tive and hyperconjugative stabilization energies are in the inductive, *not* in the Baker–Nathan, order.[16] These energetic aspects are, however, not in contradiction with the concept of charge alternation (eq 1) which concerns total charge distributions, *i.e.*, in the present case, the preferential positions for the formation of positive sites.

The final conclusion is that the simple concept of charge alternation expressed by eq 1 is basic, despite its crudeness and its obvious limitations, in that it unifies the effects exhibited by alkyl groups, *i.e.*, (i) the net electron release in the inductive order and (ii) the "hyperconjugative order" for promoting neighboring positive sites.

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The Meaning of the "Polar Effect" in Hydrogen Abstractions by Free Radicals. Reactions of the *tert*-Butoxy Radical[1]

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Abstract: Abstractions from substituted toluenes by *tert*-butoxy radicals derived from *tert*-butyl hypochlorite exhibit a Hammett ρ of -0.41; it is confirmed that previously reported higher values were due to chlorine atom chains. A plot of ρ for abstractions from toluenes by various radicals *vs.* ΔH for each radical is linear. This is interpreted as proof that ρ reflects differences in the bond dissociation energies of substituted toluenes and that its magnitude is a measure of the sensitivity of the abstracting radical to these differences. In several cases which were thought to demonstrate the importance of the "polar effect," the postulation of partial charge separation in the transition state is shown to be either unnecessary, inadequate, or inconsistent with experimental observations.

The "polar effect" in hydrogen abstractions by radicals is a widely used concept, but we have found inconsistencies in its applications. This led us to reexamine some reactions of the *tert*-butoxy radical, a typical selective hydrogen abstracting radical.

The "polar" character of the *tert*-butoxy radical has been investigated several times with the general conclusion that the radical is electrophilic. Relative reactivities of meta- and para-substituted toluenes give good Hammett $\sigma\rho$ plots. Using *tert*-butyl hypochlorite as a source of *tert*-butoxy radicals, Walling and Jacknow have reported that the reaction constant ρ for reaction 1

$$C_4H_9O\cdot + RH \xrightarrow{k_1} C_4H_9OH + R\cdot \qquad (1)$$

$$R\cdot + C_4H_9OCl \xrightarrow{k_2} RCl + C_4H_9O\cdot \qquad (2)$$

with substituted toluenes has the value of -0.82 at 40° in excess hydrocarbon solvent;[2] Gilliom and Ward found $\rho = -0.75$ at 40° in benzene,[3] and Walling and Gibian -0.96 at 0° in acetonitrile.[4] The extensive work of Kennedy and Ingold at 40° in CCl_4 gave $\rho = -0.86$; the correlation was better when log (relative reactivity) was plotted *vs.* σ^+ values, with $\rho = -0.68$.[5,6] More recent investigations employed di-*tert*-butyl peroxalate rather than the hypochlorite as a source of the oxy radical; Sakurai and Hosomi reported much lower values for the reaction constant in chlorobenzene, 1,1,2-trifluorotrichloroethane (Freon-113), and acetonitrile at 45° with ρ values between -0.36 and -0.43.[7] The correlation was better with σ^+ substituent constants and $\rho^+ = -0.32$ to -0.39 were reported. In that work, relative reactivities were obtained by the indirect method; the ratio of k_1/k_3 was determined

$$(CH_3)_3CO\cdot \xrightarrow{k_3} CH_3COCH_3 + CH_3\cdot \qquad (3)$$

with a series of substituted toluenes and was compared to k_1/k_3 with toluene. It was suggested[7] that the ρ values reported previously were near the value of -0.76 found for chlorinations of substituted toluenes by chlorine,[8] and that chlorine atom chains may become involved in chlorinations with *tert*-butyl hypochlorite. Walling and McGuinness repeated the measurements using di-*tert*-butyl hyponitrite and di-*tert*-butyl peroxalate, again employing the indirect method of k_1/k_3 ratios.[9] Their results in chlorobenzene solvent at 40° also indicated low values; $\rho = -0.39$ and $\rho^+ = -0.35$ with better statistics in the latter case.

Since direct competitions toward *tert*-butyl hypochlorite are suspect,[7,9] and k_1/k_3 ratios are known to be solvent dependent[10] and are inherently less accurate

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[1] (a) Presented at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 9–14, 1972, ORGN 60; (b) taken in part from the M.S. Dissertation of J. A. P., The Brooklyn Center, Long Island University, 1971.

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than direct competitions, the two methods giving different ρ values, we reinvestigated some aspects of chlorinations with *tert*-butyl hypochlorite including a determination of ρ with substituted toluenes, taking care to eliminate possible competing chain reactions of chlorine atoms.

Results

The relative reactivity of ethylbenzene to toluene was determined by direct competition in CCl_4 solvent at 50°; $k(\mathrm{ArEt})/k(\mathrm{ArMe}) = 2.5 \pm 0.2$ (Table I). This compares well with previously reported values of 2.30 ± 0.12 at 40° in CCl_4,[2] 2.30 ± 0.12 at 40° in CCl_3Br,[11] and 2.67 ± 0.03 at 40° in chlorobenzene solvent.[12] This ratio was also determined by comparing each aromatic hydrocarbon to 1-octene in direct competition. We obtained $k(\mathrm{ArEt})/k(\text{1-oct}) = 0.565 \pm 0.011$ and $k(\mathrm{ArMe})/k(\text{1-oct}) = 0.183 \pm 0.013$, which give a calculated ratio of $k(\mathrm{ArEt})/k(\mathrm{ArMe}) = 3.1 \pm 0.1$, at variance with the previous determinations as well as with our own direct competition results. The relative reactivity was determined again by direct competition of the two aromatic hydrocarbons in CCl_4 in the presence of a small amount (0.11 *M*) of 1-octene; we obtained 3.2 ± 0.1 in agreement with the value obtained with 1-octene as an intermediate reference.

Table I. Relative Reactivities of Hydrocarbons toward *tert*-Butyl Hypochlorite by Direct Competition

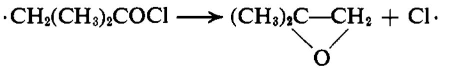
R_1H	R_2H	C_2HCl_3	Temp, °C	k_1/k_2[a]
Ethylbenzene	Toluene	None[b]	50.0	2.50 ± 0.20
Ethylbenzene	1-Octene	None[b]	50.0	0.565 ± 0.011
Toluene	1-Octene	None[b]	50.0	0.183 ± 0.013[d]
Ethylbenzene	Toluene	0.11[b,e]	50.0	3.28 ± 0.08
Ethylbenzene	Toluene	0.04[b]	50.0	3.31 ± 0.06
Ethylbenzene	Toluene	0.35[b]	50.0	3.18 ± 0.04
m-Xylene	Toluene	0.04[c]	50.0	1.96 ± 0.03
p-Xylene	Toluene	0.04[c]	50.0	2.35 ± 0.03
m-Chlorotoluene	Toluene	0.04[c]	50.0	0.699 ± 0.004
p-Chlorotoluene	Toluene	0.04[c]	50.0	0.822 ± 0.006
Cyclohexane	*p*-Xylene	0.22[c]	13.3	2.58 ± 0.01
Cyclohexane	*p*-Xylene	0.22[c,f]	31.0	2.57 ± 0.01[g]
Cyclohexane	*p*-Xylene	0.22[c,f]	50.0	2.56 ± 0.02[g]

[a] Per molecule; two determinations, each analyzed in triplicate. [b] Solvent, CCl_4. [c] Solvent, $CF_2ClCFCl_2$. [d] Five determinations. [e] 1-Octene. [f] The concentration of trichloroethylene did not decrease during the run, within experimental error. [g] Three determinations.

These findings are best explained by the incursion of chlorine atom chains in the direct competition between the ethylbenzene and toluene in CCl_4 solvent. The proposed reaction sequence 4–9 generates a chlorine chain.[9] However, in the presence of even small amounts of 1-octene, reaction 10 intercepts the chlorine atom before reaction 7 can occur. The alkyl radical from reaction 10 propagates the normal chain through reaction 2. Trichloroethylene is an effective halogen atom trap[9] and it was used for this purpose on all subsequent work. Table I shows that in the presence of as little as 0.04 *M* C_2HCl_3 the relative reactivity of ethylbenzene to toluene obtained by direct competition agrees with the value obtained with 1-octene as the intermediate standard of reference. Subsequent experiments (see Table I) established that the concentration of C_2HCl_3 did not decrease measurably during the reactions.

$$C_4H_9OCl \longrightarrow C_4H_9O\cdot + Cl\cdot \qquad (4)$$

$$C_4H_9O\cdot + C_4H_9OCl \longrightarrow C_4H_9OH + \cdot CH_2(CH_3)_2COCl \qquad (5)$$



$$\cdot CH_2(CH_3)_2COCl \longrightarrow (CH_3)_2C{-}CH_2 + Cl\cdot \qquad (6)$$

$$Cl\cdot + RH \longrightarrow HCl + R\cdot \qquad (7)$$

$$HCl + C_4H_9OCl \rightleftharpoons Cl_2 + C_4H_9OH \qquad (8)$$

$$R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot \qquad (9)$$

$$Cl\cdot + CH_2{=}CH(CH_2)_5CH_3 \longrightarrow ClCH_2CH(CH_2)_5CH_3 \qquad (10)$$

Our investigation of the kinetics of these systems found that whereas alkanes react mostly through the normal chain, reactions 1 and 2, toluene is chlorinated to large extents through reactions 7–9 in the absence of chlorine atom traps in halocarbon solvents;[13] the same conclusion has been suggested from the results of product analyses.[9] Reaction 9 competes successfully with reaction 2 only with benzyl radicals; k_2 for benzyl radicals is six times smaller than k_2 for cyclohexyl[13] at 50° and, apparently, k_9 is affected less than k_2 by the nature of the hydrocarbon radical R·. Nevertheless, there is evidence that chlorinations of the alkyl side chain of aromatic hydrocarbons by *tert*-butyl hypochlorite often proceed normally even in the absence of olefins. We have reported that the relative reactivity of ethylbenzene to cumene toward *tert*-butyl hypochlorite at 70° is 0.98 ± 0.03 by direct competition in the absence of olefins, excess hydrocarbons serving as solvent; this value is essentially identical with the relative reactivity obtained with *tert*-butoxy radicals derived from the copper-catalyzed decomposition of *tert*-butyl peracetate (1.03 ± 0.03) and *tert*-butyl perbenzoate (1.03 ± 0.03).[14] We examined the reaction of ethylbenzene with *tert*-butyl hypochlorite in excess hydrocarbon solvent; with light initiation at 30°, without any chlorine atom traps, the product distribution was 95% α-phenethyl chloride and 5% β-phenethyl chloride. This distribution is in agreement with similar previous determinations,[2,11,12] and it indicates little involvement of chlorine atoms, which would lead to a product distribution of about 60:40 in favor of the α position.[15] Thus it appears that in excess alkyl aromatics as solvents, Cl_2 forms some complex with the π electrons, and that this complexing reduces the rate of reaction 9.[16] Even though aromatics form complexes with radicals, such as *tert*-butoxy,[9,17] they apparently do not solvate benzyl radicals;[18] thus the selectivity of the benzyl radical toward the chlorine donor is not simultaneously increased in a way that could offset the effect of the ArR–Cl_2 complex on the relative rates of reactions 2 and 9. In such cases hypochlorite chlorinations proceed normally through reactions 1 and 2.

Using C_2HCl_3 as a chlorine atom trap and CF_2Cl-$CFCl_2$ solvent at 50° we determined the relative reactivi-

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Table II. Relative Reactivities of Substituted Toluenes ($Q–C_6H_4–CH_3$)

Q	This work	Ref 3	Ref 5	Ref 2	Ref 9	Ref 9	Ref 7	Ref 7
p-CH_3	1.18[a]	1.52[a]	1.47[a]	1.53[a]	1.42[a]	1.31[a]	1.32[a]	1.32[a]
m-CH_3	0.98[a]	1.14[a]	1.07[a]	1.17[a]		0.91[a]	1.07[a]	1.01[a]
H	1.00[b]	1.00[b]	1.00[b]	1.00[b]	1.00[b]	1.00[b]	1.00[b]	1.00[b]
p-Cl	0.82	0.67	0.89	0.71			1.00	0.81
m-Cl	0.70	0.52	0.59	0.52	0.61	0.67	0.77	0.68
Source	C_4H_9OCl[c]	C_4H_9OCl	C_4H_9OCl	C_4H_9OCl	C_4H_9OCl	DBPO[d]	DBPO[d]	DBPO[d]
Solvent	$C_2F_3Cl_3$	C_6H_6	CCl_4	$C_6H_5–R$	C_6H_5Cl	C_6H_5Cl	$C_2F_3Cl_3$	C_6H_5Cl
Temp, °C	50	40	40	40	40	40	45	45

[a] Statistically corrected for the two methyl groups. [b] Assumed. [c] In the presence of 0.04 *M* trichloroethylene. [d] Di-*tert*-butyl peroxalate.

ties of a series of substituted toluenes to toluene toward *tert*-butyl hypochlorite by direct competition. The values obtained are shown in Table II where they are compared to some previously reported results; our values differ from those previously obtained with hypochlorite but are similar to those found with other sources of the *tert*-butoxy radical.

Our data from Table II were plotted in terms of the Hammett equation using σ[19] and σ^+ parameters.[4] The correlations are: log (relative reactivity) = $-0.41\sigma - 0.01$ with a correlation coefficient $r = 0.987$ on a least-squares fit, and log (relative reactivity) = $-0.35\sigma^+ - 0.03$ with $r = 0.974$. The statistics are not sufficient for an unequivocal choice between σ and σ^+, a matter that has been of some interest;[3,5] nevertheless, both in terms of the value of the intercept and of the correlation coefficient, our results indicate some preference for a correlation with σ.

The Meaning of the "Polar Effect"

The existence of Hammett $\sigma\rho$ correlations in free-radical abstractions of hydrogen from substituted toluenes has been one of the reasons for the formulation of the theory of the "polar effect" in these reactions. It is thought that, in reaction 11, structures

$$R–H + X\cdot \longrightarrow \{\dot{R}\text{--}\dot{H}\text{--}\dot{X} \longleftrightarrow \underset{\text{I}}{\overset{+}{R}\text{--}\dot{H}\text{--}\overset{-}{X}}\} \longrightarrow R\cdot + H–X \quad (11)$$

such as I contribute to the character of the transition state;[20] the importance of structure I will be greatest when R can stabilize a positive charge (*i.e.*, when R· is a "donor" radical[21]) and X· is an electrophilic atom or group (*i.e.*, if X^- is more stable than X^+, X· being an "acceptor" radical[21]). In addition, strong acceptor radicals, such as the electrophilic chlorine atom, are thought to attack preferentially points of high electron density;[22] thus, in the abstraction from toluene by chlorine, reaction 12, the inductive electron-withdrawing

$$ArCH_2–H - Cl\cdot \longrightarrow \{Ar\dot{C}H_2\text{--}H\text{--}\dot{C}l \longleftrightarrow$$
$$\underset{\text{II}}{\overset{-}{A}rCH_2\text{--}\overset{+}{H}\text{--}\dot{C}l\}} \longrightarrow ArCH_2\cdot + H–Cl \quad (12)$$

effect of the phenyl group is thought to retard attack by the electrophilic chlorine atom on the electron-poor hydrogen.[23] The negative Hammett ρ values that have been obtained for abstractions from substituted toluenes by Br·, Cl·, $Cl_3C\cdot$, and t-$C_4H_9O\cdot$ are thought to be striking demonstrations of the polar effects that can arise in homolytic reactions,[23] since they are consistent with the expected behavior of structures such as I or II in the transition state. This point of view appears to have been accepted widely.[24–27]

The importance of structures such as I or II in the transition state and the magnitude of the polar effect would be expected to increase as the electrophilicity of the attacking radical increases. However, it has been recognized that the magnitude of the "polar effect" observed with various radicals abstracting from toluenes is not always in the order of electron affinities of the radicals.[28] For the five radicals studied for attack on toluenes, the electron affinities are in the order Cl· > Br· > t-$C_4H_9O\cdot$ > $Cl_3C\cdot$ > $C_6H_5\cdot$;[29] the magnitude of the "polar effect," as measured by the Hammett ρ, is in the order Br· > $Cl_3C\cdot$ > Cl· > t-$C_4H_9O\cdot$ > $C_6H_5\cdot$. The discrepancies in the two series have been attributed to differences in the amount of bond breaking in the transition state;[28] recent work has clearly demonstrated the dramatic dependence of ρ on the exothermicity of the reaction.[30]

Whereas it has been concluded that the value of ρ should be a function of both the electrophilicity of the abstracting radical and of the extent of bond breaking in the transition state,[23,26,28,30,31] we find a linear correlation between ρ and ΔH for the reaction of toluenes with the above five radicals. The plot is shown in Figure 1; considering the uncertainties in bond dissociation energies (BDE) and in the reported ρ values, it appears that ρ is a function only of the extent of bond breaking, as it is reflected by ΔH. The lack of any extensive scatter with such widely different radicals indicates that the electron affinity of the abstracting radical is not a significant factor. Thus, the correlation of Figure 1 makes the writing of structures such as I or II unjustified for these radical abstractions. It follows that differences in the reactivities of a series of substituted toluenes toward any given radical are due

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to differences in the BDE of the benzyl C–H bond in each of these substrates and that these BDE values are dependent on the electron donating or withdrawing characteristics of the substituents.[32] Semenov has pointed out that the observed relatively small ρ values could easily be the result of bond energies as they are influenced by the various substituents.[33] Thus, in effect, Hammett ρ values in these reactions measure the sensitivity of the rate of hydrogen abstraction to BDE differences in the substituted toluenes; as the exothermicity increases this sensitivity would be expected to decrease and Figure 1 indicates that for abstractions with exothermicities greater than 30 kcal/mol the existing small BDE differences become inconsequential.

There is substantial evidence, independent of the correlation in Figure 1, that charge separation in the transition state either does not occur or is an unnecessary assumption, and some of it is presented below; however, the volume of literature on the "polar effect" is too great for a detailed refutation of each such argument here.

The "polar effect" argument for hydrogen abstraction from toluenes, whether expressed in terms of structure I or II, disregards completely possible BDE differences in the benzyl C–H bond. However, in a compound Y–CH_3, where Y is an electronegative atom or group, Y withdraws electrons; the methyl group releases these electrons somewhat by using a hybrid orbital for bonding with less than 25% s character, so that the orbital is less electron attracting. The extra s character shows up in the C–H bonds.[34] The result is stronger C–H bonds. It is thus not unreasonable to expect that, when Y = *p*-nitrophenyl, the BDE of the benzyl C–H bond in *p*-nitrotoluene would be greater than that in toluene; on this basis *p*-nitrotoluene should be less reactive than toluene in hydrogen abstractions, as is observed.

Evidence from ^{13}C–H nmr coupling constant measurements strongly supports our view of the effect of ring substituents on the methyl C–H BDE of substituted toluenes. If the Fermi contact mechanism dominates the coupling constant, as appears to be the case, the latter will be related to the fractional s character of the bond.[35] In substituted toluenes, methyl ^{13}C–H coupling constants exhibit a linear dependence on Hammett σ constants; the per cent s character is a function of the substituent and the greater the effective electronegativity of the substituent, the greater the amount of s character,[36] and the higher the expected bond strength. The same conclusions have been reached on the basis of ^{15}N–H coupling constants in substituted anilines.[37]

More direct evidence of the effect of ring substituents on the BDE of benzyl C–H bonds has been presented by Lewis and Butler.[38] In the series *m*-$NO_2C_6H_4C$–H, C_6H_5C–H, *p*-$CH_3OC_6H_4C$–H the highest BDE in the benzyl C–H has been shown to be in the *m*-NO_2- and the lowest in the *p*-CH_3O-substituted compound, on the basis of significantly different primary tritium isotope effects in radical abstractions.

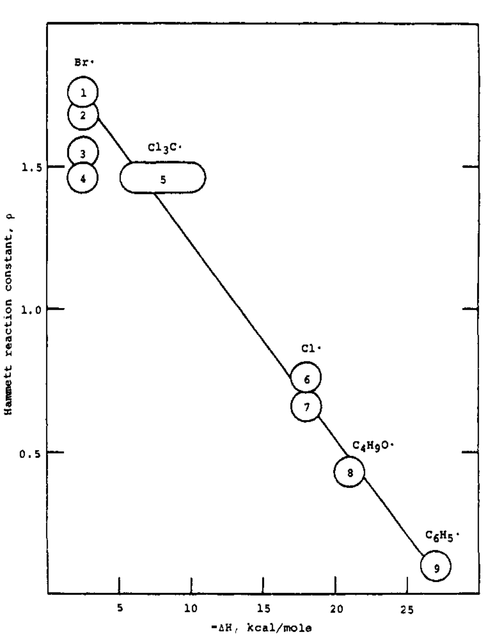

Figure 1. Values of ρ (or ρ^+) *vs.* ΔH for abstraction from toluene. Points 2, 3, 6, 8, and 9 are ρ values; 1, 4, 5, and 7 are ρ^+. Points 1 and 4 from R. E. Pearson and J. C. Martin, *J. Amer. Chem. Soc.*, **85**, 3142 (1963); point 2 from C. Walling, A. L. Rieger, and D. D. Tanner, *ibid.*, **85**, 3129 (1963); point 3 from E. C. Kooyman, R. Van Helden, and A. F. Bickel, *Kon. Ned. Acad. Wetensch., Proc., Ser. B*, **56**, 75 (1953); point 5 from E. S. Huyser, *J. Amer. Chem. Soc.*, **82**, 394 (1960); point 6 from ref 8; point 7 from ref 28; point 8 from this work; point 9 from ref 44. BDE values from S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N.Y., 1968; large uncertainty in the BDE of Cl_3C–H is due to conflicting values between Benson and B. deB. Darwent, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **No. 31**, 21 (1970). Points indicate uncertainties of ±0.1 in ρ and ±1.0 kcal in ΔH. The points are from experiments at differing temperatures, ranging from 20 to 80°. The ordinate indicates negative values.

The Hammett correlations obtained with abstractions from substituted toluenes also have been used in another way to prove the existence of charge separation in the transition state. Often it has been found that Hammett plots give better correlations with σ^+ rather than σ substituent constants.[3,4,21,23] Values of σ^+ were derived from the ionization of cumyl chlorides, with carbonium ion character in the transition state.[6] Thus, in Russell's terms the correlation with σ^+ indicates abstraction by a strongly electron-accepting radical,[39] with important contributions to the transition state by charge-transfer structures such as I or II. This plausible argument, however, is questionable. In abstractions by Br·, the correlation with σ^+ is better than that with σ;[40] however, the correlation coefficient, *r*, of the Hammett plot is even better with σ^- values, if we examine the reactivities of toluenes with substituents whose σ^- values are established. With Br· and toluenes (*p*-CH_3, H, *p*-Cl, *p*-COOH, *p*-CN, and *p*-NO_2) we obtain $\log (k/k_0) = -1.48\sigma^+ + 0.002$ (r =

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(39) G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958).

(40) C. Walling, A. L. Rieger, and D. D. Tanner, *J. Amer. Chem. Soc.*, **85**, 3129 (1963).

0.990), and log $(k/k_0) = -1.04\sigma^- + 0.099$ ($r = 0.992$). For abstractions by Br· from cumenes (p-CH$_3$, H, p-Cl, p-CO$_2$C$_2$H$_5$, p-CN, and p-NO$_2$)[41] we obtain log $(k/k_0) = -0.32\sigma^+ + 0.002$ ($r = 0.944$), and log $(k/k_0) = -0.23 \cdot \sigma^- + 0.018$ ($r = 0.959$). With *tert*-butoxy radicals and toluenes (p-CH$_3$, H, p-Cl, and p-CN[7]), log $(k/k_0) = -0.28\sigma^+ + 0.020$ ($r = 0.980$), and log $(k/k_0) = -0.21\sigma^- + 0.002$ ($r = 0.985$). For abstractions from cumenes by CCl$_3$· (p-Cl, H, p-COC$_2$C$_5$, p-CN, and p-NO$_2$),[41] we obtain log $(k/k_0) = -0.66\sigma^+ + 0.017$ ($r = 0.983$), and log $(k/k_0) = -0.44\sigma^- + 0.006$ ($r = 0.994$). Since values of σ^- are related to the ionization of phenols, and we find that correlations with σ^+ and σ^- are equally as good, it appears that σ^+ correlations do not necessarily imply carbonium ion character in the transition state. It is more likely that substituent constants must reflect the possibility of direct conjugation with the reacting site, in the cases where σ^+ and σ^- are better than σ.

We also find that nmr chemical-shift data correlate with log (k/k_0) for abstractions from toluenes by radicals. Values of the displacement in the chemical shift of the hydroxy hydrogen in substituted phenols $(\Delta\delta)$[42] correlate well ($r > 0.95$) with relative reactivities. For example, our data of Table II give log $(k/k_0) = -0.26 \cdot (\Delta\delta) - 0.001$, $r = 0.98$. Not surprisingly, these $\Delta\delta$ values correlate best with σ^-.

The combined evidence from Figure 1, from isotope effects, and from nmr coupling constant and chemical-shift measurements is overwhelming. On the basis of our argument, positive ρ values would be impossible for abstractions from toluenes and none have ever been observed.

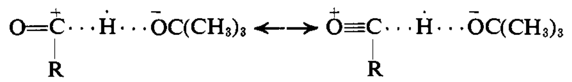
In addition to abstractions from substituted toluenes, the "polar effect" has been invoked to explain the results obtained from many other types of hydrogen abstractions. We will examine some notable cases.

The p-nitrophenyl radical has been designated as more electrophilic and more susceptible to "polar effects" in the transition state than the phenyl radical, on the basis of a more negative ρ value for abstractions from substituted toluenes.[43] In addition, the p-nitrophenyl radical was found to be more selective, suggesting that higher activation energies are associated with abstractions by p-nitrophenyl compared to phenyl; such abstractions are probably less exothermic than abstractions by phenyl radicals. The per hydrogen relative reactivity of acetone to *tert*-butylbenzene toward phenyl radicals is 2.2:1.0, reflecting primarily the lower BDE in acetone (ΔBDE = 3 kcal/mol), since the phenyl radical is thought to be fairly free of polar effects ($\rho = -0.1$ with toluenes).[44] The p-nitrophenyl radical ($\rho^+ = -0.44$) should, however, avoid acetone either in terms of structure I or II, but the relative reactivity toward this "electrophilic" radical is increased to 4.3:1.0. This increase in selectivity parallels the change in the relative reactivity of ethylbenzene to toluene: 2.3:1.0 toward phenyl, 4.2:1.0 toward p-nitrophenyl. Thus, in this case there is clearly no evidence for a special unfavorable "polar effect" for attack by the "electrophilic" p-nitrophenyl radical on acetone.

Abstractions by *tert*-butoxy radicals are also thought to provide excellent demonstrations of the operation of the "polar effect." The "polar effect" argument for such abstractions predicts strong deactivation of hydrogens α to a carbonyl, either in terms of structure I or II, and such deactivation has been cited as evidence for the existence of the effect. Since the relative reactivity of a secondary to a primary hydrogen in butane is $k_s/k_p = 11$ at 0°,[2] this ratio should be drastically lower in 3-pentanone, where the powerful electron-withdrawing effect of the carbonyl should strongly deactivate the secondary hydrogens. However, $k_s/k_p = 9.23$ in 3-pentanone,[45] so that strong deactivation is absent and the "polar effect" is nonexistent or very minor in this case.[46] Similarly, the α and β hydrogens in cyclopentanone are abstracted by the *tert*-butoxy radical with equal ease. The conclusion that electron availability plays a more important role than C–H bond strength in abstractions by *tert*-butoxy[45] is seen to be questionable.

The high reactivity of hydrogens α to an ether oxygen and of aldehydic hydrogens toward the *tert*-butoxy radical has been explained in terms of the stability of type I contributing structures in this case, with oxygen stabilizing the partial positive charge.[45] Nevertheless,

$$\mathrm{R{-}O{-}\overset{+}{C}H_2\cdots\dot{H}\cdots\bar{O}C(CH_3)_3 \longleftrightarrow R{-}\overset{+}{O}{=}CH_2\cdots\dot{H}\cdots\bar{O}C(CH_3)_3}$$



$$\mathrm{O{=}\underset{\displaystyle R}{\overset{+}{C}}\cdots\dot{H}\cdots\bar{O}C(CH_3)_3 \longleftrightarrow \overset{+}{O}{\equiv}\underset{\displaystyle R}{C}\cdots\dot{H}\cdots\bar{O}C(CH_3)_3}$$

a plot of log (relative reactivity) *vs.* BDE of the C–H bond broken for primary, secondary, and tertiary aliphatic hydrogens, *tert*-butylbenzene, dimethyl ether, tetrahydrofuran (α-C–H), and diethyl ether (α-C–H) is linear, Figure 2. Clearly, partial charge separation and structures such as the above are unnecessary postulates with these oxygen-containing compounds also. In fact, if the commonly quoted value of BDE(RCO–H) = 88 kcal/mol is used in the plot, aldehydic hydrogens are seen to be much *less* reactive than BDE considerations alone would predict, rather than the reverse as claimed by the "polar effect." If partial charge separation ever occurs in hydrogen abstractions, it should certainly occur here and the points for the ethers should lie considerably above the line defined by the alkanes and *tert*-butylbenzene in Figure 2. The reactivities of many other compounds do not fit on the line of Figure 2; this is not surprising since it is well known that bond strengths alone rarely control reactivity.

Kosower has examined abstractions of halogen atoms by substituted pyridinyl radicals and on the basis of the insensitivity of the rate to changes in solvent polarity has concluded that charge separation, the "polar effect," does not occur in these transition states, even though the pyridinyl radical would derive considerable stabilization from the corresponding positively charged species in the transition state.[47] He concluded that rate differ-

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[41] G. J. Gleicher, *J. Org. Chem.*, **33**, 332 (1968).

[42] M. T. Tribble and J. G. Traynham, *J. Amer. Chem. Soc.*, **91**, 379 (1969).

[43] W. A. Pryor, J. T. Echols, Jr., and K. Smith, *ibid.*, **88**, 118 (1966).

[44] R. F Bridger and G A. Russell, *ibid.*, **85**, 3754 (1963).

[45] C. Walling and M. J. Mintz, *ibid.*, **89**, 1515 (1967).

[46] The bond dissociation energies involved should be similar in the ketone and the alkane: K. D. King, D. M. Golden, and S. W. Benson, *ibid.*, **92**, 5541 (1970).

[47] E. M. Kosower and I. Schwager, *ibid.*, **86**, 5528 (1964).

ences within a series of similar abstractions are due to BDE effects, and, by extension, questioned the postulated charge separations in the transition states for homolytic decompositions that show Hammett correlations. No clear-cut correlations of rates with the ionizing power of the solvent appear to have been established for any hydrogen abstractions either.

The per hydrogen relative reactivity of cyclohexane to toluene is 2:1 toward the chlorine atom and 1.5:1 toward the *tert*-butoxy radical (see Table I), despite a difference of about 10 kcal/mol in the BDE of the C–H bonds involved, which should favor toluene by a very large margin. This anomaly has been explained in terms of the "polar effect," *i.e.*, the electron-withdrawing inductive effect of the phenyl group decreases the reactivity of the methyl hydrogens toward electrophilic radicals,[20,25] and the small extent of bond breaking in the transition state of these exothermic reactions does not allow the resonance stabilization of the benzyl radical to become a major factor. It is unlikely that this anomaly is due to partial charges in the transition state and to the electrophilicity of the abstracting radical. The phenomenon is not unique with strongly "electrophilic" radicals; the per hydrogen relative reactivity of cyclohexane to toluene is also about 1:1 toward the phenyl radical which is supposed to be free of significant "polar effects."[48] Toward the methyl radical, toluene is favored only by a factor of three.[49]

One obvious difference between abstraction from cyclohexane and from toluene is that entropy of activation effects may be quite different in the two cases. To the extent that the odd electron in the forming benzyl radical will conjugate with the aromatic nucleus, the free rotation of the ring with respect to the forming methylene will be lost; this loss will be reflected in an unfavorable preexponential term for abstractions from toluene, whereas no such effects would be expected with cyclohexane. We investigated this possibility by examining the relative reactivity of a hydrogen in cyclohexane to a benzyl hydrogen in *p*-xylene. The results in Table I show essentially no change between 13.3 and 50.0°; the relative reactivity of cyclohexane to *p*-xylene is 1.28:1.00 per hydrogen. A relative reactivity of cyclohexane to toluene of $2.56 \times 2.35 = 6.02:1.00$ per molecule at 50.0° can be calculated from the data of Table I; this is in fair agreement with previous determinations with hypochlorite giving 6.2 ± 0.6[9] and 6.0,[2] and by the indirect method 5.3, 6.0, and 6.1 using other sources of *tert*-butoxy radicals.[9] This lack of any significant temperature dependence in the reactivity ratio of secondary aliphatic to primary benzylic hydrogens eliminated entropy of activation effects as a major cause for the low reactivity of benzyl hydrogens toward *tert*-butoxy radicals. Available temperature dependence data on this competition toward chlorine atoms have led to the same conclusion.[22] It is unlikely that entropy effects will be more significant for the more exothermic abstractions by the phenyl radical for which even less bond breaking in the transition state is expected. Thus, no acceptable explanation in terms of polar effects or entropy effects remains for the low reactivity of benzyl hydrogens toward *tert*-butoxy, chlorine, phenyl, and methyl radicals. The only possibly viable alternative explanation at this stage is Szwarc's approach, in terms of Morse curves that are differently shaped for aliphatic and benzyl C–H bonds.[50]

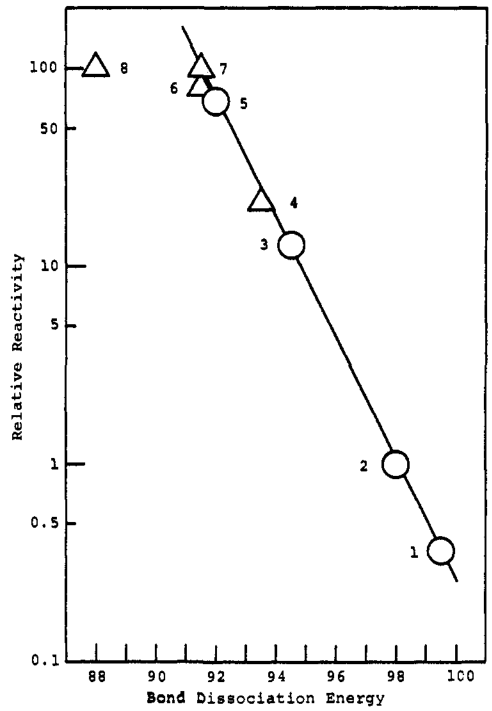

Figure 2. Relative reactivity *vs.* bond dissociation energy for attack on C–H bonds by *tert*-butoxy radicals. The line is defined by the reactivity of hydrocarbons (circles): 1, *tert*-butylbenzene; 2, primary aliphatic; 3, secondary aliphatic; 4, methyl ether; 5, tertiary aliphatic; 6, ethyl ether (α-C–H); 7, tetrahydrofuran (α-C–H); 8, aldehydic hydrogen. Reactivity data from ref 45. BDE values from: S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N.Y., 1968; D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969); and F. R. Cruickshank and S. W. Benson, *J. Amer. Chem. Soc.*, **91**, 1289 (1969).

It becomes apparent that the "polar effect" argument, as usually employed, cannot be applied in a consistent manner to explain the phenomena discussed above. However, we have shown that, for hydrogen abstractions of the type $X\text{–}H + Y\cdot \rightarrow X\cdot + H\text{–}Y$, accurate energies of activation can be obtained from a simple calculation;[51] the data needed are ir stretching frequency, BDE, masses, and bond length in the stable molecules X–H, H–Y, and X–Y. Such data lead to accurate predictions for a large variety of reactions including $CH_3O\cdot + CH_4$ and $CH_3\cdot + NH_3$, where strong "polar effects" would be expected. Antibonding interactions in $X\cdots Y$ in the transition state were found to be a major factor in controlling energies of activation. The polarity of the X–Y bond is reflected strongly in the ir stretching frequency, which in turn affects the calculated antibonding energy. Thus, the qualitative concept of the "polar effect" can be treated quantitatively without postulating charge separation in the transition state, and one may distinguish clearly between BDE and stretching frequency effects. Unfortunately, accurate molecular data are not available for the calculation of energies of activation for the

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(48) It may not be assumed that abstractions by phenyl are so exothermic that they are nonselective; phenyl is quite selective toward primary, secondary, and tertiary benzyl hydrogens.[44]

(49) W. A. Pryor, D. L. Fuller, and J. P. Stanley, *J. Amer. Chem. Soc.*, **94**, 1632 (1972).

(50) M. Szwarc, *Chem. Soc., Spec. Publ.*, **No. 16**, 96 (1962).

(51) A. A. Zavitsas, *J. Amer. Chem. Soc.*, **94**, 2779 (1972).

complex molecules whose rates of reaction have been discussed above.

Finally, it should be emphasized that our proposal that charge separation in the transition state is not a factor in controlling reaction rates for hydrogen abstractions by radicals is not merely a semantic alternative. The "polar effect" argument would predict $\rho \simeq 0$ for abstractions from substituted toluenes by the methyl radical; for abstractions by the *tert*-butyl radical ρ should be zero or positive. On the other hand, we predict $\rho \simeq -0.6$ for abstractions by methyl and as high as $\rho \simeq -1.4$ for abstractions by *tert*-butyl, near 50° on the basis of Figure 1.[52] Some data are available for the reaction of methyl radicals with substituted toluenes. From gas-phase measurements with toluene, *m*-xylene, and *p*-xylene between 100 and 250°,[53] we can extrapolate a very rough estimate of $\rho = -0.76 \pm 0.20$ at 60°. The liquid phase data of Pryor[54] and of Szwarc[55] are also limited in the range of σ values examined. A linear regression analysis of Pryor's seven points gives a poor correlation coefficient and a better fit with σ^+: $\log(k/k_0) = -0.14\sigma^+ - 0.016$ ($r = 0.83$)[56] at 100°. Szwarc's data provide four points at 0° and they exhibit superior linearity and correlate better with σ: $\log(k/k_0) = -0.57\sigma - 0.003$ ($r = 0.992$). Although the latter value of ρ is in agreement with our prediction, additional data are clearly needed for abstractions by alkyl radicals from toluenes.

Experimental Section

Materials. Reagent grade commercial materials were used. They were checked for purity by gas chromatography, the toluene was washed with concentrated H_2SO_4, and all hydrocarbons were passed through 80–100 mesh activated alumina before use. *tert*-Butyl hypochlorite was prepared from the alcohol with a twofold excess of commercial sodium hypochlorite solution neutralized with HCl, at 0°; it was extracted in the appropriate solvent, washed with sodium bicarbonate and water, and dried over $MgSO_4$.

Reactions were run in ampoules as previously described.[14,57] Relative reactivities were determined by the method of excess hydrocarbon,[14,57] with chlorobenzene as an internal standard. Each hydrocarbon was approximately 1.1 *M* and the hypochlorite 0.8 *M*. The analyses were performed with 15 ft × 1/8 in. packed columns of diisodecyl phthalate. It was established that the phenethyl chlorides did not decompose under the analytical conditions used.

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[52] Figure 1 predicts BDE ≃ 107 kcal/mol for the para C–H bond in nitrobenzene, a reasonable estimate compared to 112 ± 2 for benzene.

[53] W. A. Sanders and R. E. Rebbert, *J Phys. Chem.*, 67, 170 (1963).

[54] W. A. Pryor, U. Tonellato, D. L. Fuller, and S. Jumonville, *J. Org. Chem.*, **34**, 2018 (1969).

[55] A. E. Eachus, J. A. Meyer, J. Pearson, and M. Szwarc, *J. Amer. Chem. Soc.*, **90**, 3646 (1968).

[56] A value of $r < 0.9$ is in the so-called region of noncorrelation: G. R. Wiley and S. I. Miller, *J. Org. Chem.*, **37**, 767 (1972).

[57] A. A. Zavitsas and S. Ehrenson, *J. Amer. Chem. Soc.*, **87**, 2841 (1965).

Tricyclo[3.2.1.$0^{1,5}$]octane. A 3,2,1-Propellane[1]

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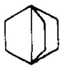
Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. Received December 11, 1971

Abstract: The synthesis of tricyclo[3.2.1.$0^{1,5}$]octane, the first hydrocarbon to possess carbons with "inverted" tetrahedral geometry, is described. It is unusual in its high reactivity toward oxygen as well as other chemical reagents. Despite its high strain it is quite unreactive thermally. Attempted syntheses of smaller ring propellanes are described. Whereas the dissolving metal reduction of 1,5-dibromobicyclo[3.2.1]octane leads to ring closure, the corresponding reaction with 1,4-dibromobicyclo[2.2.2]octane gives 1,4-dimethylenecyclohexane, and that of 1,4-dichloronorbornane gives norbornane. The reaction of the three dihalides with sodium–potassium alloy in cyclohexane gave only free-radical coupling products.

We have found it useful to consider several classes of compounds having bond angle distortion.[3] In the first class (I) we have compounds with a single constrained angle per carbon. Examples would be cyclopropane and cyclobutane. A second class (II) would contain compounds in which two angles are constrained at one or more carbons. Bicyclo[1.1.1]pentane and spiropentane would be examples. The third class (III) contains compounds in which three angles are constrained at one or more carbons. This class includes compounds **1**–**3**. Additional constraint may be realized in a compound such as **4**.



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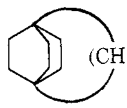

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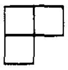

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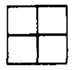
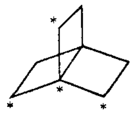


4

Whereas most of the strained compounds in classes I and II are easily considered in terms of the cyclopropane model proposed by Coulson and Moffitt,[4] the compounds in class III present some interesting aspects. In the case of **1**, which might better be drawn as



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[1] This investigation was supported by the U. S. Army Research Office.

[2] National Institutes of Health Predoctoral Fellow, 1968–1970. This has been taken from part of the Ph.D. Thesis of G. J. B., 1970.

[3] K. B. Wiberg, J. E. Hiatt, and G. J. Burgmaier, *Tetrahedron Lett.*, 5855 (1968).

[4] C. A. Coulson and W. Moffitt, *J. Chem. Phys.*, **15**, 151 (1947); *Phil. Mag.*, **40**, 1 (1949).