

The CH Bond Energy in Toluene and Xylenes

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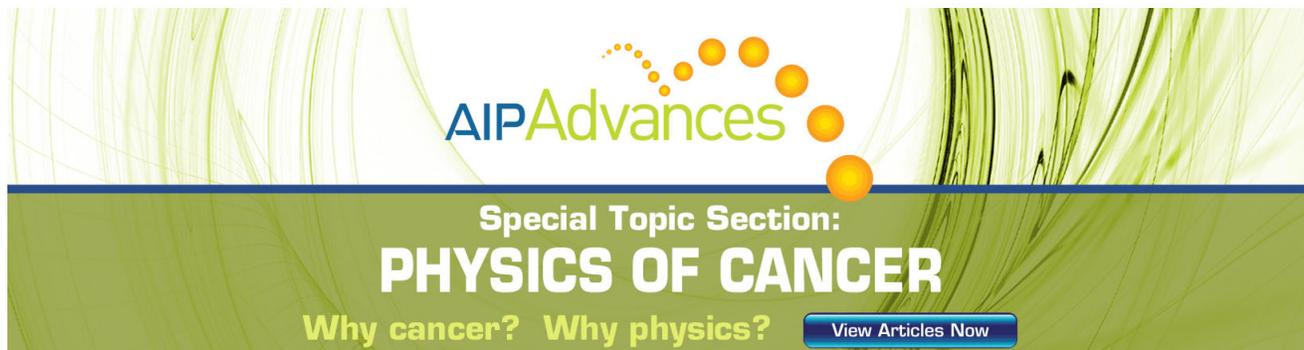
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Comings, Egly, and Mayland¹² indicate that for numerous gases the temperature dependence of the viscosity decreases with increasing pressure even at relatively low pressures in the neighborhood of 10–20 atmospheres.

The temperature dependence of the viscosity is given by

$$\eta_2/\eta_1 = (T_2/T_1)^S, \quad (10)$$

where

$$S = \frac{1}{2} + (2/\nu + 1). \quad (11)$$

So a decreasing value of S corresponds to an increasing value of ν and, thus, to a "hardening" of the molecular model with increasing pressure. If ν were only slightly pressure dependent, the value of S would not vary noticeably with pressure at ordinary pressures, but α , which is very sensitive to changes in ν , might vary appreciably.

If one substitutes Eq. (3d) for α in Eq. (4), considering $\varphi(\nu)$ as a constant to be evaluated at a pressure where the theoretical and experimental values of $\ln q$ coincide, one obtains as an approximate equation for ν over the pressure

¹² E. W. Comings, R. S. Egly and J. C. Mayland, University of Illinois Exper. Stat. Bull. 354 (1944).

range covered:

$$\nu = \frac{5 - 0.206p^{0.333}}{1 - 0.206p^{0.333}}. \quad (12)$$

Using this value in the theoretical equations one obtains approximately

$$D_T = \frac{3.98 \times 10^{-4}}{p^{0.67}}. \quad (13)$$

The values of D_T predicted from this equation agree closely with those calculated from experiment by Eq. (5), which becomes

$$D_T = 1.761p[1 + (0.495/p^4)] \times (\ln q)_{\text{exper.}} \times 10^{-4}. \quad (14)$$

This agreement is shown in Fig. 5.

Considerably more experimental work would be necessary before one could put much reliance in Eq. (12) for ν and use it to extrapolate to higher pressures or to other systems. If such a relationship is really general it would provide an incentive for operating thermal diffusion columns at slightly elevated pressure.

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The C—H Bond Energy in Toluene and Xylenes

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The pyrolysis of toluene and the xylenes was investigated by a new technique, which made it possible to study these reactions for degree of decomposition ranging from 0.01 percent up to a few percent. It was shown that these reactions are homogeneous, unimolecular reactions. It was found that the weakest bond in these molecules is the C—H bond in the methyl group. The bond energy of that C—H bond was found to be 77.5 kcal. for toluene and meta-xylene, 75 kcal. for para-xylene and 74 kcal. for ortho-xylene. These data indicate that the resonance energy of the benzyl radical is 24.5 kcal. and that the hyper-conjugation in para-xylene decreases the C—H bond energy in the methyl group of this molecule by 2.5–3 kcal.

A RECENT investigation of the pyrolysis of benzyl iodide by C. Horrex¹ and the author revealed the great stability of the benzyl radical. This work gave rise to the suspicion that the resonance energy of the benzyl radical

is much higher than was previously thought and the present study was started in the hope of further clarifying this point. It was decided to investigate the pyrolysis of toluene, and in particular the nature of the first step of its decomposition.

¹ This will shortly be published elsewhere.

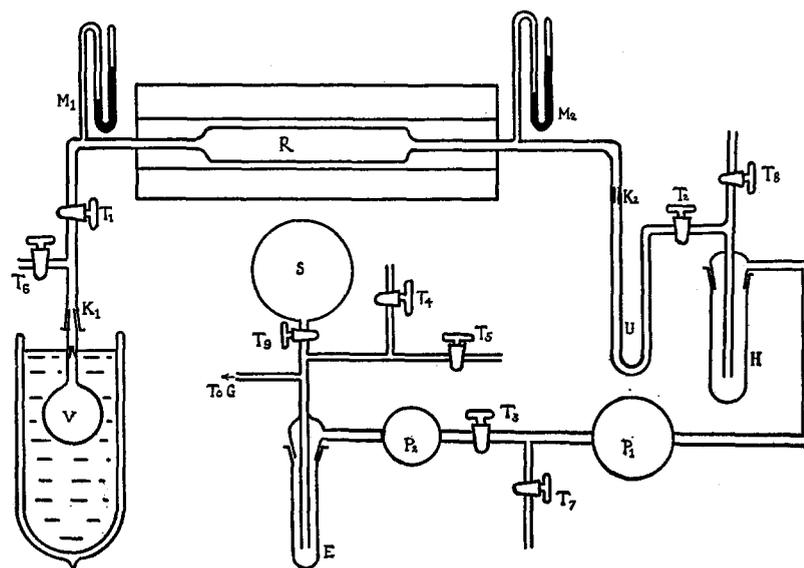


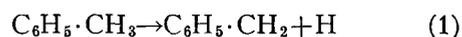
FIG. 1.

The pyrolysis of toluene and the xylenes has been investigated in the past ten years by several authors, mainly in connection with the coking process, and most of the research was devoted to studying the influence of various catalysts. It was found by Tilicheev² that toluene decomposes 13 times faster than benzene, and the energy of activation of this decomposition was found to be 70 kcal. It is interesting to compare this value with the value of 77.5 kcal. obtained in the present work.

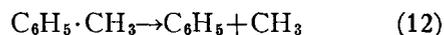
Jost and Müffling³ measured the rate of pyrolysis of a number of hydrocarbons, among them toluene, following the course of the reaction by the increase of pressure. They observed that $\text{Hg}(\text{CH}_3)_2$ had no effect on the rate of decomposition of toluene at 690°C, which indicated that the decomposition is not a chain reaction. All these investigations suffered from the common difficulty that the decomposition was carried out under conditions in which it was impossible to derive the true mechanism of the reaction, owing to the complicated mixture of products obtained.

The first successful attempt to elucidate the mechanism of the reaction was made by Hein and Mésee.⁴ These authors pyrolyzed toluene in the presence of mercury vapor, using a technique

similar to that developed by Rice. They succeeded in isolating mercury-di-benzyl as a product of the reaction, and followed the course of the decomposition by the determination of the quantities of the mercury compound formed. The rate of formation of this compound seemed to depend on a number of uncontrollable factors which prevented the determination of an energy of activation. Yet the authors concluded from the formation of mercury-di-benzyl that the first step in the decomposition of toluene is the rupture of the C—H bond,



which is followed by a reaction between benzyl radicals and mercury atoms leading to $\text{Hg}(\text{CH}_2 \cdot \text{C}_6\text{H}_5)_2$. However, it would seem that the evidence for this conclusion is not definite, for it is possible to explain the formation of the benzyl radical by a mechanism involving the rupture of the C—C bond as a first step:



followed by the reactions:



A stronger argument, put forward by Hein and Mésee, in favor of (1) is their observation of hydrogen among the products of the decomposition. There is, however, some ambiguity about

² M. D. Tilicheev, *J. App. Chem. U.S.S.R.* **12**, 741 (1939).

³ I. W. Jost and L. v. Müffling, *Zeits. f. Elektrochemie* **47**, 766 (1941).

⁴ F. Hein and H. J. Mésee, *Berichte* **76B**, 430 (1943).

TABLE I.

Run No.	Toluene partially pyrolysed	T°C	K · 10 ⁻² sec. ⁻¹	K · 10 ⁻² sec. for 845°C	% H ₂	% CH ₄
70	once at 835°C	836°	1.50	2.18	59	41
71	twice at 835°C	845°	1.90	1.90	60	40
72	once at 845°C	845°	2.02	2.02	60	40
73	twice at 845°C	848°	2.02	1.78	59	41
74	three times at 847°C	852°	2.12	1.76	61	39

the origin of this hydrogen, since Hein and Mésee worked in the region of 1000°C, when according to the present study complete cracking of toluene molecules takes place.

In the present investigation the rate of pyrolysis of toluene was observed by measuring the quantity and composition of the gaseous mixture formed. The experimental conditions were so chosen that the decomposition ranged from 0.01 percent to slightly over 1 percent. It was expected that in these conditions the reaction mechanism would be simplified. The experimental results confirmed this by showing that no other gases than hydrogen and methane were produced.

APPARATUS AND TECHNIQUE OF MEASUREMENT

The pyrolysis was investigated by the flow method in the temperature range of 680°C–850°C and under a pressure of 2–15 mm Hg. The apparatus used is shown in Fig. 1. The hydrocarbon under investigation was kept in a small vessel, *V*, fitted with a capillary *K*₁. This vessel was weighed before and after every experiment, the loss of weight giving the quantity of hydrocarbon used. During runs *V* was kept in a Dewar vessel containing water maintained at a temperature constant to 0.1°C. By opening the tap *T*₁, the vapor of the hydrocarbon was led into a silica reaction vessel *R* heated by an electrical furnace. The temperature of the furnace was kept constant by a constant voltage transformer and measured by a double chromel P-Alumel thermocouple. The variation of temperature along the reaction vessel was ±2°C. The pressure before and after the reaction vessel was measured on two manometers *M*₁ and *M*₂ by means of a cathetometer.

The vapor leaving the furnace passed through a heated tube and heated capillary *K*₂ into a

small trap *U* cooled by mixture of salt and ice to –10°C, and then through a tap *T*₂ into a big trap *H* cooled by acetone +CO₂ mixture. In the trap *U* the less volatile products such as di-benzyl, di-phenyl and others were condensed. The undecomposed hydrocarbon was condensed completely in the trap *H*. The trap *H* was connected to a system of two mercury pumps *P*₁ and *P*₂, capable of pumping all the gases into the storage vessel *S*. The pumps were chosen so as to maintain a vacuum of 10⁻³ mm of Hg in the trap *H*, while the pressure in the storage vessel *S* could rise up to 12 mm of mercury. The trap *E* placed between the pump *P*₂ and the storage vessel *S* was cooled with liquid air to trap any ethane or ethylene produced in pyrolysis. The McLeod gauge *G* was used to measure the pressure of the gases produced. The volume of the storage part between the taps *T*₃, *T*₄, and *T*₅ was exactly determined (at about 1.5 l.). The taps *T*₄, *T*₆ and *T*₇ were used for evacuation of appropriate parts of the apparatus. *T*₅ led to an analytical device and *T*₈ was used to let air into the Trap *H*. By changing the capillaries *K*₁ and *K*₂ and choosing the desired temperature of water bath, it was

TABLE II. Toluene.

Remarks	No. of run	T°C	P toluene mm Hg	Time of contact sec.	% decomp.	K · 10 ² sec. ⁻¹	% H ₂	% CH ₄
	94	738	6.4	0.310	0.0098	0.032		
	87	740	6.4	0.310	0.0114	0.037		
	88	741	6.4	0.310	0.0132	0.043		
	89	742	6.1	0.296	0.0141	0.048		
	90	742	6.0	0.291	0.0155	0.053	60	40
	91	745	5.8	0.280	0.0163	0.058		
	93	747	6.4	0.310	0.0238	0.077		
	92	749	6.4	0.310	0.0246	0.079		
	76	766	6.3	0.268	0.0336	0.125	61	39
	77	771	6.1	0.235	0.0333	0.142		
Pressure decreased	82	773	2.7	0.380	0.0600	0.158		
Time of contact increased	83	773	6.8	0.825	0.140	0.170	61	39
Surface increased 15 times	86	776	11.7	0.262	0.0344	0.131	60	40
	95	779	6.3	0.294	0.0740	0.252		
	78	792	6.2	0.256	0.0730	0.286	60	40
Pressure decreased	79	796	2.8	0.286	0.107	0.375	61	39
Time of cont. increased	81	803	5.5	0.905	0.437	0.485		
Time of cont. increased, Pressure increased	80	803	13.7	0.738	0.382	0.518	59	41
	97	819	6.3	0.284	0.244	0.860		
	98	821	6.3	0.284	0.261	0.920		
	71	845	7.6	0.306	0.581	1.90	60	40
	72	845	8.1	0.338	0.690	2.02	60	40
	73	848	5.9	0.246	0.500	2.02		
Pressure decreased	75	851	2.8	0.299	0.615	2.06	59	41
	74	852	6.3	0.246	0.520	2.12		
Surface increased 15 times	84	863	8.0	0.270	1.14	4.21	62	38
Surface increased 15 times	85	864	8.0	0.270	1.25	4.62	61	39

possible to vary both the pressure of the hydrocarbon in the reaction vessel and the time of contact.

The quantity of $H_2 + CH_4$ produced was given by the pressure in the storage part with liquid air on the trap *E*. Changing the liquid air to the acetone + CO_2 bath and measuring any consequent rise in pressure, it was possible to find the quantity of any C_2 -hydrocarbons present.

Numerous experiments showed that this arrangement gives exact results even where the quantities of gases produced are as low as 5.10^{-3} cc N.T.P./minute, so that this technique made it possible to follow the reaction down to as little as 0.01 percent decomposition. The H_2 to CH_4 ratio was estimated by combusting the H_2 , in a known quantity of $H_2 + CH_4$ mixture, by passage through a CuO cell. This method was tested by total combustion in oxygen and estimation of the CO_2 formed.

MATERIAL USED FOR PYROLYSIS

The first series of experiments in which toluene samples of different origins were used, showed that in spite of careful purification by shaking with sulphuric acid, distillation and crystallization, some impurities remained, the pyrolysis of which gave rise to considerable side reactions. These impurities could be removed by partial pyrolysis and the repeated partial pyrolysis of toluene produced samples of toluene, which pyrolyse at a steady rate when partial pyrolysis is repeated once or several times. This is seen from Table I. The final rate of pyrolysis we take to be that of toluene itself. Accordingly, the further work was carried out with toluene purified by twice repeated partial pyrolysis at $845^\circ C$, then distilled over sodium, using an efficient column, and collecting a fraction which passed within a range of $0.3^\circ C$.

EXPERIMENTAL RESULTS OF THE PYROLYSIS OF TOLUENE

The pyrolysis of toluene produced the two gases hydrogen and methane in the constant proportion 60 percent of H_2 to 40 percent of CH_4 (see Table II). No ethane or ethylene was observed. In addition to the gaseous product,

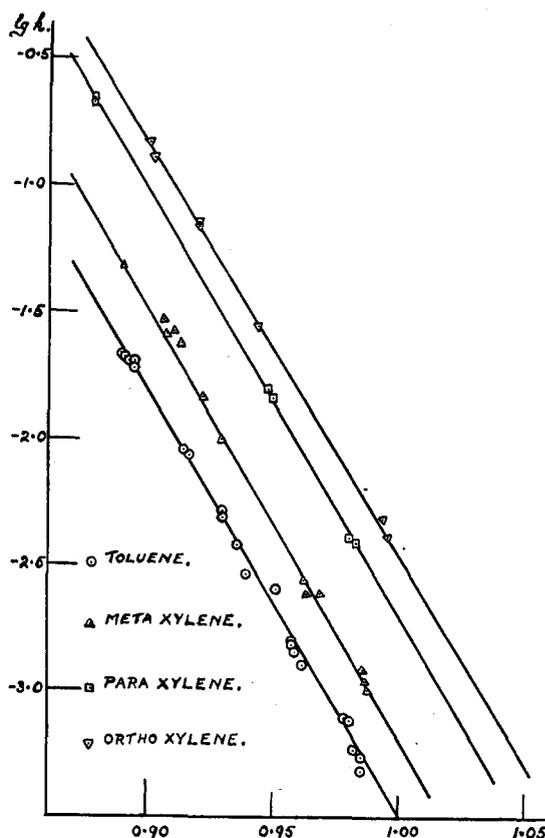


FIG. 2.

dibenzyl was isolated in quantities corresponding approximately to one mol. of dibenzyl per one mol. of gas produced. Dibenzyl was identified by its melting point and mixed melting point. The percentage of decomposition was calculated under the assumption that one mol. of gas produced corresponds to one mol. of primarily decomposed toluene. By packing the reaction vessel with silica wool which increased the surface about 15 times it was shown that the reaction is a homogeneous gas reaction (see runs 86, 84 and 85 in Table II). Reproducibility was very satisfactory, as can be seen comparing runs 89 and 90, and 71 and 72 (Table II). By changing the pressure of toluene and the time of contact, it was shown that the reaction is of the first order. The plot of $\log k$ against $1/T$ (shown on Fig. 2) can be satisfactorily drawn as a straight line, with a slope corresponding to an activation energy of 77.5 kcal. and a frequency factor of 2.10^{13} , as represented by the equation $k = 2.10^{13}$

$\cdot e^{-77.5/RT}$. A further discussion of the grounds on which these constants were determined is to follow later.

MECHANISM OF PYROLYSIS OF TOLUENE

The evidence given above shows that the reaction is a homogeneous gas reaction of the first order. The fact that the frequency factor has the theoretical value of 10^{13} , as deduced by Polanyi and Wigner⁵ suggests that we deal in this case with a true unimolecular reaction.

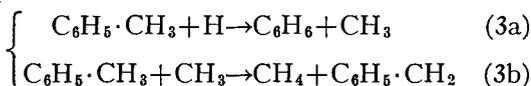
The appearance of hydrogen as one of the main products forces us to assume that the first step of the pyrolysis is the splitting of the toluene molecule into a benzyl radical and a hydrogen atom:



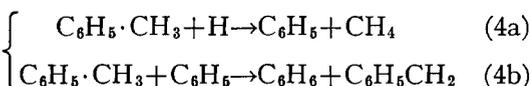
and the body of experimental evidence suggests that this step is followed by a sequence of quick reactions:



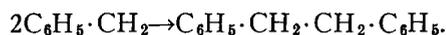
and



or



it being assumed that the benzyl radicals are finally removed by dimerization to di-benzyl,



This mechanism accounts for the observed products (H_2 , CH_4 , dibenzyl and benzene) and gives the correct proportion of one mol of dibenzyl per one mol of gas produced.

We can show that the recombination of hydrogen atoms to H_2 is very unlikely under our experimental conditions, and this justifies its omission from the suggested mechanism. We do not know the energy of activation of the reactions (3a) or (4a), but we may expect these energies of activation to be smaller than that of (4b), which was estimated by Taylor and Smith⁶

⁵ M. Polanyi and E. Wigner, *Zeits. f. Phys. Chem.* **A139**, 439 (1928). See also S. Glasstone, M. Laidler and H. Eyring, "The Theory of Rate Processes" (1941).

⁶ H. S. Taylor and J. O. Smith, *J. Chem. Phys.* **8**, 543 (1940).

at 5.6 kcal. On this basis we calculate that in (3a) and (4a) at least one in ten collisions should lead to reaction. Since the chance of three body collisions should be smaller than this by several powers of ten, the recombination of H atoms in the gas phase should be negligible. The recombination at the wall should in these conditions be also of little importance, especially since at these high temperatures the accommodation coefficient is probably extremely small.⁷

The absence of recombination of H atoms at the wall was confirmed by showing that the packing of the reaction vessel caused no change in the rate of reaction, nor any increase in the proportion of H_2 produced.

The proposed mechanism leads to the result that the reaction (1) is the rate determining step and therefore the observed energy of activation corresponds to the energy of dissociation of the C-H bond in the methyl group of toluene. This conclusion makes use of the usual assumption that there is no energy of activation involved in the recombination of a bond from a free radical and a free atom. While this is not the place to re-examine this assumption, it may be stated that the theoretical reasons in its favor seem to be very strong.

Accordingly, we give for the C-H bond energy in the methyl group of toluene the value of 77.5 kcal. The difference between this value and the bond energy of C-H in methane which may be estimated at 102 kcal.⁸ is to be accounted for by the resonance energy of the benzyl radical, which thus appears to have the value of 24.5 kcal.

PYROLYSIS OF META-XYLENE

The meta-xylene used was of German origin, produced by the "Gesellschaft für Verwehrtung von Kohlenteer." It was purified by repeated crystallization at -60°C , which was found to be sufficient.

The pyrolysis of meta-xylene produced hydrogen and methane in the same proportion as that of toluene (60 percent H_2 , 40 percent CH_4). No

⁷ F. Paneth and K. Herzfeld, *Zeits. f. Elektrochemie* **37**, 577 (1931); F. Paneth, K. Hofeditz and A. Wunsch, *J. Chem. Soc.* (1935) p. 372.

⁸ G. B. Kistiakowsky and E. B. Van Artsdalen, *J. Chem. Phys.* **12**, 469 (1944). D. P. Stevenson, *ibid.* **10**, 291 (1942).

TABLE III. Meta-xylene.

Remarks	No. of run	T°C	P meta-xylene of mm Hg	Time of contact sec.	% decomp.	$K \cdot 10^2$ sec. ⁻¹	% H ₂	% CH ₄
	121	740	3.0	0.358	0.037	0.104		
	122	741	3.0	0.360	0.040	0.111		
	123	742	3.0	0.360	0.044	0.121	60	40
	101	760	2.3	0.386	0.094	0.242		
	102	765	2.5	0.352	0.086	0.242		
	105	767	2.8	0.316	0.086	0.272	60	40
Surface increased 15 times	112	778	5.6	0.326	0.120	0.368	62	38
Pressure increased								
Time of cont. increased	106	802	5.9	0.840	0.825	0.98	57	43
Time of cont. increased								
Pressure increased	109	812	5.5	0.891	1.29	1.45	59	41
Time of cont. increased								
Pressure increased	113	815	2.5	0.910	1.37	1.50	59	41
Time of cont. increased								
	128	822	2.8	0.336	0.80	2.38	60	40
	129	825	2.8	0.336	0.88	2.62	60	40
Time of contact and pressure increased	107	828	5.5	0.908	2.52	2.78		
	108	829	5.5	0.876	2.60	2.96	60	40
	103	850	3.0	0.311	1.51	4.86	60	40
Pressure increased	114	851	5.8	0.320	1.60	5.00	59	41
Surface increased 15 times	110	867	4.4	0.400	3.33	8.31	61	39
	111	867	3.7	0.410	3.54	8.75	61	39

ethane or ethylene was observed. The droplets of liquid collected in the *U* trap were identified by their boiling point as 3, 3' di-methyl-di-benzyl.

The percentage of decomposition was calculated as before by assuming that one mol of each gas produced corresponds to one mol of meta-xylene primarily decomposed. By changing the time of contact and pressure of xylene the reaction was proved to be of the first order, and packing experiments confirmed it to be a homogeneous gas reaction. The results are summarized in Table III, and the plot of $\log K$ against $1/T$ is given in Fig. 2.

The graph of $\log K$ against $1/T$ demonstrates strikingly that the pyrolysis of meta-xylene is represented by a straight line parallel to that of toluene but displaced towards higher values of $\log K$ by logarithm of 2. Accordingly, the activation energy is taken once more at 77.5 kcal. while the temperature independent factor is chosen as $4.0 \cdot 10^{13}$ —that is twice the value for toluene. A more precise justification of these figures will be given later.

The interpretation which we place on these facts is that the mechanism of pyrolysis of meta-xylene is analogous to that of toluene. The recurrence of the same value for the energy of activation indicates the same C—H bond energy, while the twofold value of the frequency factor indicates a twice increased probability of reac-

tion, owing to the presence of two independent methyl groups.

The recurrence of the same composition of gas in the products of the pyrolysis of meta-xylene as was observed for toluene is in itself a powerful argument for assuming the same mechanism of decomposition in both cases.

PYROLYSIS OF PARA-XYLENE

The para-xylene used was manufactured by Chance and Hunt. After purification by repeated crystallization the substance had a sharp melting point at 12.8°C, and gave steady results in repeated pyrolysis showing that it was pure enough for our purposes.

Table IV gives the experimental results, and the plot of $\log K$ against $1/T$ is to be found in Fig. 2. Hydrogen and methane are once more the only gaseous products and no ethane or ethylene was observed. The gas produced is slightly richer in hydrogen than the gas obtained by pyrolysis of toluene and meta-xylene, the composition being 65 percent of hydrogen and 35 percent of methane. The packing experiments proved that the reaction is a homogeneous gas reaction. The rate of decomposition is at all temperatures three times greater than that of meta-xylene.

From these results we conclude that in the pyrolysis of para-xylene the first step is again the rupture of a C—H bond of a CH₃ group. The main result clearly consists in the fact that para-xylene is proved to decompose three times faster than meta-xylene. As a further discussion will presently show, this can be best accounted for by a reduction of the activation energy (which is the energy of the C—H bond) to 75

TABLE IV. Para-xylene.

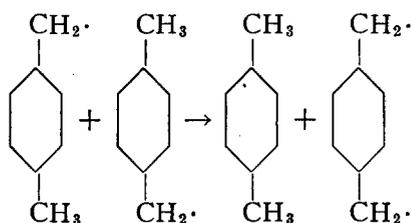
Remarks	Run No.	T°C	P. para-xylene of mm Hg	Time of contact sec. ⁻¹	% decomp.	$K \cdot 10^2$ sec. ⁻¹	% H ₂	% CH ₄
	134	745	3.2	0.419	0.158	0.378		
	135	745	3.2	0.419	0.159	0.381	67	33
	130	746	3.3	0.425	0.168	0.395		
	136	747	3.3	0.428	0.178	0.415	67	33
	138	781	2.6	0.239	0.344	1.44	67	33
Surface increased 15 times	133	782	6.2	0.715	0.365	1.35	64	36
	137	783	2.0	0.238	0.372	1.56		
	139	866	3.7	0.344	7.73	22.4		
	140	866	3.8	0.354	7.73	21.8	65	35
Surface increased 15 times	131	860	4.5	0.410	10.0	25.0	63	37

kcal; the temperature independent factor being retained at the $4 \cdot 10^{13}$.

The slight change in the proportion of hydrogen to methane is probably the result of the decrease in the C—H bond energy, as this would increase the probability of the reaction between the hydrogen atom and para-xylene molecules which leads to the production of hydrogen molecules. (Reaction 2.)

The pyrolysis of para-xylene differs from that of toluene and of meta-xylene in the following particular. The last two give rise to dimers of the free radicals primarily produced. The radical produced in the pyrolysis of para-xylene gives no dimer but only a high polymer which accumulates in trap *U* and trap *H*.

The problems arising from this polymerization are discussed elsewhere.⁹ It appears that the primarily produced para-xylyl radicals disproportionate in the gas phase according to the following equation:



and the biradical (or its quinonoid form



polymerizes rapidly on condensation at a cooled surface.

PYROLYSIS OF ORTHO-XYLENE

The ortho-xylene used was a B.D.H. product, which was additionally purified by crystallization at -30°C , followed by a careful distillation. Since this product was not pure enough, it was further purified by partial pyrolysis. The necessity of this purification is seen from Table V. (Compare runs 153 and 150, 151 and 152, also 146 and 147 with 148 and 149.) The concordant results obtained with pyrolyzed ortho-xylene, proved that they represent the pyrolysis of ortho-xylene itself.

⁹ M. Szwarc, "Discussion on labile molecules," Trans. Faraday Soc., in press.

The main features of the pyrolysis of ortho-xylene are the same as those of the previously investigated hydrocarbons. The principal gaseous products are hydrogen and methane. The rate of their formation is somewhat (about 70 percent) greater than that observed for para-xylene, the percentage of hydrogen being smaller (50 percent H_2 50 percent CH_4). In this case the formation of a small quantity of C_2 hydrocarbon was observed; about 10 percent of $\text{H}_2 + \text{CH}_4$.

It seems reasonable to explain the formation of C_2 hydrocarbons from ortho-xylene by the presence of two adjoining methyl groups. This may also account for the low H_2/CH_4 ratio if the steric interaction of the two CH_3 groups is assumed to decrease the Ph—C bond energy and consequently increase the probability of the reaction leading to the formation of CH_4 .

These considerations leave unaffected the conclusion that the main process in the pyrolysis of ortho-xylene is again the rupture of the C—H bond. The slightly higher rate of decomposition of ortho-xylene compared to that of the para isomer may be taken to indicate that the C—H bond is weaker in the former.

The values of $\log K$ are plotted against $1/T$ in Fig. 2, and are represented as lying on a straight line corresponding to an energy of activation of 74 kcal., indicating the decrease in C—H bond energy of ortho-xylene as compared to meta-xylene.

FURTHER DISCUSSION OF THE RESULTS

We shall now present the more detailed consideration on the ground of which the activation energies and the temperature independent factors

TABLE V. Ortho-xylene.

Remarks	No. of run	$T^{\circ}\text{C}$	<i>P</i> ortho-xylene mm Hg	Time of contact sec.	% decomp. into $\text{H}_2 + \text{CH}_4$	$K \cdot 10^2$ sec. ⁻¹	% decomp. into C_2 hydrocarb.	% H_2	% CH_4
Partially pyrolyzed at 836°C	156	730	3.5	0.370	0.140	0.379	0.010		
	157	734	3.6	0.385	0.185	0.480	0.014		
	155	777	3.2	0.338	0.745	2.20	0.028		
	154	788	3.0	0.340	1.06	3.12	0.045	46	54
	150	815	3.4	0.330	2.26	6.85	0.22	52	48
Partially pyrolyzed at 870°C	151	815	3.4	0.330	2.33	7.07	0.25		
	152	815	3.5	0.339	2.30	6.90	0.20	52	48
Not pyrolyzed	153	815	3.5	0.339	3.24	9.55	2.72	42	58
Partially pyrolyzed at 836°C	148	836	4.0	0.372	4.83	13.0	0.35	52	48
	149	838	3.8	0.335	4.93	14.7	0.55	52	48
	146	835	3.5	0.326	6.00	18.4	2.6	50	50
Not pyrolyzed	147	837	3.5	0.326	6.20	19.0	2.4		

quoted above were determined. Using the method of least mean squares we obtain for the assumed linear dependence of $\log K$ on $1/T$ the parameters of the equation

$$\log K = -\frac{E}{2.3RT} + \nu$$

shown in Table VI. The standard deviations listed in the second column show that the accuracy is not sufficient to distinguish definitely between the activation energies of the reaction proceeding at different speeds. The situation can, however, be clarified further by assuming that the temperature independent factor is the same for the decomposition of *one methyl group* in each of the four investigated hydrocarbons. We note that all the results can be represented on this basis within the experimental errors. Such a representation limits the possible values of the temperature independent factor for the decomposition of *one methyl group* to $\nu_0 = 2.0 \cdot 10^{13} - 2.5 \cdot 10^{13}$. We can make use of the choice of any particular value within this range for a more accurate determination of the differences between the activation energies of the four pyrolytic reactions.

Table VII shows the calculated values for energy of activation on the basis $\nu_0 = 2.0 \cdot 10^{13}$, the following equations were used:

$$E = 2.3 \cdot RT(13.3 - \log K) \text{ for toluene.}$$

$$E = 2.3 \cdot RT(13.6 - \log K) \text{ for xylenes.}$$

Calculations are based on experiments at low temperature.

From these results we conclude that the C—H bond energy is the same in toluene and meta-xylene, while it is smaller by 2.3–2.5 kcal. in para-xylene and by 3.5 kcal. in ortho-xylene. We may recall the observations of Dobryanskii and Saprykin¹⁰ on the relative stability of xylenes

TABLE VI.

Hydrocarbon	E kcal.	Mean deviation of $E = \Delta E$ kcal.	
toluene	77.3	± 1.3	$2 \cdot 10^{13}$
meta-xylene	77.1	± 1.9	$4 \cdot 10^{13}$
para-xylene	76.2	± 1.5	$5 \cdot 10^{13}$
ortho-xylene	74.8	± 1.1	$5 \cdot 10^{13}$

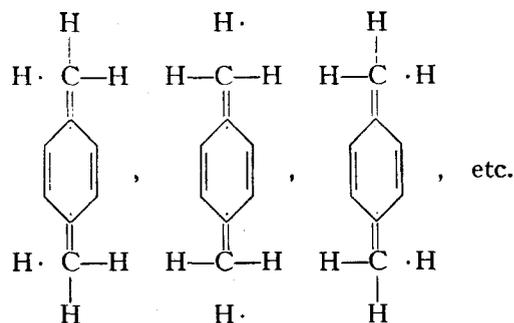
¹⁰ A. F. Dobryanskii and F. Y. Saprykin, J. Gen. Chem. (U.S.S.R.) 9, 1313 (1939).

TABLE VII.

No. of run	$T^\circ\text{C}$	E	ΔE
Toluene			
87	740	77.9	+0.4
88	741	77.9	+0.4
89	742	77.5	0.0
90	742	77.5	0.0
91	745	77.0	-0.4
92	749	77.1	-0.3
93	747	76.9	-0.5
94	738	78.3	+0.8
average 77.5 ± 0.14			
Meta-xylene			
101	760	77.0	-0.2
102	765	77.1	-0.1
105	767	77.4	+0.2
121	740	77.4	+0.2
122	741	77.4	+0.2
123	742	77.0	+0.2
average 77.2 ± 0.18			
Para-xylene			
130	746	74.9	+0.1
134	745	74.9	+0.1
135	745	74.9	+0.1
136	747	75.0	+0.2
137	783	74.5	-0.3
138	781	74.6	-0.2
average 74.8 ± 0.20			
Ortho-xylene			
156	730	73.9	-0.1
157	734	73.7	-0.3
155	777	74.9	+0.9
average 74.0 ± 0.55			

by pyrolytic isomerization. They found that meta-xylene was the most stable and did not isomerize, para-xylene isomerized only slightly to meta, while ortho-xylene isomerized very easily giving mainly meta- and partially para-xylene. These facts agree well with the sequence of activation energies derived above.

The weakening of the C—H bond in the methyl groups of para- and ortho-xylene as compared with toluene and meta-xylene was to be expected on the assumption of hyperconjugation occurring for example in para-xylene as follows:



The effect of hyperconjugation weakening in the C—H bond in C_2H_6 as compared with that in CH_4 has been estimated at 7 kcal.¹¹ A detailed discussion of the disparity between this value and that obtained for para-xylene seems premature in view of the inaccuracy of the results obtained up to date. But we would like to emphasize that in the case of the weakening of C—H bonds in para-xylene as compared with meta-xylene we can see no other possible explanation than hyperconjugation, whereas in the

¹¹ E. C. Baughan, M. G. Evans, and M. Polanyi, *Trans. Faraday Soc.* **37**, 377 (1941).

case of the weakening of the C—H bond in ethane as compared with methane, the proximity of the two interacting methyl groups offers additional possibilities—for example, steric effects or dipole interactions—of an explanation.

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Absorption of the Alkyl Cyanides in the Vacuum Ultraviolet*

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The vacuum ultraviolet spectra of methyl and ethyl cyanide have been determined in the region 1000A to 1800A. Three members of a Rydberg series were found for methyl cyanide starting at 1292A, the limit of the series corresponding to an ionization potential of 11.96 ev. Vibrational band changes which have been found to accompany the first two members have been assigned to fundamental frequencies of the molecule by comparison with Raman data. The electronic transition, expressed by the Rydberg series, was ascribed to excitation of a π electron in the triple bond. At higher pressures, a continuous absorption appeared which was followed only to 1600A. No structure could be observed in the spectrum of the ethyl cyanide, although it paralleled that of methyl cyanide in having a stronger absorption starting at 1342A and a weaker one appearing at higher pressures and spreading to longer wave-lengths.

INTRODUCTION

THE following communication contains a study of the absorption spectra of methyl and ethyl cyanides in the vacuum ultraviolet. Previously, Herzberg and Scheibe¹ studied the spectrum of methyl cyanide down to about 1540A, finding a weak band extending from 1820A to 1600A with a maximum at about 1670A. Below 1600A, there was an indication of the beginning of a stronger absorption which would extend to shorter wave-lengths. They also

observed the same indications in the spectra of the methyl halides. Price² extended this work on the halides to shorter wave-lengths and found discrete Rydberg series, assigning the excitation to the $p\pi$ electrons on the halide. From this it was felt that if the work on methyl cyanide were also extended to shorter wave-lengths, a Rydberg series might be identified.

EXPERIMENTAL

The far ultraviolet spectra were photographed on a Lyman continuum as a background, using hydrogen as the inert gas, by means of a vacuum spectrograph at nearly normal incidence. A lightly ruled glass grating was used, of focal length 1 meter, with 30,000 lines per inch, ruled by R. W.

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¹ G. Herzberg and G. Scheibe, *Zeits. f. physik. Chemie* **B7**, 390 (1930).

² W. C. Price, *J. Chem. Phys.* **4**, 539 (1936).