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Kinetic vs Thermodynamic Factors in α-Hydrogen Atom Abstractions from Alkylaromatics. 2. Reactivities of α-Alkylnaphthalenes and Several Conformationally Locked Alkylaromatics toward Bromine Atom

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The relative reactivities of α-methyl-, α-ethyl-, and α-isopropylnaphthalene toward bromine atom have been determined. A partial breakdown in the normal reactivity pattern (tertiary > secondary > primary) is observed: CH_3 (1.00) < CH_2CH_3 (5.7) > $CH(CH_3)_2$ (4.7) per hydrogen at 80 °C. These data (in conjunction with earlier results for the phenyl and 9-anthryl series) show that for alkylaromatics in general, the anticipated correlation between log (k_{rel}) and $\Delta H°$ for α-hydrogen abstractions by bromine atom is poor. This breakdown in the Evans and Polanyi (E&P) relationship and the observed selectivity reversals in the α-naphthyl and 9-anthryl series are attributed to stereoelectronic factors, specifically the alignment of the α-C–H bond with the adjacent π-system in the starting alkylaromatic. The reactivities of indane, 1,8-ethylenenaphthalene, and 1,9-ethyleneanthracene (relative to the corresponding ethylarenes) provide further evidence for the role of stereoelectronic factors. These stereoelectronic factors are reconciled with the E&P equation quantitatively: An excellent correlation between log k_{rel} and ($\sin^2\theta \times \Delta H°$) is observed (where θ is the angle defined by the α-C–H bond with respect to the aromatic plane). The basis for this treatment and its relationship to the E&P equation is discussed.

Introduction

In an earlier report, we noted an inverted order in the relative rates of α-hydrogen abstraction from several 9-alkylanthracenes by bromine atom: methyl (1.00) > cyclopropyl (0.33) > ethyl (0.063) > isopropyl (<0.001, per hydrogen at 80 °C).[1] Two factors were considered in order to explain this unusual reactivity order: (1) steric inhibition to resonance in the resulting radicals and (2) stereoelectronic effects (i.e., the degree of alignment of the α-C–H bond with the π-system).

If the thermodynamic stability of the resulting free radical bore primary responsibility for this reactivity order, then it was anticipated that this effect would be reflected in the α-C–H bond dissociation energies of these substrates. To check this hypothesis, bond dissociation energies of the 9-alkylanthracenes were estimated (kcal/mol) using semiempirical MO theory (AM1 approximation): $c\text{-}C_3H_5$ (83) > CH_3 (82) > CH_2CH_3 (80) > $CH(CH_3)_2$ (76). Because a similar inversion in the BDE order was not found, we concluded that steric inhibition to resonance in the free radicals was not the primary factor responsible for the unusual reactivity order.

In contrast, the reactivity order could be directly related to the lowest energy conformation of the substrate. Defining θ_{C-H} as the angle of the α-C–H bond with respect to the aromatic plane, for 9-methyl, 9-cyclopropyl-, 9-ethyl-, and 9-isopropylanthracene, θ_{C-H} = 90, 90, 33 and 16°, respectively. Based upon this correlation (reactivity is maximal when the α-C–H bond is parallel to the adjacent π-system), we argued that stereoelectronic factors were responsible for the inverted reactivity order.

We have determined the relative reactivities of (1) several α-alkylnaphthalenes and (2) conformationally locked alkylaromatics towards bromine atom. In this paper, we summarize these findings and amplify our earlier conclusions regarding the interplay of kinetic and thermodynamic factors in these hydrogen atom abstractions.

Results

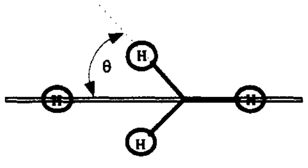
A. α-Alkylnaphthalenes. 1. Relative Reactivities. The relative reactivities of α-methyl-, α-ethyl-, and α-isopropylnaphthalene were determined via competition experiments for bromine atom (NBS/CCl_4).[2] Our results are summarized in Table I. In order to obtain an absolute rate constant for a member of this series, a competition pitting α-methylnaphthalene vs toluene found the former to be more reactive by a factor of 8.3 (±1.2 per molecule at 80 °C). The absolute rate constant for $PhCH_3 + Br^\bullet \rightarrow PhCH_2^\bullet + HBr$ is 6×10^5 M^{-1} s^{-1} at 80 °C;[3] therefore, the absolute rate constant for abstraction of hydrogen from α-methylnaphthalene by bromine atom is estimated to be about 1 order of magnitude faster, $k = 5 \times 10^6$ M^{-1} s^{-1}.

Table I. Relative Rates of α-Hydrogen Abstraction for α-Alkylnaphthalenes by Bromine Atom (CCl_4 Solvent)

	relative rate[a]	
alkyl group	80 °C[b]	13 °C[c]
$-CH_3$	1.00	1.00
$-CH_2CH_3$	5.7	6.2
$-CH(CH_3)_2$	4.7	4.9

[a] Per hydrogen, triplicate determinations, ±5%. [b] Initiated thermally with benzoyl peroxide. [c] Photoinitiated with a 450-W medium-pressure mercury arc lamp through two Pyrex layers.

2. Conformational Analysis. The conformations of the α-alkylnaphthalenes were examined using AM1.[4] For α-methylnaphthalene, the lowest energy conformation is depicted below (1, θ = 60°). The barrier to rotation is calculated to be 1.3 kcal/mol.



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The two lowest energy conformations of α-ethylnaphthalene are 2 and 3. Of these, the former is found to

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[1] Tanko, J. M.; Mas, R. H. *J. Org. Chem.* **1990**, *55*, 5145.

[2] The Ziegler conditions (NBS/CCl_4) are generally accepted as the best experimental method for determining bromine atom selectivities. For a review, see: Poutsma, M. L. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, pp 159–229.

[3] Based upon an activation energy of 7.6 kcal/mol and log A = 13.5 (cm^3 mol^{-1} s^{-1}): Anderson, H. R., Jr.; Scherage, H. A.; VanArtsdalen, E. R. *J. Chem. Phys.* **1953**, *21*, 1258.

[4] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

[5] McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493.

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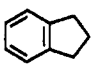
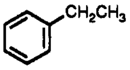
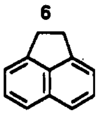
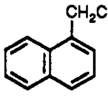
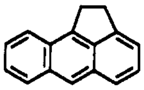
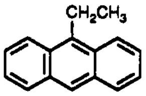
Table II. AM1-Calculated Bond Dissociation Energies of α-Alkylnaphthalenes[a]

alkyl group	BDE,[b] kcal/mol
$-\mathit{C}H_3$	[85]
$-\mathit{C}H_2CH_3$	80
$-\mathit{C}H(CH_3)_2$	80

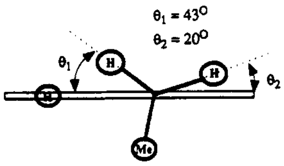
[a] MOPAC Version 5.0 (QCPE 455). [b] Obtained by calculating ΔH_{rxn} for $ArCH_3 + Ar\dot{C}R_2 \rightarrow Ar\dot{C}H_2 + ArCHR_2$ (ΔH_{rxn} = BDE(ArCH$_3$) − BDE(ArCHR$_2$)) using AM1-calculated ΔH°_f's (see ref 1). Experimental BDE for ArCH$_3$ from ref 5.

Table III. Rates of α-Hydrogen Abstraction by Br$^•$ from Conformationally Locked Alkylaromatics 6 → 8 Relative to the Corresponding Ethylarene at 80 °C

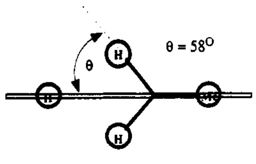
compd			
A	B	k_A/k_B[a]	ΔBDE,[b] kcal/mol
 6		2.7 (1.8)[c]	2.5
 7		1.9	3.5
 8		180	2.3

[a] Per hydrogen. [b] BDE(A) − BDE(B), calculated using AM1 (see text). [c] Reference 7, 40 °C.

be slightly (0.1 kcal/mol) lower in energy (with a 1.1 kcal/mol barrier to interconversion).

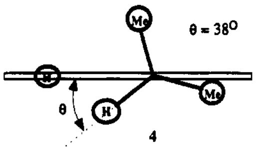


2



3

Two degenerate conformations of α-isopropylnaphthalene were found, 4 and 5 with θ_{C-H} = 38 and 0°, respectively. 4 and 5 are separated by a 0.3 kcal/mol rotational barrier.



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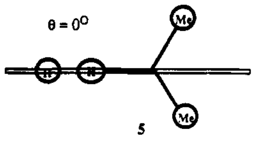

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3. α-C–H Bond Dissociation Energies. These values (Table II) were obtained using AM1 to calculate the heats of formation of the α-alkylnaphthalenes and corresponding free radicals as described previously.[1]

B. Conformationally Locked Alkylaromatics 6 → 8. The reactivities of indane (6), 1,8-ethylenenaphthalene (7), and 1,9-ethyleneanthracene (8) relative to the corresponding ethylarenes toward bromine atom were determined via direct competitions (NBS/CCl$_4$). The results are summarized in Table III. The difference in bond dissociation energies (Δ BDE) between 6, 7, and 8 and the corresponding ethylarenes were calculated according to the exchange reaction depicted in eq 1 using heats of formation obtained from AM1. These values are also summarized in Table III.

$$\text{Ar-}\dot{\text{C}}\text{HCH}_3 + \text{Ar}\frown\text{CH}_2 \longrightarrow \text{Ar-CH}_2\text{CH}_3 + \text{Ar}\frown\text{CH}^\bullet \qquad (1)$$

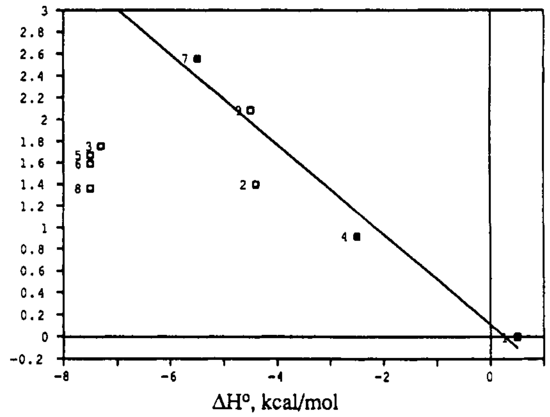

Figure 1. Relative reactivites of alkylaromatics toward bromine atom vs ΔH° (data from Table IV; straight line from linear regression analysis using only the methylarene data). Key: 1, toluene; 2, ethylbenzene; 3, cumene; 4, α-methylnaphthalene; 5, α-ethylnaphthalene; 6, α-isopropylnaphthalene; 7, 9-methylanthracene; 8, 9-ethylanthracene; 9, 9-cyclopropylanthracene.

Discussion

A. α-Alkylnaphthalenes. In Table IV, the reactivities of several alkylaromatics toward bromine atom, ΔH° for the hydrogen abstraction process, and θ_{C-H} are compiled. The α-alkylnaphthalenes exhibit a partial breakdown in the normal reactivity pattern toward bromine atom with CH_3 (1.00) < CH_2CH_3 (5.7) > $CH(CH_3)_2$ (4.7). These selectivities encompass a much narrower range of values compared to the corresponding alkylbenzenes[6-8] or 9-alkylanthracenes.[1]

The α-alkylnaphthalenes were selected for study because of the three (methyl, ethyl, and isopropyl), only the radical resulting from the isopropyl derivative was expected to suffer from any appreciable steric interaction with the peri-hydrogen. In fact, the AM1-optimized geometry of this radical indicates a 24° deviation from planarity. This steric effect is also manifested in the thermochemistry, in that α-ethyl- and α-isopropylnaphthalene have identical BDE's (Table II).

α-Ethyl- and α-isopropylnaphthalene are nearly equally suited for α-hydrogen abstraction with θ_{C-H} = 43 and 38°, respectively. While at both 80 and 13 °C the ethyl derivative is slightly (1.2–1.3×) more reactive, these observations by themselves do not help clarify the relative importance of α-C–H bond alignment vs radical stability.

B. Methylarenes. In the series Ar = phenyl → α-naphthyl → 9-anthryl, the relationship between the rate constant and ΔH° for the methylarenes is unmistakable (Table IV). In accordance with the Evans and Polanyi relationship ($\log k = C - \alpha\text{-}\Delta H^\circ$),[9] a plot of $\log k_{rel}$ vs ΔH° yields a straignt line (Figure 1) with $\alpha = 0.41 \pm 0.05$. This correlation demonstrates that for methylarenes at least, the transition state is stabilized by resonance interactions analogous to those present in the resulting radicals and that stereoelectronic factors are of minor significance in this series.

C. Conformationally Locked Alkylaromatics 6 → 8. The results summarized in Table III provide compelling

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(6) Friedrich, S. S.; Friedrich, E. C.; Andrews, L. J.; Keefer, R. M. *J. Org. Chem.* **1969**, *34*, 900.

(7) Russell, G. A.; Desmond, K. A. *J. Am. Chem. Soc.* **1963**, *85*, 3139.

(8) Russell, G. A. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, pp 275–331.

(9) Walling, C.; Rieger, A. L.; Tanner, D. D. *J. Am. Chem. Soc.* **1963**, *85*, 3129.

(10) Benson, S. W. *J. Chem. Educ.* **1965**, *42*, 502.

(11) Bockrath, B.; Bittner, E.; McGrew, J. *J. Am. Chem. Soc.* **1984**, *106*, 135.

Table IV. Relative Reactivities of Alkylaromatics (Ar–R) toward Bromine Atom at 80 °C

Ar	R	$r(\mathrm{ArR/ArCH_3})^a$	$r(\mathrm{ArR/PhCH_3})^b$	k^c ($M^{-1}\,s^{-1}$)	$\theta_{C\text{-}H}{}^d$ (deg)	$\Delta H^{\circ\,e}$ (kcal/mol)
phenyl						
	$-CH_3$	1^f	1^f	$6 \times 10^{5\,g}$	90, 21, 21 (0.0) 60, 60, 0 (0.2)	0.5
	$-CH_2CH_3$	25^f	25^f		31, 31 (0.0) 58, 58 (0.4)	−4.4
	$-CH(CH_3)_2$	57^f	57^f		6 (0.0) 43 (0.4)	−7.3
α-naphthyl						
	$-CH_3$	1	8.3	5×10^6	60, 60, 0	−2.5
	$-CH_2CH_3$	5.7	47		20, 43, (0.0) 58, 58 (0.1)	−7.5
	$-CH(CH_3)_2$	4.7	39		38 (0.0) 0.1 (1.9) 0.8 (0.5)	−7.5
9-anthryl[h]						
	$-CH(CH_2)_2$	0.33	120	2×10^8	90 (0.0) 0 (6.3)	−4.5
	$-CH_3$	1	360		90, 30, 30	−5.5
	$-CH_2CH_3$	0.063	23		33, 33 (0.0) 66, 66 (7.0)	−7.5
	$-CH(CH_3)_2$	<0.001			16 (0.0) 4 (1.0)	−11.5

[a] Relative reactivity (per hydrogen) vs corresponding methylarene. [b] Relative reactivity (per hydrogen) vs toluene. [c] Absolute rate constant for $ArCH_3 + Br^\bullet \rightarrow ArCH_2^\bullet + HBr$ at 80 °C. [d] Angle of α-C–H bond(s) with respect to aromatic ring. The values in parantheses represent the relative enthalpies (kcal/mol) of the different conformations (when more than one exist). [d] ΔH° = BDE(ArR) − BDE(HBr). BDE(ArR) was calculated using AM1 (see text and ref 1); BDE(HBr) from ref 10. [f] Relative reactivities from refs 6–8. [g] Gas phase, ref 3. [h] Data for the 9-anthryl series from ref 1.

evidence for the importance of stereoelectronic factors in the hydrogen abstraction process. Despite the fact that 6 → 8 each has a higher bond dissociation energy than the corresponding ethyl derivative, each shows enhanced reactivity toward bromine atom.

The enhanced reactivity of indane relative to ethylbenzene (for Br• and several other free radicals) has been noted by others and discussed in terms of a stereoelectronic effect.[9] For indane, the α-CH_2 groups are effectively locked in a conformation where $\theta_{C\text{-}H}$ = 60°, while for the freely rotating ethyl group of ethylbenzene two low energy conformations are available for which $\theta_{C\text{-}H}$ = 31 and 57°, respectively (the former of which is 0.4 kcal/mol lower in energy). Similarly, 7 is found to be more reactive than α-ethylnaphthalene, although the differences between the two are smaller, a fact explicable by the fact that $\theta_{C\text{-}H}$ = 60° for both compounds (vide supra).[12]

A compelling argument for stereoelectronic control is provided by comparing the relative reactivities of 8 vs 9-ethylanthracene. While ΔBDE for 8 is similar to 6 and 7, 8 is found to be 180× more reactive toward Br• than its corresponding ethyl derivative. The difference in this system is that the while the ethyl group of the phenyl or α-naphthyl systems is freely rotating and can achieve a low-energy conformation with $\theta_{C\text{-}H} \approx 60°$ (≤0.4 kcal/mol difference, Table IV), the ethyl group of 9-ethylanthracene is effectively locked in a conformation wherein $\theta_{C\text{-}H}$ = 33° (rotation of the C_{Ar}–CH_2 bond brings the methyl group prohibitively close to one of the peri-hydrogens; the conformation where $\theta_{C\text{-}H}$ = 66° is 7.0 kcal/mol higher in energy). In contrast, $\theta_{C\text{-}H}$ = 60° for 8 and hydrogen abstraction is more facile.

D. Kinetic vs Thermodynamic Factors in Hydrogen Atom Abstractions. Utilizing the data compiled in Table IV, the relative reactivities of all the alkylaromatics in the phenyl, α-naphthyl, and 9-anthryl series relative to toluene (log k_{rel}) are plotted (Figure 1) vs ΔH° (calculated as the difference in BDE between the alkylaromatic and HBr). While there is a general trend that shows enhanced reaction rate as the reaction becomes increasingly exothermic, the overall correlation is poor (R = −0.684). From Figure 1 it is clear that increased alkyl substitution at the α-position induces significant deviation from the Evans–Polanyi equation. Our interpretation is that the expected correlation between log k_{rel} and ΔH° is obscured because of stereoelectronic factors.

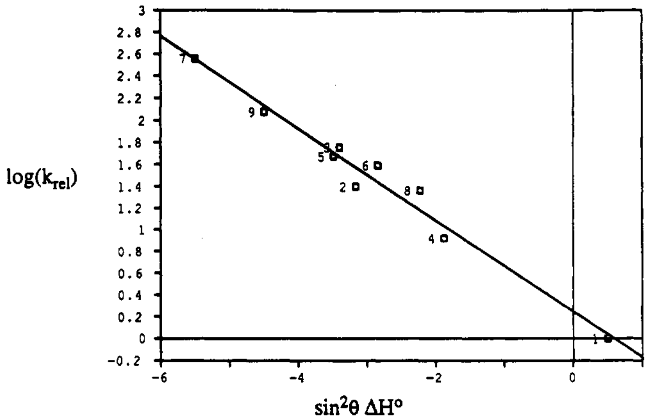

Figure 2. Relative reactivities of alkylaromatics toward bromine atom vs $\sin^2\theta(\Delta H^\circ)$ (data from Table IV). Key: 1, toluene; 2, ethylbenzene; 3, cumene; 4, α-methylnaphthalene; 5, α-ethylnaphthalene; 6, α-isopropylnaphthalene; 7, 9-methylanthracene; 8, 9-ethylanthracene; 9, 9-cyclopropylanthracene.

In an attempt to account for stereoelectronic factors quantitatively, we propose a modification of the Evans–Polanyi relationship for alkylaromatics (eq 2). Our rationale for this relationship is that hydrogen abstraction is most facile when the α-C–H bond is aligned with the adjacent π-system (θ = 90°) and least facile when $\theta_{C\text{-}H}$ = 0°, hence the $\sin^2\theta$ term in eq 2.[14] A linear least-squares

$$\log k_{rel} = C - \alpha\text{-}\sin^2\theta(\Delta H^\circ) \qquad (2)$$

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[12] Similar results have been reported by Bockrath et al. who observed an analogous reactivity order toward benzyl radical: 1,8-ethylenenaphthalene (7.0) > α-ethylnaphthalene (2.6) > α-methylnaphthalene (1.0), per hydrogen at 170 °C, ref 11.

[13] Sales, K. D. In *Advances in Free Radical Chemistry*; Williams, G. H., Ed.; Academic Press: New York, 1969; Vol. III, pp 39–198.

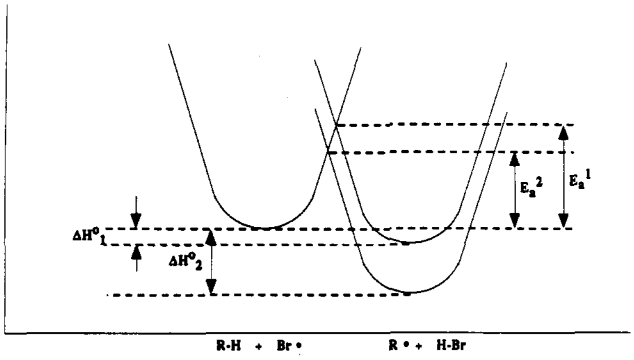

Figure 3. Reaction coordinate diagram for hydrogen abstraction reactions (relationship between E_a and ΔH°).

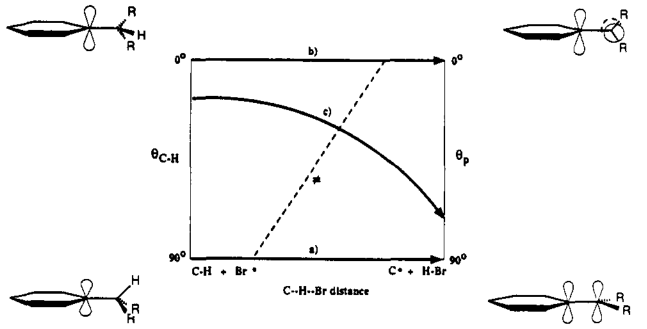

Figure 4. Proposed reaction coordinate diagram for hydrogen abstraction reactions involving alkylaromatics.

regression analysis of the data in Table IV according to eq 2 yields $\alpha = 0.42 \pm .02$, which within experimental error is identical with that obtained using the methylarene data alone.

Equation 2 is remarkably successful in quantifying both the contribution of thermodynamic factors (radical stability) and stereoelectronic factors (θ) on log k_{rel} as evidenced by the plot of log k_{rel} vs $\sin^2 \theta(\Delta H^\circ)$ (Figure 2). The reasons for the success of eq 2 and its relationship to the Evans–Polanyi equation can be derived by considering the underlying assumptions of each.

For the Evans–Polanyi relationship, α is a measure of the sensitivity of the transition state to the stability of the resulting free radical. As the two-dimensional reaction coordinate diagram depicted in Figure 3 illustrates, substituents which stabilize the resulting radical (making ΔH° more exothermic) lower the activation energy and shift the transition state towards reactants (i.e., the Hammond postulate).[9]

Unlike simple alkanes, however, the reaction coordinate for hydrogen abstraction from alkylaromatics has an extra dimmension—θ_{C-H}. This notion is illustrated by the three-dimensional reaction coordinate diagram depicted in Figure 4. (Note: To relate the starting geometry of the substrate to the resulting free radical, θ_p is introduced to define the angle of the singly-occupied p orbital of the radical with respect to the aromatic plane).

Horizontal lines a and b represent two possible extremes. For line a, it is assumed that the aryl moiety is in full conjugation with the developing radical center through the entire reaction coordinate ($\theta = 90°$), while the opposite is assumed for line b. On the basis of the Hammond postulate, line a is reckoned to proceed via an earlier transition state than line b. Presumably, a continuum of transition states are available for intermediate values of θ (the dotted line in Figure 4).

The simple reaction coordinate diagram based upon intersecting Morse curves (Figure 3) is valid only if θ is constant during the course of the reaction. Only under these conditions will the effect of the aryl group in stabilizing the resulting radical and the transition state be the same. (In essence, Figure 3 is a horizontal cross-section of Figure 4).

In every case involving alkylaromatics in which free rotation can occur, $\theta_{C-H} \ll \theta_p$. This observation results from the fact that electronic interactions involving the aryl moiety in the product radical are stronger than in the substrate. While steric factors have considerable influence on θ_{C-H}, the effect on θ_p is less. Consequently, the reaction coordinate is not a horizontal cross-section of the potential energy surface, and the Evan–Polanyi relationship breaks down. We suggest that the reaction coordinate is better represented by line c in Figure 4. The ability of the aryl moiety to stabilize the transition state compared to the free radical is not the same because θ changes during the course of the reaction. Thus, as depicted for line c, very little of the resonance stabilization associated with the free radical is manifested in the transition state ($\theta_{C-H} \approx \theta^{\neq} \ll \theta_p$). This analysis serves to explain (and predict) the observed selectivity reversals, the breakdown of the Evans–Polanyi equation, and the success of eq 2.

Conclusion

The rate of α-hydrogen abstraction from alkylaromatics can be related to both the stability of the resulting free radical and the conformation of the starting alkylaromatic (i.e., the degree of alignment of the α-C–H bond with the adjacent π-system). This relationship can be described *quantitatively* by incorporating a correction ($\sin^2 \theta$, where θ is the angle of the α-C–H bond with respect to the aromatic plane) into the Evans and Polanyi equation. The failure of the Evans and Polanyi equation (in its standard form) in these systems can be understood because unlike simple alkanes, *two independant variables are needed to describe the reaction coordinate: C···H···Br distance and* θ_{C-H}.

Experimental Section

General. The following materials were obtained from Aldrich Chemical Co. and used as received unless otherwise noted: benzoyl peroxide, α-bromonaphthalene, chlorobenzene, 1,8-ethylenenaphthalene, α-ethylnaphthalene, hexamethyldisiloxane, indane,

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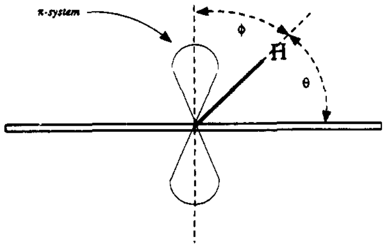
(14) For molecules that possess more than one abstractable hydrogen and/or several low-energy conformations (≤0.4 kcal/mol energy difference), the largest value of θ_{C-H} was selected for this analysis for the following reason: Suppose two conformations exist: A ⇄ B where B is ≤0.4 kcal/mol higher in energy and the reactive conformation. At equilibrium, B would constitute at least 36% of the equilibrium composition. Consequently, the error in log k_{rel} will be small. While a more rigorous treatment which would account for (a) the equilibrium distribution of the different conformations and (b) the fact that all α-hydrogens in a given conformation may not be equivalent is feasible, such an added degree of complexity is not needed to satisfactorily interpret the data. The correlation of log k_{rel} to $\sin^2 \theta$ was significantly better than to $\sin \theta$, $R = -0.986$ and -0.935, respectively, and suggests that interaction between the developing radical center and adjacent π-system is proportional to $\cos^2 \phi$ (note: $\phi + \theta = 90°$, $\cos^2 \phi = \sin^2 \theta$):



This observation is reminiscent of the effect of hyperconjugation in alkyl radicals for which the β-hyperfine coupling constant is related to ϕ by the following relation: $a_H{}^\beta = B_0 + B_2 \cos^2 \phi$ (ref 13).

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and α-methylnaphthalene. α-Isopropylnaphthalene was prepared in two steps via reaction of the Grignard reagent of α-bromonaphthalene with acetone, followed by reduction of the resulting carbinol according to a published literature procedure.[15] A sample of 1,9-ethyleneanthracene was provided by Prof. Laren Tolbert (Georgia Institute of Technology). Carbon tetrachloride was slurried with potassium hydroxide for 24 h, decanted, and fractionally distilled from phosphorus pentoxide. The middle portion was stored over molecular sieves. NBS (Aldrich) was recrystallized from water and dried in vacuo before use. Gas chromatographic analyses were performed on a Hewlett-Packard HP 5890A instrument equipped with both FID and TCD detectors and an HP 3393A reporting integrator. Nuclear magnetic resonance spectra were recorded on a 270-MHz Bruker FT NMR spectrometer.

Competition Experiments. Competitive brominations (NBS/CCl_4) were carried out as described earlier.[1] Reaction mixtures were analyzed by GLC (vs chlorobenzene as internal standard) in triplicate. Relative rate constants were calculated by $k_A/k_B = \ln (A_o/A)/\ln (B_o/B_f)$, where the subscripts "o" and "f" refer to the initial and final concentrations of substrate, respectively. Mass balances were nearly quantitative, although elimination products were detected by NMR and GCMS in the reactions involving α-isopropylnaphthalene, 1,8-ethylenenaphthalene, and 1,9-ethyleneanthracene.

Theoretical. Semiempirical MO calculations were performed using the AM1 approximation developed by Dewar et al.[4] and implemented through MOPAC Version 5.0 (QCPE 455). Full geometry optimizations were performed on the parent hydrocarbon. For the open-shell species, geometries were optimized using UHF, followed by a single-point calculation using the half-electron approximation.[16,17]

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Registry No. 6, 496-11-7; 7, 83-32-9; 8, 641-48-5; Br, 10097-32-2; PhEt, 100-41-4; α-methylnaphthalene, 90-12-0; α-ethylnaphthalene, 1127-76-0; α-isopropylnaphthalene, 6158-45-8; 9-ethylanthracene, 605-83-4.

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Rate Constants and Arrhenius Parameters for the Reactions of Some Carbon-Centered Radicals with Tris(trimethylsilyl)silane

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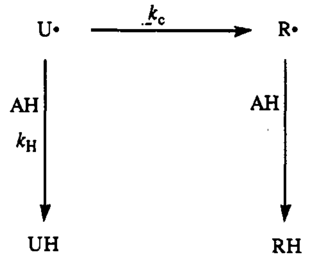
Rate constants for the reactions of some carbon-centered radicals with $(Me_3Si)_3SiH$ have been measured over a range of temperatures by using competing unimolecular radical reactions as timing devices. For example, the rate constants (at 298 K) are 3.7, 1.4, and 2.6 × 10^5 M^{-1} s^{-1} from primary, secondary, and tertiary alkyl radicals, respectively. Comparison of the radical trapping abilities of tri-*n*-butylstannane and tris(trimethylsilyl)silane is discussed. The use of 1,1-dimethyl-5-hexenyl cyclization as a radical clock has been recalibrated by using new data and data from the literature.

Introduction

Free radicals are of considerable importance in the development of organic chemistry, and many methodologies in radical-based synthesis employ tributyltin hydride.[2-4] It has recently been shown that tris(trimethylsilyl)silane is a valuable reducing agent for a variety of organic substrates.[5,6] This reagent has proved to be an attractive alternative to tributyltin hydride for the majority of these reactions although in a few cases the two reagents can complement each other. The key step in these straightforward radical-chain reduction reactions,[5,6] as well as in those processes where their use as a mediator for the formation of carbon–carbon bonds[7] via an inter- or intramolecular addition, is

$$R^\bullet + X_3MH \rightarrow RH + X_3M^\bullet \qquad (1)$$

Scheme I



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