(17) J. Landauer and H. McConnell, *J. Am. Chem. Soc.*, **74**, 1221 (1952); D. M. G. Lawrey and H. McConnell, *J. Am. Chem. Soc.*, **74**, 6175 (1952).
(18) D. A. Deranleau, *J. Am. Chem. Soc.*, **91**, 4050 (1969).
(19) R. Foster, "Molecular Complexes", Vol. 2, R. Foster, Ed., Elek Science, London; Crane Russak, New York, 1974, Chapter 3.
(20) R. Foster and N. Kulevsky, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1427 (1973).
(21) B. Dodson, R. Foster, A. A. S. Bright, M. I. Foreman, and J. Gorton, *J. Chem. Soc, B*, 1283 (1971).
(22) W. C. Herndon, J. Feuer, and R. E. Mitchell, *J. Chem. Soc., Chem. Commun.*, 435 (1971).
(23) K. H. Michaelian, K. E. Rieckhoff and E.-M. Voigt, *J. Phys. Chem.*, **81**, 1489 (1977).
(24) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).
(25) L. E. Orgel and R. S. Mulliken, *J. Am. Chem. Soc.*, **79**, 4839 (1957).
(26) J. Grundnes and S. D. Christian, *J. Am. Chem. Soc.*, **90**, 2239 (1968).
(27) M. Tamres and J. Grundnes, *J. Am. Chem. Soc.*, **93**, 801 (1971).
(28) M. Tamres and R. L. Strong, "Molecular Association", Vol. 2, R. Foster, Ed., Academic Press, London, 1979, Chapter 5.
(29) O. B. Nagy, M. W. Muanda, and J. B. Nagy, *J. Chem. Soc., Faraday Trans. 2*, **74**, 2210 (1978).
(30) R. J. Laub and J. H. Purnell, *J. Am. Chem. Soc.*, **98**, 35 (1976).
(31) R. J. Laub and C. A. Wellington, "Molecular Association", Vol. 2, R. Foster, Ed.; Academic Press, London, 1979, Chapter 3.
(32) K. Morokuma, *Acc. Chem. Res.*, **10**, 294 (1977).
(33) See, for example, "The Exciplex", M. Gordon and W. R. Ware, Ed., Academic Press, New York, 1975; M. Ottolenghi, *Acc. Chem. Res.* **6**, 153 (1973); N. Mataga and M. Ottolenghi in "Molecular Association", Vol. 2, R. Foster, Ed., Academic Press, New York, 1979.
(34) Th. Förster and K. Kasper, *Z. Phys. Chem. (Frankfurt am Main)*, **1**, 19 (1954).
(35) H. Leonhardt and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **67**, 791 (1963).
(36) R. Postashnik and M. Ottolenghi, *Chem. Phys. Lett.*, **6**, 525 (1970).
(37) H. Knibbe, Dissertation, Vrije Universiteit te Amsterdam, 1969, quoted by T. Förster in "The Exciplex", M. Gordon and W. R. Ware, Ed., Academic Press, New York, 1975, p 9.
(38) (a) K. B. Eisenthal, *J. Chem. Phys.*, **62**, 2213 (1975); (b) *Acc. Chem. Res.*, **8**, 118 (1975).
(39) H. Beens and A. Weller, *Chem. Phys. Lett.*, **2**, 140 (1968); T. Mimura and M. Itoh, *J. Am. Chem. Soc.*, **98**, 1095 (1976); T. Mimura, M. Itoh, T. Ohta, and T. Okameto, *Bull. Chem. Soc. Jpn.*, **50**, 1665 (1977).
(40) M. Yoshida, H. Tatemitsu, Y. Sakata, S. Misumi, H. Masuhara, and N. Mataga, *J. Chem. Soc., Chem. Commun.*, 587 (1976).
(41) K. A. Zachariasse and Kühnle, *Z. Phys. Chem. (Frankfurt am Main)*, **101**, 267 (1976).
(42) B. Mayoh and C. K. Prout, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1072 (1972).
(43) E. g., H. A. Staab and C. P. Herz, *Angew. Chem., Int. Ed. Engl.*, **16**, 799 (1977).
(44) H. A. Staab and C. P. Herz, *Angew. Chem., Int. Ed. Engl.*, **16**, 393 (1977).
(45) H. M. Powell and G. Huse, *Nature (London)*, **144**, 177 (1939).
(46) F. H. Herbstein and J. A. Snyman, *Phil. Trans. R. Soc., Ser. A*, **264**, 239 (1969). See also F. H. Herbstein in "Perspectives in Structural Chemistry", Vol. 4, J. D. Dunitz and J. A. Ibers, Ed., Wiley, New York, 1971, p 166.
(47) C. A. Fyfe, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1633 (1974).
(48) C. A. Fyfe, D. Harold-Smith, and J. Ripmeester, *J. Chem. Soc., Faraday Trans. 2*, **73**, 2269 (1977).
(49) C. A. Fyfe, unpublished work.
(50) R. M. Shaffert, *IBM J. Res. Develop.*, **15**, 75 (1971).
(51) B. Scrosati, M. Torroni, and A. D. Butherus in "Power Sources", Vol. 4. "Research and Development in Non-mechanical Electrical Power Sources". 8th International Power Resources Symposium, Brighton, U.K., 1972, D. H. Collins, Ed., Oriel Press, 1973, p 453.
(52) A. A. Schneider, W. Greatbatch, and R. Read, paper presented at the 9th International Power Resources Symposium, Brighton, U.K., 1974.
(53) E.g., A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, **7**, 232 (1974).
(54) E. P. Kyba, R. C. Helgeson, K. Madan, G. W. Gokel, T. L. Tarnowski, S. S. Moore, and D. J. Cram, *J. Am. Chem. Soc.*, **99**, 2564 (1977).
(55) M. Grätzel in "Micellation, Solubilization and Microemulsions", Vol. 2, K. L. Mittal, Ed., Plenum, New York, 1977, p 531.
(56) From the ^{13}C shifts due to the aromatic carbons of the hexamethylbenzene moiety in a number of EDA complexes compared with that for solid hexamethylbenzene itself, the degree of electron transfer in the ground state of the complexes in the solid state has been estimated at $\leq 10\%$. This is in good general agreement with earlier estimates based on various solution experiments (W. G. Blann, C. A. Fyfe, J. R. Lyerla, and C. S. Yannoni, unpublished work).

Pyrolysis of Alkyl Benzenes. Relative Stabilities of Methyl-Substituted Benzyl Radicals

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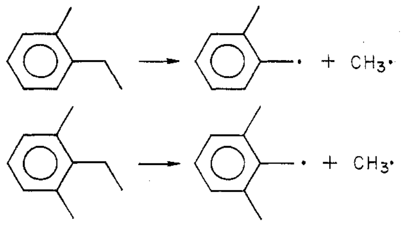
Decomposition rates for β C–C bond scission in several methyl-substituted ethylbenzenes were measured in a very low pressure pyrolysis (VLPP) system from 1050 to 1200 K, and relative stabilities of the resulting substituted benzyl radicals were derived. Relative to ethylbenzene, rates were highest for *o*-methyl-substituted ethylbenzenes, and little affected by meta and para substitution. Activation energy differences were approximately separable into ortho and nonortho contributions, amounting to a lowering of the activation energy, relative to ethylbenzene, of 1.3–1.7 kJ mol^{-1} per *m*- or *p*-CH_3, and 5.0–6.3 kJ mol^{-1} per *o*-CH_3. Rate differences were explained in terms of a partial relaxation of steric interaction in the activated complex. Methyl inductive effects were found to be very small, amounting to a decrease of <1.7 kJ mol^{-1} per CH_3 in the Gibbs energy of formation of the radicals produced.

Introduction

The effect of substituents on the properties of aromatic compounds has traditionally played an important role in organic chemistry. Much effort has been expended toward reducing the bulk of empirical information concerning substituent effects into systematic relationships. In an attempt to discover thermodynamic factors of influence in reactions of aromatic free radicals, our laboratory has been investigating the effect of substituents on the kinetics of decomposition in aromatic compounds. We present here the results of very low pressure pyrolysis (VLPP) studies completed for a series of methylethylbenzenes and dimethylethylbenzenes.

The chemical reactions reported here involve β C–C bond fission, as exemplified in eq 1 and 2 for two of the



compounds. The kinetics of β C–C bond fission for methyl-substituted ethylbenzenes has not been previously reported. However, some studies have been reported relating to the bond strengths in substituted toluenes and benzyl bromides. We summarize below the information available on bond strengths in these compounds.

Szwarc has studied the kinetics of C–H bond fission in toluene and the three xylenes and deduced bond dissociation energies of 324.3 kJ mol^{-1} for toluene and *m*-xylene, 313.8 kJ mol^{-1} for *p*-xylene, and 309.6 kJ mol^{-1} for *o*-xylene.[1] Hyperconjugation was invoked to explain the decreased bond energies in *o*- and *p*-xylene. Later investigators found good agreement with Szwarc's results for *p*-xylene.[2,3] However, Benson has suggested that the rates for *o*-xylene decomposition may be too high, hence derived bond dissociation energies too low, because of contibutions from chain decomposition.[4]

A number of methyl-substituted benzyl bromide decompositions have been investigated by Szwarc and coworkers. They found the C–Br bond dissociation energy in *m*-xylyl bromide to be the same as that in benzyl bromide, but lower for *o*-xylyl and *p*-xylyl by 8.4 and 5.8 kJ mol^{-1}, respectively.[5] These results are in agreement with previous results for toluene and the xylenes.[1] The authors suggested increased resonance energy in *o*- and *p*-xylyl radicals to explain the results but expressed some reservation due to "peculiarities" encountered in the pyrolysis of *p*-xylyl bromide. In a later paper, it was found that decomposition rates for benzyl bromide and *p*-xylyl bromide were essentially the same in the lower temperature range.[6] The discrepancy was believed to arise from impurities in the *p*-xylyl bromide in the earlier study.

There exists a substantial amount of information concerning H-atom abstraction rates in the liquid phase for methyl-substituted benzenes. Meyer, Stannett, and Szwarc found essentially identical abstraction rates for toluene, the xylenes, and mesitylene with methyl radicals.[7] These authors also summarized results from previous investigators involving ROO·,[8] *t*-BuO·,[9] and CCl_3·[10] radicals. The collective results show fair agreement, although the data for ROO· radical gave relative abstraction rates of 1.9, 1.6, 1.15, and 1.00 for mesitylene, *p*-xylene, *m*-xylene, and toluene, respectively. In all of the studies, abstraction rates for *p*-xylene are slightly (ca. 10–20%) higher than for the other compounds. Sanders and Rebbert also studied H-atom abstraction from the xylenes by methyl radicals.[11] The observed order of reactivity was *o*-xylene > *m*-xylene > *p*-xylene > toluene. However, Pearson and Szwarc have contended that these data indicate little if any difference in reactivity, the apparent differences being due to systematic error and experimental uncertainty.[12] Bridger and Russell studied H-atom abstraction by phenyl radicals for numerous hydrocarbons.[13] They reported relative abstraction rates of 9.0, 13.2, and 9.4 for toluene, *p*-xylene, and mesitylene, respectively.

The present situation can be summarized as follows. There seems to be agreement on the approximate equality of bond strengths within 4 kJ mol^{-1} for C–H bonds in toluene, *m*-xylene, and mesitylene and for benzylic C–Br bonds in benzyl and *m*-xylyl bromide. Hence, *m*-methyl substitution appears to have little effect on the stabilities of benzyl radicals. Decomposition data indicate a weaker C–H bond in *p*-xylene than in toluene, whereas *p*-xylyl bromide decomposition rates indicate a C–Br bond strength equal to, or very slightly weaker than, the C–Br bond strength in benzyl bromide. Finally, *o*-xylene and *o*-xylyl bromide decompositions occur faster than toluene and benzyl bromide, respectively, although H-atom abstraction rates are nearly the same for *o*-xylene, *p*-xylene, and toluene. Thus, the relative stabilities of *o*- and *p*-methyl-substituted benzyl radicals is unclear. The present study substantially clarifies the subject of bond strengths in substituted benzenes because of the precision available in comparative VLPP experiments.

TABLE I: Results of Flow Study for 13DM2EB at 1117 K

flow rate, molecules s^{-1}	% decomposition (decrease in parent peak)
4×10^{13}	53 ± 18
2×10^{14}	53 ± 5
2×10^{15}	51 ± 4

Experimental Section

Apparatus. General operating principles of very low pressure pyrolysis (VLPP) have been reviewed previously.[14] The VLPP apparatus is described elsewhere.[15] The fused silica reactor used was the same as that used in previous experiments[16] and had a collision number of 1160 and an escape aperture of area 9.08 mm^2.

Reagents. All reagents were obtained from Chemical Samples Co. with the following stated purities: 1-ethyl-2-methylbenzene (99.9%), 1-ethyl-3-methylbenzene (99%), 1-ethyl-4-methylbenzene (99.9%), 1,3-dimethyl-2-ethylbenzene (99%), 1,4-dimethyl-2-ethylbenzene (99.8%), and 1,3-dimethyl-5-ethylbenzene (99.7%). These compounds were used without further purification.

Results

Examination of the mass spectra of reactant and products for 1-ethyl-2-methylbenzene (1E2MB), 1-ethyl-3-methylbenzene (1E3MB), and 1-ethyl-4-methylbenzene (1E4MB) indicated the expected β C–C bond scission as in eq 1. For 50% decomposition, increases in m/e 15 (CH_3) and m/e 105 (C_8H_9) corresponded well with decreases in the parent peak at m/e 120 (C_9H_{12}). No evidence of molecular H_2 or CH_4 elimination from any pyrolysis was detected. Minor product peaks were detected at m/e 104 and 106 that we attribute to secondary reaction of the methylbenzyl radicals. Similar observations were made for 1,3-dimethyl-2-ethylbenzene (13DM2EB), 1,4-dimethyl-2-ethylbenzene (14DM2EB), and 1,3-dimethyl-5-ethylbenzene (13DM5EB). However, for pyrolyses of these molecules, relative differences were found in the product spectra at m/e 118 (C_9H_{10}) and 119 (C_9H_{11}), as illustrated by the following m/e 118/119 ratios at 14 eV: 13DM2EB (1.0), 14DM2EB (2.9), 13DM5EB (0.2). The differences are believed to arise from the formation of xylylenes either by secondary reaction or within the ionizing region of the mass spectrometer, as suggested by Levy, Szwarc, and Throssell.[6]

The conversion of observed mass spectral intensity to the low pressure unimolecular rate constant, k_{uni}, has been described previously.[14] The reactor escape rate $k_e/s^{-1} = 4.0(T/M)^{1/2}$ includes a Clausing factor correction as described previously.[16]

Decomposition rates of 13DM2EB were found to be independent of flow rate between 4×10^{13} and 2×10^{15} molecules s^{-1}, as illustrated by the data in Table I. VLPP studies for the ethylmethylbenzenes were carried out in the temperature range 1070–1200 K and a flow rate of 8×10^{13} molecules s^{-1}; percent decomposition ranged from 11 to 69%. Studies for the dimethylethylbenzenes were carried out in the temperature range 1050–1198 K and a flow rate of 2×10^{14} molecules s^{-1}; percent composition ranged from 13% to 80%.

The experimental data are presented for the ethylmethylbenzenes in Figure 1 and for the dimethylethylbenzenes in Figure 2. RRKM fits to the experimental data

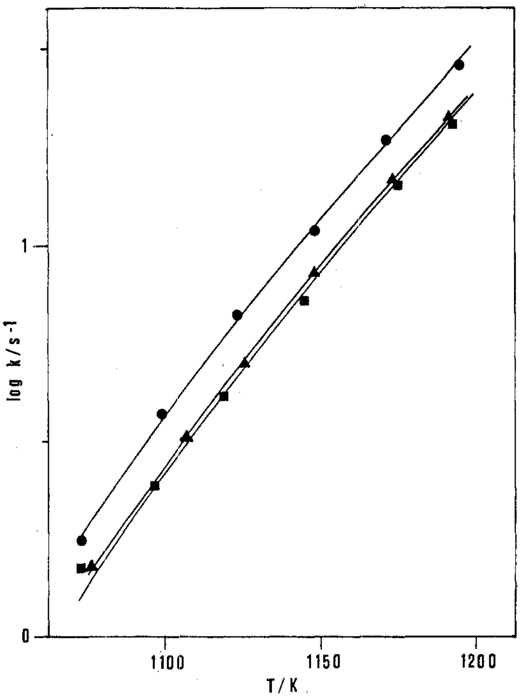


Figure 1. Rate constants measured for the decomposition of ethylmethylbenzenes: 1E2MB (●), 1E3MB (■), 1E4MB (▲). Solid curves shown are RRKM fits to the data.

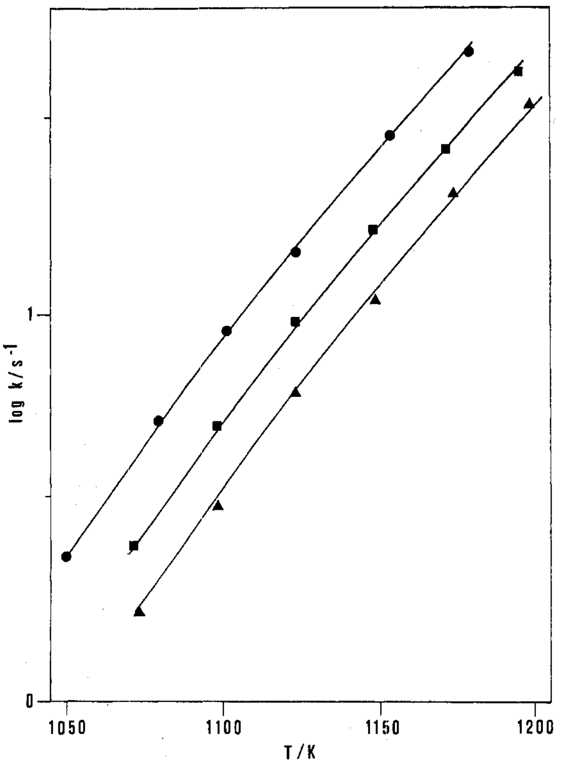


Figure 2. Rate constants measured for the decomposition of dimethylethylbenzenes: 13DM2EB (●), 14DM2EB (■), 13DM5EB (▲). Solid curves shown are RRKM fits to the data.

are shown as solid lines. The models used for the RRKM calculations are included in the Appendix. An A factor of $\log A/\mathrm{s}^{-1} = 15.0$ was assumed in these calculations. This value has been found to be appropriate for the decomposition of ethylbenzene.[4,15] (A more thorough investigation of the A factor is covered in the Discussion.) Relative rates under identical experimental conditions indicate that the observed rates of decomposition are in the following order: 1E2MB > 1E4MB ~ 1E3MB and 13DM2EB > 14DM2EB > 13DM5EB.

TABLE II: Activation Energies (kJ mol^{-1}) with $\log A/\mathrm{s}^{-1} = 15.0$

	E_a	ΔE_a
ethylbenzene	300.8[a]	0
1E2MB	295.8	−5.0 ± 1.1
1E3MB	299.5	−1.3 ± 0.8
1E4MB	299.1	−1.7 ± 0.8
13DM2EB	288.5	−12.3 ± 1.3
14DM2EB	293.9	−6.9 ± 1.1
13DM5EB	298.1	−2.7 ± 0.8

[a] Reference 15.

TABLE III: Bond Dissociation Enthalpy at 298 K

	$D[(\mathrm{CH_3})_n\mathrm{C_6H_{5-n}CH_2CH_3}]$, kJ mol^{-1}
ethylbenzene	310.2[a]
1E2MB	305.2
1E3MB	308.9
1E4MB	308.5
13DM2EB	297.9
14DM2EB	303.3
13DM5EB	307.5

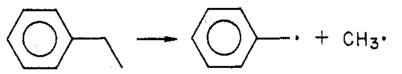
[a] Reference 15.

Activation energies and differences in activation energies relative to that of ethylbenzene,[15] assuming $\log A/\mathrm{s}^{-1} = 15.0$, are presented in Table II. Differences are expressed as $\Delta E_a = E_a(\text{substituted ethylbenzene}) - E_a(\text{ethylbenzene})$.

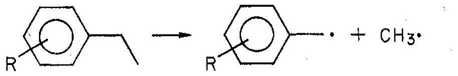
One may define the bond dissociation enthalpy in a simple bond fission reaction by eq 3. One may then relate

$$D(\mathrm{R{-}R'}) = \Delta H_R^\circ = \sum_{\text{products}} \Delta H_f^\circ - \sum_{\text{reactants}} \Delta H_f^\circ \qquad (3)$$

ΔE_a to differences in bond dissociation enthalpies between reactions 4 and 5, ΔD, as given by eq 6. The derived bond



(4)

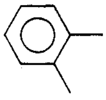


(5)

$$\Delta D = \Delta H_f^\circ(\text{substituted benzyl}) - \Delta H_f^\circ(\text{benzyl}) - \Delta H_f^\circ(\text{substituted ethylbenzene}) + \Delta H_f^\circ(\text{ethylbenzene})$$
$$= \Delta(\Delta H_f^\circ)(\mathrm{R}\cdot) - \Delta(\Delta H_f^\circ)(\mathrm{RCH_3}) = \Delta E_a \qquad (6)$$

dissociation enthalpies relative to a value of 310.2 kJ mol^{-1} for ethylbenzene[15] are presented in Table III.

The ΔE_a values were used to derive ΔH_f° (298 K) for the methylbenzyl radicals (1–6), relative to a value of 196.6 kJ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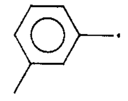
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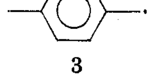
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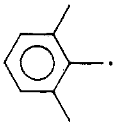
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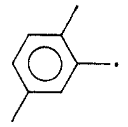
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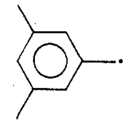
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mol^{-1} for the benzyl radical.[17] For these calculations, we make the assumption that the difference in heat capacities between the benzyl radical and methyl-substituted benzyl radical is the same as the difference in heat capacities between ethylbenzene and the corresponding methyl-substituted ethylbenzene, i.e., $\Delta C^\circ_{P,T}(\text{reaction 4}) = \Delta C^\circ_{P,T}(\text{reaction 5})$. Since the vibrational frequencies and internal rotational barriers associated with the methyl substituents are not expected to differ substantially in the molecule and the radical, this assumption is expected to

TABLE IV: Enthalpies (kJ mol^{-1}) of Formation at 298 K

RH	$\Delta H_f°(RH)$[a]	$\Delta(\Delta H_f°)(RH)$[b]	R·	$\Delta H_f°(R\cdot)$[c]	$\Delta(\Delta H_f°)(R\cdot)$[d]
toluene	50.17 ± 0.42		benzyl	196.6 ± 4.2[e]	
1,2-dimethylbenzene	19.1 ± 1.1	−31.1 ± 1.5	methylbenzyl (1)	160.5 ± 6.8	−36.1 ± 2.6
1,3-dimethylbenzene	17.32 ± 0.75	−32.8 ± 1.2	methylbenzyl (2)	162.5 ± 6.2	−34.1 ± 2.0
1,4-dimethylbenzene	18.0 ± 1.0	−32.2 ± 1.4	methylbenzyl (3)	162.7 ± 6.4	−33.9 ± 2.2
1,2,3-trimethylbenzene	−9.4 ± 1.2	−59.6 ± 1.6	dimethylbenzyl (4)	124.6 ± 7.1	−71.9 ± 2.9
1,2,4-trimethylbenzene	−13.8 ± 1.1	−64.0 ± 1.5	dimethylbenzyl (5)	125.7 ± 6.8	−70.9 ± 2.6
1,3,5-trimethylbenzene	−15.9 ± 1.4	−66.1 ± 1.8	dimethylbenzyl (6)	127.8 ± 6.8	−68.8 ± 2.6
RCH_3	$\Delta H_f°(RCH_3)$[a]	$\Delta(\Delta H_f°)(RCH_3)$[f]	R·	$\Delta H_f°(R\cdot)$[c]	$\Delta(\Delta H_f°)(R\cdot)$[g]
ethylbenzene	29.92 ± 0.80		benzyl	196.6 ± 4.2[e]	
1E2MB	1.6 ± 1.1	−28.3 ± 1.9	methylbenzyl (1)	163.3 ± 7.2	−33.3 ± 3.0
1E3MB	−1.8 ± 1.2	−31.7 ± 2.0	methylbenzyl (2)	163.6 ± 7.0	−33.0 ± 2.8
1E4MB	−3.2 ± 1.4	−33.1 ± 2.2	methylbenzyl (3)	161.8 ± 7.2	−34.8 ± 3.0

[a] Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. [b] $\Delta(\Delta H_f°)(RH) = \Delta H_f°(RH) - \Delta H_f°(\text{toluene})$. [c] $\Delta H_f°(R\cdot) = \Delta(\Delta H_f°)(R\cdot) + \Delta H_f°(\text{benzyl})$. [d] $\Delta(\Delta H_f°)(R\cdot) = \Delta/\Delta H_f°)(RH) + \Delta E_a$ (Table II). [e] Reference 17. [f] $\Delta(\Delta H_f°)(RCH_3) = \Delta H_f°(RCH_3) - \Delta H_f°(\text{ethylbenzene})$. [g] $\Delta(\Delta H_f°)(R\cdot) = \Delta(\Delta H_f°)(RCH_3) + \Delta E_a$ (Table II).

be a good one. Then, the difference in enthalpies of formation at 298 K between substituted benzyl radicals (**1**–**6**) and benzyl radical is given by eq 7. Since $\Delta H_f°$ values for

$$\begin{aligned}\Delta(\Delta H_f°)(R\cdot) &= \Delta H_f°(\text{substituted benzyl}) - \Delta H_f°(\text{benzyl}) \\ &= \Delta E_a + \Delta H_f°(\text{substituted ethylbenzene}) - \Delta H_f°(\text{ethylbenzene}) \\ &= \Delta E_a + \Delta(\Delta H_f°)(RCH_3) \qquad (7)\end{aligned}$$

the dimethylethylbenzenes have not been reported in the literature, $\Delta(\Delta H_f°)(RCH_3)$ for these compounds was taken to be the same as the difference between $\Delta H_f°$(trimethylbenzene) and $\Delta H_f°$(toluene). For comparison, $\Delta(\Delta H_f°)(RCH_3)$ for the ethylmethylbenzenes were set equal to $\Delta H_f°$(dimethylbenzene) − $\Delta H_f°$(toluene), as well as $\Delta H_f°$(ethylmethylbenzene) − $\Delta H_f°$(ethylbenzene). Values of the enthalpies of formation are presented in Table IV. The results show the enthalpies of formation of methylbenzyl radicals (**1**–**3**) to be within 2.1 kJ mol^{-1} of one other, and those of dimethylbenzyl radicals (**4**–**6**) to be within 3.2 kJ mol^{-1} of one other.

Discussion

One may note from Figures 1 and 2 and Table II that decomposition rates are highest for compounds having methyl groups ortho to the ethyl group. This fact appears to be best explained as a relaxation of steric interaction in the activated complex. Benson et al.[18] have obtained "ortho correction" values for entropy and enthalpy by fitting observed chemical thermodynamic properties of a number of aromatic compounds. One may use Benson's values for the "ortho correction" entropy and enthalpy to estimate the maximum increase in rate constant for bond scission due to steric relaxation. One then obtains a ratio of rate constants given by eq 8, where k_{NO} is the rate

$$k_{NO}/k_O = \exp[-\Delta(\Delta G^\ddagger)/RT] \qquad (8)$$

constant for the nonortho model, k_O is the rate constant for the ortho model with complete steric relaxation, and $\Delta(\Delta G^\ddagger) = \Delta(\Delta H^\ddagger) - T\Delta(\Delta S^\ddagger)$, where $\Delta(\Delta H^\ddagger)$ and $\Delta(\Delta S^\ddagger)$ are set equal to Benson's ortho correction values. Extrapolation of the entropy and enthalpy values to 1150 K, using $C°_P$ values,[18] leads to a $\Delta(\Delta G^\ddagger)$ of 6.7 kJ mol^{-1} for this model. Examination of the range of values exhibited by the compounds in ref 18 used for deriving the above ortho correction value leads to a range of $\Delta(\Delta G^\ddagger)$ from 3.3 to 5.1 kJ mol^{-1} at 298 K, and 5.6 to 7.4 kJ mol^{-1} at 1150 K. A comparision of Benson's $\Delta(\Delta G^\ddagger)$ values with values obtained from our measured rate constants for ortho and nonortho isomers, e.g., 1E2MB and 1E3MB, is shown in Table V. The ratios of measured rate constants lead to smaller $\Delta(\Delta G^\ddagger)$ values than those derived from the ortho correction model by 1.3 to 3.3 kJ mol^{-1}. This result seems reasonable in view of the fact that the ortho steric interaction may not be completely removed in the activated complex.

TABLE V: Rate Constant Ratios at 1150 K

	k_1^∞/k_2^∞	$\Delta G^\ddagger$, kJ mol^{-1}
ortho correction	0.49	6.7
1E4MB/1E2MB	0.70	3.4
1E3MB/1E2MB	0.68	3.8
13DM5EB/14DM2EB	0.64	4.2
14DM2EB/13DM2EB	0.57	5.4

Also, inductive effects can amount to a lowering of activation energy by no more than 1.3–1.7 kJ mol^{-1} per *o*- or *p*-methyl group, as seen in Table II, an amount that, in fact, may not be experimentally significant. Thus, all major differences in bond dissociation rates are best explained in terms of changes in steric interaction.

Let us briefly consider the values of *A* factors used in our calculations. At 1150 K, the $\Delta(\Delta S^\ddagger)$ value associated with Benson's ortho correction has a value of only −0.80 J K^{-1} mol^{-1}; hence, the effect of the ortho correction model on the *A* factor is very small. Applying the full ortho correction would raise log *A* from 15.00 to 15.04 for 1E2MB and 14DM2EB, and to 15.08 for 13DM2EB. To match observed rates, activation energies would be increased by at most 0.8 kJ mol^{-1}. Hence, the values of the activation energies presented in Table II, assuming log *A* = 15.0, are felt by the authors to be the best representation of the data at the present time.

Differences in activation energies shown in Table II are approximately separable into individual methyl group contributions relative to ethylbenzene. Substitution of *m*- or *p*-CH_3 lowers the activation energy by 1.3–1.7 kJ mol^{-1} per CH_3; substitution by *o*-CH_3 lowers the activation energy by 5.0–6.3 kJ mol^{-1} per CH_3.

Enthalpies of formation of isomeric radicals are found to be the same within experimental error (Table IV). A similar observation was found previously for the case of isomeric picolinyl radicals.[16] Differences in stabilities of these isomeric radicals seem to have little, if any, dependence on structure.

Conclusions

Results of the present study may be summarized as follows: (1) Relative to ethylbenzene, rates of C–C bond scission for a number of methyl-substituted ethylbenzenes are significantly accelerated by the presence of a methyl group adjacent to the ethyl group and are little affected by the presence of methyl groups at the meta and para positions. (2) Differences in activation energy relative to ethylbenzene are approximately separable into individual ortho and nonortho contributions. (3) Rate differences in ortho-substituted ethylbenzenes may be explained in terms of a partial relaxation of steric interaction in the activated complex. (4) Methyl inductive effects on the relative stabilities of radicals produced are small, amounting to a decrease of <1.7 kJ mol^{-1} per CH_3 in their Gibbs energy of formation.

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Appendix

The following models were used for the RRKM calculations. It should be noted that the degree of falloff depends primarily on values of the Arrhenius parameters, and is rather insensitive to exact details of the transition-state model.[19]

I. Ethylmethylbenzenes. a. Complex. $I = 4.519 \times 10^{-112}$ g^3 cm^6; $\sigma = 9$.

Vibrational frequencies: 3050(3), 1490(6), 1200(4), 990(1), 940(1), 810(1), 670(3), 490(5), 330(1), 250(5), 2950(6), 1430(5), 1050(4), 50(2), 3100(2), 1450(2), 1150(3), 10(1).

b. Molecule. $I = 1.736 \times 10^{-112}$ g^3 cm^6; $\sigma = 9$.

Vibrational frequencies: 3050(3), 1490(6), 1200(4), 990(1), 940(1), 810(1), 670(3), 490(5), 310(1), 250(5), 2950(6), 1430(6), 1050(4), 140(2), 3100(2), 1450(2), 1150(3), 1000(1), 30(1).

II. Dimethylethylbenzenes. a. Complex. $I = 6.148 \times 10^{-112}$ g^3 cm^6; $\sigma = 54$.

Vibrational frequencies: 3050(3), 1490(6), 1200(4), 990(1), 940(1), 860(1), 670(3), 490(5), 310(1), 250(5), 2950(9), 1430(9), 1050(6), 20(3), 2740(2), 1450(2), 1150(3), 10(1).

b. Molecule. $I = 3.006 \times 10^{-112}$ g^3 cm^6; $\sigma = 54$.

Vibrational frequencies: 3050(3), 1490(6), 1200(4), 990(1), 940(1), 810(1), 670(3), 490(5), 310(1), 250(5), 2950(9), 1430(9), 1050(6), 40(3), 3100(2), 1450(2), 1150(3), 1000(1), 30(1).

References and Notes

(1) Szwarc, M. *Nature (London)* **1947**, *160*, 403; *J. Chem. Phys.* **1948**, *16*, 128–36.
(2) Schaefgen, J. R. *J. Polym. Sci.* **1955**, *15*, 203–19.
(3) Errede, L. A.; DeMaria, F. *J. Phys. Chem.* **1962**, *66*, 2664–72.
(4) Benson, S. W.; O'Neal, H. E. *Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.)* **1970**, *No. 21*.
(5) Leigh, C. H.; Sehon, A. H.; Szwarc, M. *Proc. R. Soc. London, Ser. A* **1951**, *209*, 97–110.
(6) Levy, M.; Szwarc, M.; Throssell, J. *J. Chem. Phys.* **1954**, *22*, 1904–11.
(7) Meyer, J. A.; Stannett, V.; Szwarc, M. *J. Am. Chem. Soc.* **1961**, *83*, 25–9.
(8) Russell, G. A. *J. Am. Chem. Soc.* **1956**, *78*, 1047–54.
(9) Williams, A. L.; Oberright, E. A.; Brooks, J. W. *J. Am. Chem. Soc.* **1956**, *78*, 1190–3.
(10) Kooyman, C. *Discuss. Faraday Soc.* **1951**, *10*, 163–74.
(11) Sanders, W. A.; Rebbert, R. E. *J. Phys. Chem.* **1963**, *67*, 170–1.
(12) Pearson, J. M.; Szwarc, M. *Trans. Faraday Soc.* **1964**, *60*, 553–63.
(13) Bridger, R. F.; Russell, G. A. *J. Am. Chem. Soc.* **1963**, *85*, 3754–65.
(14) Golden, D. M; Spokes, G. N.; Benson, S. W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 534–45.
(15) Robaugh, D. A.; Stein, S. E., to be submitted for publication in *Int. J. Chem. Kinet.*
(16) Barton, B. D.; Stein, S. E., accepted for publication in *J. Chem. Soc., Faraday Trans. 1.*
(17) Rossi, M.; Golden, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 1230–5.
(18) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279–324.
(19) Robinson, P. J.; Holbrook, K. A. "Unimolecular Reactions"; Wiley-Interscience: New York, 1972.