Reactions of Alkyl Radicals with Substituted Toluenes and the Effect of Substituents on Dissociation Energies of Benzyl C–H Bonds

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Dedicated to Professor *Hanns Fischer*, deceased on February 22, 2005

Reactions of isopropyl and of undecyl radicals with *meta-* and *para*-substituted toluenes are reported. The results demonstrate that the reactivities of toluenes are due to both benzyl-H abstraction and addition of the alkyl radicals to the aromatic ring. Relative reactivities yield curved *Hammett* plots, consistent with kinetic data reported by *Dütsch* and *Fischer*. Abstractions and ring additions occur with comparable rates, but opposite *Hammett* slopes. Addition is favored by electron-withdrawing and abstraction by electron-donating substituents. The effects of substituents on the dissociation energies of benzyl C–H bonds are shown to be the major factor influencing reaction rates for benzyl-H abstraction by alkyl radicals.

Introduction. – In 1982, *Dütsch* and *Fischer* published 'Nucleophilic Character of the *tert*-Butyl Radical. Absolute Rate Constants for the Reactions with Substituted Toluenes' [1]. *tert*-Butyl radicals were produced by pulsed photolysis of di(*tert*-butyl) ketone at 48°. The decay of *tert*-butyl radicals was measured by time-resolved electron paramagnetic resonance (EPR) spectroscopy in eleven *meta-* or *para*-substituted toluenes. A plot according to the *Hammett* equation (*Eqn. 1*) of the rate constants *vs.* *Hammett* substituent constants, σ, was found to have a positive slope, ρ. The σ values reflect the electron-donating or -withdrawing abilities of the substituents, k_X is the rate constant for reaction of *tert*-butyl radicals with the *meta-* or *para*-substituted toluene and k_H is that with toluene. Because electron-withdrawing groups enhanced the rate of disappearance of *tert*-butyl radicals, following usual practice, these results were interpreted to mean that the transition state for benzyl-H abstraction by *tert*-butyl radicals is stabilized by a 'polar effect', with charge separation in contributing dipolar structures as shown in *Eqn. 2*. This conclusion was based on the assumption that the only mode of reaction between *tert*-butyl radicals and the toluenes is benzyl-H abstraction. The positive slope, $\rho = 0.59$, classified the abstracting *tert*-butyl radical as 'nucleophilic', capable of accommodating a partial positive charge, with a partial negative charge on the benzyl C-atom. Electron-withdrawing substituents, positive σ, would stabilize the negative charge and speed the reaction. Electron donors, negative σ, would do the reverse.

$$\log(k_X/k_H) = \rho\sigma \tag{1}$$

$$XC_6H_4\dot{C}H_2\text{---}H\text{---}\dot{C}(CH_3)_3 \leftrightarrow XC_6H_4^{\delta-}CH_2\text{---}H\text{---}\overset{\delta+}{C}(CH_3)_3 \qquad (2)$$

The reason for interest in H abstractions from toluenes by alkyl radicals was a proposal that *Hammett* correlations in radical reactions might not always be due primarily to 'polar effects' in the transition state but effects of substituents on the bond-dissociation energy (*BDE*) of benzyl C–H bonds [2]. On the basis of *Hammett* correlations of $^{13}C,^{1}H$-NMR coupling constants of toluenes and other evidence, it had been postulated that electron-withdrawing substituents strengthen the bond and electron-donating substituents weaken it. The same was postulated for anilines on the basis of $^{15}N,^{1}H$ coupling constants. If this were the case, then all H abstractions from toluenes would have negative ρ values, as was the case up to then for abstractions by 'electrophilic' radicals such as chlorine, bromine, trichloromethyl, phenyl, *etc*., radicals. Positive slopes would disprove the proposal.

There ensued several reports of good *Hammett* correlations with positive slopes for reactions of *meta*- and *para*-substituted toluenes with primary-, secondary-, and tertiary-alkyl radicals. Undecyl radicals generated by thermolysis of dilauroyl peroxide (=bis(1-oxododecyl) peroxide), $Me(CH_2)_{10}CO_2)_2$, were reported to abstract a benzyl H-atom from toluenes with $\rho = 0.45$ in relative-reactivity determinations of each toluene *vs*. CCl_4 by measuring the amounts of the products undecane and 1-chloroundecane produced [3]. Possible addition of undecyl radicals to the aromatic ring was dismissed as a significant competing reaction because the amount of undecyltoluenes found was less than 1%. Undecyl radicals were also reported to abstract a H-atom from toluenes with $\rho = 0.5$ in relative-reactivity determinations of pairs of toluenes by NMR determinations of the amounts of toluenes remaining at the conclusion of the reaction *vs*. those at the start [4]. Again, possible addition to the ring was dismissed as a complicating factor because undecyltoluene was 'not a significant product.'

The 1-ethylpentyl radicals from thermolysis of *tert*-butyl 2-ethylhexaneperoxoate were also reported to abstract a benzyl H-atom with $\rho = 0.7$ by measurements of the amounts of the products heptane and 3-chloroheptane produced in competitions between each toluene *vs*. CCl_4 [5]. The possibility of secondary-alkyl radicals adding the aromatic rings was not considered. Another secondary radical, isopropyl, produced by photolysis of 'azoisopropane' (=bis(1-methylethyl)diazene), was also reported to give a positive $\rho = 0.8 \pm 0.1$ by competition measurements of substituted toluenes *vs*. deuterated thiol, RSD. The ratio of products Me_2CH_2 to Me_2CHD was determined by mass spectrometry from the ratio of *m/z* 43 to *m/z* 44 ($[M-1]^+$) [6].

tert-Butyl radicals were reported to abstract a benzyl H-atom with $\rho = 1.0 \pm 0.1$ in competitions of toluenes *vs*. C_6H_5SD by measuring the ratio of the mass fragments *m/z* 43 to *m/z* 44 ($[M-15]^+$) of the products [6][7]. Again, the possibility of alkyl-radical addition to aromatic rings was discounted because reaction of *tert*-butyl radicals with benzene or toluene did not produce significant amounts of isopropylbenzene or (*tert*-butyl)toluenes, respectively.

The argument has been advanced that the ρ values reported for methyl ($\rho = -0.17$ [8]), primary-, secondary-, and tertiary-alkyl radicals followed the trend of the ionization energies plus electron affinities, *Mulliken*'s electronegativities, of the alkyl radicals. The sum decreases from methyl to *tert*-butyl. The lower the sum, the greater the ability to accommodate positive charge [5]. As a result of these reports, the proposal that differences in the *BDE* of benzyl C–H bonds were a major factor for the *Hammett* correlations observed for H abstractions from toluenes appeared disproved.

The kinetic measurements of *Dütsch* and *Fischer* with *tert*-butyl radicals [1], however, provided data inconsistent with those described above in several important ways and generated the impetus for much of the work to be reported here. The absolute rate constants reported indicate that only *ca.* 4% of the *tert*-butyl radicals reacted with toluene immediately after the pulse and 8% at 50% decay of the radicals[1]) [9] with the remainder being self-reactions, coupling, and disproportionation. Nevertheless, the technique used was capable of following the reactions down to *ca.* 0.5%. *Dütsch* and *Fischer* noted that the *Hammett* correlation of his kinetic data was a very poor one, unlike the other reports described above. Specifically, 'for $\sigma < 0.23$ our absolute rate constants do not vary systematically with σ and are nearly equal for all toluenes'. The authors also added that 'we do not think that the substituent effects found in this study should be taken as unambiguous proof of the general applicability of Eq. (1) to radical reactions', and they concluded that a linear *Hammett* equation did not seem to fit the kinetic data. We have re-plotted the data of *Dütsch* and *Fischer* in *Fig. 1*.

Tanner and co-workers [10] also have questioned the validity of the interpretation of the results with 1-ethylpentyl(=heptan-3-yl) radicals because little of the heptane reported [5] came from H abstraction from toluenes and concluded that 'the nucleophilicity or electrophilicity of a secondary-alkyl radical has not yet been experimentally demonstrated'.

In the following section, we make some comments regarding interpretations of previously reported results and then present new measurements of reactions of isopropyl and undecyl radicals.

Results and Discussion. – The solid straight line in *Fig. 1* is plotted according to *Dütsch* and *Fischer*, who reported $\rho = 0.59 \pm 0.09$, quite different from the $\rho = 1.0$ previously reported by *Pryor* and co-workers [6][7]. It can be seen that the straight line fits only about three points and that it does not pass through the point at $\sigma = 0.0$ (toluene), as it should. The dashed line curve, drawn by us, fits virtually all points with the exception of one, due to *p*-Cl, which is not accommodated by either line or by any line that would pass near the origin. The curve is similar in shape with what is obtained if our reported [11] relative reactivities of toluenes toward undecyl radicals are plotted. A nonlinear *Hammett* plot often indicates either a change in mechanism within the range of σ values examined, or that there are two different reactions occurring with comparable rates but different *Hammett* slopes. In this case, a second possible reaction is addition to the aromatic rings. The curve in *Fig. 1* is not a free-hand drawing through the points. It was generated by plotting the logarithm of the sum of k_{abs} for abstraction and k_{add} for addition, obtained from $\log k_{\mathrm{abs}} = 1.03 - 0.80\sigma$ and $\log k_{\mathrm{add}} = 0.52 + 1.70\sigma$, respectively. The coefficients were selected to produce a reasonable fit to the kinetic measurements of *Dütsch* and *Fischer*. The positive slope for addition is consistent

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[1]) Calculated with a rate constant of $2k_{\mathrm{t}} = 2 \cdot 10^9$ for the self-termination of *tert*-butyl radicals [9].

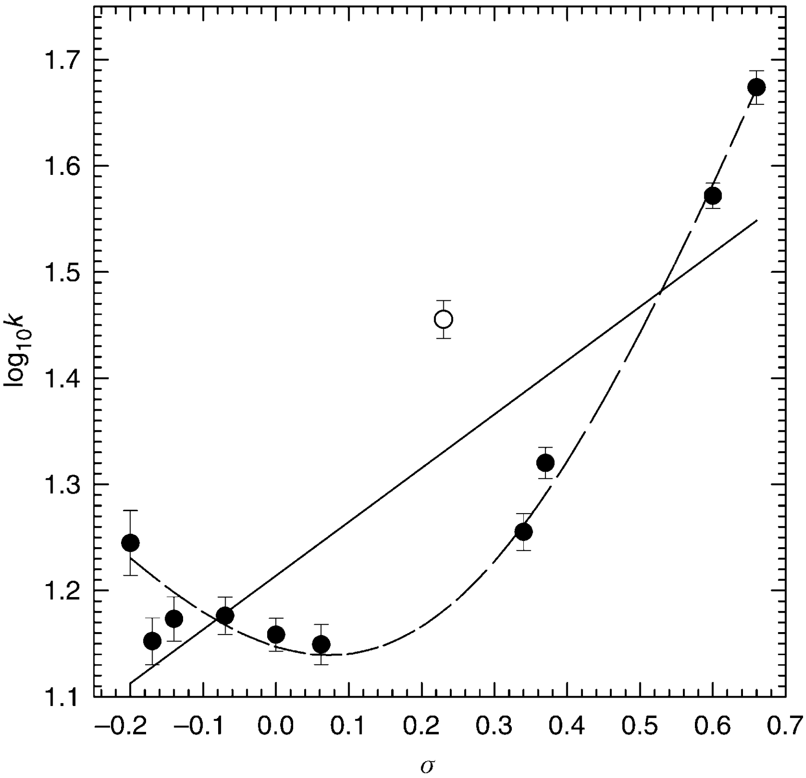
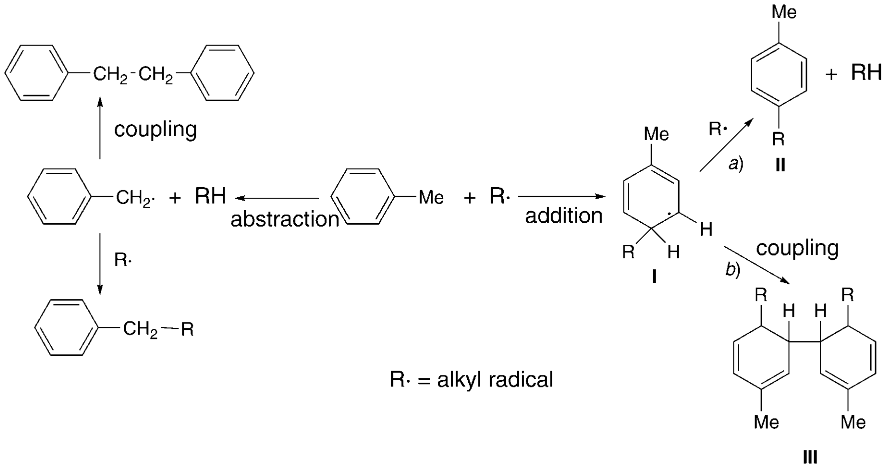


Fig. 1. *Plot of the logarithm of the absolute rate constants for reaction of* tert-*butyl radicals with substituted toluenes* vs. Hammett *substituent constants*, σ [1]. Solid circles from left to right: *p*-^{t}Bu, *p*-Me, *m,m'*-diMe, *m*-Me, H, *p*-F, *m*-F, *m,p*-diCl, *p*-CN. Open circle: *p*-Cl.

with the report that k_{add} of the less selective cyclohexyl radicals adding to the *meta-* and *para*-positions of substituted benzenes plot with a positive ρ of 1.1 [12]. The negative slope for benzyl-H abstraction is consistent with our proposal [2].

Addition of alkyl radicals to the ring of toluene has long been known to compete with abstraction of a benzyl H-atom. Methyl radicals react with toluene by both benzyl-H abstraction and addition to the ring [8][13]. Cyclohexyl radicals react with toluene to produce an 11% yield of cyclohexyltoluenes and a 47% yield of high-boiling material described as arising from coupling of the cyclohexadienyl-type adduct of cyclohexyl to the ring, indicating substantial ring addition [12]. Such radical additions to the ring complicate considerably the interpretation of reported experimental results. The *Scheme* shows some of the major reaction pathways. Alkane can be produced not only from abstraction of a benzyl H-atom but also by *Path a* and by abstraction from all isomers of **III**. For reactions of *tert*-butyl radicals, given the small amounts reacting with toluenes, *Tanner* and co-workers reported that disproportionation of *tert*-butyl radicals is the major contributor to the formation of isobutane (=2-methylpropane) [14]. Absence of large amounts of alkylated toluene **II** does not necessarily reflect a small amount of addition. It has long been known that the ratio of reaction of the radical

Scheme



adduct **I** through *Paths a* or *b* is very much dependent on the concentration of alkyl radicals. At low concentrations of R˙, *Path b* is by far the most favored, as expected [15][16]. In the reaction of methyl radicals with toluene $C_6H_2D_3CH_3$, there was an 8% yield of CH_3D, arising from abstraction by methyl radicals from the adduct **I**, with 1.2M diacetyl peroxide precursor, but the yield of CH_3D was less than 1% with 0.1M diacetyl peroxide. It was understood that this did not indicate a smaller ratio of addition *vs.* abstraction at the lower concentration of peroxide [13].

Because of experimental problems found by *Tanner* and co-workers [14] with the work that reported $\rho = 1.0$ for *tert*-butyl radicals, *Pryor* and co-workers re-investigated the reactivity of *tert*-butyl radicals from azoisobutane (= bis(2-methylpropyl)diazene) photolysis with toluenes and reported $\rho = 0.49$ [17] ascribed to benzyl-H abstraction, in good agreement with the ρ value reported by *Dütsch* and *Fischer* [1]. However, there was serious disagreement in the reactivities relative to toluene of many substituents, *e.g.*, *p*-(*tert*-butyl) 1.22 [1] and 0.78 [17], *p*-CN 3.28 [1] and 2.23 [17], *etc.* Both reports of positive ρ did not include strongly electron-withdrawing substituents such as *p*-methoxy or *p*-phenoxy. *Tanner* and co-workers found quite high reactivity for *p*-phenoxytoluene toward *tert*-butyl radicals, 4.8 times higher than that of toluene [14]. If H abstraction were the only reaction occurring, this value should have been much lower than unity, on the basis of the positive ρ values reported [1][17]. Absence of (*tert*-butyl)toluenes has been cited as evidence against addition to the ring [17], but there is another report that *o*- and *p*-(*tert*-butyl)toluenes (from ring addition) are present in a ratio of 2 : 11 to neopentylbenzene (= (2,2-dimethylpropyl)benzene; from abstraction) in the products of decomposition of azoisobutane in toluene [18].

The values of ρ near 0.5 reported both by *Dütsch* and *Fischer* and by *Pryor* and co-workers for *tert*-butyl radicals invalidate the previously reported ρ values for primary- and secondary-alkyl radicals. According to the argument of 'polar effects' at the transition state of benzyl-H abstraction, primary- and secondary-alkyl radicals should have lower ρ values than tertiary ones, and they do not, having been reported as 0.5 and 0.8, respectively. In addition, the argument of 'polar effects' at the transition state being consistent with the trends of ionization energies (*IE*) of the series of methyl, primary-, secondary-, and tertiary-alkyl radicals is self contradictory. In H abstractions of a benzyl H-atom by alkyl radicals, polar resonance structures to be considered at the transition state are as shown in *Eqn. 3*.

In deciding whether structure **A** or **B** is appropriate, ionization energies of both the benzyl radical and the alkyl radical must be considered. Primary-alkyl radicals have $IE = 8.1$ eV (ethyl, propyl), and benzyl radicals have $IE = 7.2$ eV. The benzyl radical is better capable of accommodating a positive charge and, therefore, structure **B** is the appropriate one. This would require that electron-withdrawing groups retard the rate and electron-donating groups enhance it, resulting in a negative ρ. Nevertheless, ρ values were reported and justified by the ionization-potential argument. If electron affinities are also added to *IE* (*Mulliken*'s electronegativity), then $IE + EA = 7.9$ eV for primary-alkyl and 8.2 eV for benzyl radicals. Again, primary-alkyl radicals are the more electronegative of the two. Hence, primary-alkyl radicals should be considered electrophilic, not nucleophilic, *vs.* benzyl radicals. Actually, electronegativity differences between alkyl and benzyl radicals are so small that they are unlikely to produce large *Hammett* slopes, negative or positive ones. Benzyl C–H *BDE* differences, however, may do so.

$$\mathrm{Ph\dot{C}H_2}\text{---}\mathrm{H}\text{---}\mathrm{\dot{R}} \leftrightarrow \underset{\mathbf{A}}{\mathrm{Ph}\overset{\delta-}{\mathrm{CH_2}}\text{---}\mathrm{H}\text{---}\overset{\delta+}{\mathrm{R}}} \leftrightarrow \underset{\mathbf{B}}{\mathrm{Ph}\overset{\delta+}{\mathrm{CH_2}}\text{---}\mathrm{H}\text{---}\overset{\delta-}{\mathrm{R}}} \qquad (3)$$

It is relevant that our postulate [2] of the effects of substituents on benzyl C–H bonds or quasi-benzyl bonds is validated by the measurements of *Mahoney* and *DaRooge* with substituted phenols [19]. Electron-donating substituents weaken the O–H bond and electron-withdrawing substituents strengthen it. Other studies followed[2]) [20], and *BDE*(O–H) was found to increase by a large amount, 10–11 kcal mol^{-1}, from 4-MeO to 4-NO_2 substituents. Our postulate that *BDE*(N–H) of substituted anilines would also show such an effect was borne out by subsequent measurements [21], with *BDE*(N–H) increasing by 6.8 kcal mol^{-1} from 4-$MeOC_6H_4NH_2$ to 3,5-$(CF_3)_2C_6H_4NH_2$ [21a]. Similar trends were found for *BDE*(S–H) in thiophenols [20d][3]) [22], for *BDE*(ArO–C) of anisoles [23][4]), *etc.* More directly relevant to abstractions from substituted toluenes are measurements pertaining to *BDE*(C–H) of the methyl group. *Pryor* and co-workers measured substituent effects on *BDE*(benzyl C–H) of toluenes by iodination studies and found a good correlation with σ^+, correlation coefficient $r = 0.97$ [24]. The data of *Pryor* and co-workers lead to *BDE* increasing by 2.56 kcal mol^{-1} per unit increase of σ^+. This corresponds to an increase of 4.0 kcal mol^{-1} from *p*-methoxytoluene to *p*-nitrotoluene, consistent with the same estimate made previously by *Howard* and *Chenier* [25]. From kinetics of brominations, we reported that benzyl *BDE*(C–H) in *m*-chlorotoluene is 2.2 ± 0.6 kcal mol^{-1} stronger that in *p*-xylene (=1,4-dimethylbenzene) [26], which is consistent with *Pryor* and co-

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[2]) *BDE* correlated with σ^+ [20a].

[3]) Correlation with σ^+ [20d].

[4]) Correlation with σ^+ [23a].

workers' value of 1.9. *Bordwell* and co-workers reported that benzyl C$-$H bonds in *meta-* and *para*-substituted arylacetonitriles, $XC_6H_4CH_2CN$, are strengthened by electron-withdrawing groups and weakened by electron donors, *BDE*(C$-$H)$=$77.9 kcal mol^{-1} with X$=$4-Me_2N and 83.0 with X$=$4-CF_3 [27], and reported confirmation of our *BDE* postulate. Similar results were obtained for the benzyl C$-$H bonds of benzyl phenyl sulfones, $XC_6H_4CH_2SO_2Ph$ [28]. In all the above cases, electron-withdrawing substituents strengthen the benzyl or quasi-benzyl bond and the reverse holds for electron donors. On the other hand, experimental values for *BDE*(S$-$NO) of substituted *S*-nitrosothiophenols show the opposite trend, $BDE = 20.1 - 1.4\sigma^+$, with a rather poor $r = -0.65$ [29]. Theoretical calculations of a series of *para*-substituted $ArSiH_2-F$ also showed a decrease in *BDE* in going from electron-donating to electron-withdrawing substituents, $\Delta BDE = -2.34\sigma^+$, and the same trend holds for *para*-substituted $ArSiH_2-Cl$, $\Delta BDE = -1.70\sigma^+$. The trend reverses for $ArSiH_2-Li$, $\Delta BDE = 9.12\sigma^-$, and there is no discernible trend for $ArSiH_2-H$ [30]. Experimental measurements by *Marque*, *Studer*, and co-workers of rates of homolytic cleavage of the C$-$O bond in *para*-substituted benzyl nitroxides, *p*-$XC_6H_4CHR-ONR_2$ (alkoxyamines derived from TEMPO ($=$2,2,6,6-tetramethylpiperidin-1-yloxy), also showed a decrease in energy of activation for bond cleavage with electron-withdrawing substituents [31]: $\Delta E_a = -1.81\sigma$. Rather than being contradictory, all these results lend support to the proposals that the direction of the dipole of the bond being broken, a ground-state effect, can be a significant factor in determining the slope of *Hammett* correlations in atom abstractions by radicals [32]. When the dipole of the bond points toward the ring (toluenes, anilines, phenols, anisoles, thiophenols, and $ArSiH_2-Li$), electron-withdrawing substituents strengthen the benzylic or quasi-benzylic bond, ArG$-$Y. When the dipole points away ($ArSiH_2-F$, $ArSiH_2-Cl$, ArS$-$NO, $ArCHR-ONR_2$), they weaken it. Although this conclusion was questioned on the basis of theoretical calculations for benzyl halides [33], the results cited above support it.

Because of the *BDE* results for toluenes, it seemed unlikely that substituent effects on the *BDE* of benzyl C$-$H would have little or no effect on the rates of abstraction, all being explained by 'polar effects' at the transition state between two C-radicals, alkyl and benzyl, of similar electronegativities. Also because of the kinetic complexity of the *Scheme* and the additional complicating fact that *tert*-butyl radicals not only couple but disproportionate with benzyl radicals to regenerate the toluenes and produce isobutylene ($=$2-methylprop-1-ene), we re-investigated reactions between alkyl radicals and toluenes. Measurements of alkane products formed or relative rates of disappearance of reactant toluenes are not easily interpreted (see *Scheme*). An unequivocal method of determining the relative importance of benzyl-H abstractions *vs.* additions to the rings is the determination of relative reactivities of each toluene *vs.* a similarly substituted benzene, $XC_6H_4CH_3$ *vs.* C_6H_5X, by measuring the disappearance of reactants. This simple and direct competition has not been done in any of the previous relevant studies mentioned above, except for our work with undecyl radicals [11].

We report here such experiments with secondary-alkyl radicals. They should be more reactive than tertiary-alkyl radicals and decrease the extent of self-reactions, consume more substrate, and be more selective than primary ones so that ρ values near zero would not be obtained. We avoided using *tert*-butyl peroxyesters as sources of alkyl radicals [5][6][14], because the generated *tert*-butoxy radicals immediately abstract a benzyl H-atom and lead to high concentrations of benzyl radicals, evidenced by large amounts of bibenzyls (=1,1′-(ethane-1,2-diyl)bis[benzenes]) found in such studies. Benzyl radicals accumulating in the system are excellent radical traps for the alkyl radicals.

We generated isopropyl radicals by thermal decomposition of diisobutyryl peroxide (=bis(2-methyl-1-oxopropyl peroxide), $Me_2CHCO_2OCOCHMe_2$, on dropwise addition of its cyclohexane solution into refluxing cyclohexane, under a slow stream of 'oxygen-free' Ar. The identified products are listed in *Table 1*. *Walling* and *Sloan* have shown that such peroxide decompositions would produce not only isopropyl radicals and 2 CO_2, but also substantial amounts of ester $Me_2CHCO_2CHMe_2$ and CO_2, and of the carboxy inversion product $Me_2CHCO_2CO_2CHMe_2$ [34]. On GLC analysis, pyrolysis of the carboxy inversion product was reported to produce nonquantitative yields of alcohol and carboxylic acid. *Table 1* shows that our results are consistent. Propane and prop-1-ene escape from our experimental system, but their combined amount can be calculated confidently from the amount of 2,3-dimethylbutane: the ratio of disproportionation to combination of isopropyl radicals is 1.2 at 30° in hydrocarbon solvent [35], very near the gas-phase value of 1.1 [36]. *Table 1* shows adequate yields of isopropyl radicals.

Table 1. *Gas Chromatographic Analyses of the Products of Decomposition of Diisobutyryl Peroxide in Refluxing Cyclohexane*

	Yield [mol/mol peroxide]		
	Exper. 1[a])	*Exper. 2*[b])	*Exper. 3*[c])
2,3-Dimethylbutane (^iPr-^iPr)	0.30	0.37	0.35
Isopropyl alcohol (^iPrOH)	–[d])	0.004	0.08
Isopropyl isobutyrate ($^iPrCO_2{}^iPr$)	0.07	0.11	0.05
Isopropylcyclohexane[e]) ($^iPrC_6H_{11}$)	0.03	0.04	0.03
Isobutyric acid ($^iPrCO_2H$)	–[f])	0.14	0.08
Bicyclohexyl (C_6H_{11}–C_6H_{11})	0.03	0.02	trace
Propane/pro-1-ene[g]) ($MeCH_2Me$/$MeCH{=}CH_2$)	(0.36)	(0.44)	(0.42)
Total as % of theoretical[h])	–	79	71

[a]) 15.0 ml of 0.73M peroxide in cyclohexane added to 30.0 ml of refluxing cyclohexane. Products analyzed in triplicate on a *SE-30* GLC column. [b]) Same as *Footnote a*, analyzed in triplicate on a *FFAP* GLC column. [c]) 15.0 ml of 1.10M peroxide added to 37.5 ml of refluxing cyclohexane, analyzed in triplicate on a *FFAP* GLC column. [d]) Not separated from cyclohexane. [e]) Identity assumed on the basis of retention time. [f]) Small, trailing peak, not quantifiable. [g]) Calculated from 2,3-dimethylbutane, see text. [h]) Counting isopropyl groups in the products and assuming a theoretical yield of two isopropyl groups per mol of diisobutyryl peroxide.

To establish the reactions that occur between isopropyl radicals and toluene, we added cyclohexane solutions of diisobutyryl peroxide dropwise into a refluxing solution of toluene in cyclohexane under a slow stream of Ar. The identified products are shown in *Table 2*. The yield is lower than in the absence of toluene shown in *Table 1*. The missing yield is due to dimers and high-boiling materials arising from the addition branch of the *Scheme*. Cyclohexadiene-type materials would polymerize easily under the reaction

Table 2. *Gas-Chromatographic Analyses of Products of Decomposition of Diisobutyryl Peroxide in Refluxing Solutions of Toluene in Cyclohexane*

	Yield [mol/mol peroxide]			
	Exper. 4[a])	*Exper. 5*[b])	*Exper. 6*[c])	*Exper. 7*[d])
2,3-Dimethylbutane (^{i}Pr-^{i}Pr)	0.250	0.175	–[e])	0.213
Isopropyl alcohol (^{i}PrOH)	– [e])	0.005	0.041	0.096
Isopropyl isobutyrate (^{i}PrCO$_2$^{i}Pr)	0.124	0.127	0.216	0.052
Isobutylbenzene (^{i}PrC$_6$H$_5$)	0.076	0.096	0.076	0.090
m- and *p*-Isopropyltoluene[f]) (*m*- and *p*-^{i}PrC$_6$H$_4$Me)	0.025	0.031	0.022	0.028
o-Isopropyltoluene (*o*-^{i}PrC$_6$H$_4$Me)	0.009	0.010	0.014	0.011
Isobutyric acid (^{i}PrCO$_2$H)	–[e])	0.197	0.350	0.127
1,1′-(Ethane-1,2-diyl)bis[benzene] (PhCH$_2$CH$_2$Ph)	0.010	0.026	0.025	0.007
Propane/prop-1-ene[g]) (MeCH$_2$/MeCH=CH$_2$)	(0.300)	(0.210)	–[e])	(0.256)
Total as % of theoretical[h])	–	58	–	57

[a]) 15.0 ml of 0.63M peroxide in cyclohexane were added at 20 drops/min to 30.0 ml of gently refluxing 4.72M toluene in cyclohexane at 84°. [b]) Same as *Footnote a*, but with 0.73M peroxide. [c]) 23.5 ml of 0.28M peroxide were added over 15 min to 5.0 ml of gently refluxing 4.60M toluene in cyclohexane. [d]) 15.0 ml of 1.10M peroxide were added over 15 min to 37.5 ml of gently refluxing 4.27M toluene in cyclohexane. [e]) Not quantified. [f]) Eluted together. [g]) Calculated from 2,3-dimethylbutane, see text. [h]) Counting isopropyl groups in the products and assuming a theoretical yield of two isopropyl groups per mol of diisobutyryl peroxide.

conditions, and they are excellent sources of abstractable H-atoms. *Table 3* shows the normalized results of *Table 2* for identified products of addition to the ring of toluene and of abstraction of a benzyl H-atom. The ratio of addition (alkylated toluenes) to abstraction (number of benzyl groups) varies between 0.27 and 0.38. This ratio is a minimum because the amount of alkylated toluenes reflects only a part of the products of addition shown in the *Scheme*. The fact that we found significant amounts of isopropyltoluenes, while others have not, is due to the fast rates of decomposition of our radical source yielding high concentrations of alkyl radicals. The half-life of diisobutyryl peroxide has been reported as 34 min at 40° [37]; it would be about 20 s at 84°, unlike the slow photolysis experiments mentioned above. We also note that photolysis of azoisobutane at 30° in toluene has been reported to yield both isopropyltoluene and isobutylbenzene in a ratio of 1:10 (Table X in [16]), even though the slow rate of photolysis would suppress the formation of isopropyltoluene from radical adducts to the ring.

The next series of experiments were competitions between a substituted toluene with a similarly substituted benzene. Isopropyl radicals were generated by dropwise addition of solutions of diisobutyryl peroxide in cyclohexane into solutions of toluenes and substituted benzenes in gently refluxing cyclohexane under a slow stream of N_2. Relative reactivities were obtained by measuring (GLC) the concentration of the two reactants before and after completion of the reaction. *Eqn. 4* was used to calculate relative reactivities.

$$k_X/k_H = \log([XC_6H_4Me]_i/[XC_6H_4Me]_f)/\log([C_6H_5Me]_i/[C_6H_5Me]_f) \qquad (4)$$

Table 3. *Identified Products of Abstraction from and of Addition to Toluene by Isopropyl Radicals, Normalized to 100 Parts*[a])

	Exper. 4	*Exper. 5*	*Exper. 6*	*Exper. 7*
Isobutylbenzene ($^iPrCH_2Ph$)	63	59	55	66
m- and *p*-Isopropyltoluenes (*m*- and *p*-$^iPrC_6H_4Me$)	21	19	16	21
o-Isopropyltoluene (*o*-$^iPrC_6H_4Me$)	8	6	10	8
1,1′-(Ethane-1,2-diyl)bis[benzene] ($PhCH_2CH_2Ph$)	8	16	18	5
Min. ratio addition/abstraction[b])	0.37	0.27	0.29	0.38

[a]) From *Table 2*. [b]) Isopropyltoluenes/(isobutylbenzene + 2 × 1,1′-(ethane-1,2-diyl)bis[benzene]).

The subscripts i and f refer to initial and final concentrations. The results are given in *Table 4*. In this system, isopropyl radicals do not attack cyclohexane extensively: little isopropylcyclohexane is reported in *Table 1* and none in *Table 2*. Even if they do to a small extent, the radical generated is also a secondary-alkyl radical. The results are plotted in *Fig. 2 vs.* σ^+, a substituent parameter better suited to reflecting any resonance effects, often found to give better correlations in a variety of radical reactions [2] [38] and in their correlation with *BDE* of benzyl C−H bonds [24], and better correlating with the ionization potentials of substituted benzyl radicals [39]. The similarity of the curve of our results with that of *Dütsch* and *Fischer*'s data in *Fig. 1* is striking, even though the latter did not include *p*-methoxytoluene. Whether one plots *vs.* σ or σ^+, the nonlinearity noted by *Dütsch* and *Fischer* remains. The curve of *Fig. 2* was obtained from the logarithm of the sum of k_{add} and k_{abs}, which were obtained from $\log k_{add} = 0.90\sigma^+ - 0.13$ and $\log k_{abs} = -0.90\sigma^+ - 0.48$, where the coefficients were optimized to produce a reasonable fit to the experimental results; k_{abs} and k_{add} are not rate constants but relative reactivities. We note that $\rho = 0.9$ for isopropyl-radical addition to the ring is compatible with the reported $\rho = 1.1$ for cyclohexyl-radical addition to the *meta*- and *para*-positions of substituted benzenes [12]. For benzyl-H abstraction, a negative ρ is found as originally predicted on the basis of our postulate of ring substituents affecting the *BDE* of benzyl C−H bonds [2]. *Fig. 2* is only a qualitative *Hammett* plot in that it includes the reactivities of addition *ortho* to a ring substituent, a reaction not correlating with *Hammett* substituent constants. This introduces some scattering in the points. Therefore, the ρ values used to produce the curve shown are only qualitative indicators.

Hammett correlations are not necessary for understanding the reactivity patterns of isopropyl radicals. It is clear from *Table 4* that substituted benzenes are quite reactive and that benzonitrile is much more reactive than anisole, consistent with the previous reports of positive *Hammett* slopes for addition to the ring by secondary-alkyl radicals. Benzonitrile is twice as reactive as toluene, even though it does not have benzyl H-atoms. From the relative reactivities, it can be seen that, with the strongly electron-withdrawing CN substituent, the reactivity ratio of *p*-cyanotoluene[5]) to benzonitrile is only 1.6 : 1 and that of *m*-cyanotoluene[5]) to benzonitrile only 1.4 : 1. Most of the reactivity of the cyanotoluenes is not due to benzyl-H abstraction. With the strongly electron-donat-

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[5]) For systematic names, see *Table 4*.

Table 4. *Relative Reactivities of Benzenes and Toluenes toward Isopropyl Radicals*[a])

	σ	σ^+	Relative reactivity[b])
p-Cyanotoluene (=4-methylbenzonitrile; *p*-MeC_6H_4CN)	0.66	0.67	3.18 ± 0.03 (3)
m-Cyanotoluene (=3-methylbenzonitrile; *m*-MeC_6H_4CN)	0.56	0.62	2.81 ± 0.01 (4)
m-Chlorotoluene (=1-chloro-3-methylbenzene; *m*-MeC_6H_4Cl)	0.37	0.37	1.75 ± 0.04 (3)
p-Chlorotoluene (=1-chloro-4-methylbenzene;*p*-MeC_6H_4Cl)	0.23	0.11	1.39 ± 0.04 (3)
m-Methoxytoluene (=1-methoxy-3-methylbenzene; *m*-MeC_6H_4OMe)	0.12	0.05	1.23 ± 0.04 (3)
Toluene (=methylbenzene; MeC_6H_5)	0.00	0.00	1.00[c])
p-Xylene (=1,4-dimethylbenzene; *p*-MeC_6H_4Me)	−0.17	−0.31	0.99 ± 0.04 (3)[d])
p-Methoxytoluene (=1-methoxy-4-methylbenzene; *p*-MeC_6H_4OMe)	−0.27	−0.78	1.88 ± 0.06 (4)
Benzonitrile (PhCN)			1.99 ± 0.04 (3)
Chlorobenzene (PhCl)			0.83 ± 0.04 (3)
Anisole (=methoxybenzene; PhOMe)			0.62 ± 0.03 (4)

[a]) 5.00 ml of 2.00M toluene and 2.00M substituted toluene or substituted benzene in cyclohexane were brought to gentle reflux under N_2 (79–80°). Then, 8.00 ml of 1.4–1.5M diisobutyryl peroxide in cyclohexane were added over 60 min, followed by refluxing for 8 h. [b]) ± is the average deviation of the performed analyses (number in parentheses). [c]) Standard of reactivity. [d]) Normalized to one methyl group.

ing *p*-methoxy substituent, the reactivity ratio of *p*-methoxytoluene[5]) to anisole[5]) is 3.0:1. Most of the reactivity of *p*-methoxytoluene is due to benzyl-H abstraction. The corresponding ratios for the *m*- and *p*-chlorotoluenes[5]) and for *m*-methoxytoluene follow the trend required by their intermediate σ^+ values. Possible side reactions such as additions to the triple bond of the cyano group, *ipso* attack, and replacement of the Cl-atom, or H abstraction from the methyl group of the methoxy substituent are irrelevant because they would happen in both the substituted benzenes and the similarly substituted toluenes. The high reactivity of *p*-methoxytoluene cannot be ascribed to abstraction of a H-atom from the methyl group of the methoxy group, because *m*-methoxytoluene in *Fig. 2* is not farther away from the curve than is the average scatter of any other points, and its reactivity is normal, lying between those of toluene and *p*-chlorotoluene, its σ^+ neighbors on either side.

The high reactivity of *p*-methoxytoluene toward isopropyl radicals is consistent with the high reactivity of *p*-phenoxytoluene found by *Tanner* and co-workers with *tert*-butyl radicals, 4.8 times more reactive than toluene [14], while the reactivity of *m*-phenoxytoluene was normal and similar to that of *p*-chlorotoluene, its neighbor on the σ or σ^+ scale[6]). H Abstraction of aromatic H-atoms of the *p*-phenoxy substituent can be discounted.

It may be tempting to dismiss the meaning we have attributed to the plot of *Fig. 2* as being based on one point only, that of *p*-methoxytoluene. However, such dismissal must also dismiss the reactivities found for benzonitrile, chlorobenzene, and anisole in this work, as well as the behavior of *tert*-butyl radicals from *Dütsch* and *Fischer*'s kinetic results [1] and *Tanner* and co-workers' relative reactivities [14].

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[6]) A *Hammett* plot was not made in the original publication. We use the values designated 'corrected' of Me_3CH/Me_3CD from Table V of [12].

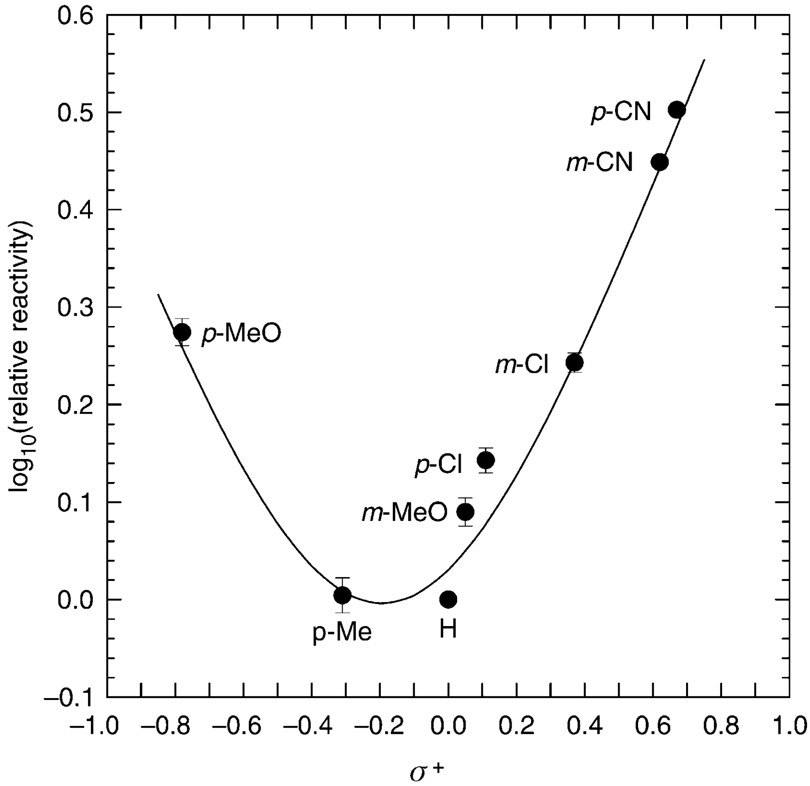

Fig. 2. *Plot of the logarithm of the relative reactivities of substituted toluenes toward isopropyl radicals* (*Table 4*) vs. σ^+

We have also repeated some of our previously reported relative-reactivity experiments with undecyl radicals, where benzene was an unfortunate choice as a solvent because addition to the ring was not suspected at the time [11]. The two substrates combined were about 1.3M, while the benzene solvent was of the order of 6M, and relative reactivities were determined by measuring disappearance of toluenes. The yield of undecane was only 13% based on peroxide, and it exceeded the amounts of substrates reacted, evidently because it was produced from reactions with products of addition to benzene and disproportionation of undecyl radicals. Nevertheless, using benzene solvent should not affect significantly the relative rates of disappearance of substrate toluenes and benzenes examined, even though undecyl radicals are also consumed by reaction with the benzene solvent. In this work, we determined again some relative reactivities by adding solid dilauroyl peroxide (5.00 g) to a gently refluxing mixture of toluene (3.25 g), *p*-methoxytoluene (3.63 g), anisole (3.72 g), and benzene (3.07 g), under a slow stream of 'oxygen-free' N_2 over 60 min and determined relative reactivities by *Eqn. 4*. In three independent runs, we obtained $k_X/k_H = 1.46 \pm 0.03$ for *p*-methoxytoluene relative to toluene = 1.00 and $k_X/k_H = 0.43 \pm 0.2$ for anisole. Disappearance of benzene could not be quantified because blank runs indicated some loss by evaporation. There is a serious discrepancy between our value of k_X/k_H for *p*-methoxytoluene and the value of 0.69 reported by *Pryor* and *Davis* [4]. Therefore, we also determined relative reactivities by measuring reactant disappearance in some mixtures of toluene and a substituted toluene (or substituted benzene) and dilauroyl peroxide placed in a constant-temperature bath at $80 \pm 0.3°$ for 5 h under a very slow stream of 'oxygen free' Ar. Relative reactivities obtained by *Eqn. 4* were for *m*-cyanotoluene 2.62 ± 0.36, for benzonitrile 2.02 ± 0.17, for *p*-xylene 2.25, for anisole 0.35 ± 0.10, and for *p*-methoxytoluene 1.45 ± 0.15[7]). Comparing the reactivity of *m*-cyanotoluene to benzonitrile shows that most of the reactivity of the former is not due to benzyl-H abstraction. Comparing the reactivity of *p*-methoxytoluene to anisole shows the reverse. The yield of undecane was $30 \pm 2\%$ on peroxide, more than twice as much as previously obtained with benzene as the solvent. The yield calculated from disappearance of reactants was only $21 \pm 2\%$. The excess undecane is produced by disproportionation with **I** and abstraction from **III** (see *Scheme*), without consuming starting substrates. The possibility of addition to aromatic rings had been discounted in [4] because 'undecyltoluene is not a significant product'. However, the amount of undecyltoluene from mixtures of toluene in benzene as the solvent and dilauroyl peroxide was reported [4] as 0.024M and the amount of undecane produced as 0.18M, indicating that undecyltoluenes were a significant 16% of the undecane formed after accounting for 0.03M undecane reported as formed by disproportionation of undecyl radicals with themselves. It was also reported [4] that the amount of undecane produced was 80% higher than the amount of toluenes reacted, with the note that 'we cannot account for all of the excess undecane'. Abstraction of a H-atom by undecyl radicals from radical adducts **I** and **III** of the *Scheme* explains the formation of this apparent 'excess'. Our original note for undecyl radicals [11] did not include a *Hammett* plot, and we provide one here, *Fig. 3*, for comparison with *Fig. 2*. *Fig. 3* includes relative-reactivity values obtained in this work, averaged with those previously reported. The curve of *Fig. 3* was obtained from the logarithm of the sum of k_{add} and k_{abs}, which were obtained from $\log k_{add} = 1.00\sigma^+ - 0.45$ and $\log k_{abs} = -0.40\sigma^+ - 0.20$, where the coefficients were optimized to produce a reasonable fit to the data. The plot is qualitative and scatter should be expected because the reactivities include ring additions to *ortho* positions, which do not correlate with *Hammett* constants. Nevertheless, a negative ρ for abstraction is evident.

Abstractions of halogen atoms from substituted benzyl halides by tributylstannyl radicals and by triethylsilyl radicals show *Hammett* correlations with positive ρ [40]. This is consistent with the proposal that electron-donating substituents strengthen benzyl–halogen bonds and electron-withdrawing substituents weaken them [30], producing an effect opposite to what is seen with abstractions of benzyl H-atoms.

We turn to the question of how differences in *BDE* relate to the ρ values reported here. The benzyl C–H bond of *p*-methoxytoluene is 2.56 ($\Delta\sigma^+$) stronger than that of

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[7]) The source of the discrepancy between our value of 1.45 for the reactivity of *p*-methoxytoluene *vs.* toluene and 0.69 of [4] is unresolved. However, we note that the two values are the reciprocal of each other. In the NMR determinations of [4], if the signals of the benzyl H-atoms of *p*-methoxytoluene (δ 2.26) and of toluene (δ 2.34) were identified as the reverse, the discrepancy would disappear. In our GLC analyses, the retention times are quite different.

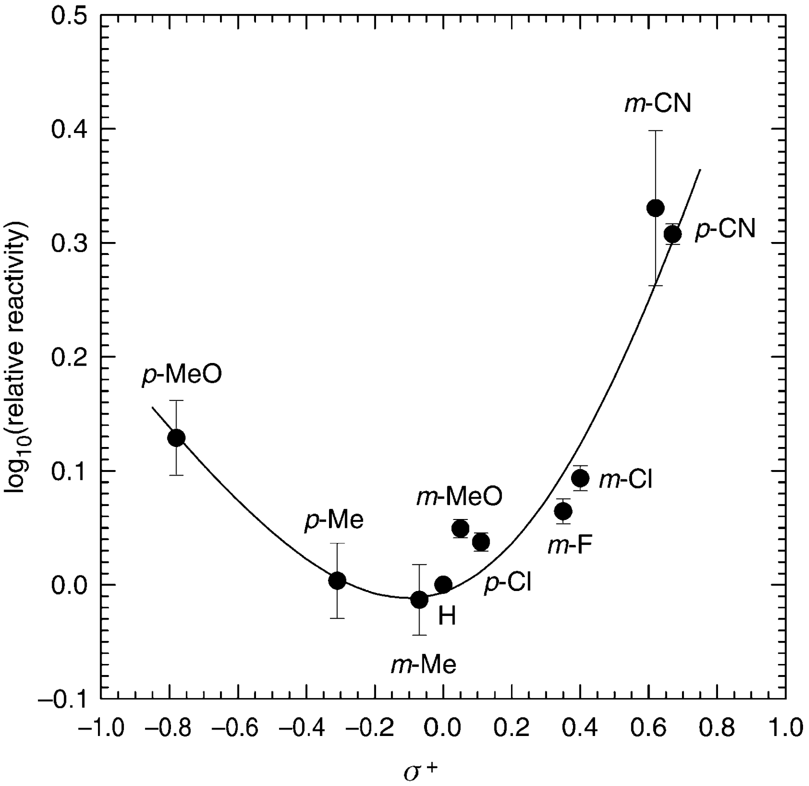

Fig. 3. *Plot of the logarithm of the relative reactivities of substituted toluenes toward undecyl radicals* vs. σ^+. Relative reactivities from [11] averaged with those reported in this work.

p-cyanotoluene [24], or 3.71 kcal mol^{-1}. With isopropyl radicals, from $\log k_{abs} = -0.90\sigma^+ - 0.48$, $k_{abs}(p\text{-MeO}) = 1.667$ and $k_{abs}(p\text{-CN}) = 0.0826$. The relative reactivity of the two is 20.182. Assuming similar pre-exponential factors at 84° (reflux temp.), $\ln(20.182) = \Delta E_a/RT = \Delta E_a/(1.987 \cdot 354.15)$, where ΔE_a is the difference in the *Arrhenius* energy of activation. $\Delta E_a = 2.13$ kcal mol^{-1}, or 57% of the difference in *BDE*. This is a reasonable expectation for a reaction whose exothermicity is *ca.* 9.0 kcal mol^{-1} for abstraction of a benzyl H-atom from toluene. With undecyl radicals, from $\log k_{abs} = -0.40\sigma^+ - 0.20$ at 80° (refluxing benzene), $k_{abs}(p\text{-MeO}) = 1.294$ and $k_{abs}(p\text{-CN}) = 0.340$. The relative reactivity is 3.806 and $\Delta E_a = 0.938$ kcal mol^{-1}, or 25% of the *BDE* difference. The exothermicity is *ca.* 11.4 kcal mol^{-1} for abstraction from toluene and a smaller percentage of the *BDE* is reflected in ΔE_a. Therefore, even though the *Hammett* plots of *Figs. 2* and *3* are only qualitative, the resulting ρ values lead to reasonable agreement with what would be expected from differences in *BDE*.

The topic of the extent to which *BDE* values reflect ground-state effects of the substituents or their effects on the stabilization of the benzyl radicals is of current interest. A recent report outlines some views on the current state of affairs [41], but the issue is outside the scope of this work. The point made previously [2] and in this work is that, if

BDE values of the bond being broken yield good *Hammett* correlations and reaction rates are consistent with *BDE* trends, then postulating 'polar effects' on the transition state or any other effects is unnecessary by *Occam*'s razor[8]). This is not to dismiss the effect of dipoles on the ground-state or on the transition state, as we have shown for both [42], but to point out that not all *Hammett* correlations reflect dipolar structures at the transition state. For a recent example, H abstractions from *para*-substituted phenols by the phthalimide-*N*-oxyl (=1,3-dihydro-1,3-dioxo-2*H*-isoindol-2-yloxy; PINO radical) were found to yield a good *Hammett* correlation of relative reactivities with σ^+, $\rho = -3.1$ ($r = -0.989$). On this basis, partial proton-coupled electron transfer (PCET) from the phenol ring to the PINO radical was postulated [43]. However, when a plot is made of log(relative reactivity) *vs.* ΔBDE of O−H of the phenols [20a–c], we find an equivalently good correlation ($r = 0.986$). When *BDE* effects are sufficient to explain the facts, there is no need to postulate other effects. In fact, the *BDE* correlation may well disprove involvement of any other effects not related to it.

Conclusions. – *Fischer*'s accurate kinetic measurements and his acumen in recognizing and pointing out that *tert*-butyl radicals reacted with toluenes in a suspect, nonlinear *Hammett* correlation opened the door to a reexamination of much of the work that had been reported previously for such alkyl-radical reactions. Direct measurements of reactivities of substituted benzenes and similarly substituted toluenes demonstrate that addition of alkyl radicals to aromatic rings is a major reaction pathway. V-Shaped *Hammett* plots are obtained with primary-, secondary-, and tertiary-alkyl radicals. Positive ρ values previously reported as due to benzyl-H abstractions were due primarily to ring additions to toluenes with electron-withdrawing substituents. H Abstractions occur with negative ρ.

Experimental Part

General. Materials were obtained from commercial sources and were redistilled before each use. Toluene and *p*-xylene were also distilled from sodium, but this had no effect on results. Dilauroyl peroxide was used as received. Isopropyl isobutyrate was prepared from isobutyryl chloride and isopropyl alcohol by standard methods of esterification. Identification of products was made by comparison of GLC retention times with authentic materials on three different GLC columns (*SE-30*, *FFAP*, and *Supelco* pesticide).

Diisobutyryl Peroxide (=*Bis(2-methyl-1-oxopropyl) Peroxide*). A 50% excess of sodium peroxide was dissolved in H_2O, keeping the temp. below 15°, and a soln. of isobutyryl chloride in cyclohexane was added in an ice bath with vigorous stirring at such a rate as to keep the temp. between 8 and 15°. Then the org. layer was quickly separated, washed to neutrality, and dried ($MgSO_4$). *Care must be exercised in controlling the temp. during synthesis to avoid detonation*. The yield of peroxide was *ca.* 40% by iodometric titration. The cyclohexane soln. was stored in the refrigerator (8°) for not more than three days, when decomposition reached *ca.* 2%.

Typical Kinetic Run. Toluene (0.05 mol) and a substituted toluene (or substituted benzene) were made up to 25.0 ml with cyclohexane. A 5.00-ml aliquot was brought to gentle reflux under a slow flow of N_2 (2 ml per min) and 8.00 ml of 1.45–1.50M isobutyryl peroxide in cyclohexane were added drop-

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[8]) *William of Occam* (*ca.* 1285–1349): '*Entia non sunt multiplicanda praeter necessitatem*'. Also, *I. Newton*: 'We are to admit no more causes of natural things than such as are both true and sufficient to explain their appearances'.

wise over *ca.* 45 min. Two aliquots of the toluene and substituted-toluene solns. were used as blanks, after the addition of 8.00 ml of cyclohexane. To check for evaporative losses, one blank was sealed and kept refrigerated, and the other was refluxed in the same way as the competition experiment. No evaporative losses of substrates were found, except for benzene for which no reactivity is reported. Additional information is provided in footnotes to the *Tables.*

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