4 | — | 14.60 | 33.0 |
| 973.7 | 0.56 | 48.3 | 7.35 | 9.92 | 41.1 |
| 979.2 P | 0.39 | 43.2 | — | 6.94 | 44.3 |
| 984.7 | 0.54 | 48.5 | 10.60 | 13.60 | 60.6 |
| 998.9 | 0.55 | 45.0 | 15.60 | 18.10 | 94.8 |
| 1010.5 | 0.55 | 51.1 | 22.20 | 7.90 | 143.0 |
| 1020.2 | 0.55 | 50.4 | 30.00 | 32.50 | 183.0 |
| 1021.0 | 0.54 | 46.7 | 31.00 | 30.50 | 197.0 |

Total pressure was between 10.0 and 11.7 mm. Condensables were entirely C₂ hydrocarbons. M, Runs of the competitive pyrolysis in which ethylbenzene was present. P, packed vessel.

First-order rate constants for the pyrolysis of n-propylbenzene were calculated from the rates of formation of ethane and ethylene according to the scheme:



The benzyl and anilino-radicals are supposed to react as in the ethylbenzene system. The constants were independent of contact time, reactant pressure, and packing of the reaction vessel. Much more ethylene than ethane was formed, as would be expected because the ethylene-hydrogen bond is weak. Methane found in the products was always less than 10% of the hydrogen. Leigh and Szwarc¹⁵ also found methane in the products and attributed it to a reaction of the toluene that was present. When aniline is the carrier, methane is presumably formed by reaction of a methyl radical from n-propylbenzene, as

TABLE 3.
Pyrolysis of n-butylbenzene.

| Temp. (°K) | Contact time (sec.) | PhBu ^a (10 ⁻⁵ mole) | CH ₄ (10 ⁻⁵ mole) | C ₂ H ₄ (10 ⁻⁵ mole) | H ₂ (10 ⁻⁵ mole) | 10 ³ k (sec. ⁻¹) |
|---------------|---------------------------|--|--|--|---|--|
| 863.9 | 3.19 | 37.4 | 0.370 | 0.643 | 0.135 | 0.314 |
| 877.2 | 2.85 | 28.6 | 0.509 | 0.871 | 0.195 | 0.616 |
| 883.4 | 1.06 | 54.6 | 0.497 | 0.710 | 0.117 | 0.859 |
| 884.7 | 1.09 | 71.0 | 0.726 | 1.090 | 0.144 | 0.936 |
| 911.7 | 1.09 | 27.4 | 0.714 | 1.103 | 0.235 | 2.440 |
| 920.0 | 1.09 | 32.9 | 1.248 | 1.970 | 0.390 | 3.579 |
| 929.3 | 1.01 | 21.9 | 1.224 | 1.751 | 0.233 | 5.754 |
| 934.2 | 1.01 | 46.7 | 2.930 | 4.883 | 0.817 | 6.530 |
| 934.4 | 0.98 | 18.9 | 1.280 | 1.790 | 0.423 | 6.834 |
| 939.4 P | 0.42 | 21.6 | 0.938 | 1.033 | 0.085 | 10.48 |
| 941.9 | 0.64 | 25.9 | 1.560 | 2.183 | 0.243 | 9.79 |
| 944.2 | 0.61 | 34.0 | 2.010 | 2.906 | 0.508 | 10.15 |
| 944.3 P | 0.40 | 19.5 | 0.945 | 0.951 | — | 12.00 |
| 944.8 | 0.61 | 29.5 | 1.870 | 2.584 | 0.287 | 10.79 |
| 948.3 P | 0.41 | 27.2 | 1.374 | 1.649 | 0.240 | 12.65 |
| 950.6 P | 0.40 | 26.6 | 1.530 | 1.807 | 0.276 | 14.72 |
| 959.4 | 1.03 | 31.8 | 4.620 | 7.910 | 1.790 | 16.15 |
| 962.3 | 0.60 | 30.3 | 3.171 | 4.888 | 1.260 | 18.91 |
| 962.7 | 1.01 | 19.4 | 2.950 | 4.960 | 1.136 | 17.18 |
| 971.0 | 0.59 | 29.5 | 4.090 | 6.401 | 1.149 | 27.6 |
| 971.2 P | 0.40 | 24.3 | 2.842 | 3.349 | 0.507 | 31.4 |
| 971.6 P | 0.39 | 21.9 | 2.602 | 3.224 | 0.116 | 32.3 |
| 983.2 | 1.01 | 25.3 | 6.450 | 11.42 | 2.62. | 33.3 |
| 991.2 | 0.59 | 29.2 | 6.750 | 11.84 | 2.946 | 50.2 |
| 998.9 | 0.56 | 31.3 | 8.790 | 14.93 | — | 67.0 |
| 1008.5 | 0.93 | 49.8 | 17.34 | 36.52 | 11.6 | 67.5 |

Total pressure was between 8.9 and 14.1 mm. P, Packed reaction vessel.

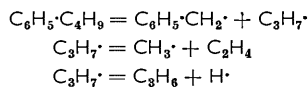
the work of Blades and Steacie¹⁶ rules out the possibility that methane is directly eliminated. The relative amount of hydrogen and hydrocarbons formed are in keeping with this mechanism. The amount of n-propylbenzene that decomposes in this way is small and no correction was made to allow for it. The rate constants are best expressed by

$$\log k \text{ (sec.}^{-1}\text{)} = (14.9 \pm 0.1) - (68,600 \pm 500/2.3RT),$$

derived by a least-squares computation. The Arrhenius parameters are very different from those of Leigh and Szwarc,¹⁵ and the rate constants agree only at the highest temperature.

From these results and the heats of formation of the methyl (33.9) and ethyl radicals (26.0),¹³ the heat of formation of the benzyl radical is found to be 43.2 and 44.5 kcal. mole⁻¹, respectively. Hence $D(\text{C}_6\text{H}_5\text{-CH}_2\text{-H}) = 83.3$ or 84.6 kcal. mole⁻¹. The higher value is preferred because more work was done with n-propylbenzene during the present investigation. There is no real disagreement, as an error of 1—1.5 kcal. mole⁻¹ should probably be attached to each figure.

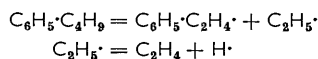
A principal reason for the interest in the heat of formation of the benzyl radical is that once it is known the heats of formation of other radicals can be found from studies of the pyrolyses of their benzyl compounds. This principle can be applied to the results from n-butylbenzene. The decomposition was expected to involve the steps:



Methane, hydrogen, and perhaps very small amounts of propane should be formed by reaction with the aniline. Ethane, propane, and propene accounted always for less than

¹⁶ Blades and Steacie, *Canad. J. Chem.*, 1954, **32**, 1142.

1% of the total gaseous products. n-Propyl radicals do not appear to decompose with loss of a hydrogen atom. The simple mechanism cannot be complete, as considerably more ethylene than methane is formed, together with much hydrogen. As with ethylbenzene, decomposition of the type



must be assumed. First-order rate constants were calculated for the overall rate of decomposition from the yields of ethylene. The rate constants for the decomposition to benzyl were calculated from the yields of methane. They can be expressed by

$$\log k \text{ (sec.}^{-1}\text{)} = 14.5 - (67,100/2.3RT).$$

The ratio of ethylene to methane increases with temperature. The second process by which ethylene is formed clearly has the higher activation energy, as would be expected. The overall rate constant is given by

$$\log k \text{ (sec.}^{-1}\text{)} = 14.7 - (67,200/2.3RT),$$

but the results are not sufficiently accurate to warrant computation of the rate constant for the fission yielding ethyl radicals.

The activation energy for the fission to n-propyl radicals yields $D(\text{n-C}_3\text{H}_7\text{-H}) = 96.2$ kcal. mole⁻¹ and $\Delta H_f^\circ(\text{n-C}_3\text{H}_7) = 19.1$ kcal. mole⁻¹. These values are considerably lower than those usually quoted, which are based on Stevenson's determinations¹⁷ by electron impact and those of Leigh and Szwarc,¹⁵ who used an incorrect value for $\Delta H_f^\circ(\text{C}_6\text{H}_5\cdot\text{CH}_2)$. The high bond strength was supported by early work on the pyrolysis of propyl radicals (cf. ref. 18). Calvert and Sleppey,¹⁹ and Kerr and Calvert,²⁰ recently found 34.9 and 34.5 kcal. mole⁻¹ as the activation energy for the decomposition of n-propyl. In combination with Brinton's²¹ activation energy for the addition of methyl to ethylene, these values give $D(\text{Pr}^\text{n}\text{-H}) = 97.3$ kcal. mole⁻¹. The reactivities of primary C-H bonds with most radicals appear to vary little.²² A value of $D(\text{Pr}^\text{n}\text{-H})$ close to that of $D(\text{Et-H})$ can therefore be accepted on general grounds.

Eight runs were performed with isobutylbenzene. The condensable products consisted of propene and ethylene in the ratio of 3—4 : 1. Much hydrogen was formed. Rate constants derived from the (propene + ethylene) are given by

$$\log k \text{ (sec.}^{-1}\text{)} = 13.2 - (63,200/2.3RT).$$

The mechanism of the reaction is too complicated to permit the relation of this activation energy to any process in the reaction.

EXPERIMENTAL

Materials.—Aniline was purified by passage twice through a quartz tube at 850°/20 mm. and subsequent fractionation. Degassing aniline is difficult; bulb-to-bulb distillation is of little use for large quantities. Hydrogen, from which oxygen and water were removed, was bubbled through the aniline for several hours. A high vacuum was then applied and the aniline boiled for several minutes in a flask with a water-condenser. The aniline was distilled into a container and stored under a vacuum. Toluene was also pyrolysed, fractionated, and degassed by bulb-to-bulb distillation. The alkylbenzenes were commercial samples, tested by gas chromatography.

Typical toluene-carrier apparatus and procedure were slightly adapted to permit the use of the higher-boiling aniline as carrier. The reactants were all injected into the gas stream

¹⁷ Stevenson, *Trans. Faraday Soc.*, 1953, **49**, 867.

¹⁸ Kerr and Trotman-Dickenson, *Trans. Faraday Soc.*, 1959, **55**, 572.

¹⁹ Calvert and Sleppey, *J. Amer. Chem. Soc.*, 1959, **81**, 1544.

²⁰ Kerr and Calvert, *J. Amer. Chem. Soc.*, 1961, **83**, 3391.

²¹ Brinton, *J. Chem. Phys.*, 1958, **29**, 781.

²² See Bérces and Trotman-Dickenson, *J.*, 1961, 4281.

through a capillary stopcock. The products were separated on a low-temperature distillation train. Hydrogen-methane mixtures were measured in a gas burette. The methane was condensed in a silica-gel trap, attached to the top of the burette, at liquid-air temperature. The non-condensable materials were also analysed by gas chromatography on an 8 ft. column packed with Linde molecular sieve 5A. The C₂-C₄ fractions were analysed on a 6 ft. temperature-controlled column packed with 40-60 mesh alumina containing 2% of squalane.

This research was sponsored by the Office of Scientific Research, OAR, through its European Office, United States Air Force.

EDWARD DAVIES CHEMICAL LABORATORY,
ABERYSTWYTH, WALES.

[Received, January 31st, 1963.]
