Substituent Effects on Benzyl Radical ESR Hyperfine Coupling Constants. The $\sigma_\alpha\cdot$ Scale Based upon Spin Delocalization

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Abstract: The electron spin resonance spectra of 21 para- and meta-substituted benzyl radicals have been analyzed. A substituent constant, $\sigma_\alpha\cdot$, has been defined from the benzylic α-hydrogen hyperfine coupling constant. The $\sigma_\alpha\cdot$ constant reflects the component of energy that may be attributed to spin delocalization in a substituted benzyl radical in comparison to the unsubstituted radical. For the derivatives studied, para substitution is stabilizing, except when fluorine is the substituent; meta substitution destabilizes the benzyl radical. A series of radical reactions is reexamined with an extended Hammett relation. The relative importance of spin delocalization vs. polar effects is assessed by the ratio of $\rho\cdot$ to ρ. The importance of choosing substituents for which $\sigma_\alpha\cdot$ and σ differ widely for such an assessment is emphasized.

The application of linear free energy relationships to explain and predict rates of reactions involving ions is a major achievement of modern physical organic chemistry.[1] In contrast, the effect of substituents on the rates of free radical reactions is less well understood.[2] Several attempts have been made to establish a σ dot ($\sigma\cdot$) scale by kinetic methods,[3] but it is difficult to assess the relatively small influence of the substituent on the radical nature of a transition state that is significantly polar. In fact, relative rates of many free radical reactions correlate reasonably well with the substituent parameters (σ, σ^+, σ^-) devised for ionic reactions; they are apparently insensitive to variation in radical stability.[4]

The variation in rate which results from the effect of the substituent on the stability of the starting material is also difficult to assess[5] and has been ignored. This approximation may be acceptable when defining substituent effects on reactions of ions, in that the variation of the stability of the ion is large in comparison to the variation of the reaction center in the initial neutral molecule. As a result the substituent parameters (σ, σ^+, σ^-) are taken as reflecting the relative stability of the ionic intermediate.[6] For example, the variation of the rate of solvolysis of substituted cumyl chlorides, expressed as σ^+ values, reflects the stability of the intermediate carbocation. The variation of the stability of the initial carbon–chlorine bond of the neutral molecule is neglected. A similarly derived definition of relative radical stability is clearly inappropriate since the magnitude of the substituent effect on the starting material may be comparable to the effect on the stability of the intermediate radical.

Table I. Benzyl Radical Hyperfine Coupling Constants[a]

X	a_1	a_2	a_3	a_4	a_5	a_6
4-COMe	15.26	4.90	1.75	(0.52)[b]	1.75	4.90
4-COPh	15.29	5.00	1.72		1.72	5.00
4-COOMe	15.55	5.12	1.78		1.78	5.12
4-CN	15.64	5.06	1.81	(0.92)[c]	1.81	5.06
4-*t*-Bu	15.76	5.10	1.97		1.97	5.10
4-OMe	15.78	5.00	1.60	(0.75)[b]	1.60	5.00
4-Cl	16.06	5.22	1.85	0.55[d]	1.85	5.22
4-Me	16.10	5.00	1.70	(6.25)[b]	1.70	5.00
4-SOMe	16.24	5.00	1.72		1.72	5.00
4-SO₃Me	16.29	5.00	1.70		1.70	5.00
4-OCOMe	16.32	5.27	1.80		1.80	5.27
4-CF₃	16.32	5.15	1.74	(6.37)[e]	1.74	5.15
H	16.34	5.12	1.75	6.25	1.75	5.12
3-Me	16.35	4.23	(0.78)[b]	5.25	1.95	4.23
3-Cl	16.35	4.99		5.10	1.72	4.76
3-COOMe	16.40	5.38	(0.76)[b]	5.79	1.70	4.90
4-F	16.52	5.17	1.72	14.0[f]	1.72	5.17
3-OPh	16.55	5.30		5.95	1.74	4.70
3-CF₃	16.57	5.16	(6.40)[e]	5.99	1.73	4.81
3-F	16.64	5.40	4.90[f]	6.30	1.83	5.14
3-CN	16.98	5.30	(0.64)[c]	6.17	1.72	5.19

[a] Positions given in Chart 1. X is the substituent. Values are believed to be accurate ±0.02 G. [b] Hydrogen of CH₃. [c] Nitrogen of CN. [d] Cl. [e] Fluorine of CF₃. [f] Fluorine.

Radical stability (as distinguished from radical persistence, which is largely a steric phenomenon[2c]) has usually been equated with carbon–hydrogen bond dissociation energy. However, in this case also, bond dissociation energy is the difference in the heat of formation of the radical and the initial molecule, and therefore, the effect of substituents on the bond dissociation energy cannot be attributed to variation in the stability of the radical alone. Bond dissociation energies are known to be dependent on steric effects[7] and on polar substituent effects on the bond being broken.[5] In fact, it has been suggested that benzylic carbon–hydrogen bond homolysis correlates with the ionic substituent parameter, σ^+, because of a substituent effect on the initial bond.[8]

Recent work by Brown and colleagues has defined a new ionic substituent parameter (σ^{C+}) based upon ^{13}C NMR chemical shifts of substituted benzylic carbocations.[9] This method measures the

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Table II. Comparison of Benzylic α-H hfc^a (G)

substituent	exptl^b	lit
4-COMe	15.26	15.25^c
4-COPh	15.29	15.29^d
4-CN	15 64	15.64,^{c} 15.49^d
4-OMe	15.78	15.93,^{c} 15.99^d
4-Cl	16.06	16.08,^{c} 16.07,^{d} 16.20^e
H	16.34	16.34,^{c} 16.47,^{d} 16.50^e
		16.28,^{f} 16.35,^{g} 16.3^h
		16.1,^{i} 16.5,^{j} 16.35^k
		16.22^l
4-F	16.52	16.43,^{c} 16.29,^{d} 16.89^g
3-F	16.64	16.54^g

^{a} Literature data vary in experimental conditions and were obtained over a 20-year period. In general, the benzylic α-H hfc's found in our study agree with literature values to within 0.1 G. ^{b} This work. ^{c} Reference 29. ^{d} Reference 3g. ^{e} Hudson, A.; Hussain, H. A. *J. Chem. Soc. B* 1969, 793. ^{f} Paul, H.; Fischer, H. *Helv. Chim. Acta* 1973, *56*, 1575. ^{g} Hudson, A.; Lewis, J. W. E. *Mol. Phys.* 1970, *19*, 241. ^{h} Krusic, P.; Kochi, J. K. *J. Am. Chem. Soc.* 1968, *90*, 7155. ^{i} Lloyd, R. V.; Wood, D. E. *Mol. Phys.* 1971, *20*, 735. ^{j} Tolkachev, V.; Chkheidze, I.; Buben, N. *Dokl. Akad. Nauk SSR* 1962, *147*, 643. ^{k} Carrington, A.; Smith, I. C. P. *Mol. Phys.* 1965, *9*, 137. ^{l} Reference 15.

electron delocalization directly and charge density is equated to stabilization of the cations. A similar direct approach for determining substituent effects on radical stability would be desirable.
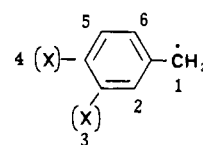
We have suggested that a substituent scale ($\sigma_\alpha.$) based upon hyperfine coupling constants (hfc) due to the α-hydrogens in the electron spin resonance (ESR) spectra of substituted benzyl radicals could accurately reflect relative spin delocalization.^{3f} The α-hydrogen coupling constant is related to the spin density at the benzylic position^{10} and is an intrinsic property of the radical. Other factors which, in general, can influence the hfc (such as the hybridization of the half-filled orbital, steric interactions which could cause deviations from planarity, interaction with β substituents, etc.^{11}) would be insensitive to ring substitution. Variation in the hfc should, therefore, represent spin delocalization, relative to that of the benzyl radical. Increased spin delocalization should increase radical stability.

Results

Static solutions of di-*tert*-butyl peroxide (DTBP), 4-methoxyacetophenone (PMA) and the substituted toluene, or the toluene and solvent, were irradiated in the ESR cavity to generate the various benzyl radicals. Such a procedure has been recommended^{12} as a method of increasing radical concentration. The PMA triplet-sensitized cleavage of DTBP ultimately generates benzyl radicals in detectable concentrations even under unfavorable conditions, a relatively small hydrogen atom transfer constant ($\sim 10^5$ M^{-1} s^{-1}, where *tert*-butoxyl is the abstracting radical^{13}) as compared to the diffusion-controlled rate constant for benzyl radical dimerization.^{14}

The benzyl radical spectra were solved manually and the hyperfine coupling constants (hfc) thus determined were refined by computer simulation. The data represent a consistent series (Table I), produced under similar conditions. Typically, the best signal was obtained at the lowest temperature possible, above the freezing point of the solution. Consequently, temperatures vary from 20 to –60 °C, though the majority of spectra were recorded at –60 °C. Control experiments were undertaken to ascertain the effects of moderate solvent and temperature changes on the ESR spectra of three representative derivatives (benzyl, 4-fluorobenzyl, and 3-cyanobenzyl). It is not surprising that, over the range of temperatures used throughout our study, no hfc changes were noted;

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Chart I

Table III. $\sigma_\alpha.$ Values^a Compared with σ, σ^+, and σ^- Values^b

substituent	$\sigma_\alpha.$	σ	σ^+	σ^-
4-COMe	0.066	0.50	0.57	0.85
4-COPh	0.064			
4-COOMe	0.048	0.39	0.49	0.68
4-CN	0.043	0.66	0.67	0.89
4-*t*-Bu	0.036	-0.20	-0.28	
4-OMe	0.034	-0.27	-0.65	-0.2
4-Cl	0.017	0.23	0.04	
4-Me	0.015	-0.17	-0.26	
4-SOMe	0.006	0.49	0.39	
4-SO$_3$Me	0.003			
4-OCOMe	0.001	0.31	0.18	
4-CF$_3$	0.001	0.54	0.58	
H	0.000	0.00	0.00	0.00
3-Me	-0.001	-0.07	-0.06	
3-Cl	-0.001	0.37	0.40	
3-COOMe	-0.004	0.32	0.37	
4-F	-0.011	0.06	-0.25	0.02
3-OPh	-0.013	0.25		
3-CF$_3$	-0.014	0.43	0.52	
3-F	-0.018	0.34	0.35	
3-CN	-0.039	0.56	0.56	

^{a} Defined by eq 1. ^{b} Taken from Murov (Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973, pp 203–206).
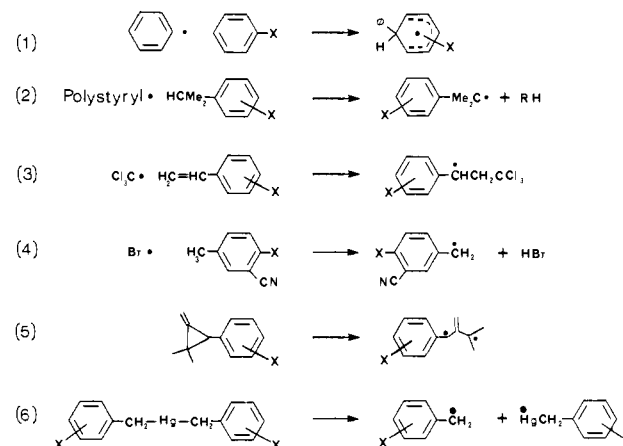
Figure 1. Standard reactions for previous σ· scales: (1) phenyl radical addition to substituted benzenes (ref 36), (2) hydrogen abstraction from substituted cumenes (ref 3c), (3) trichloromethyl radical addition to substituted styrenes (ref 3d), (4) hydrogen abstraction from 4-substituted 3-cyanotoluenes (ref 3e), (5) methylenearylcyclopropane rearrangement (ref 3f and 22), and (6) dibenzylmercurial decompsitions (ref 3g).

a previous investigation of the unsubstituted benzyl radical showed a 0.12-G decrease in benzylic α-hydrogen hyperfine coupling constant, over a 540 °C temperature range.^{15}

The coupling constants were assigned to various positions (Chart I) either by comparison with literature values (Table II) or on the basis of hfc from calculated spin densities.^{16} In meta-substituted benzyl radicals hfc for the para position and the two ortho positions were all similar in magnitude. Confidence in the designation of the hfc at these positions is less than that in the

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Table IV. Comparison of Kinetic Radical Substituent Constants ($\sigma\cdot$)

substituent	$\tau_P{}^a$	$E_R{}^b$	$E_D{}^c$	$E_R{}^{N\,d}$	$\sigma_F\cdot{}^e$	$\sigma_C\cdot{}^f$	$\sigma_J\cdot{}^g$
4-NO$_2$	0.90	0.41	0.27	0.41	0.27		0.76
4-N=NPh	0.90				0.33		
4-N(Me)$_2$		0.24		-0.11			
4-Ph					0.12		0.42
4-COMe		0.24		0.24	0.53		
4-CN		0.24	0.32	0.23	0.34	0.46	
4-SMe						0.43	
4 COOMe						0.35	
4-OMe	0.14	0.11	0.19	-0.008	-0.12	0.24	0.42
4-Si(Me)$_3$						0.17	
4-Br		0.12		0.072	0.17	0.14	
4-t-Bu		0.03		0.014		0.13	
4-i-Pr		0.03		0.034			
4-Cl	0.16	0.10	0.07	0.062	0.08	0.12	0.18
4-I		0.12		0.037	0.16		
4-OPh		0.13		-0.147			
4-Me	0.09	0.03	0.11	-0.020	-0.02	0.11	0.39
4-CF$_3$						0.08	
H	0	0	0	0	0	0	0
3-Si(Me)$_3$						0.03	
3-Me						-0.02	
3-OMe						-0.02	
3-Cl						-0.04	
3-F						-0.05	
3-CF$_3$						-0.07	
4-F						-0.08	
3-CN						-0.12	

^{a} Reference 3b; reaction 1, Figure 1. ^{b} Reference 3c; reaction 2, Figure 1. ^{c} Reference 3d; reaction 3, Figure 1. ^{d} Reference 17; reaction 2, Figure 1. ^{e} Reference 3e; reaction 4, Figure 1. ^{f} Reference 3f and 22; reaction 5, Figure 1. ^{g} Reference 3g; reaction 6, Figure 1.

assignment of positions in the para-substituted radicals.

Also listed (Table III) are $\sigma_\alpha\cdot$ values, defined (eq 1) from the

$$\sigma_\alpha\cdot = 1 - \frac{\text{hfc } \alpha\text{-H}_x}{\text{hfc } \alpha\text{-H}_0} \qquad (1)$$

benzylic α-hydrogen hfc so that the $\sigma_\alpha\cdot$ value for the unsubstituted benzyl radical is zero and substituents which decrease the spin density at the benzylic position have positive values.

Discussion

Previous $\sigma\cdot$ Scales. Before discussion of the $\sigma_\alpha\cdot$ scale, previous attempts to establish a $\sigma\cdot$ scale base on kinetic schemes (Figure 1; Table IV) will be reviewed. In every case, the radical substituent parameter has been defined *after assumption of some polar contribution*. A polar substituent scale is correlated with the radical reaction in question, and the residual factor needed for agreement is attributed to the radical stabilization effect. In this case, the dual-parameter (extended) Hammett equation has been criticized,[17] because it is highly subject to the a priori choice of the polar substituent constant in the two-parameter equation.

The earliest approach to radical substituent effects was the work of Alfrey and Price,[3a] in which the radical copolymerization of various monomers yield two constants, Q and e.

$$r_1 = k_{11}/k_{12} = (Q_1/Q_2)e^{-e_1(e_1-e_2)} \qquad (2a)$$

$$r_2 = k_{22}/k_{21} = (Q_1/Q_2)e^{-e_2(e_2-e_1)} \qquad (2b)$$

The constant Q was meant to represent radical stabilization due to conjugation, whereas e was taken as a measure of permanent polarization of the initial monomer. The concept of permanent polarization has not been well received.[18] Further, Q and e are not specifically defined for any particular monomer. Some arbitrary choice must be made for a standard monomer. As a result *differences* between Q and e for one monomer vs. another (co-

polymerized with the same comonomer) are significant, but the actual magnitudes are not. In fact, originally styrene was selected as the standard with Q and e of 1 and -1, respectively. However, these values were later modified and are now accepted as 1.0 and -0.8, so that better agreement was obtained with copolymer relative reactivity data.[18] Overall, the $Q-e$ scheme has proven itself to be a qualitatively useful method of estimating relative reactivities in radical copolymerization,[19] but, the relationship between Q and radical stability is obscure.

Simamura and co-workers suggested a $\sigma\cdot$ scale (named τ_p in this case), based on product analysis for phenyl radical addition to substituted benzenes[3b] (Figure 1).

$$k_x = k_{para} + 2k_{meta} + 2k_{ortho} \qquad (3a)$$

$$\log (k_x/k_H) - \rho\sigma = \tau_p \qquad (3b)$$

The kinetic treatment is complicated. Ipso addition is apparently ignored. Other difficulties such as spin trapping by the nitro group in the case where nitrobenzene is the substrate[20] and spin trapping by the N-nitrosoacetanilide starting material[21] make this system unsuitable. Finally, the limited number of substituents studied markedly decreases the applicability of this scale.

Yamamoto and Otsu[3c] examined the chain transfer reaction between polystyryl radical and ring-substituted cumenes (Figure 1). By use of the extended Hammett approach, a substituent constant, representing the resonance energy of the radical, E_R, was proposed (eq 4). The Hammett ρ value, however, was chosen

$$\log (k_x/k_H) - 0.7\sigma = E_R \qquad (4)$$

as +0.7 so that the Yamamoto–Otsu equation would agree with the Alfrey–Price $Q-e$ system. Given the empirical nature of the $Q-e$ scheme, this fit is difficult to justify.

The E_D constant ($\sigma\cdot$) of Sakurai et al.[3d] is based on trichloromethyl radical addition to substituted styrenes (Figure 1). The dual-parameter Hammett equation defined the radical delocalization energy constant, E_D, eq 5. Correction was not made for products arising from radical addition to the aromatic ring itself.

$$\log (k_x/k_H) - \rho\sigma = E_D \qquad (5)$$

In 1978 Fisher and Meierhoefer[3e] postulated that hydrogen abstraction from substituted toluenes bearing a cyano function in the meta position should result in a transition state in which radical stabilization effects would be prominent. The polarity of an electrophilic abstracting radical and the benzyl radical would be nearly balanced. A $\sigma\cdot$ scale was then devised ($\sigma_F\cdot$), using the bromination of the para-substituted 3-cyanotoluenes as the standard reaction. The two-parameter Hammett relation (eq 6).

$$\log (k_x/k_H) + 1.46\sigma^+ = \sigma_F\cdot \qquad (6)$$

uses the ρ value (-1.46) from the bromination of the corresponding toluenes *lacking the balancing meta substitution*. Some substituents may also have been forced out of conjugative planarity by, or otherwise interact with, the adjacent cyano group.

On the basis of the extensive rate data provided by Creary[22] for the rearrangement of methylenearylcyclopropanes, we[3f] have proposed a $\sigma\cdot$ scale ($\sigma_C\cdot$, Figure 1), according to eq 7. The polar

$$\log (k_x/k_H) = \sigma_C\cdot \qquad (7)$$

effect on the carbon–carbon bond scission, to generate a transition state with considerable benzyl radical character, would be anticipated to be small. This radical substituent parameter, $\sigma_C\cdot$, has been applied successfully to a number of systems.[23]

Recently, Jackson and co-workers[3g] have put forward a $\sigma\cdot$ scale ($\sigma_J\cdot$), in which the decomposition of substituted dibenzylmercury

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compounds forms the standard reaction (Figure 1). In the dual-parameter treatment (eq 8), the polar substituent constant

$$\log (k_x/k_H) - \rho\sigma^0 = \sigma_J\cdot \qquad (8)$$

chosen by Jackson was σ^0 (Taft's inductive substituent parameter). The ρ value was determined by the slope of the three-point plot for the meta derivatives, assuming no radical substituent effect for meta substitution. The ^{13}C NMR coupling constants (J-($^{13}C_\alpha$–^{199}Hg)) correlated best with σ^0, providing the rationale for the use of these substituent constants in the two-parameter equation. However, Kitching and Drew[24] have recently reported a much better correlation of these coupling constants using Hammett's σ, albeit for a more restricted series of dibenzyl-mercurials. The kinetics may be complicated by two-bond cleavage and induced decomposition of the mercurials, even though the reactions were carried out in dilute (10^{-3} M) solutions to minimize this effect.

A companion paper[25] by Jackson enumerates stringent criteria for an ideal kinetic radical substituent scale to meet. It is apparent that no scale has met more than a few of the requirements. The $\sigma_J\cdot$ scale is flawed in that it too fails to meet a major criterion; the range of substituents considered was limited by the difficulties involved in making the starting mercurials.

Agreement between all these $\sigma\cdot$ scales is understandably poor (Table IV).

Basis of the ESR Approach. Based on an MO study,[26] Walter suggested a qualitative method of evaluating radical substituent effects on a wide range of radical properties, (including ESR hfc), using ionic substituent parameters.[27] Two classes of radicals were recognized by Walter: class S (same) and class O (opposite). He postulated that (1) para-acceptor groups can delocalize both a pair of electrons and an unpaired electron, (2) para-donor groups can only delocalize spin density, and, (3) electron pair delocalization is more important than radical delocalization. In class O radicals donor and acceptor functions will operate to produce opposite substituent effects. Considering postulate (3), substituent effects should be proportional to the normal Hammett parameters, specifically $\sigma/2$ for donors and σ for acceptors.

In class S radicals only spin density can be withdrawn by substituents; all substituents affect the radical in the same manner. Walter proposed that for this class, rates should correlate with $\sigma/2$ for electron-donating functions ($\sigma < 0$) and with σ^- for electron-withdrawing substituents ($\sigma > 0$). Substituted benzyl radicals are class S. However, rates of formation of substituted benzyl radicals, by hydrogen abstraction, are not correlated by this approach.[27]

Janzen has reviewed the substituent effects on ESR hyperfine coupling constants.[28] For the species studied (nitroxyls, nitro anions, hydrazyls, and phenylpropanesemidionyls) the correlations were good, utilizing the expression 9, relating the ratio of hfc to

$$\text{hfc}_x/\text{hfc}_0 = \rho\sigma \text{ or } \rho\sigma^- \qquad (9)$$

the Hammett constants σ and σ^-. This would be expected for such class O radicals, where delocalization of the pair of electrons dominates. Following Janzen's proposal, but ignoring the fact that Walter classified benzyl radicals as class S, Neta and Schuler[29] attempted to fit the substituted benzylic α-H hfc to eq 9. No agreement was found.

A previous scale of alkyl radical stabilities incorporated β-H hfc.[30] However, in addition to spin delocalization, through-bond spin polarization also affects the hfc.[11] The effect of spin polarization, as well as changes in hybridization at the radical center,

can lead to a complex substituent effect. Molecular orbital calculations show significant deviation from planarity with substituent in methyl radicals.[31,32] Therefore, the α-H hfc of substituented benzyl radicals provide a better system upon which to base a $\sigma\cdot$ scale, in that spin polarization effects and changes in hybridization should be minimal.

Three criteria must be met to define an ESR-based $\sigma\cdot$ scale: (1) The radical must be generated in an unambiguous manner. (2) The ESR parameters must be determined accurately. (3) The substituents, both electron-withdrawing and -releasing groups in ionic situations, should be able to interact with the radical center, but must be far enough away so that changes in substitution influence only spin delocalization. Criterion 1 has been considered and shown to be fulfilled (see Results). The second prerequisite is particularly important in that Jackson has, on the basis of an ESR study of a limited number of para-substituted benzyl radicals, stated that the range of α-hydrogen hyperfine coupling constants is too small to be significant.[25] The data presented here, however, represent a consistent series done under similar conditions. The accuracy of the determinations as well as the precision compares favorably with that of kinetics used to define previous $\sigma\cdot$ scales. The variation observed (10%) certainly is significant. Finally, requirement 3 has led us to consider a large series of substituents, electron-withdrawing and -donating in ionic terms, located in both meta and para positions of benzyl radicals.[33] It seems likely that, with the range of derivatives studied, in some cases the substituent effect on spin delocalization will differ significantly from the effect on charge delocalization.

Substituents. Inasmuch as the $\sigma_\alpha\cdot$ scale measures the component of energy that may be attributed to spin delocalization in the substituted benzyl radical in comparison to the unsubstituted case, each of the $\sigma_\alpha\cdot$ values (Table III) is of interest. The $\sigma_\alpha\cdot$ values indicate relative radical stabilization. This reasoning is similar to that applied in the aforementioned study of substituent effects on ^{13}C NMR chemical shifts, where the measured charge delocalization was equated to carbocation stabilization.[9]

Generally, para substitution increases spin delocalization. This is true for substituents recognized as being both electron withdrawing and electron-releasing in ionic reactions. An important exception is para-fluoro, which significantly decreases spin delocalization. In contrast the second-row halogen, chlorine, increases unpaired electron delocalization when placed in the para position.

Notice that p-$tert$-butyl increases spin withdrawal to a greater extent than p-methyl substitution. The opposite order is observed in carbocation stability ($\sigma^+ = -0.256$ vs. -0.311[34]), where hyperconjugation with an adjacent proton is apparently stabilizing.

The effect of p-cyano functionalization is reasonable, considering the additional resonance structure that can be drawn. Significant spin density *is* found on the cyano nitrogen (Table I). Other unsaturated substituents should exhibit similar stabilizing effects. p-Acetyl and p-benzoyl substitution both result in large spin delocalization, in accord with resonance forms which place unpaired electron density on the carbonyl oxygen.

The sulfur-containing groups define an interesting subset. Substitution in the para position by methylsulfinyl or methoxysulfonyl functions increases unpaired electron delocalization; methylsulfinyl is twice as effective as methoxysulfonyl. This series is obviously incomplete; methylsulfenyl and methylsulfonyl are missing. In experiments, using these substituted toluenes, triplets (1:2:1), characteristic of substituted methyl radicals without further coupling, were recorded and the benzyl radicals were not detected. Apparently, hydrogen abstraction occurred at the methyl adjacent to sulfur. Other evidence[22,23] indicates that a p-methylsulfenyl group stabilizes the benzylic radical to a much larger extent than the carbocation ($\sigma = 0.0$; $\sigma^+ = -0.16$). This is consistent with

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Table V. Correlation of σ_α. with Radical Reaction Kinetics

reaction	ρ·	$r_1{}^a$	ρ	$r_2{}^b$	ρ^c	ρ·^{c}	$r_3{}^d$	no. of points
methylenearylcyclopropane rearrangement[e]	6.12	0.909	0.028	nil	0.152	6.52	0.946	14
NBS bromination of 4-substituted 3-cyanotoluenes[f]	-1.83	nil	-1.07	0.969	-1.09	5.19	0.992	7
NBS bromination of substituted toluenes[g]	-3.43	nil	-1.43	0.997	-1.43	0.672	0.997	6
H abstraction from substituted toluenes by t-Bu·[h]	3.62	nil	0.484	0.962	0.462	1.30	0.978	7
electroreduction of benzyl chlorides[i]	9.70	0.727	0.816	0.942	0.651	4.38	0.989	9

[a] Correlation constant (r) for log (k_{rel}) vs. σ_α·, least-squares plot. All r's are corrected for degrees of freedom. [b] Correlation constant (r) for log (k_{rel}) vs. σ or σ^+; σ values are taken from Brown and McDaniel (Brown, H. C.; McDaniel, D. M. *J. Org. Chem.* 1958, *37*, 420). σ^+ values are those of ref 34. [c] Defined by eq 10. [d] Correlation constant for eq 10. [e] Reference 22, 3f, correlation with σ. [f] Reference 3e, correlation with σ^+. [g] Reference 37, correlation with σ^+. [h] Reference 8b, correlation with σ^+. Pryor correlates his data with σ ($r = 0.957$), rather than σ^- ($r = 0.941$) or σ^+ ($r = 0.962$), in apparent contradiction of the nucleophilicity ($\rho > 0$) of the *tert*-butyl radical. [i] Reference 4f.

a recent theoretical calculation.[31] Our attempts to complete this subset will continue.

All meta substituents studied decrease spin delocalization. The contrast between *p*- and *m*-cyano substitution is particularly marked. *m*-Cyano functionalization results in the largest destabilizing effect on the benzyl radical, whereas *p*-cyano substitution increases the unpaired electron withdrawl substantially. The relative occupancy of *p*-quinoidal and diallylic MO's offers a qualitative account of these effects.

A thorough MO study could provide an explanation of the effects observed. However, several semiempirical calculations have already been carried out[16] and the agreement is poor. An ab initio approach may be more successful.

Applications. Previous studies of free radical reactions (Table V) in which substituent effects were considered can now be reexamined with a two-parameter Hammett relationship (eq 10)

$$\log k_{rel} = \rho \cdot \sigma_\alpha \cdot + \rho \sigma \ (\text{or } \sigma^+, \ \sigma^-, \ \text{etc.}) \qquad (10)$$

to assess the relative importance of spin delocalization and polar factors on the transition-state energy. Note that now radical stabilization has been defined separately. It is not dependent on the choice of ionic substituent constant. Since the values of σ_α· are not normalized with σ or σ^+, only ratios of the respective ρ values can be considered. There is no relationship between σ_α· and σ or σ^+; therefore, if the relative rates of a free radical reaction correlate well with σ or σ^+, spin delocalization of the intermediates is unimportant and an early transition state, influenced by polar factors, is indicated.[35]

Since bond dissociation energy has traditionally been used as a measure of radical stability (subject to the criticism above), it would be interesting to apply eq 10 to the relative carbon–hydrogen bond dissociation energy of substituted toluenes. Unfortunately, too few derivatives have been studied.[8] Furthermore, the substituent effect on the benzylic bond dissociation energy may be masked within the experimental accuracy (1–1.5 kcal mol^{-1}[36]).

The effect of substituents on the thermal rearrangement of methylenearylcyclopropanes has been studied by Creary.[22] The transition state for this reaction should have radical (biradical) character and polar factors should be relatively unimportant. In fact, Creary noticed that the relative rates did not correlate with any of the ionic substituent parameters. In this case a reasonable correlation is observed with σ_α· alone (Figure 2). Consideration of both σ_α· and σ, using eq 10, improves the correlation. The relative importance of spin delocalization is indicated by the ratio of $\rho \cdot / \rho$ which is 43. Notice also that fluoro is the only para substituent that slows the rearrangement and that the *p-tert*-butyl increases the rate of rearrangement more than *p*-methyl. *m*-Cyano substitution has the largest effect in slowing the rate of rearrangement.

An estimate of the energetics involved over the σ_α· scale can be obtained from this study. If the polar effect is neglected the ρ· value is 6.12. Based on the change in rate constant with substituent, and assuming a constant preexponential factor, a ρ_α· unit is equivalent to 12 kcal mol^{-1} in activation energy.

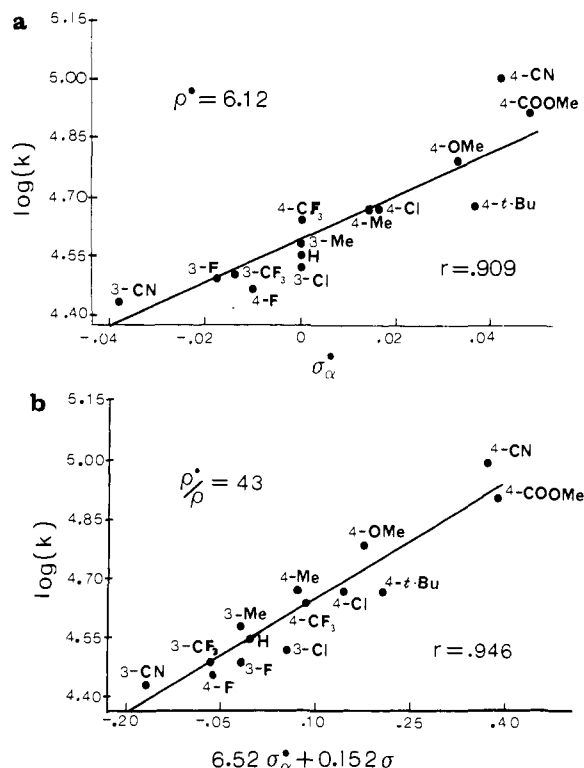**Figure 2.** Plot of the logarithm of the rates of rearrangement in the methylenearylcyclopropane rearrangement vs. (a) σ_α· alone and (b) the two parameters σ_α· and σ (eq 10).

In the bromination of substituted toluenes[37] (*N*-bromosuccinimide in benzene), the relative rates do not correlate solely with σ_α·, a good correlation is obtained by using σ^+ alone, and use of σ_α· and σ^+, in the two-parameter equation, leads to no improvement. Spin delocalization is obviously unimportant, and the ratio of $\rho \cdot / \rho^+$ from the two parameter equation is only 0.5.

The comparable bromination of substituted 3-cyanotoluenes has been studied with the view that the cyano group should cause the transition state to be less polar.[3e] Again, in this case, no correlation is evident between the relative rates and σ_α· alone. However, the correlation with σ^+ is not as good as in the toluene series. The ρ^+ value indicates that the transition state *is* less polar as the result of 3-cyano substitution. Now the two-parameter Hammett equation significantly improves the correlation and the ratio of $\rho \cdot / \rho^+$ increases to 5.

Few radical reactions have been found with positive ρ values.[4a,5,38,39] However, a recent investigation by Pryor[8] has determined a positive ρ for the abstraction of hydrogen from substituted toluenes by *tert*-butyl radical. The logarithm of the

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relative rates does not correlate with $\sigma_\alpha\cdot$ alone, the agreement with σ^+ alone is good. However, the two-parameter treatment with $\sigma_\alpha\cdot$ and σ^+ yields an even better correlation and *both ρ^+ and $\rho\cdot$ are positive.* Interestingly, *p-tert*-butyl substitution increases the relative rate beyond that caused by *p*-methyl substitution.

Streitwieser and Perrin[4e] were the first to advocate the use of a two-parameter Hammett equation, incorporating σ and $\sigma\cdot$, to correlate the substituent effects on the electrochemical reduction of benzyl chlorides. They pointed out that no $\sigma\cdot$ scale was available at that time and plotted the data vs. σ alone. Correlation was, not unexpectedly, poor ($r = 0.817$); they discuss the examples which deviate from the line in terms of additional radical stabilization. Tanner and co-workers extended the study, including conjugative electron-withdrawing substituents. They found a much better correlation ($r = 0.911$) with σ^-.

We can now reassess these data with eq 10. We have chosen not to combine the two sets of data; experimental conditions were significantly different, the error limits were smaller in Tanner's work, and eq 10 was applied to his data.[4f]

Using the nine data points available, the correlation ($r = 0.942$) with σ^- alone is much improved ($r = 0.989$) by including $\sigma\cdot$ (eq 10). The ratio of $\rho\cdot/\rho^-$ is 6.7 which indicates a significant contribution of radical stabilization at the transition state.

In conclusion, the $\sigma_\alpha\cdot$ scale offers an attractive approach to determining the relative importance of radical stabilization vs. polar factors in radical reactions. Exner[33] has put forward a minimum set of groups that must be considered to obtain any overall picture in ionic reactions. These are 4-OCH_3, 3-CH_3, H, 4-Cl, 3-Cl, 3-NO_2, and 4-NO_2. Given the known spin-trapping problem (vide supra) at the nitro function, the lack of this group in the $\sigma_\alpha\cdot$ series is not critical. The electron-withdrawing and conjugating cyano group achieves a similar purpose. The results presented argue in favor of the inclusion of 4-F, 4-CH_3, 4-*tert*-C_4H_9, 4-CN, and 3-CN, as well as the groups mentioned by Exner, in any study of substituent effects on radical reactions. Unfortunately, many of the previous studies of relative free radical reactivity have not included these important derivatives.

Experimental Section

General Information. ESR spectra were recorded on a Varian Associates E-109E[40] or E-109B electron paramagnetic resonance spectrometer, both equipped with a liquid nitrogen variable-temperature accessory. The ESR reactor tube has been described previously.[41] Melting points were determined on a Sybron Corp. Thermolyne hotstage (uncorrected). ^{1}H NMR data, obtained from a Varian Associates T-60 nuclear magnetic resonance spectrometer, and IR data, obtained from a Perkin-Elmer 237 Infracord infrared spectrometer, were in agreement with literature data.

Materials. Di-*tert*-butyl peroxide (DTBP) and triethylsilane were bought from Pfaltz and Bauer and used without further purification. 4-Methoxyacetophenone (PMA) was supplied by Aldrich and recrystallized twice from 95% ethanol prior to use. Substituted toluenes, which were obtained commercially, were purified by conventional methods. Aldrich: 4-*tert*-butyltoluene, 4-chlorotoluene, 3-chlorotoluene, 3-cyanotoluene, 4-fluorotoluene, 3-fluorotoluene, 4-methylanisole. Anachemia: 4-methylacetophenone, toluene, 4-xylene. J. T. Baker: 4-cyanotoluene, 3-xylene. Eastman: methyl 4-toluate, methyl 3-toluate. Nitrogen and argon gases were purchased (Union Carbide Corp.) and utilized without subsequent treatment. Carbon tetrachloride was fractionally distilled and then stored over 4-Å molecular sieve. Chlorobenzene (J. T. Baker) was stirred with concentrated sulfuric acid, washed successively with water, saturated sodium bicarbonate solution, and water, dried over magnesium sulfate, and distilled through a Vigreux column.

Preparation of Substituted Benzyl Bromides. The method of Grice and Owen[42] was used for the conversion of the substituted benzyl alcohols to the bromides. Typically, the benzyl alcohol (0.2 mol) was dissolved in benzene (100 mL). Hydrogen bromide gas (Matheson) was passed through the solution for 1 h or until the solution was saturated. The reactants were heated to reflux and the water which formed was removed via a Dean-Stark trap. The solution was dried over anhydrous calcium

chloride and the bromide isolated by fractional distillation at reduced pressure.

3-(Trifluoromethyl)benzyl Bromide. The benzyl alcohol (3.0 g, 0.017 mol) was obtained from Aldrich and brominated by the method outlined above. The product (2.0 g, 49%) was distilled (bp 50 °C (0.25 torr); lit.[43] bp 69 °C (4 torr)).

4-(Trifluoromethyl)benzyl Bromide. The 4-(trifluoromethyl)benzoic acid (4.0 g, 0.021 mol) was purchased from Pfaltz and Bauer and was esterified with ethanol to give 3.2 g (70%) of the ethyl ester (bp 78–80 °C (5 torr); lit.[43] bp 80–80.5 °C (5.5 torr)). The benzoate was reduced to the benzyl alcohol (2.5 g, 96%; bp 70–72 °C (3.5 torr); lit.[43] bp 78.5–80 °C (4 torr)) with lithium aluminum hydride.

The benzyl alcohol was brominated as before[42] to give 1.25 g (37%) of the bromide which was distilled (bp 37–40 °C (1.5 torr); lit.[44] bp 65–66 °C (5 torr)).

Toluenes. Methyl 4-Tolyl Sulfoxide. Methyl 4-tolyl sulfide was prepared from 4-methylthiophenol (12.4 g, 0.1 mol) with sodium hydroxide (6.0 g, 0.15 mol) in dimethyl sulfoxide (40 mL), followed by dropwise addition of iodomethane (21.3 g, 0.15 mol). The reaction mixture was extracted twice with ether. The ethereal extracts were washed with water and dried over sodium sulfate, and the ether was removed at reduced pressure. Distillation yielded 6.0 g (44%) of the product (bp 92–94 °C (20 torr); lit.[45] bp 95 °C (21 torr)). The toluene (5.0 g, 0.036 mol) was oxidized to the sulfoxide with sodium periodate (8.0 g, 0.027 mol) in water/methanol (100 mL:20 mL). The solution was extracted with dichloromethane, dried over sodium sulfate, the dichloromethane distilled at reduced pressure and the isolated sulfoxide recrystallized from pentane:carbon tetrachloride to give 3.2 g (57%) pure product (mp 42–43 °C; lit.[46] 42–43 °C).

Methyl 4-Tolyl Sulfone. The sulfoxide (vide supra) (1.5 g, 0.01 mol) was oxidized to the sulfone with 3-chloroperbenzoic acid (1.9 g, 0.011 mol) to yield 1.27 g (75%) (mp 87–88.5 °C; lit.[47] mp 89 °C).

Methyl 4-Toluene Sulfonate. The toluene was prepared by the reaction of 4-toluenesulfonyl chloride (10 g, 0.057 mol) with excess methanol[47] to give 8.1 g (82%) (mp 27 °C; lit.[48] mp 27–28 °C).

4-Tolyl Acetate. The 4-methylphenol (10 g, 0.09 mol) was reacted with excess acetyl chloride to afford 10.4 g (77%) of the ester (bp 212–214 °C; lit.[49] 213 °C).

ESR Experiments. Toluenes. A static solution (0.5 mL) of DTBP and the toluene (1:4) with PMA (45 mg, 0.6 M) or diluted with carbon tetrachloride or chlorobenzene (up to 33%) was irradiated in the ESR spectrometer cavity,[21] using a filtered (Corning 0-53) 1-kW Xe or Xe–Hg high-pressure lamp. Temperatures ranged from +20 to –60 °C, with the majority of samples examined at –60 °C. All samples were purged with nitrogen or argon (10 min) before irradiation.

Benzyl Bromides. The method of Bassindale et al.[50] was used for the bromides. The benzyl bromide and triethylsilane (3:1) were placed in the ESR tube with 1 drop of DTBP. Solutions were irradiated, as described above, in the ESR cavity. All samples were purged before use.

Control Experiments. Linearity of field was checked against the lines of [Cr(NH$_3$)$_5$Cl]Cl$_2$ doped with 2% [Co(NH$_3$)$_5$Cl]Cl$_2$.[51] Accuracy of the field was checked against the couplings for Würster's blue perchlorate in ethanol.[52] In some cases signal averaging (Nicolet 1170) was found useful. Control experiments were undertaken with three representative benzyl radicals: benzyl, 4-fluorobenzyl, and 3-cyanobenzyl. The spectrum of the benzyl radical was recorded at 10-deg intervals from –20 to +20 °C. The 4-fluorobenzyl spectrum was observed at –60, –20, and +20 °C. The 3-cyanobenzyl radical was noted at –60 and –40 °C. In all cases field positions for the lines were invariant. Dilution with up to 50% (v/v) chlorobenzene or carbon tetrachloride also did not affect the spectra.

Coupling constants were measured directly and refined by computer simulation.

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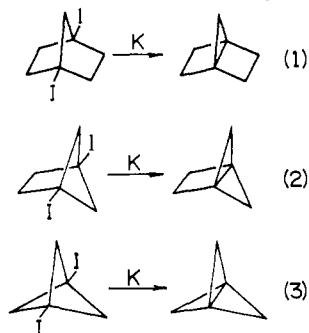
Strain Energies of Small Ring Propellanes

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Abstract: Energies of hydrogenolysis of carbon–carbon bonds have been calculated by using extended basis sets and have been compared with experimental data. In most cases, a consistent difference between calculated and observed values of 5 ± 1 kcal/mol was obtained. It was found that the energies of hydrogenolysis of the propellanes became progressively more negative in the order [1.1.1], [2.1.1], [2.2.1]. Since the [2.2.1]propellane has been obtained from its bicyclic precursor, the calculations suggested that the other propellanes may be prepared in a similar fashion, and with greater ease. Subsequently, this was confirmed experimentally. The enthalpies of formation and strain energies were estimated. The effect of polarization functions on the energies and structures of the propellanes is discussed, and the electron density changes for the central bonds of the propellanes have been calculated.

We have recently observed that the gas-phase dehalogenation of 1,4-diiodobicyclo[2.2.1]heptane leads to the [2.2.1]propellane.[1] In this context, we should like to know the relative strain energy increases in the series of reactions: This might suggest whether or not the second and third reactions are practical.

In addition, we have examined the rates of thermolysis of a series of small ring propellanes containing cyclobutane rings and have suggested that strain energy relief,[2] rather than orbital symmetry considerations,[3] provides the main driving force leading to changes in activation energies. Better information on strain energies would be valuable in determining whether or not this is correct. Since it is unlikely that direct calorimetric measurements will be practical for many of these compounds and for other small ring propellanes of current interest,[4–7] we have attempted to es-

timate the energies via molecular orbital calculations. These calculations will also provide structural data for some of the propellanes for which such data are not available.[8,9]

Reasonably good energies and geometries are normally obtained for hydrocarbons with the 4-31G basis set.[10] Complete geometry optimizations have been carried out for four propellanes as well as a set of relevant small ring hydrocarbons, and the resulting energies are given in Table I. Some calculations dealing with the propellanes have been reported,[3,11] but in no case has complete geometry optimization been carried out.

It is known that polarization functions (d orbitals) are needed at carbon if one is to obtain reasonable estimates of energies of reaction of highly strained compounds.[12,13] Therefore, the energies of the 4-31G[14] optimized structures also were calculated with the 6-31G* basis set, and these energies are given in Table I, along with the zero-point energies and the change in enthalpy of formation on going from 0 to 298 K.[15]

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