291. *Homolytic Reactions of Aromatic Side Chains. Part II.*[1] *Relative Rates of α-Hydrogen Abstraction by t-Butoxy-radicals.*

By K. M. Johnston and Gareth H. Williams.

Measurements are reported of the relative rates of abstraction by t-butoxy-radicals of α-hydrogen atoms from alkyl side chains attached to aromatic nuclei. The radicals were formed by the thermal decomposition of t-butyl peroxide, and the measurements made by the use of the competitive technique. The influence of nuclear substituents is determined by their polar character, since the results are in accord with Hammett's " ρσ " relation. A value of approximately −0·5 was obtained for the parameter ρ for this reaction, which is therefore assisted by electron-repelling and hindered by electron-attracting substituents. Alkyl substituents at the α-carbon atom of the side chain assist the reaction, probably because of their stabilising influence on the radicals formed by α-hydrogen abstraction. The theoretical significance of the results is discussed.

The reactions reported in Part I[1] provide a convenient vehicle for the investigation of the relative rates of abstraction of α-hydrogen atoms from the side chains of aromatic and heterocyclic compounds by t-butoxy-radicals, and a number of determinations of this kind, carried out by means of competitive experiments, are now reported.

The relative rates of analogous processes of this type have already been investigated in considerable detail, and have been considered to be influenced by structural features which are present in the molecules in two ways, namely, by the effect of structure on the stability of the radical which is the product of hydrogen-abstraction, and by the polar effects

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[1] Part I, *J.*, 1960, 1168.

of the substituent groups. Reactivity series for free-radical reactions have, for many years, been interpreted in terms of the resonance stabilisation of the radicals formed in these reactions, on the reasonable assumption that the stability of the transition states parallels that of the products (see, *e.g.*, Mayo and Walling [2] and Wheland [3]). More recently, however, the contribution of polar forms, resulting from electron-transfer between the radical and the substrate, to the transition states of these reactions has been considered to be of importance in determining the activation energies of these processes. Russell [4] has regarded the transition state for the reactions of a radical X· with a compound RH as a resonance hybrid of three canonical forms, one (I) resembling the reactants and another (III) the products. In the third form (II), electron-transfer is regarded as having taken place between the radical and the substrate, as originally suggested by Walling, Briggs, Wolfstirn, and Mayo.[5]

$$\begin{array}{ccccc} \mathrm{R{:}H{\cdot}X} & \longleftrightarrow & \mathrm{R^{+}{\cdot}H{:}X^{-}} & \longleftrightarrow & \mathrm{R{\cdot}H{:}X} \\ \text{(I)} & & \text{(II)} & & \text{(III)} \end{array}$$

Polar effects would be expected to be most important in form (II), and Russell has argued that they should be more important in form (I) than in form (III). The more electronegative the radical X, the more favoured form (II) should become, and hence the greater the importance of polar effects. Again, a highly reactive radical X should give rise to a transition state more nearly approaching (I), while an unreactive radical should lead to a transition state approaching (III). Since these forms are expected to reflect the polar effects of groups differently, the influence of polar effects should therefore be dependent on the intrinsic reactivity of the radicals as well as on their electronegativity.

The conformity to the Hammett " $\rho\sigma$ " relation [6] has been taken as an indication of the determination of reactivity by polar factors in a number of homolytic hydrogen-abstraction reactions, and the value of the parameter ρ derived from the application of this relationship to a particular reaction with a series of substrates has been considered to be a measure of the magnitude of the polar effect in that reaction. From an examination of the ρ-values obtained for the reaction of various free radicals (chlorine and bromine atoms, and trichloromethyl and succinimido-radicals) with derivatives of alkylbenzenes, van Helden and Kooyman [7] concluded that a correlation exists between the value of ρ and the electronegativity of the atom which formally carries the unpaired electron in the free radical, the most pronounced polar effects being associated with highly electronegative radicals. It was therefore predicted that, since oxygen is highly electronegative, very pronounced polar effects, corresponding to values of ρ of about -2, should be found for reactions of this type with alkoxy- or peroxy-radicals. The reactions with peroxy-radicals were studied by Russell,[4] and values of ρ of $-0{\cdot}6$ and $-0{\cdot}4$ were obtained for the two series studied (toluene and cumene derivatives). It was therefore considered that, while the electronegativity of the attacking radical must obviously make a contribution, other factors, as indicated in the foregoing summary, must also be considered in assessing the magnitude of the polar effect in a given reaction.

The establishment of the existence, and determination of the magnitude, of the polar effect in the reaction of alkoxy-radicals with derivatives of alkylbenzenes is therefore of great importance in this connection. This requires the determination of the relative reactivity of a series of compounds of this type towards a radical such as t-butoxy. In the competitive method, as used in the present determinations, t-butyl peroxide was allowed to react with a large excess of an equimolar mixture of the two solvents to be compared, and the resulting mixture of binuclear products isolated and analysed. A higher-boiling

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[2] Mayo and Walling, *Chem. Rev.*, 1950, **46**, 191.

[3] Wheland, " Resonance in Organic Chemistry," John Wiley & Sons Inc., New York, 1955, Chap. 8.

[4] Russell, *J. Amer. Chem. Soc.*, 1956, **78**, 1047.

[5] Walling, Briggs, Wolfstirn, and Mayo, *J. Amer. Chem. Soc.*, 1948, **70**, 1537.

[6] Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 96; " Physical Organic Chemistry," McGraw-Hill Book Co., New York, 1940, Chap. 7.

[7] van Helden and Kooyman, *Rec. Trav. chim.*, 1954, **73**, 269.

fraction consisting mainly of dehydrogeno-trimers, which is usually formed in small amount (cf. Part I [1]), was also isolated and analysed. The relative reactivities of the two solvents could then be calculated from the relative amounts of the radicals derived from them which were incorporated in the dehydrogeno-dimer and -trimer fractions. In order to facilitate the analysis of the product mixtures, either β- or γ-picoline was always used as one component of the mixture of solvents. In a competitive reaction in which the other component of the solvent mixture was a compound $Ar{\cdot}CH_3$, for example, three binuclear products would be formed, namely, the two dehydrogeno-dimers, $Ar{\cdot}CH_2{\cdot}CH_2Ar$, and $C_5H_4N{\cdot}CH_2{\cdot}CH_2{\cdot}C_5H_4N$ and the "mixed" product $Ar{\cdot}CH_2{\cdot}CH_2{\cdot}C_5H_4N$. The analysis of this mixture could be accomplished by an acid–base titration of the mixture of mono- and di-acidic bases, after removal of the neutral dehydrogeno-dimer by acid-extraction. The reactions were conducted at a fairly low temperature (110°) in order to minimise the decomposition of t-butoxy-radicals to methyl radicals and acetone. The extent of this decomposition in a typical reaction was estimated by measurement of the amount of methane formed. The reaction chosen for this determination was a competitive reaction of t-butyl peroxide with a mixture of *p*-chlorotoluene and γ-picoline, since both these solvents were shown to be rather unreactive towards t-butoxy-radicals, and hence the decomposition of these radicals would be expected to be most important in such a medium. The amount of methane formed corresponded to about 1/14 of the amount expected if all of the t-butyl peroxide used had been decomposed to give methyl radicals. The competitive reactions were, however, not allowed to proceed to completion, but were stopped after about 50% of the reaction had taken place, in order to minimise the formation of dehydrogeno-trimers. Calculation from the yields of methane and of bi- and tri-nuclear products obtained then reveals that not more than about 1/7 of the total amount of hydrogen-abstraction is brought about by methyl radicals under these conditions. This process is therefore regarded as only a minor contribution to the total reaction, about 85% of which is due to t-butoxy-radicals.

It was also established by experiment that the extent to which a competitive reaction of t-butyl peroxide with a mixture of toluene and γ-picoline was allowed to proceed had no effect on the relative reactivity deduced from its results.

The experimental results reported below indicate that β- and γ-picoline are less reactive towards t-butoxy-radicals than any of the other substrates investigated. Thus, in principle, processes such as

$$C_5H_4N{\cdot}CH_2{\cdot} + C_6H_5{\cdot}CHMe_2 \longrightarrow C_5H_4N{\cdot}CH_3 + C_6H_5{\cdot}CMe_2{\cdot}$$

are energetically favoured, and would tend to reduce the yield of nitrogen-containing dehydrogeno-dimers. To the extent to which such processes occur, therefore, the measured rate ratios exaggerate the actual differences in reactivity. The extent of these processes of radical-transfer brought about by picolinyl radicals has not been directly measured, but it is considered to be fairly small, as benzyl and 4-chlorobenzyl radicals have been shown to react only to a minute extent with isopropylbenzene in an analogous process which, on the basis of the foregoing argument, should also be energetically favoured.[8] These processes of radical-transfer are therefore not considered to affect the results seriously.

EXPERIMENTAL

Solvents were purified as described in Part I.[1] t-Butyl peroxide (Light and Co.) was used without further purification (cf. Part I [1]).

Preparation of Reference Compounds.—Bibenzyl was prepared by the reaction of t-butyl peroxide with toluene, as described in Part I.[1]

2-*Phenethylpyridine*. This was prepared by Bergstrom, Norton, and Seibert's method,[9] *i.e.*, treatment of α-picoline with potassamide in liquid ammonia, and then with benzyl chloride.

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[8] Hey, Shingleton, and Williams, unpublished observations.

[9] Bergstrom, Norton, and Seibert, *J. Org. Chem.*, 1945, **10**, 452.

After the ammonia had been allowed to evaporate, the residue was treated with water and extracted with ether, and the extracts were washed with water and dried ($MgSO_4$). Distillation gave 2-phenethylpyridine (b. p. 99°/2 mm.) in 65% yield.

4-*Phenethylpyridine.* This was prepared in almost theoretical yield from γ-picoline by a similar method, and purified by crystallisation from light petroleum (m. p. 71°; Bergstrom, Norton, and Seibert[9] reported m. p. 70—71°).

($\pm$)-2-*Phenyl*-1-4′-*pyridylpropane.* A similar method was used for the preparation of this compound. Potassium (3·5 g.) was dissolved in liquid ammonia (400 ml.), anhydrous ferric oxide (50 mg.) added, and the mixture stirred for about ½ hr. until the deep blue colour of the solution was replaced by the amber colour of potassamide in liquid ammonia. γ-Picoline (8 g.) was then added, followed by 1-phenylethyl chloride (11 g.), which was prepared by Norris, Watt, and Thomas's method[10] from 1-phenylethanol. The mixture was worked up by the method described for the preparation of 2-phenethylpyridine and gave 2-*phenyl*-1-4′-*pyridylpropane*, b. p. 130—131°/2·5 mm., n_D^{19} 1·5620 (Found: C, 84·9; H, 7·8; N, 7·0. $C_{14}H_{15}N$ requires C, 85·2; H, 7·7; N, 7·1%). The *methiodide* had m. p. 128° (Found: C, 52·7; H, 5·6; N, 4·1; I, 37·5. $C_{15}H_{18}NI$ requires C, 53·1; H, 5·3; N, 4·1; I, 37·4%), and the *picrate*, m. p. 103° (Found: C, 56·3; H, 4·0; N, 13·3. $C_{20}H_{18}O_7N_4$ requires C, 56·3; H, 4·3; N, 13·1%).

1,2-Di-3′- and 1,2-di-4′-pyridylethane were prepared as described in Part I.[1]

Analysis of Mixtures of Dehydrogeno-dimers.—It was first established by experiment that the following mono- and di-acidic bases, which are typical of the binuclear products which would be formed in competitive experiments by union of radicals formed from basic and neutral substrates, could be satisfactorily titrated against hydrochloric acid by Kolthoff's method,[11] using Bromophenol Blue as indicator: 2- and 4-phenethylpyridine, ($\pm$)-2-phenyl-1-4′-pyridylpropane, and 1,2-di-3′- and 1,2-di-4′-pyridylethane. It was also shown that these bases could be estimated by dissolution in an excess of standard hydrochloric acid and back-titration against sodium hydroxide, using the same indicator.

The following method for the analysis of mixtures containing a neutral component as well as a mono- and di-acidic base was then tested by the analysis of a synthetic mixture made up so as to simulate the mixture of dehydrogeno-dimers formed in a competitive experiment with a mixture of toluene and γ-picoline as substrate. This mixture, which contained bibenzyl (0·5738 g.), 4-phenethylpyridine (0·3756 g.), and 1,2-di-4′-pyridylethane (0·1170 g.), was treated with 0·369N-hydrochloric acid (20 ml.), and the resulting mixture warmed on a water-bath. The mixture was cooled in a refrigerator, and the insoluble bibenzyl removed by filtration through a weighed No. 4 sintered-glass crucible, and washed with water. The crucible and its contents were dried *in vacuo* at room temperature, and re-weighed to give the amount of bibenzyl present. The filtrate was diluted with water (5 ml.) and made up to 50 ml. with ethanol. The resulting solution was titrated, in 10 ml. portions, against 0·119N-sodium hydroxide. This titration permitted the calculation of the normality of the solution of the mixture of bases, and, since the combined weight of the bases could be obtained from the weights of the original mixture and of the bibenzyl present, also of the amounts of the two bases originally present. Complete analysis of the mixture could therefore be accomplished. The amounts of the three components present, as determined by this procedure, were: bibenzyl, 0·572 g.; 4-phenethylpyridine, 0·373 g.; 1,2-di-4′-pyridylethane, 0·121 g. This method of analysis was therefore considered to be satisfactory, and was employed in the competitive experiments.

Competitive Experiments.—t-Butyl peroxide (4·0 g., 0·027 mole) was allowed to decompose in a mixture of 0·5 mole of each of the two solvents for 72 hr. at 110° (thermostat). The reactions were conducted, and the products worked up, as described in Part I[1] for reactions of t-butyl peroxide with single solvents. Owing to the difficulty of preparing large quantities of 4-methylbiphenyl, competitive experiments involving this substance were conducted on a reduced (¼ of the above) scale. The dehydrogeno-dimer fractions were analysed by the method described above. The amounts of radicals derived from the two solvents and incorporated in the binuclear products were calculated in two ways, (*a*) from the titration alone, since a knowledge of the normality of the mixture of bases permits the calculation of the amount of picoline-derived radicals, and (*b*) from the complete analysis, based on the gravimetric estimation of the neutral components as well as on the titration. The second method failed for competitive

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[10] Norris, Watt, and Thomas, *J. Amer. Chem. Soc.*, 1916, **38**, 1078.

[11] Kolthoff, *Biochem. Z.*, 1925, **162**, 289; Kolthoff and Stenger, " Volumetric Analysis II," Interscience Publishers Inc., New York, 1947, p. 126.

experiments involving ethylbenzene as one component of the mixture of solvents, since racemic 2,3-diphenylbutane is a liquid (cf. Part I [1]), and could not therefore be estimated gravimetrically. The first method of calculation was therefore the only one used in this instance. Good agreement was obtained between relative rates calculated by the two methods.

The relative rates calculated from the composition of the mixture of binuclear products were corrected for the removal of some of the solvent-derived radicals by incorporation in the higher-boiling fractions, which were shown, by molecular-weight determinations, to consist very largely of dehydrogeno-trimers, the formation of which was discussed in Part I.[1] Since these corrections were relatively small, accurate analysis of the high-boiling fractions was unnecessary, and their composition was estimated by means of microanalysis for nitrogen. The observations made, and the methods of calculation employed, are illustrated in Table 1, with reference to competitive experiments in which the substrate was an equimolar mixture of toluene (M, 92) and γ-picoline (M, 93).

TABLE 1. *Reaction of t-butyl peroxide with an equimolar mixture of toluene and γ-picoline.*

	Expt. 1	Expt. 2
(*a*) Dehydrogeno-dimer fraction, b. p. 90—126°/2 mm. (g.)	1·7219	1·6852
(*b*) Dehydrogeno-trimer fraction, b. p. 170—220°/2 mm. (g.)	0·2732	0·2518
(*c*) Mol. wt. of (*b*)	249	262
(*d*) N (%) in (*b*)	5·35	5·10
(*e*) Benzyl radicals in (*a*) calc. from titration alone (g.)	1·3052	1·2872
(*f*) γ-Picolyl radicals in (*a*) calc. from titration alone (g.)	0·4167	0·3980
(*g*) Relative rate of reaction (toluene : γ-picoline) calc. from (*e*) and (*f*)	3·25	3·23
(*h*) Bibenzyl in (*a*) (g.)	1·0240	1·0077
(*i*) 4-Phenethylpyridine in (*a*) (g.)	0·5679	0·5558
(*j*) 1,2-Di-4′-pyridylethane in (*a*) (g.)	0·1300	0·1217
(*k*) Benzyl radicals in (*a*) calc. from (*h*) and (*i*) (g.)	1·3080	1·2853
(*l*) γ-Picolinyl radicals in (*a*) calc. from (*i*) and (*j*) (g.)	0·4140	0·3993
(*m*) Relative rate of reaction (toluene : γ-picoline) calc. from (*k*) and (*l*)	3·28	3·22
(*n*) γ-Picolinyl radicals in (*b*) calc. from (*d*) (g.)	0·0934	0·0862
(*o*) Benzyl radicals in (*b*) calc. from (*d*) (g.)	0·1798	0·1656
(*p*) Corrected relative rate of reaction (toluene : γ-picoline) $= 93(e + o)/92(f + n)$	2·98	2·99

The results of competitive experiments performed in this way are given in Table 2, from which it may be seen that the agreement in duplicate experiments is good.

TABLE 2. *Relative reactivities towards homolytic α-hydrogen abstraction.*

Solvent A	Solvent B	Relative reactivity A/B		$k_{\text{rel.}}$ of solvent
β-Picoline	Toluene	0·45	0·43	0·44
γ-Picoline	,,	0·33	0·33	0·33
o-Chlorotoluene	γ-Picoline	2·2	2·2	0·73
m-Chlorotoluene	,,	2·1	2·1	0·70
p-Chlorotoluene	,,	2·7	2·7	0·90
4-Methylbiphenyl	,,	5·3	—	1·75
Ethylbenzene	,,	7·8	7·8	2·6
Isopropylbenzene	,,	9·2	9·1	3·1
p-Cymene	,,	9·6	—	3·2

The volume of the gaseous products formed from a competitive reaction of t-butyl peroxide (4·0 g.) with an equimolar mixture of *p*-chlorotoluene and γ-picoline was measured by collection in a graduated vessel over brine. The corrected volume of this gas, which may be assumed to consist almost entirely of methane (cf. Bell, Rust, and Vaughan [12]) was 90 ml. (S.T.P.). The combined yield of bi- and tri-nuclear products in this reaction was 3·0 g.

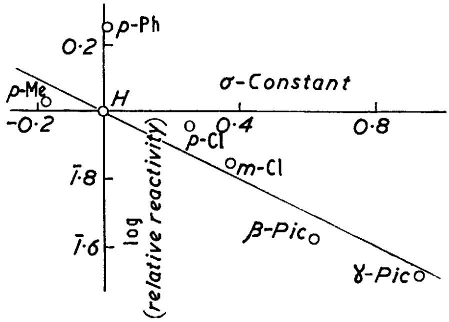
A competitive reaction in which t-butyl peroxide (4·0 g.) was allowed to react with an equimolar mixture of toluene and γ-picoline at 110° for 168 hr. gave increased yields of all of the products, and the value of the corrected relative rate of reaction (toluene : γ-picoline) calculated from the composition of these products was 3·0.

DISCUSSION

The relative reactivities ($k_{\text{rel.}}$) of the compounds investigated, on a scale in which toluene is considered to have a reactivity of unity, are given in the last column of Table 2.

[12] Bell, Rust, and Vaughan, *J. Amer. Chem. Soc.*, 1950, **72**, 337.

The polar effects of nuclear substituents (except the *o*-chloro-group, for which steric factors render the Hammett equation inappropriate) are illustrated by the Figure, in which log $k_{rel.}$ is plotted against the appropriate Hammett σ-constant. The point corresponding to the *p*-methyl group was obtained by using the relative reactivity of *p*-cymene expressed on a scale on which isopropylbenzene has a reactivity of unity. This relative reactivity is 1·04. This procedure is justified, since it has previously been shown (cf. Part I [1]) that hydrogen-abstraction from *p*-cymene takes place virtually entirely from the isopropyl group. The σ-constants used are those given by Jaffe,[13] except for β- and γ-picoline, for which those given by Simonetta and Favini [14] were employed. The slope of the best straight line drawn by the method of least squares through all the points except that corresponding to 4-methylbiphenyl was found to be —0·49. The value of the reaction constant ρ is therefore approximately —0·5. This observed correlation between the relative reactivities of derivatives of toluene and the Hammett σ-constants for the appropriate substituents demonstrates clearly that the effects of nuclear substituents on the rate of this reaction are governed by their polar influences. The relative insignificance of considerations of the stability of the product radicals is doubtless due to the fact that nuclear substituents, apart from aryl groups, impart little resonance stabilisation to radicals analogous to benzyl, and hence the relatively small polar influences become effective in determining reactivity. This contention is supported by a comparison of the values of the ($C_5H_4N{\cdot}CH_2$–H) bond dissociation energies in β- and γ-picoline (76·5 and 77·5 kcal. mole^{-1} respectively [15]) with that of the ($C_6H_5{\cdot}CH_2$–H) bond dissociation energy in toluene (77·5 kcal. mole^{-1}).[16] If the relative reactivities of these compounds were determined mainly by the stability of the product-radicals, then on the basis of these values for the bond-dissociation energies they would be expected to be closely similar. The fact that the picolines are only about one-third as reactive as toluene shows conclusively that the reactivities are determined by other factors, of which polar effects appear to be the most probable. On the other hand, the importance of the resonance-stabilisation effect in the case of the strongly conjugating *p*-phenyl group is clearly indicated by the fact that the point corresponding to 4-methylbiphenyl in the Figure lies well above the line. Walling and Miller [17] observed a similar situation in the homolytic side-chain chlorination of this compound.



Effect of substituents on relative reactivity.

The magnitude of the polar effect in the reaction with t-butoxy-radicals, as indicated by the value of ρ, is closely similar to those obtained by Russell [4] for the reaction of nuclear-substituted toluene and cumene derivatives with peroxy-radicals. The present results therefore lend further support to Russell's contention that other factors besides the electronegativity of the atom carrying the unpaired electron in the attacking free radical

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[13] Jaffe, *Chem. Rev.*, 1953, **53**, 191.

[14] Simonetta and Favini, *Gazzetta*, 1954, **84**, 566.

[15] Roberts and Szwarc, *J. Chem. Phys.*, 1948, **16**, 981.

[16] Szwarc, *J. Chem. Phys.*, 1948, **16**, 128; *Discuss. Faraday Soc.*, 1947, **2**, 39.

[17] Walling and Miller, *J. Amer. Chem. Soc.*, 1957, **79**, 4181.

are significant in determining the importance of polar effects in reactions of this type. On the basis of Russell's theory, as outlined in the introduction, the present results indicate that the t-butoxy-radical in aromatic solvents should be regarded as a rather unreactive species.

Hydrogen-abstraction by the relatively non-polar methyl radical would, of course, tend to reduce the observed ρ-value, and the foregoing argument therefore depends on the observation that this process makes only a small contribution to the total reaction.

The relative reactivities of the hydrocarbons toluene, ethylbenzene, and isopropylbenzene are in accord with the well-established theory that the effects of side chain, as distinct from nuclear, substituents on reactions of this type are governed chiefly by the resonance-stabilisation of product radicals.[4,7,17] The numerical values obtained in this work, however, are not in complete agreement with the values reported by Williams, Oberright, and Brooks [18] and by Brook.[19] The three sets of results, expressed as relative reactivities per α-hydrogen atom on a scale on which the reactivity of the single α-hydrogen atom of isopropylbenzene is unity, are given in Table 4. Williams, Oberright, and Brooks have not commented on their rather surprising conclusion that the total reactivity of ethylbenzene towards attack in the side chain by t-butoxy-radicals (*i.e.*, double the value given in Table 4, since ethylbenzene has two α-hydrogen atoms) is greater than that of isopropylbenzene. This is not in accord with the behaviour of these hydrocarbons in other free-radical reactions, such as their reactions with phenyl radicals from benzoyl peroxide,[20] trichloromethyl radicals,[21] and polystyrene radicals.[22] In all these various processes, each of which involves α-hydrogen abstraction, the reactivity series toluene < ethylbenzene < isopropylbenzene was found to be obeyed. This anomaly was recognised by Brook,[19] who considered steric factors to be responsible for the low reactivity of isopropylbenzene in its reaction with t-butyl peroxide. Examination of models, however, indicates that there should be no appreciable hindrance to the approach of a t-butoxy-radical to the α-hydrogen atom of isopropylbenzene. Hence, it is difficult to rationalise the comparatively high reactivity of ethylbenzene as measured by the aforementioned workers, and it is therefore considered that the relative reactivities of toluene, ethylbenzene, and isopropylbenzene obtained in the present work are probably more reliable.

TABLE 4. *Relative reactivities of α-hydrogen atoms of aralkyl hydrocarbons.*

	Relative reactivity *		
Hydrocarbon	(*a*)	(*b*)	(*c*)
Toluene	0·23	0·16	0·11
Ethylbenzene	0·66	0·63	0·42
Isopropylbenzene	1·00	1·00	1·00

* Results obtained by (*a*) Williams, Oberright, and Brooks,[18] (*b*) Brook,[19] and (*c*) in present work.

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KING'S COLLEGE (UNIVERSITY OF LONDON),
STRAND, LONDON, W.C.2.

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[18] Williams, Oberright, and Brooks, *J. Amer. Chem. Soc.*, 1956, **78**, 1190.
[19] Brook, *Trans. Faraday Soc.*, 1957, **53**, 327.
[20] Hey, Pengilly, and Williams, *J.*, 1956, 1463.
[21] Kooyman, *Discuss. Faraday Soc.*, 1951, **10**, 163.
[22] Gregg and Mayo, *Discuss. Faraday Soc.*, 1947, **2**, 328.