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Relative Reactivities of Some C–H Bonds in Hydrogen Abstraction by Methyl Radicals at 950 K

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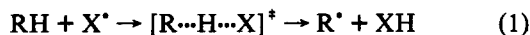
Received: August 23, 1993; In Final Form: November 3, 1993*

Relative reactivities of C–H bonds in alkylbenzenes in the hydrogen abstraction by methyl radicals at about 950 K were determined by means of labeled compounds. The following values normalized to the primary aliphatic C–H bond were obtained: $r_{\text{Ph-H}} = 0.7 \pm 0.1$; $r_{\text{Bz-H}} = 4.6 \pm 0.5$; $r_{\text{sec,benzyl}} = 8.7 \pm 1.0$; $r_{\text{tert,benzyl}} = 9.0 \pm 1.0$. The combination of these high-temperature values with low-temperature kinetic data from the literature reveals the absence of a straight connection between strength and reactivity of C–H bonds.

Introduction

Methyl radicals are among the most important radicals in hydrocarbon chemistry, particularly in reactions at elevated temperatures, such as pyrolysis and combustion. There is a lot of data in the literature describing the kinetics of methyl radical reactions in solution and in the gas phase at moderate temperatures.^{1–7} Tsang et al. have compiled and evaluated the presently available data on reactions with relevance to hydrocarbon pyrolysis and combustion covering a broad temperature range.⁸ This comprehensive data base is limited, however, to relatively simple hydrocarbons: methane,⁹ propane,¹⁰ isobutane,¹¹ and propene.¹² Aromatic hydrocarbons are not yet included. Even the most recent data collection of Baulch et al.¹³ for combustion modelling involves few reactions of aromatic hydrocarbons only. Relative reactivities of C–H bonds in aromatic hydrocarbons in the hydrogen abstraction reaction by methyl radicals at about 950 K are the subject of the present paper.

The bimolecular H abstraction



is one of the propagation steps in radical chain reactions. In order to describe the inter- and the intramolecular selectivity of X^* , it is profitable to use the concept of relative reactivities instead of absolute rate constants. The relative reactivity r of a particular C–H bond i in a molecule j that is attacked by a radical X^* is defined as a dimensionless relative rate constant:

$$r_{ij\text{X}} = \left\{ \frac{k_{ij}/m_{ij}}{k_{\text{stand}}/m_{\text{stand}}} \right\}_{\text{X}} \quad (2)$$

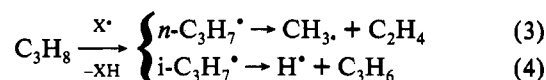
The absolute rate constant k_{ij} is related to the rate constant k_{stand} of a standard C–H bond, usually the primary aliphatic one. Both rate constants are normalized to one C–H bond, if more than one equivalent C–H bond (m_{ij} , m_{stand}) is present in the molecule. Relative reactivities are convenient tools to quantify the hydrogen-donating potential of hydrocarbons by summing up the reactivities of all the C–H bonds in the hydrocarbon molecule.

The experimental determination of relative reactivities is obviously much easier to perform and more precise than that of absolute rate constants. Imperfect measurement of radical concentration, residence time, and reaction temperature do not deteriorate the result. The change from a relative to an absolute base of reactivities is possible knowing only one reliable absolute

rate constant in the whole data set. Such a value can usually be found in the literature. Tsang gives $k_{\text{prim}} (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = 0.25 \times 10^{-24} T^{3.65} \exp(-3600/T)$ as a best approximation of the rate constant of the abstraction of one primary H atom in propane¹⁰ and in isobutane¹¹ by the methyl radical in the gas phase.

There are three principal methods to determine relative reactivities of C–H bonds at elevated temperatures:

(i) Measurement of the pattern of primary fragmentation products of the radicals R^* if this reflects unambiguously the position of the original radical center (no radical isomerization must occur), e.g., for propane (n_j as number of moles)



with

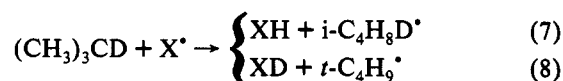
$$r_{\text{sec,propane}} = 3n_{\text{H}_2}/n_{\text{CH}_4} = 3n_{\text{C}_3\text{H}_6}/n_{\text{C}_2\text{H}_4} \quad (5)$$

(ii) Measurement of relative rate constants of the overall conversion of hydrocarbons as components of a feedstock mixture if the conversion is dominated by the bimolecular hydrogen abstraction. This holds true for saturated hydrocarbons in radical reactions having a sufficiently long chain, e.g., for the pyrolysis of a propane– n -butane mixture

$$k_{n\text{-butane}}/k_{\text{propane}} = [6r_{\text{prim}} + 4r_{\text{sec}}]/[6r_{\text{prim}} + 2r_{\text{sec}}] \quad (6)$$

Both methods cannot distinguish between different attacking radicals X^* .

(iii) Measurement of the intra- or intermolecular competition between different C–H bonds by use of labeled compounds ($^2\text{H} = \text{D}$, $^3\text{H} = \text{T}$) and the isotope analysis of the radical products (in the case of the methyl radical methane), e.g., for isobutane



with

$$r_{\text{tert,isobutane}} = 9(n_{\text{XD}}/n_{\text{XH}})(k_{\text{H}}/k_{\text{D}}) \quad (9)$$

Utility and limitations of these methods are discussed in more detail by Kopinke et al.¹⁴ The present investigation uses method (iii).

Experimental Section

All the hydrocarbons used were commercially available with a GC purity higher than 99%. Tritium-labeled benzene and

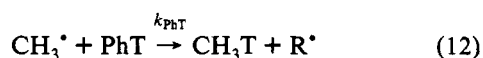
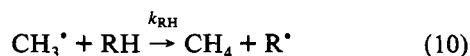
* Abstract published in *Advance ACS Abstracts*, January 1, 1994.

toluene were synthesized by hydrolysis of phenyl magnesium bromide and benzyl magnesium chloride, respectively, with HTO in etheric solution, followed by a preparative GC purification. Their specific activity amounted to 100 MBq/g. They were found to be radiochemically pure (>99.9 act %).

The pyrolysis experiments were conducted in a flow system with use of an electrically heated reactor tube of quartz glass ($4 \times 0.7 \times 200$ mm, $V_R \approx 0.3$ cm³) surrounded by a stainless steel tube and on-line coupled to a radio gas chromatograph.¹⁵ The apparatus worked in a pulse regime: 0.5–5 μ L of the feedstock was injected with a microsyringe into a hot carrier gas stream (2 L h⁻¹ He at 0.15–0.25 MPa), which passed the reactor tube with a residence time of about 0.1 s at the adjusted temperatures between 650 and 700 °C. The pyrolysis products were analyzed on packed columns (6 m \times 4 mm SE54 or 3 m \times 4 mm alumina for hydrocarbons \geq C₅ and 2 m \times 4 mm activated molecular sieve for methane). We used a double TCD as a mass detector and a flow proportional counter tube (10 cm³) as a radioactivity detector.

Kinetic Data Acquisition

Pyrolysis experiments with labeled benzene used the competitive reactions 10–12 with RH as any hydrogen donor in the mixture



except benzene. It is a safe assumption that all the methane is formed by bimolecular hydrogen abstraction of the methyl radical. The division of the rate laws for the formation of unlabeled and labeled methane gives

$$\frac{dn_{\text{CH}_4}}{dn_{\text{CH}_3\text{T}}} = \frac{k_{\text{benzene}}n_{\text{benzene}} + k_{\text{RH}}n_{\text{RH}}}{k_{\text{PhT}}n_{\text{PhT}}} \quad (13)$$

If the conversion of the feedstock components is kept low (<25%), i.e., all n_i can be considered approximately constant, then integration of eq 13 gives

$$\frac{n_{\text{CH}_4}}{n_{\text{CH}_3\text{T}}} = \frac{k_{\text{benzene}}n_{\text{benzene}} + k_{\text{RH}}n_{\text{RH}}}{k_{\text{PhT}}n_{\text{PhT}}} \quad (14)$$

and by transformation

$$\frac{n_{\text{CH}_4}n_{\text{PhT}}}{n_{\text{CH}_3\text{T}}n_{\text{benzene}}} = \frac{1}{\alpha} = \frac{k_{\text{RH}}}{k_{\text{PhT}}} \frac{n_{\text{RH}}}{n_{\text{benzene}}} + \frac{k_{\text{benzene}}}{k_{\text{PhT}}} \quad (15)$$

Equation 15 is well suited for a linear regression. It contains two variables which are measured with the radio GC device: the molar radioactivity of the formed methane relative to that of benzene, named α , and the molar ratio of the hydrocarbon RH and benzene in the feedstock. This ratio is varied as the independent variable within one series of experiments. The regression parameters in eq 15 are the ratio $k_{\text{benzene}}/k_{\text{PhT}}$, which is in fact equal to 6 times the kinetic isotope effect (KIE) $k_{\text{PhH}}/k_{\text{PhT}} = k_{\text{benzene}}/6k_{\text{PhT}}$, and the relative rate constant $k_{\text{RH}}/k_{\text{PhT}}$. The latter one contains the actual information on the reactivity of C–H-bonds in the hydrocarbon RH. Under the worst conditions, the approximated value of the intersection can be very erroneous. Therefore, a transformed version of eq 15 was used to calculate the KIE, whereby $k_{\text{benzene}}/k_{\text{PhT}}$ is obtained from the slope of a straight line.

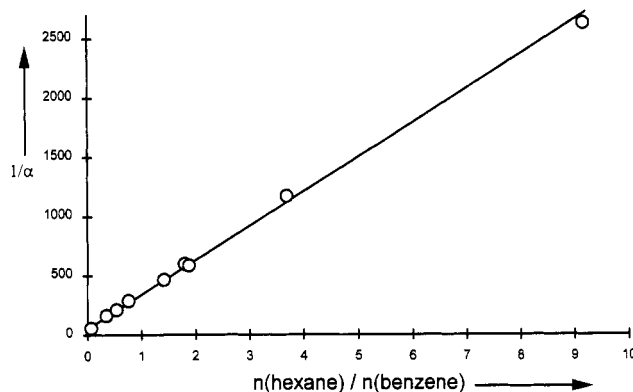


Figure 1. Pyrolysis of tritium-labeled benzene-hexane mixtures.

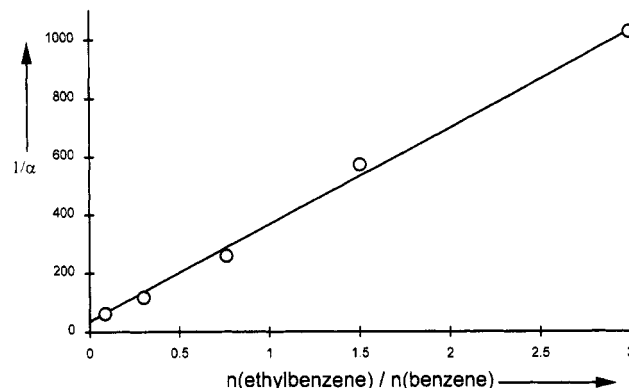


Figure 2. Pyrolysis of tritium-labeled benzene-ethylbenzene-hexane mixtures.

The strategy of hydrogen labeling has been extensively used by several groups of researchers in order to measure the hydrogen donation potential of organic compounds. The problems resulting from an extension of the method to higher reaction temperatures consist in the selection of well defined reaction channels. The basic eq 13 only holds if there is no other way but reaction 12 for the tritium input into methane. Benzene is the ideal tritium donor with respect to its high thermal stability and the very low probability of conversion of an aromatic methine group to methane. In case that the hydrogen donor RH does not generate enough methyl radicals by its spontaneous decomposition *n*-hexane (30–50% of RH) was added as a methyl source. Then eq 15 has to be modified because *n*-hexane reacts as a hydrogen donor too

$$\frac{1}{\alpha} = \frac{k_{\text{RH}} + k_{\text{hexane}}(n_{\text{hexane}}/n_{\text{RH}})}{k_{\text{PhT}}} \frac{n_{\text{RH}}}{n_{\text{benzene}}} + \frac{k_{\text{benzene}}}{k_{\text{PhT}}} \quad (16)$$

$k_{\text{RH}}/k_{\text{PhT}}$ can easily be recalculated from the slope of the regression line if $k_{\text{hexane}}/k_{\text{PhT}}$ is known and the ratio $n_{\text{hexane}}/n_{\text{RH}}$ is kept constant during variation of $n_{\text{RH}}/n_{\text{benzene}}$.

The effect of reaction products on the absolute rate of pyrolysis, which can be greatly accelerating or inhibitory, is insignificant for the results of the labeling technique, because relative rates are measured.

Results

All pyrolysis experiments with tritium-labeled benzene were carried out in the temperature range 930–970 K in such a way that the conversion of tritium in benzene did not exceed 0.5% and the conversion of the aromatic hydrogen donors (toluene, xylenes, etc.) did not exceed 25%. Figures 1–3 and Table 1 present results of tracer experiments.

The linear relationship according to eq 16 holds over the entire range of feedstock composition ($n_{\text{RH}}/n_{\text{benzene}} \approx 0.05$ –10). The KIE, however, which is assumed to be independent of the hydrogen donor, scatters considerably (4.6–7.9).

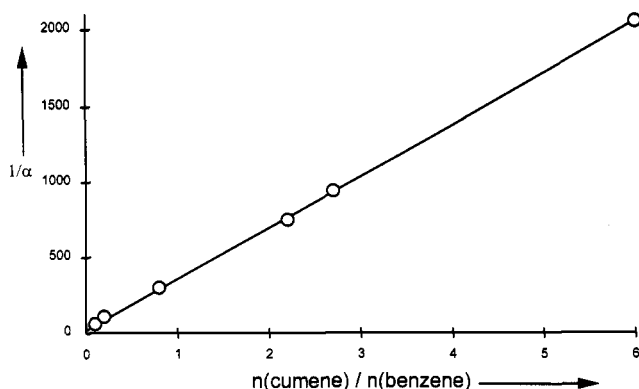


Figure 3. Pyrolysis of tritium-labeled benzene-cumene-hexane mixtures.

TABLE 1: Relative Rate Constants of Hydrogen Abstraction by Methyl Radicals at about 950 K

hydrocarbon RH	k_{RH}/k_{PhT}	k_{PhH}/k_{PhT}	type of C-H bond	rel reactivity ^a
<i>n</i> -hexane	281 ± 5^b	6.5 ± 0.3	Ph-H	0.68 ± 0.1
	301 ± 10^c	4.6 ± 0.5	Ph-H	0.72 ± 0.1
isooctane	283 ± 7	4.8 ± 0.6	Ph-H	0.69 ± 0.1
toluene	162 ± 6	5.6 ± 0.4	PhCH ₂ -H	4.9 ± 0.5
<i>o</i> -xylene	289 ± 22	7.4 ± 0.9	<i>o</i> -MePhCH ₂ -H	4.9 ± 1.0
<i>m</i> -xylene	276 ± 25	7.9 ± 1.5	<i>m</i> -MePhCH ₂ -H	4.7 ± 1.0
<i>p</i> -xylene	238 ± 9	7.6 ± 0.1	<i>p</i> -MePhCH ₂ -H	4.0 ± 0.5
ethylbenzene	214 ± 8	5.6 ± 0.6	PhCH(CH ₃)-H	8.7 ± 1.0
cumene	165 ± 2	6.2 ± 0.2	PhC(CH ₃) ₂ -H	9.0 ± 1.0

^a Related to the reactivity of a primary aliphatic C-H bond. ^b One standard deviation. ^c Replicate with another charge of labeled benzene.

The way to extract relative reactivities r_{ij} of particular C-H bonds i in RH_{*j*} from the measured relative rate constants k_{RH}/k_{PhT} is as follows:

$$\frac{k_{RH}}{k_{PhT}} = \frac{k_{RH}}{k_{hexane}} \frac{k_{hexane}}{k_{PhT}} = \frac{(\sum_i m_i r_i)_{RH} k_{prim}}{31.6 k_{prim}} \times 281 = \frac{281}{31.6} (\sum_i m_i r_i)_{RH} \quad (17)$$

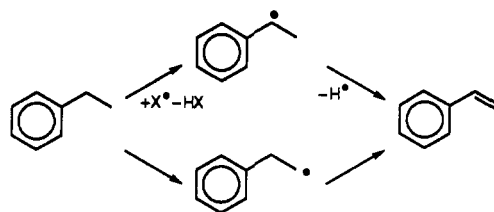
The values 31.6 and 281 result from $(\sum_i m_i r_i)_{hexane} = 6 \times 1 + 8 \times 3.2 = 31.6$ (with $r_{sec,aliphatic} = 3.2$)¹⁴ and k_{hexane}/k_{PhT} from Table 1, respectively. In the same way, isooctane can be used as H donor with known reactivity: $(\sum_i m_i r_i)_{isooctane} = 15 \times 1 + 2 \times 3.2 + 1 \times 10.0 = 31.4$. If all the r_i except one in the hydrogen donor RH are known, the unknown r_i can be calculated resolving the sum in eq 17. The procedure works reasonably only if the unknown C-H bond contributes substantially to the hydrogen donation potential of the molecule. This likely holds for benzylic C-H bonds in alkylbenzenes. Nonbenzylic primary C-H bonds in ethylbenzene and cumene were assumed to be as reactive as ordinary aliphatic ones, i.e., $r_{prim} = 1.0$, and the phenylic C-H bonds in the alkylbenzenes as reactive as those in the unsubstituted benzene, i.e., $r_{PhH} = 0.7$. r_{PhH} was calculated with an average of the KIE = 6.2 according to

$$r_{PhH} = \left(\frac{k_{PhH}}{k_{PhT}} \times \frac{k_{hexane}}{k_{prim}} \right) : \left(\frac{k_{hexane}}{k_{PhT}} \right) = (6.2 \times 31.6) : (281) = \frac{k_{PhH}}{k_{prim}} = 0.68 \quad (18)$$

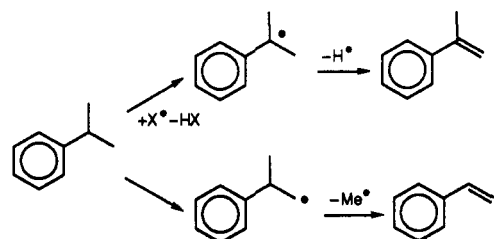
The same r_{PhH} value is obtained with isooctane instead of hexane.

It is always interesting to compare relative reactivities determined from an intermolecular competition with those from an intramolecular competition. Ethylbenzene is not accessible to such an approach because the primary as well as the benzylic radical will fall into styrene (Scheme 1).

SCHEME 1



SCHEME 2



Cumene offers a better chance to reveal the position of the primary attack from the products ratio (Scheme 2).

The molar ratio of styrene to α-methylstyrene, both formed from cumene at low degrees of conversion, should be a reasonable measure of the corresponding C-H bond reactivities. At 950 K a ratio of 2.1 yields

$$r_{tert,benzyl} = 6 \frac{n_{styrene}}{n_{methylstyrene}} = 12.6 \quad (19)$$

This value is in reasonable conformity with that from the tracer experiments ($r_{tert,benzyl} = 9.0 \pm 0.5$). Bach et al.¹⁶ give the primary products composition of the pyrolysis of some isoalkylbenzenes. At about 950 K (10% conversion) they found 20% α-methylstyrene and 40% styrene from cumene which is in good conformity with our results. The more complex deconvolution of the pyrolysis products of *n*-octylbenzene¹⁷ leads to a ratio $r_{sec,benzyl}:r_{sec,aliphatic} \approx 2.8$ which is in excellent conformity with our direct measurement (Table 2, $r_{sec,benzyl}:r_{sec,aliphatic} = 8.7:3.2 = 2.75$). One should take into consideration that product patterns reflect always the selectivity of the pool of all β-radicals, not of one special radical.

Discussion

The latest study on the reactivity of benzene and toluene in the intermediate temperature range (650–770 K) has been performed by Back et al.¹⁸ Their method is based on the competition between ethylene, which generates, among others, methyl radicals, and an added H donor. The measured relative rate constants are related to the hydrogen abstraction from ethylene. Taking the Arrhenius parameters estimated by the authors for the attack of the methyl radical on benzene ($E_A = 63 \text{ kJ mol}^{-1}$), toluene ($E_A = 29 \text{ kJ mol}^{-1}$), and cyclopentane ($E_A = 36 \text{ kJ mol}^{-1}$) one obtains the following relative rate constants

$$\text{at 770 K: } k_{benzene} = 0.15 k_{cyclopentane}, \quad k_{toluene} = 0.38 k_{cyclopentane}$$

$$\text{at 950 K: } k_{benzene} = 0.33 k_{cyclopentane}, \quad k_{toluene} = 0.31 k_{cyclopentane}$$

Normalization to the reactivity of a primary aliphatic C-H bond (with $r_{sec,cyclopentane} = 4.0$ and 2.8 at 770 and 950 K, respectively)¹⁴ gives $r_{PhH} = 1.0$ (770 K) to 1.65 (950 K) and $r_{BzH} = 3.3$ (770 K). The measured reactivity of toluene as a H donor at 950 K can be completely accounted for by its five phenylic C-H bonds ($k_{toluene}/k_{benzene} = 0.31/0.33 \approx 5/6$). It does not remain a significant contribution of the benzylic C-H bonds in toluene! Obviously, the kinetic data of Back et al. do not permit an extrapolation to higher reaction temperatures.

TABLE 2: Kinetic Data of Hydrogen Abstraction by Methyl Radicals

type of C-H bond	$\log A$ ($M^{-1} s^{-1}$) ^a	E_A ($kJ mol^{-1}$) ^a	r at 350 K (calcd) ^a	r at 950 K (measd) ^b	ΔE_A^c ($kJ mol^{-1}$)	D_{C-H} ($kJ mol^{-1}$)
aliphatic						
primary	9.0	55.4	1.0	1.0	0	422 [ref 24]
secondary	9.2	52.2	4.8	3.2 [ref 14] 3.3 [ref 10]	1.9	411 [ref 25]
tertiary	9.4	46.1	61	10.0 [ref 14] 6.4 [ref 11]	8.3	401 [ref 26]
benzylic						
primary	8.0	40.7	15.6	4.9	5.3	369 [ref 27]
secondary	8.2	37.8	69	8.7	9.5	359 [ref 27]
tertiary	8.4	35.7	204	9.0	14.4	354 [ref 27]
phenylic			0.7 ^d –1.2 ^e	0.7	0	464 [ref 27]

^a From ref 6. ^b This work. ^c $\Delta E_A = E_{A,prim\ aliphatic} - E_{A,R-H}$ recalculated from r values in columns 4 and 5. ^d From ref 20. ^e With $r_{PhH}/r_{BzH} = 0.067$ –0.082 at 373 K.¹

Besides their own values, the authors discussed compiled literature data in the temperature range 450–770 and 350–1250 K. We extracted from these data average Arrhenius parameters:

$$\log k_{benzene} = 8.3 - 47000/2.3RT = 5.85 M^{-1} s^{-1} \text{ at } 1000 \text{ K}$$

$$\log k_{toluene} = 9.2 - 45000/2.3RT = 6.85 M^{-1} s^{-1} \text{ at } 1000 \text{ K}$$

The resulting difference between the activation energies (2 $kJ mol^{-1}$) is much lower than could be expected from the strength of the attacked C–H bonds ($D_{PhH} = 464 kJ mol^{-1}$, $D_{BzH} = 369 kJ mol^{-1}$), even if one takes into consideration that the toluene is attacked at both types of C–H bonds. According to the k values at 1000 K as calculated above, the contribution of the benzylic C–H bonds is quite dominant in toluene. Taking the non-Arrhenius expression for k_{prim} recommended by Tsang,^{10,11} one can estimate the following relative reactivities at 1000 K: $r_{PhH} = 0.3$ and $r_{BzH} = 6.4$. Although these values are based on independent absolute rate constants and are uncertain within a factor of 3 at least, they give a reasonable rank of reactivity which is close to the results of our relative measurements (Table 1; $r_{PhH} = 0.7$ and $r_{BzH} = 4.9$).

Recently, Freund and Olmstead published a modeling study on the pyrolysis of *n*-butylbenzene.¹⁹ Calculation of relative reactivities from their master set gives $r_{sec,aliphatic,Me} = 3.3$ and $r_{sec,benzylic,Me} = 5.6$ at 950 K. The difference between the corresponding activation energies is assumed as 4 $kJ mol^{-1}$ only! The attack of radicals on the phenylic C–H bond is not included in the model.

Another way to extract Arrhenius parameters is to combine the more certain data from the low-temperature region with our relative reactivities determined at 950 K. Fundamental low-temperature studies are from Berezin et al.,²⁰ Szwarc et al.,²¹ and Pryor et al.²² A comprehensive compilation of kinetic data for hydrogen abstraction in the liquid phase is given in ref 1. We use here the data collected and evaluated in the review of Hendry et al.⁶ Unfortunately, the attack on phenylic C–H bonds is not considered there, but k_{prim} is in excellent conformity with the more recent recommendation of Tsang^{10,11} in the low-temperature region. Table 2 presents a compilation of relative reactivities at 350 K calculated from Hendry's Arrhenius parameters and those measured in the present study at 950 K. The ΔE_A values in Table 2 are calculated using these two supporting points. Such an approach seems to be risky, but it does not suppose a linear Arrhenius behavior of the abstraction reactions. Only the difference between the activation energies is supposed to be approximately constant.

The resulting ΔE_A values are much lower than expected from the corresponding bond dissociation energies. A ΔD_{C-H} value of 95 $kJ mol^{-1}$ between the phenylic and the benzylic C–H bond results in a ΔE_A of only 5 $kJ mol^{-1}$ which is far from the prediction of the Evans–Polanyi relation in the form $\Delta E_A = 0.609\Delta D_{C-H}$.²³ It is well-known, however, that LFE relationships of that type

hold within a homologous series only. It fails if the type of the attacked bond varies. Though we have some doubts on the validity of the estimated ΔE_A values, the conclusions drawn from the data in Table 2 and from averaged literature kinetic data (see the compilation of Back et al.¹⁸) are consistent: the difference between the activation energies of abstraction of phenylic and benzylic hydrogen atoms by the methyl radical is very low.

The influence of a phenyl substituent on the rate of a hydrogen abstraction can be considered as composed of two contrary effects: (i) the resonance stabilization of the transition state and (ii) its stiffening. The first contribution decreases the activation energy, and the entropic effect lowers the preexponential factor. Therefore, the net effect will have a strong temperature dependence in such a way that the promoting effect on the reaction rate dominates at low temperatures, while the retarding effect prevails at high temperatures. The results confirm this view.

Regarding the relative reactivities of different types of C–H bonds the most striking feature is that the phenyl substituent loses its promoting effect on the reactivity of a benzylic C–H bond at 950 K the more the alkyl group is branched. The reactivities of a tertiary aliphatic and a tertiary benzylic C–H bond are equal. Apparently, the resonance stabilization of the transition state is not very effective. Recently, Tanko and Mas discussed the relative importance of kinetic versus thermodynamic factors in α -hydrogen atom abstraction from alkylaromatics.²⁸ If the aromatic skeleton is bulky, e.g., in 9-alkylanthracenes, stereoelectronic factors, specifically a hindered alignment of the α -C–H bond with the aromatic π -system, can significantly influence the reactivity. For monoalkylbenzenes, such as cumene, a stereoelectronic resonance inhibition is, however, less probable. It has been known for more than 20 years that the ability of a phenyl substituent to activate C–H bonds more than a methyl substituent falls off as the reactivity of the system increases. This increase in reactivity applies to tertiary C–H bonds. The explanation given by Russell⁷ is based on the Hammond postulation: the higher the exothermicity of the reaction, the earlier the transition state, the less preformed the incipient radical, the less effective its resonance stabilization can be. Our results clearly illustrate the more general assertion that the reactivity of C–H bonds depends on other factors besides their bond strength. This holds true even for reactions in pure hydrocarbon systems where polar factors can be assumed as negligible.

A second methyl group at the aromatic ring has no significant influence on the reactivity of the first one. Benzylic C–H bonds in toluene and in xylenes have the same reactivity within the range of experimental error. This result is in full conformity with conclusions of Barton and Stein²⁹ about the stability of substituted benzyl radicals, who estimated a decrease in E_A of 1.3–1.7 $kJ mol^{-1}$ for the unimolecular formation of *m*- or *p*-methylbenzyl over unsubstituted benzyl radicals from the corresponding ethylbenzenes. If the resonance stabilization of the transition state is not well developed, minor changes in the

aromatic system will be, of course, even less important. Furthermore, there is no specific ortho effect observable in *o*-xylene.

The reactivity of the phenylic C–H bond is very near to that of a primary aliphatic one at low as well as at high reaction temperatures despite the great difference in bond strengths. This phenomenon needs an explanation. It is important insofar as the abstraction of phenylic hydrogen is often underestimated or even neglected. The intermediate formation of phenyl radicals is masked because of the dominance of its hydrogen abstraction instead of decomposition. Actually, benzene is about as reactive as ethane as a hydrogen donor and toluene; e.g., is attacked by about 20% at the aromatic ring at 1000 K.

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