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Evaluation of the Kinetic Data for Intramolecular 1,*x*-Hydrogen Shifts in Alkyl Radicals and Structure/Reactivity Predictions from the Carbocyclic Model for the Transition State

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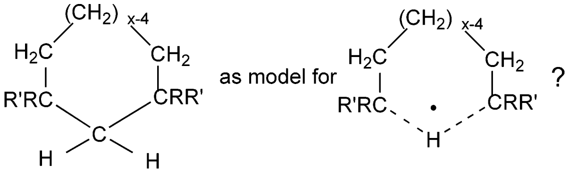

Experimental and computational kinetic data for the intramolecular 1,*x*-hydrogen shift in alkyl radicals are compiled in Arrhenius format for $x = 2-5$. Significant experimental disparity remains, especially for $x = 2$ and 3. Experimental data for radicals with tert centers or bearing spectator substituents are lacking for all *x*, and none exist for $x = 6$. The common use of the strain energy of the unsubstituted $(x+1)$-carbocycle to coarsely model the activation energy for the 1,*x*-shift is extended to explore more subtle differences in progressively methyl-substituted systems by use of molecular mechanics estimates of differences in strain between radicals and carbocycles. For $x = 5$ and 6, a sterically driven increase in E is predicted for shifts in the tert → tert class that apparently runs counter to the behavior of bimolecular hydrogen transfers. In contrast, a sterically driven decrease in E is predicted to result from spectator methyl groups for the prim → prim reaction class for all *x*. There is no experimental basis to test these predictions; fragmentary computational evidence lends some support to the second but is ambiguous concerning the first. Possible deficiencies in the use of carbocycles as transition state models are discussed.

Introduction

Isomerization of alkyl free radicals by intramolecular 1,*x*-hydrogen shift is an important elementary process in phenomena as diverse as the pyrolysis and combustion of fuels and polymers, the formation of short branches during radical vinyl polymerization, and the translocation of radical centers in multistep organic syntheses. A simple "carbocycle model" to rationalize reactivity has emerged in which the geometry of the cyclic transition state **1** is compared to that of the carbocycle **2** in which a $-CH_2-$ group replaces the transferring hydrogen.[1−9] Reactivity as a function of *x* falls in the order $5 \geq 4 \approx 6 \gg 3 \approx 2$. The conventional strain enthalpies of cyclopropane, cyclobutane, cyclopentane, and cycloheptane are 27.5, 26.5, 6.2, and 6.2 kcal mol^{-1},[10] or 27.6, 26.2, 6.3, and 6.4 kcal mol^{-1},[11,12] referenced to cyclohexane as "strain-free", and the ring strain pattern in **2** can be seen to parallel the reactivity pattern for

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(1) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976; pp 257−258.

(2) Dobe, S.; Berces, T.; Reti, F.; Marta, F. *Int. J. Chem. Kinet.* **1987**, *19*, 895.

(3) (a) Viskolcz, B.; Lendvay, G.; Kortvelyesi, T.; Seres, L. *J. Am. Chem. Soc.* **1996**, *118*, 3006. (b) Viskolcz, B.; Lendvay, G.; Seres, L. *J. Phys. Chem. A* **1997**, *101*, 7119. (c) Cf.: Barker, J. R.; Ortiz, N. F. *Int. J. Chem. Kinet.* **2001**, *33*, 246.

(4) Lehrle, R. S.; Pattenden, C. S. *Polym. Degrad. Stab.* **1999**, *63*, 153.

(5) Matheu, D. M.; Green, W. H., Jr.; Grenda, J. M. *Int. J. Chem. Kinet.* **2003**, *35*, 95.

(6) (a) Yamauchi, N.; Miyoshi, A.; Kosaka, K.; Koshi, M.; Matsui, H. *J. Phys. Chem. A* **1999**, *103*, 2723. (b) Miyoshi, M.; Widjaja, J.; Yamauchi, N.; Koshi, M.; Matsui, H. *Proc. Comb. Inst.* **2002**, *29*, 1285.

(7) (a) Endrenyi, L.; Le Roy, D. J. *J. Phys. Chem.* **1966**, *70*, 4081. (b) Mintz, K. J.; Le Roy, D. J. *Can. J. Chem.* **1973**, *51*, 3534. (c) Endrenyi, L.; Le Roy, D. J. *J. Phys. Chem.* **1967**, *71*, 1334.

(8) (a) Imbert, F. E.; Marshall, R. M. *Int. J. Chem. Kinet.* **1987**, *19*, 81. (b) Marshall, R. M. *Int. J. Chem. Kinet.* **1990**, *22*, 935.

(9) Kortvelyesi, T.; Seres, L. *React. Kinet. Catal. Lett.* **1996**, *58*, 27.

(10) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970.

(11) Based on the ring correction factors in Benson's group additivity scheme; see ref 1, Tables in Appendix.

(12) Lias, S. G.; Liebman, J. F.; Levin, R. D.; Kafifi, S. A.; Stein, S. E. *NIST Standard Reference Data Base 25; Structures and Properties*; Version 2.02, 1994.

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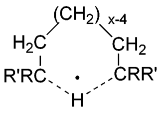
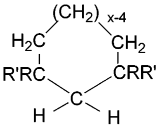
1,x-shift. Hence, in the carbocycle model, $E_{1,x} \approx E_H + \Delta H°_{strain}$, where $E_{1,x}$ is the Arrhenius activation energy for the 1,x-shift, E_H is that for an analogous bimolecular hydrogen abstraction, and $\Delta H°_{strain}$ is the strain enthalpy of **2**. The model also predicts that the Arrhenius $A_{1,x}$ factor should decrease monotonically as x increases because additional free rotations need to be frozen out as the open-chain starting radical is converted to the cyclic **1**.



1



2

CH_3--H- -CH_3

3

Kinetic data on 1,x-shifts are limited almost entirely to cases in which the initial and final radical centers are prim or sec, especially the (p → s) conversion,[13] rather than tert, and the radical bears no additional spectator alkyl substituents. With rare exception,[6b] data consist of rates of formation and distributions of stable products as a function of temperature (T) that lead to mathematical products of A values and sums of E values; obtaining the individual $A_{1,x}$ and $E_{1,x}$ values requires deconvolution based on the A and E values of one or more anchoring elementary reactions whose kinetics are already known. Most commonly, these have been either for k_c or k_β, the rate constants for combination or β-scission of the radical that is simultaneously undergoing rearrangement. A diagnostic product may arise from multiple elementary reactions, and further assumptions are then required about their rate constants that do not appear in the composite A and E values. Added uncertainty arises because experimenters have not always demonstrated the absence of a pressure effect and falloff behavior; hence k_{exp} may be less than k_∞, the desired high-pressure-limit rate constant. Inversely, in cases for which radical generation leads to chemically activated radicals, simultaneous rearrangement of activated and thermalized radicals may lead to inflated k values.[14a] For high-T shock-tube experiments, Tsang and co-workers[15a−c] have demonstrated that competition between energy transfer and rapid reactions, as well as the occurrence of multiple decay pathways for a radical, may lead to rate constants that are time-dependent. In all such cases, obtaining the desired A_∞ and E_∞ values requires modeling (e.g., RRKM and/or TST) that in turn depends on the geometry and vibrational frequencies of **1**, either estimated or, more recently, obtained from ab initio computations.

Ab initio electronic structure calculations and statistical kinetic methods have reached a level of accuracy approaching that of experimental data from these complex systems, especially for revealing structure−reactivity trends. Computed values of k_∞ for selected 1,x-shifts as a function of T have been presented in Arrhenius format or, given the probable role of tunneling at lower T, three-parameter $A'T^n \exp(-E'/RT)$ format. Lendvay and co-workers[3] optimized radical and transition state structures at the UHF/6-31G* level and calculated threshold energies E_0 by several methods, with most results from the MP-SAC2 protocol; $\Delta S^\ddagger$ values from calculated vibrational frequencies and moments of inertia gave A_∞ values;[3c] however, there was no explicit consideration of tunneling. These methods were applied to the ($x = 2-5$, p → p) cases and to all possible shifts in 2-methylhexyl; in the latter set, a tert center and one example for $x = 6$ were addressed. Green and co-workers[5] presented a complete set of generic recommended k_∞ values, in three-parameter Arrhenius format, for (p → p) through (t → t) and $x = 2-5$. For $x = 2-4$, a "full" TST calculation was performed for each (p → p) class, explicitly including hindered rotor effects, which were said to have been neglected by Lendvay and co-workers,[3] with input from B3LYP-ccpVDZ calculations for the radical and transition state; fitting the TST-calculated k_∞ values for 300−1500 K gave recommended values for A_∞, n_∞, and E_∞ for each x value; again there was no explicit consideration of tunneling. These A_∞ and n_∞ values for the (p → p) class were then used for all of the other classes with the same x, and the E_∞ values for the latter were estimated from calculated zero-point energy differences for model examples. For $x = 5$, the full calculation was also used for the (p → p) class, but E_∞ values for the other classes were estimated by an Evans−Polanyi approach with $\alpha = 0.6$. Jitariu and co-workers[16] optimized structures for the $x = 2-5$ shifts in 1-pentyl at the UMP2/6-311G** level and carried out direct dynamics calculations at the PUMP-SAC2/6-311G** level, including canonical variational TST and tunneling corrections; however, we shall see below that these calculations for $x = 4$ conform better to experimental data if the tunneling correction is not included.

Curran and co-workers[17] earlier presented a set of recommended rate constants in three-parameter Arrhenius format[18] for interconversions within n-heptyl and i-octyl radicals. These represent a "hybrid" approach in that the E values were derived directly from the carbocycle model (albeit with an atypically low value for the strain enthalpy for cyclobutane[17b]), while the A values were derived from calculations of $\Delta S^\ddagger$ based on loss/gain of internal rotors, specific vibrations, and optical isomers (which were not described in detail). As we shall see below, this set of recommendations is characterized by the greatest dependence of A on x.

We will review and compare the available experimental and computational data; for the latter, we emphasize the recommendations from Green and co-workers[5] because of their

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[13] Our nomenclature "(x = a, b → c)" specifies x and the reaction class in terms of the substitution pattern of the original and rearranged radical, either p(rim), s(ec), or t(ert); this differs from a common literature convention that gives (x+1), the number of atoms in the cyclic transition state, and inverts the order of radical types. All reactions that share the same substitution pattern of the starting and rearranged alkyl radicals are considered to be in the same "reaction class", for example, (p → t).

[14] (a) Watkins, K. W.; Lawson, D. R. *J. Phys. Chem.* **1971**, *75*, 1632. (b) Watkins, K. W. *J. Phys. Chem.* **1973**, *77*, 2938. (c) Watkins, K. W.; Ostreko, L. A. *J. Phys. Chem.* **1969**, *73*, 2080. (d) Watkins, K. W. *J. Am. Chem. Soc.* **1971**, *93*, 6355. (e) Watkins, K. W. *Can. J. Chem.* **1972**, *50*, 3738.

[15] (a) Tsang, W. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **2005**, *50*, 105. (b) Knyazev, V. D.; Tsang, W. *J. Phys. Chem. A* **2000**, *104*, 10747. (c) Tsang, W.; Bedanov, V.; Zachariah, M. R. *Ber. Bunsen-Ges. Phys. Chem.* **1997**, *101*, 491. (d) Tsang, W. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **2004**, *49*, 385. (e) Tsang, W.; Walker, J. A.; Manion, J. A. *Chem. Phys. Proc. Comb.* **1996**, 515. (f) Tsang, W.; Walker, J. A.; Manion, J. A. *Proc. 27th Int. Symp. Comb.* **1998**, 135.

[16] Jitariu, L. C.; Jones, L. D.; Robertson, S. H.; Pilling, M. J.; Hillier, I. H. *J. Phys. Chem. A* **2003**, *107*, 8607.

[17] (a) Curran, H. J.; Gaffuri, P.; Pitz, W. J.; Westbrook, C. K. *Combust. Flame* **1998**, *114*, 149. Curran, H. J.; Gaffuri, P.; Pitz, W. J.; Westbrook, C. K. *Combust. Flame* **2002**, *129*, 253. (b) The strain enthalpies of cyclopropane, cyclobutane, and cyclopentane used can be deduced to be 27, 22, and 8 kcal mol^{-1}, referenced to cyclohexane.

[18] All three-parameter Arrhenius expressions have been plotted as such in Figures 1−4, but are converted for convenience of comparison with the typical two-parameter Arrhenius expressions derived from experimental studies by the usual approximations $E_\infty = E' + nRT$ and $A_\infty = A'(eT)^n$, evaluated at 773 K, where $k_\infty = A_\infty \exp(-E_\infty/RT)$ or $A'T^n \exp(-E'/RT)$.

broadest coverage of reaction classes.[18] We will extend the use of the carbocycle model from the (p → p) class to other reaction classes and compare predictions with the data base. We have recently suggested,[19] based on simple molecular mechanics simulations applied to the carbocycle model, that the presence of spectator alkyl substituents may accelerate 1,*x*-shifts for the (p → p) class, but that steric congestion at sec or tert reaction sites may decelerate 1,*x*-shifts. We will explore such predictions further and also compare them with the database.

Background

Bimolecular Hydrogen Abstraction: Reaction Class Effects. The prototypical bimolecular hydrogen abstraction (methyl + methane) proceeds with $E_{exp} \approx 14.5$ kcal mol^{-1}.[20,21] Ab initio calculations[22−27] have become increasingly successful in reproducing this value when the relationships between the computed barrier height, tunneling, and E_{exp} are considered. These have converged on d(C−H) = 1.34 Å and θ(C−H−C) = 180° for the D_{3d} transition state **3**.

Suggestions have been made that E for the symmetrical reactions (R$^\bullet$ + H−R) decreases modestly as R is varied from methyl to prim to sec to tert, even though each is thermoneutral. In other words, in the Evans−Polanyi formalism [$E = E^0 + \alpha(\Delta H^\circ_{rxn})$], there is no single intrinsic E^0 that applies to all alkyl radical abstractions.[28] The empirical correlation of Roberts,[29] which was parametrized for a wide variety of (A$^\bullet$ + H−B) hydrogen abstractions, predicts E(methyl + methane) = 13.4 > E(ethyl + ethane) = 12.6 > E(*i*-propyl + propane-2-*H*) = 12.2 > E(*t*-butyl + *i*-butane-2-*H*) = 11.9 kcal mol^{-1}. The empirical correlation ("method II") of Ma and Schobert,[30] which was parametrized for a wide variety of (R$^\bullet$ + H−R′) hydrogen abstractions, similarly predicts E(methyl + methane) = 13.5 > E(ethyl + ethane) = 12.7 > E(*i*-propyl + propane-2-*H*) = 12.4 > E(*t*-butyl + *i*-butane-2-*H*) = 12.0 kcal mol^{-1}. The less parametric, semiempirical Zavitsas formulation[31] also predicts E(methyl + methane) = 14.5 > E(ethyl + ethane) = 13.8 kcal mol^{-1}, but the molecular data to estimate the sec and tert classes were not given. In contrast, a formulation of Formosinho and co-workers[32a] predicts essentially no differences: E(methyl + methane) = 14.6, E(ethyl + ethane) = 14.3, E(*i*-propyl + propane-2-*H*) = 14.4, and E(*t*-butyl + *i*-butane-2-*H*) = 14.3 kcal mol^{-1}. Similarly, their ISM method[32b] gives a nonmonotonic pattern: E(methyl + methane) = 14.2, E(ethyl + ethane) = 14.6, E(*i*-propyl + propane-2-*H*) = 13.4, and E(*t*-butyl + *i*-butane-2-*H*) = 13.7 kcal mol^{-1}.

Early calculations[33] gave E(methyl + methane) = 22.4, E(ethyl + ethane) = 20.5, E(*i*-propyl + propane-2-*H*) = 18.2, and E(*t*-butyl + *i*-butane-2-*H*) = 15.3 kcal mol^{-1}; while the authors did not consider these absolute values to be accurate, they did consider the downward trend meaningful. Later calculations[34] gave the same order except for the (methyl + methane) case: E(methyl + methane) = 19.2, E(ethyl + ethane) = 20.5, E(*i*-propyl + propane-2-*H*) = 18.2, and E(*t*-butyl + *i*-butane-2-*H*) = 16.4 kcal mol^{-1}. Modified semiempirical MNDO/PM3 calculations by Franz and co-workers[35] gave a non-monotonic trend of E(methyl + methane) = 15.8, E(ethyl + ethane) = 10.1, E(*i*-propyl + propane-2*H*) = 8.3, and E(*t*-butyl + *i*-butane-2-*H*) = 10.5 kcal mol^{-1}, but the authors considered the last value anomalous, based on the ab initio calculations.[33] A recent benchmarking comparison of the highest-level computational methods[22] gave consensus values of the classical barrier heights (excluding ZPE) for (methyl + methane) = 17.53 > (ethyl + ethane) = 16.69 kcal mol^{-1}, and the authors assigned less credence to methods that produced the reverse inequality.

Several of these correlative and computational studies[29−32,35] cited experimental data to support the inequality: E(methyl + methane) > E(ethyl + ethane). However, the difference was comparable to the data spread cited for each value: E(methyl + methane) = 12.9−14.9 and E(ethyl + ethane) = 12.6−14.1 kcal mol^{-1}. Unfortunately, the uncertainty because of this dispersion in the experimental data is exacerbated by the paucity of data for E(s → s) and E(t → t). In summary, it seems prudent to characterize the hypothesis that the intrinsic E^0 for symmetrical hydrogen abstraction decreases as the radical becomes more highly alkylated as highly probable albeit not fully definitive. Only for convenience, and taking no position on its exact origin, we label this effect as a "prim-tert electronic acceleration".

One could imagine a counter-acting inverse effect, a "prim-tert steric deceleration", based on a build-up of unfavorable gauche-like interactions as methyl substituents are progressively added to the core of **3**. However, high-level ab initio calculations could barely distinguish any energy difference (<0.1 kcal mol^{-1}) for the gauche and trans conformers of the transition state for the (ethyl + ethane) reaction,[22] whereas the gauche−trans energy difference in butane is 0.9 kcal mol^{-1}. This is not surprising because the gauche CH_3–CH_3 distance will be significantly longer in **3** than in butane. For comparison of the underlying skeletons to which CH_3 groups would be added, the nearest H−H distance increases from 2.55 Å in D_{3d} ethane to 3.40 Å in **3**.[23] If these hydrogens are replaced with methyl groups, the closest CH_3–CH_3 distances will each be somewhat longer because of the longer C−C rather than C−H bonds, but the relative order will persist. However, anticipating the discussion below, if we model **1** for the 1,5-shift, which is bent at C−H−C as compared to **3**, by chair-cyclohexane, the analogous H−H distance for this comparison becomes the 1,3-diaxial H−H distance, which is 2.63 Å, only 0.08 Å longer

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[19] Poutsma, M. L. *J. Anal. Appl. Pyrolysis* **2005**, *73*, 159.

[20] *NIST Standard Reference Database 17*, Version 7.0 (Web Version), Release 1.3 {http://kinetics.nist.gov/index.php}.

[21] Kerr, J. A. In *Free Radicals*; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. I.

[22] Dybala-Defratyka, A.; Paneth, P.; Pu, J.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 2475.

[23] Isborn, C.; Hrovat, D. A.; Borden, W. T.; Mayer, J. M.; Carpenter, B. K. *J. Am. Chem. Soc.* **2005**, *127*, 5794.

[24] Kang, J. K.; Musgrave, C. B. *J. Chem. Phys.* **2001**, *115*, 11040.

[25] Kungman, N.; Truong, T. N. *J. Phys. Chem. A* **2005**, *109*, 7742.

[26] Coote, M. L.; Collins, M. A.; Radom, L. *Mol. Phys.* **2003**, *101*, 1329.

[27] Saeys, M.; Reyniers, M.-F.; Marin, G. B.; Van Speybroeck, V.; Waroquier, M. *J. Phys. Chem. A* **2003**, *107*, 9147.

[28] We use the phrase "simple Evans−Polanyi behavior" to refer to the idealized case of a single E^0 applicable to an entire reaction family, in this case, hydrogen transfer between alkyl radical sites.

[29] Roberts, B. P.; Steel, A. J. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2155. Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2719.

[30] Ma, X.; Schobert, H. H. *Ind. Eng. Chem. Res.* **2003**, *42*, 1151.

[31] Zavitsas, A. A.; Chatgilialoglu, C. *J. Am. Chem. Soc.* **1995**, *117*, 10645.

[32] (a) Pais, A. A. C. C.; Arnaut, L. G.; Formosinho, S. J. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2577. (b) Arnaut, L. G.; Pais, A. A. C. C.; Formosinho, S. J.; Barroso, M. *J. Am. Chem. Soc.* **2003**, *125*, 5236.

[33] Yamataka, H.; Nagase, S. *J. Org. Chem.* **1988**, *53*, 3232.

[34] Chandra, A. K.; Rao, V. S. *Chem. Phys.* **1994**, *187*, 297.

[35] Camaioni, D. M.; Autrey, S. T.; Salinas, T. B.; Franz, J. A. *J. Am. Chem. Soc.* **1996**, *118*, 2013.

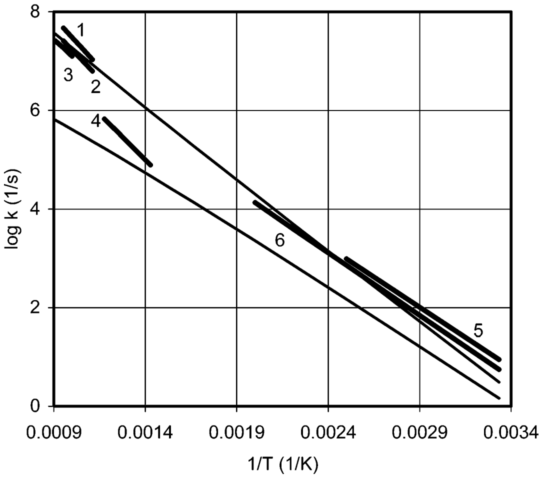

FIGURE 1. Arrhenius plots for k(1-hexyl → 2-hexyl) and log A (s^{-1}) and E (kcal mol^{-1}) values. #1, 11.5, 18.5 (ref 15d); #2, 11.1, 17.7 (ref 15e); #3, 10.5, 15.7 (ref 6a); #4, 10.2, 17.0 (ref 8a); #5, 9.1, 11.2 (ref 14c as re-evaluated in ref 14b); #6, 9.2, 11.6 (ref 2). Continuous (curved) lines in ascending order: ~7.85, ~10.15, hybrid recommendation for 1-heptyl → 3-heptyl (ref 17) and ~10.3, ~13.7, experimental/computational recommendation (ref 6a).

than that in D_{3d} ethane. Hence, the bent transition states for the unimolecular 1,*x*-shift may well be more susceptible to a "prim-tert steric deceleration" than analogous bimolecular hydrogen abstractions.

Experimental Results and Suggested Correlations for 1,*x*-Shifts. The Arrhenius parameters given below may differ slightly from the original reports if we have adjusted those for the anchoring reactions to more recent recommendations. We have also converted reported A factors to a "per H" basis. In the figures, the Arrhenius correlation line for each data set is shown for its experimental T range with no attempt to show the experimental points.

$\boldsymbol{x = 5.}$ Data for the prototypical ($x = 5$, p → s) shift in 1-hexyl are shown in Figure 1. In the low-T range, Watkins[14b,c] produced 1-hexyl by photolysis of azoethane in the presence of ethylene; telomerized and rearranged hexyl radicals were captured by the "bath" of ethyl. Anchoring to k_c(ethyl + ethyl) and k_c(ethyl + 1-hexyl) gave k(1-hexyl → 2-hexyl) = $10^{9.1}$ exp(−11 200/RT) s^{-1}.[36] Dobe and co-workers[2] generated 1-hexyl in a "bath" of methyl by co-photolysis of 2-octanone and excess acetone or azomethane and obtained $10^{9.2\pm0.3}$ exp(−11 600 ± 300/RT) s^{-1}, anchored to k_c(1-hexyl + 1-hexyl), which was assumed to be the same as k_c(ethyl + ethyl).[37] Tsang and co-workers carried out shock-tube pyrolyses of 1-hexyl iodide in the high-T range where exhaustive β-scission of the original and rearranged radicals to methyl or H was dominant. Production of propylene along with ethylene was diagnostic of partial rearrangement, and analysis of the olefin product ratios gave the desired rate constant, anchored to k_β values. Two values were extracted (see above) from the same data set, $10^{11.5}$ exp(−18 500/RT) s^{-1} [15d] and $10^{11.1}$ exp(−17 700/RT) s^{-1};[15e] the difference of almost 2-fold at 1000 K is somewhat larger than the difference in k_β values used as anchors. Miyoshi and co-workers[6a] also carried out shock-tube pyrolyses of 1-hexyl iodide but monitored directly the yield of H by atomic resonance absorption spectroscopy; a less than quantitative yield was diagnostic of partial rearrangement. TST calculations performed with HF/6-31G(d) inputs for geometries and vibrational frequencies indicated that the reaction conditions (900−1400 K and ~1 atm) were into the falloff regime, and RRKM adjustments gave $10^{10.5}$ exp(−15 700/RT) s^{-1}, anchored to k_β(1-hexyl). An estimate of $10^{10.2}$ exp(−17 000/RT) s^{-1} used by Imbert and Marshall[8a] for modeling the pyrolysis of hexane in the mid-T range gives rate constants lower by an order of magnitude, but it had no direct experimental basis. The data collected in Figure 1 suggest a trend for E to increase with increasing T from 11−12 at low T to 16−18 kcal mol^{-1} at high T; correspondingly, A appears to increase from $10^{9.0}$−$10^{9.5}$ to $10^{10.5}$−$10^{11.5}$ s^{-1}. Such curvature commonly results from the intrusion of tunneling in hydrogen abstractions at lower T. The Miyoshi group[6a] offered a nonlinear correlation over the whole T range, based on their data, RRKM calculations, and tunneling considerations, of $3.33 \times 10^7 T^{0.823}$ exp(−12 450/RT) ≈ $10^{10.3}$ exp(−13 700/RT) s^{-1}, which is overlaid in Figure 1. Also overlaid is the quite different hybrid recommendation from Curran and co-workers[17] for 1-heptyl → 3-heptyl of $4.28 \times 10^{11} T^{-1.05}$ exp(−11 760/RT) ≈ $10^{7.85}$ exp(−10 150/RT) s^{-1}, which gives lower values. A forced least-squares correlation (not shown) through the end points of the T ranges for the five data sets (excluding that of Imbert and Marshall) gives $10^{10.0}$ exp(−12 700/RT) s^{-1}. The computational recommendation of Green and co-workers[5] for the corresponding (p → p) shift (see below), adjusted with $\Delta H°$(p,s) = 2.8 kcal mol^{-1} (the stability difference between a prim and sec radical) and $\alpha = 0.5$, would give E = 13.0 kcal mol^{-1}. These values of $E_{1,5}$ are thus not inconsistent with that for the bimolecular (ethyl + ethane) analogue discussed above. Simply for ease of comparative visualization with results described below for other x, we assign $E_{1,5}$(p → s) ≈ 13 kcal mol^{-1}.

Dobe and co-workers[2] generated 3-octyl in a "bath" of methyl by photolysis of excess acetone or azomethane in the presence of 1-heptene. From the distribution among C_9 cross-combination products and a complex steady-state analysis, they derived for the ($x = 5$, s → s) process k(3-octyl → 2-octyl) = $10^{9.1\pm0.7}$ exp(−11 200 ± 1000/RT) s^{-1} from a two-point Arrhenius plot (300−385 K), with the anchoring assumption that k_c is not sensitive to radical size.[37,38]

We have not found data for the unadorned ($x = 5$, p → p) process that would require labeling in 1-pentyl. The computational recommendation from Green and co-workers[5] is $3.67 \times 10^{12} T^{-0.6}$ exp(−15 300/RT) ≈ $10^{10.6}$ exp(−14 400/RT) s^{-1}, which has the opposite curvature from the Miyoshi correlation[6a] for the ($x = 5$, p → s) process. If simple Evans−Polanyi behavior applied and if the A factors were not dependent on the radical class, we would expect k(p → s) > k(p → p) ≈ k(s → s). A direct comparison of the Dobe data,[2] the Miyoshi correlation,[6a] and the Green recommendation[5] gives instead a ratio of 1.6:1.0:2.2 at 400 K. While this order is closer to a conclusion drawn by Dobe and co-workers[2] that E depends on $D°$ of the C−H bond being broken but not on that of the C−H bond being formed, that is, k(p → s) > k(p → p) but k(p → s) ≈ k(s → s), this conclusion was based on limited data and appears inherently unlikely. In summary, comparison of such

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[36] An earlier "low-A" result (ref 14c) was later refined (ref 14b) by more extensive analysis of cross-combination products, including those from octyl radicals that result from further telomerization.

[37] If k_c is smaller for the larger radicals (ref 8b), the effect in both of these studies will be to decrease the derived A factors.

[38] The treatment also seems to require a rate constant assignment for addition of methyl to 1-heptene, which is not discussed.

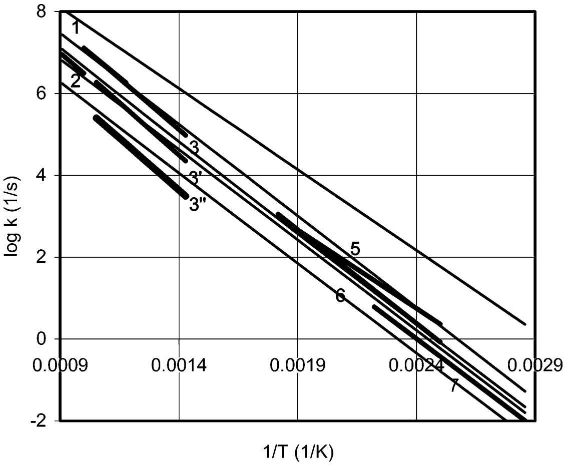

FIGURE 2. Arrhenius plots for k(1-pentyl → 2-pentyl) and log A (s^{-1}) and E (kcal mol^{-1}) values. #1, 11.9, 21.9 (ref 15f); #2, 11.5, 22.8 (ref 6a); #3, #3′, and #3″ for extremes, 10.7, 23.2 (low), 11.7, 23.4 (preferred), 12.1, 22.8 (high) (ref 8b); #5, 10.0, 17.6 (ref 6b); #6, 11.4, 21.0 (ref 7a as reinterpreted in ref 14e); #7, 10.5, 20.0 (ref 14e). Continuous lines, in ascending order: ~10.3, 20.3, (curved) hybrid recommendation for 1-heptyl → 4-heptyl (ref 17); 10.8, 20.2, canonical variational TST without tunneling (ref 16); 11.2, 20.8, experimental/computational recommendation (ref 6a); ~11.5, ~20.4, (curved) generic computational recommendation (ref 5); 11.7, 18.1, canonical variational TST with tunneling (ref 16).

small differences from multiple sources is dangerous given the error limits and differences in dependences on T that are involved.

$x = 4$**.** Data for the prototypical ($x = 4$, p → s) shift in 1-pentyl are shown in Figure 2. Early Arrhenius expressions[7,14d] obtained at low T had unrealistically low A values ($\leq 10^{8.5}$ s^{-1}) and are not plotted, but later adjustments[14e] to parameters more consistent with estimates of $\Delta S^{\ddagger}$ are included. Endrenyi and Le Roy[7a] produced 1-pentyl by photolysis of excess acetone in the presence of ethylene; telomerized and rearranged pentyl radicals were captured by the “bath” of methyl. Anchoring to k_c(methyl + methyl) and k_c(methyl + 2-pentyl) gave k(1-pentyl → 2-pentyl) $= 10^{6.85} \exp(-10\,800/RT)$ s^{-1}. Watkins[14e] revised these data by adding in the propylene[7c] formed by β-scission of 2-pentyl at the higher end of the T range to obtain $10^{11.4} \exp(-21\,000/RT)$ s^{-1} (Figure 2). A second “low-A” result of $10^{8.2} \exp(-15\,100/RT)$ s^{-1} was obtained by Watkins[14d] from analysis of the isomeric C_{10} combination products from photolysis of 1-pentylazomethane. However, he later concluded[14e] that this study also had unspecified “complications” and recast the data to obtain $10^{10.5} \exp(-20\,000/RT)$ s^{-1}, based on a “most reliable” rate constant value at 433 K and an assigned E. Not plotted is still another similar value from the Watkins group,[14a] $10^{10.3} \exp(-18\,000/RT)$ s^{-1}, based on an RRKM treatment of data for chemically activated 1-pentyl at low pressure. From an analysis of the pyrolysis of pentane at higher T, Marshall[8b] extracted the desired rate constant, anchored to k_β(1-pentyl). However, variations among numerous other rate constant ratio assumptions led to six models with differing Arrhenius parameters. Shown in Figure 2 are the extremes that give the highest and lowest rate constants and the author’s preferred intermediate expression.[39] Tsang and co-workers[15f] carried out shock-tube pyrolyses of 1-pentyl iodide at still higher T. Analysis of the olefin product ratios, anchored to k_β values, gave $10^{11.9} \exp(-21\,900/RT)$ s^{-1}. Miyoshi and co-workers[6a] also carried out shock-tube pyrolyses of 1-pentyl iodide; monitoring of the H yield from 2-pentyl and RRKM adjustments gave $10^{11.5} \exp(-22\,800/RT)$ s^{-1}, anchored to k_β(1-pentyl). Finally, Miyoshi and co-workers[6b] reported a direct measurement at low T and pressure without the need for an anchoring reaction. After laser flash generation of 1-pentyl from a 1-pentyl halide, formation of 2-pentyl was directly monitored by photoionization/MS, based on its lower ionization potential. An RRKM/master equation treatment, including DFT calculations of radical properties and a tunneling correction, gave $10^{10.0} \exp(-17\,600/RT)$ s^{-1}. The data collected in Figure 2 show less curvature than for the analogous 1,5-shift in Figure 1; E increases from 18−21 at low T to 22−23 kcal mol^{-1} at high T; correspondingly, A appears to increase from $10^{10.0}$−$10^{11.5}$ to $10^{11.5}$−$10^{12.0}$ s^{-1}. Overlaid in Figure 2 are the computational recommendation from Green and co-workers[5] of $k_{1,4}(\mathrm{p} \rightarrow \mathrm{s}) = 7.85 \times 10^{11} T^{-0.12} \exp(-20\,600/RT) \approx 10^{11.5} \exp(-20\,400/RT)$ s^{-1}; two computed values from Jitariu and co-workers[16] for k(1-pentyl → 2-pentyl) $= 10^{11.7} \exp(-18\,100/RT)$ s^{-1} and $10^{10.8} \exp(-20\,200/RT)$ s^{-1}, with and without a tunneling correction; a correlation from the Miyoshi group[6a] again based on their data, RRKM calculations, and tunneling considerations of $2.44 \times 10^{8} T^{0.846} \exp(-19\,530/RT)$ s^{-1} $\approx 10^{11.2} \exp(-20\,800/RT)$ s^{-1};[40] and the hybrid recommendation from Curran and co-workers[17] for 1-heptyl → 4-heptyl of $2.54 \times 10^{9} T^{0.35} \exp(-19\,760/RT) \approx 10^{10.3} \exp(-20\,300/RT)$ s^{-1}. Three of these agree quite well and overlap the data, while the Jitariu expression with tunneling is notably larger and the Curran expression is somewhat lower. If we focus on the parallel Miyoshi recommendations that give good fits in both Figures 1 and 2 for (p → s) shifts, we conclude that E increases by ~7 (20.8 − 13.7) kcal mol^{-1} and A increases by $\sim 10^{0.9}$ ($10^{11.2}/10^{10.3}$) s^{-1} as x decreases from 5 to 4. This difference in E corresponds well with the strain enthalpy of cyclopentane, and the directionality of the change in A is also consistent with the carbocycle model (see above).

Data on the ($x = 4$, p → s) shift in 1-hexyl, a minor competitor with the dominant ($x = 5$, p → s) shift, are limited to the high-T shock-tube pyrolyses of 1-hexyl iodide by Tsang and co-workers, who detected minor production of 1-butene. The rate expressions extracted from the same data set were $10^{11.2} \exp(-22\,100/RT)$[15e] and $10^{12.2}$ $(-24\,800/RT)$ s^{-1},[15d] a 2.5-fold difference in rate constant at 1000 K. These expressions are comparable with those in Figure 2. The estimate of $10^{10.7} \exp(-24\,000/RT)$ s^{-1} used by Imbert and Marshall[8a] for modeling the pyrolysis of hexane again gives rate constants lower by an order of magnitude, but it had no direct experimental basis.

As part of their study of the (3-octyl → 2-octyl) rearrangement in the low-T range (see above), Dobe and co-workers[2] also reported k(2-octyl → 4-octyl) $= 10^{10.2} \exp(-17\,000/RT)$ s^{-1} for an ($x = 4$, s → s) shift. However, this value rests on a complex reaction sequence (methyl + 1-heptene → 3-octyl → 2-octyl → 4-octyl), numerous assignments of anchoring reactions, a single-T data point at 385 K, and an assumed A factor, and hence we consider it provisional. The computational recommendation from Green and co-workers[5] of $k_{1,4}(\mathrm{s} \rightarrow \mathrm{s}) = 7.85 \times 10^{11} T^{-0.12}$

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[39] This preference was influenced by an assumption that linear Arrhenius behavior should be expected between these data and those in the lower T range discussed above. The author proposed $10^{10.8} \exp(-20\,000/RT)$ s^{-1} over a wide T range.

[40] This group also offered an alternate two-term empirical correlation of $[2.43 \times 10^{3} T^{2.324} \exp(-16\,260/RT) + 9.11 \times 10^{5} \exp(-10\,934/RT)]$ s^{-1} (ref 6b).

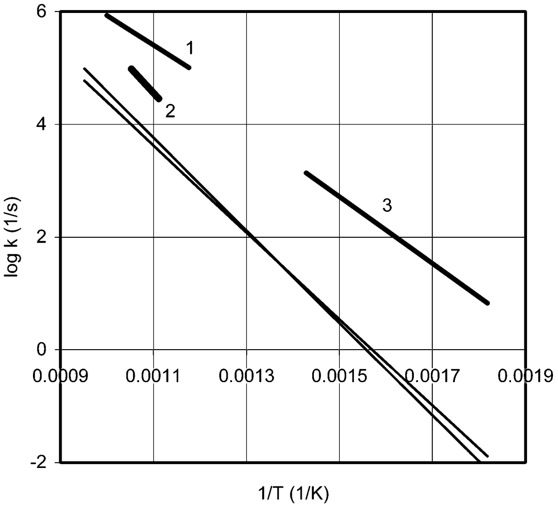

FIGURE 3. Arrhenius plots for $k_{1,3}$ and log A (s^{-1}) and E (kcal mol^{-1}) values. #1, 1-pentyl → 3-pentyl, 11.2, 24.0 (ref 15f); #2, 1-butyl → 2-butyl, 14.4, 41.0 (ref 41); #3, 1-butyl → 2-butyl, 11.6, 27.1 (ref 42a). Continuous (curved) lines: ~12.8, ~37.6, generic computational recommendation (ref 5); ~12.1, ~35.3, hybrid recommendation for 1-heptyl → 3-heptyl (ref 17).

exp($-23\,500/RT$) ≈ $10^{11.5}$ exp($-23\,300/RT$) s^{-1} and the hybrid recommendation from Curran and co-workers[17] for 2-heptyl → 3-heptyl of $3.22 \times 10^9 T^{0.13}$ exp($-20\,700/RT$) ≈ $10^{9.6}$ exp($-20\,900/RT$) s^{-1} are some 200-fold less at 385 K.

We have not found data for the unadorned ($x = 4$, p → p) process, which would require labeling in 1-butyl. The computational recommendation from Green and co-workers[5] is $7.85 \times 10^{11} T^{-0.12}$ exp($-23\,500/RT$) ≈ $10^{11.5}$ exp($-23\,300/RT$) s^{-1}. Again, there is not enough self-consistent data to allow a valid comparison of k(p → s) with k(p → p) and k(s → s) for $x = 4$. The Green recommendations[5] give a ratio of 23:1.0:0.6 at 400 K; that is, the modestly exothermic member is predicted to be significantly more rapid than the thermoneutral ones (see discussion above for $x = 5$).

$x = 3$. The very limited data are shown in Figure 3. In an oft-cited study, Lin and Back[41] proposed that methane formation from pyrolysis of ethane with added ethylene resulted from the sequence (ethyl + ethylene → 1-butyl → 2-butyl → propylene + methyl). From multiple anchorings to k_i(ethane → 2 methyl) (in the falloff region), k_t(ethyl + ethyl), and K(ethyl + ethylene ↔ 1-butyl), they derived k(1-butyl → 2-butyl) = $10^{14.4}$ exp($-41\,000/RT$) s^{-1}. Although this has usually been taken to represent an ($x = 3$, p → s) shift, it is an upper limit to the extent that any ($x = 2$, p → s) shift also contributed. However, even earlier, Kerr and Trotman-Dickenson[42a] had considered the same (1-butyl → propylene + methyl) process in a lower T range during photolysis of 1-pentanal and obtained notably different Arrhenius parameters: $10^{11.6}$ exp($-27\,100/RT$) s^{-1} (we have adjusted their k_c(1-butyl + 1-butyl) anchor from 10^{11} to 10^{10} M^{-1} s^{-1}[20]). An ($x = 3$, p → s) shift was also claimed in 1-pentyl, based on formation of 1-butene, as a minor competitor with the dominant ($x = 4$, p → s) shift during shock-tube pyrolyses of 1-pentyl iodide by Tsang and co-workers,[15f] and a value of k(1-pentyl → 3-pentyl) = $10^{11.2}$ exp($-24\,000/RT$) s^{-1} was extracted, anchored to β-scission. The order-of-magnitude disparity in $k_{1,3}$ at high T and the major difference in Arrhenius parameters between the studies are shown in Figure 3. Overlaid are the computational recommendation from Green and co-workers[5] of $k_{1,3}$(p → s) = $3.80 \times 10^{10} T^{0.67}$ exp($-36\,600/RT$) ≈ $10^{12.8}$ exp($-37\,600/RT$) s^{-1}, which has intermediate Arrhenius parameters and leads to $k_{1,3}$ still another order of magnitude lower, and the hybrid recommendation from Curran and co-workers[17] for 1-heptyl → 3-heptyl of $1.39 \times 10^9 T^{0.98}$ exp($-33\,760/RT$) ≈ $10^{12.1}$ exp($-35\,270/RT$) s^{-1}, which in this case is very similar. Tsang and co-workers[15f] suggested that the relationship between E and strain energy should be re-examined. Tardy[43] studied the formation of 1-butene, presumably from 3-pentyl, from a mixture of chemically activated 1-pentyl and 2-pentyl radicals; RRKM analyses gave $E_0 = 31 \pm 1$ kcal mol^{-1} if this channel originated from a 1,3-shift in activated 1-pentyl or $E_0 = 33 \pm 1$ kcal mol^{-1} if it originated from a 1,2-shift (see below) in activated 2-pentyl. Similar studies and data treatment for formation of ethane from chemically activated 2-butyl in the presence of H_2S, presumably via β-scission of 1-butyl, by Gierczak and co-workers[44] gave, after conversion by thermochemical balance to the 1-butyl → 2-butyl direction, $A = 10^{11.8}$ s^{-1} and $E_0 = 32.8$ kcal mol^{-1} if the conversion occurred by a 1,3-shift and $A = 10^{12.95}$ s^{-1} and $E_0 = 38.3$ kcal mol^{-1} if by a 1,2-shift. If for the (p → s) class we again take $E_{1,5} \approx 13$ kcal mol^{-1} (see above), the carbocycle model would predict $E_{1,3} \approx [13 + \Delta H^\circ_{\text{strain}}(\text{cyclobutane})] \approx (13 + 26) \approx 39$ kcal mol^{-1}. In summary, the experimental evidence to support this high a value for $E_{1,3}$ is weak; stronger computational evidence will be considered below.

$x = 2$. Gordon and co-workers[45] used the $CHD{=}CD_2$ from pyrolysis of CH_3CD_3 as diagnostic of an ($x = 2$, p → p) shift. Consideration of isotope effects and anchoring to k_β(ethyl) (we slightly revised their value to k_β(ethyl) = $10^{13.9}$ exp($-39\,900/RT$) s^{-1}[20]) gave k(ethyl → ethyl) = $10^{(12.7\pm1.1)}$ exp($-39\,900 \pm 4000/RT$) s^{-1} (793−851 K). The generic Green recommendation[5] of $3.56 \times 10^{10} T^{0.88}$ exp($-40\,000/RT$) ≈ $10^{13.5}$ exp($-41\,400/RT$) s^{-1} compares favorably, the difference in rate constants at 773 K being <2.5-fold.

Attempts to isolate an ($x = 2$, p → s) shift in larger 1-alkyl radicals are usually foiled by much more rapid C−C β-scission. However, several early studies found an (ethylene + methyl)-forming channel from 2-propyl, generated from carbonyl or azo compounds, that is competitive with C−H β-scission, and its rate-controlling step is generally considered to be the modestly endothermic ($x = 2$, s → p) shift to form 1-propyl that then rapidly undergoes C−C β-scission. Data for k(2-propyl → 1-propyl) are collected in Figure 4. Kerr and Trotman-Dickenson[42b] obtained composite Arrhenius parameters anchored to k_c(2-propyl + 2-propyl); to obtain the deconvoluted values shown, we adjusted k_c from 10^{11} to $10^{9.5}$ M^{-1} s^{-1}.[20] These authors also deconvoluted earlier composites of Heller and Gordon,[46] which they considered to involve less experimental uncertainty; the values shown use the same downward adjustment of k_c. Jackson and McNesby[47] obtained four rate constants anchored to k_β(2-propyl) that varied only modestly, and non-

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[41] Lin, M. C.; Back, M. H. *Can. J. Chem.* **1966**, *44*, 2369.

[42] (a) Kerr, J. A.; Trotman-Dickenson, A. F. *J. Chem. Soc.* **1960**, 1602. (b) Kerr, J. A.; Trotman-Dickenson, A. F. *Trans. Faraday Soc.* **1959**, *55*, 921.

[43] Tardy, D. C. *Int. J. Chem. Kinet.* **1974**, *6*, 291.

[44] Gierczak, T.; Gawlowski, J.; Niedzielski, J. *React. Kinet. Catal. Lett.* **1988**, *36*, 435.

[45] Gordon, A. S.; Tardy, D. C.; Ireton, R. *J. Phys. Chem.* **1976**, *80*, 1400.

[46] Heller, C. A.; Gordon, A. S. *J. Phys. Chem.* **1958**, *62*, 709.

[47] Jackson, W. M.; McNesby, J. R. *J. Chem. Phys.* **1962**, *36*, 2272.

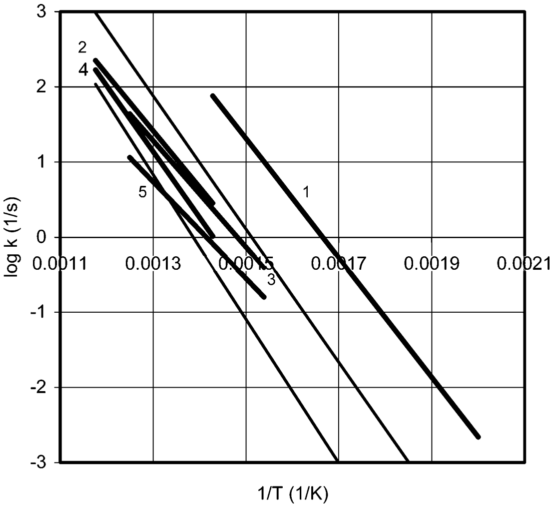

FIGURE 4. Arrhenius plots for k(2-propyl → 1-propyl) and log A (s^{-1}) and E (kcal mol^{-1}) values. #1, 13.2, 36.3 (ref 50); #2, 11.2, 34.5 (ref 48); #3, 10.5, 32.5 (ref 46 as discussed in ref 42b); #4, 12.6, 40.2 (ref 47 and see text); #5, 9.1, 29.5 (ref 42b). Continuous (curved) lines in ascending order: ~13.4, ~44.4, hybrid recommendation for 2-heptyl → 1-heptyl (ref 17); ~13.5, ~40.8, generic computational recommendation (ref 5).

monotonically, with T. We forced these data to an Arrhenius format (r^2 is only 0.42) and used as the anchor k_β(2-propyl) = $10^{13.2}\exp(-35\,800/RT)\ s^{-1}$;[20] clearly the error bars will be large. In studies of pyrolysis of *i*-butane, Konar, Marshall, and Purnell[48] concluded that there were two routes from 2-propyl to 1-propyl.[49] The extracted parameters shown for the unimolecular 1,2-shift were anchored to hydrogen abstraction from *i*-butane. Finally, the parameters from Szirovicza and Marta,[50] already anchored to the current value of k_c, give rate constants notably larger than those from the other studies, as noted by the authors. The data in Figure 4 show major variations in A values in the range $10^{9.1}-10^{13.2}\ s^{-1}$ and in E values in the range 29.5−40.2 kcal mol^{-1}, although considerable compensation occurs. Overlaid in Figure 4 are the generic computational recommendation from Green and co-workers[5] for $k_{1,2}(s \rightarrow p) = 3.56 \times 10^{10}T^{0.88}\exp(-39\,440/RT) \approx 10^{13.5}\exp(-40\,800/RT)\ s^{-1}$ [51] and the hybrid recommendation from Curran and co-workers for 2-heptyl → 1-heptyl of $1.74 \times 10^{7}T^{2.01}\exp(-41\,280/RT) \approx 10^{13.4}\exp(-44\,400/RT)\ s^{-1}$. These flank the four clustered lower values, are notably lower than singularly higher rate constants of Szirovicza and Marta,[50] and may support the "higher" A and E values of Jackson and McNesby,[47] although these would appear to have the least experimental rigor (see above). If we again take $E_{1,5} \approx 13$ kcal mol^{-1} for the (p → s) case (see above), the carbocycle model would predict $E_{1,2}$ for this (s → p) case ≈ $[13 + \Delta H°_{strain}(\text{cyclopropane}) + \Delta H°(p,s)] \approx (13 + 27 + 3) \approx 43$ kcal mol^{-1}. None of the experimental or computational values (see below) reaches a value this high and several are notably less; the only exception is the Curran value, which presupposes the correctness of the carbocycle model.

$x = 6$. We are not aware of direct kinetic measurements for $x = 6$. Conflicting estimates of $k_{1,4}/k_{1,6}$ have been made. Lehrle and Pattenden[4] proposed a ratio of ~5:1 at ~600 K based on strain-free energies rather than strain enthalpies of the carbocycle models; this approach was proposed to account better for both entropic and enthalpic differences in the transition states, but it did not incorporate any experimental data. We proposed[52] the inverted ratio of ~1:5 based on the observed distribution of short side-chains in high-pressure polyethylene.

Branched Activated Radicals. Rabinovitch and co-workers[53] studied competitive rearrangement and β-scission of more branched but also chemically activated radicals (~35 kcal mol^{-1} excess energy) formed by addition of H to olefins. Translation of observed k_a values for shifts in such an activated radical into E_0 for the corresponding thermalized radical is model-dependent. RRKM analyses with estimated geometries and vibrational frequencies led to E_0 values for several 1,x-shifts, but these do not vary smoothly with the k_a value; the authors noted that "our data are not directly suited to determination of activation energies and A factors." We note three series (1)−(3); each represents a single shift class with differing numbers of spectator methyl groups on the intervening carbons. For the ($x = 4$, p → t) shift in reaction (1), adding one and then two methyl groups adjacent to the initial radical center led to a steady decrease in k_a from 100×10^6 to 18×10^6 to $5 \times 10^6\ s^{-1}$, but the derived E_0 values remained identical (all 12.0 kcal mol^{-1}). In contrast, for the ($x = 5$, s → p) shift in reaction (2), adding one and then two methyl groups adjacent to the product radical center did not lead to resolvable changes in k_a (all $>1 \times 10^6\ s^{-1}$), but the derived E_0 values steadily decreased from ≤20.8 to ≤15.8 to ≤14.3 kcal mol^{-1}. Finally for the ($x = 5$, p → s) shift in reaction (3), adding one and then two methyl groups at the "center carbon" did not lead to monotonic changes in either k_a ($>30 \times 10^6$ to $>100 \times 10^6$ to $>80 \times 10^6\ s^{-1}$) or E_0 (≤11.0 to ≤13.0 to ≤10.0 kcal mol^{-1}). Thus, unfortunately these tantalizing data on branched radicals do not produce a clear picture of the effects of spectator substituents.

$$CH_3CH_2CH(CH_3)CH_2CH_{2-n}(CH_3)_nCH_2^{\bullet} \rightarrow CH_3CH_2C(^{\bullet})(CH_3)CH_2CH_{2-n}(CH_3)_nCH_3, \quad n = 0-2 \quad (1)$$

$$CH_3CH_{2-n}(CH_3)_nCH_2CH(CH_3)CH(^{\bullet})CH_3 \rightarrow {}^{\bullet}CH_2CH_{2-n}(CH_3)_nCH_2CH(CH_3)CH_2CH_3, \quad n = 0-2 \quad (2)$$

$$RCH_2CH_2CH_{2-n}(CH_3)_nCH_2CH_2(^{\bullet}) \rightarrow RCH(^{\bullet})CH_2CH_{2-n}(CH_3)_nCH_2CH_3, \quad n = 0-2 \quad (3)$$

Computational Results for 1,x-Shifts. Transition State Geometry. Lendvay and co-workers[3] obtained C−H bond lengths in **1** for the symmetrical (p → p) cases of d = 1.28, 1.43, 1.39, and 1.36 Å and C−H−C bond angles of θ = 71°, 102°, 131°, and 151° for x = 2−5, respectively. Jitariu and co-workers[16] obtained d = 1.29, 1.38, 1.36, and 1.33 Å for x = 2−5, respectively, in 1-pentyl. A calculation at the HF/6-31G*

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[48] Konar, R. S.; Marshall, R. M.; Purnell, J. H. *Trans. Faraday Soc.* **1968**, *64*, 405.

[49] The second, involving a bimolecular interaction with *i*-butane through a five-membered cyclic transition state, has neither precedent nor confirmation.

[50] Szirovicza, L.; Marta, F. *Int. J. Chem. Kinet.* **1976**, *8*, 897.

[51] This value was derived from $k_{1,2}(p \rightarrow s) = 3.56 \times 10^{10}T^{0.88}\exp(-37\,300/RT)\ s^{-1}$ (ref 5) by using $K_{773} = 4.03$ from group additivity estimates and, following the Green protocol (ref 5), assigning all of the thermochemical balance to E.

[52] Poutsma, M. L. *Macromolecules* **2003**, *36*, 8931.

[53] (a) Hardwidge, E. A.; Larson, C. W.; Rabinovitch, B. S. *J. Am. Chem. Soc.* **1970**, *92*, 3278. (b) Larson, C. W.; Chua, P. T.; Rabinovitch, B. S. *J. Phys. Chem.* **1972**, *76*, 2507.

TABLE 1. Comparison of Computed Activation Barriers for 1,x-Shift and Strain Energies for (x+1)-Carbocycles[a]

x	E_0[b]	ΔE[b,c]	E_0[d]	ΔE[d]	E_∞[e]	ΔE[e]	ΔH_{strain}[f]	ΔH_{rel}[g]
2	41.1	23.9	37.0	23.8	41.4	27.0	27.5	24.3
3	41.6	24.4	36.0	22.8	39.8	25.4	26.5	25.5
4	24.6	7.4	19.1	5.9	22.9	8.5	6.2	5.7
5	17.2	0.0	13.2	0.0	14.4	0.0	0.0[h]	0.0[h]

[a] All values in kcal mol^{-1}; $\Delta E = E_{1,x} - E_{1,5}$. [b] Computed for (p → p) cases (ref 3); at this level of theory, $E_0 = 18.0$ for (methyl + methane). [c] 24.3, 22.2, 6.3, and 0.0, respectively, for alternate BAC-MP4 protocol. [d] Computed for 1-pentyl (ref 16); because this series represents (p → s) cases for $x = 2-4$, the calculated value for $x = 5$ (p → p) was decreased by 1.0 kcal mol^{-1}, based on a calculated $\Delta H°(\text{p,s}) = 2.1$ kcal mol^{-1} and $\alpha = 0.5$. [e] Computed for generic (p → p) cases (ref 5); converted from three-parameter Arrhenius format at 773 K. [f] Classical strain enthalpy of (x+1)-carbocycle referred to cyclohexane as "strain-free" (ref 10). [g] From MMX simulations; see text below. [h] Value for cycloheptane is 6.2 (6.9) kcal mol^{-1}; see text for an "unusually low" computed $E_0 = 15.1$ for $x = 6$ (ref 3b).

level[54] gave $d = 1.36-1.37$ Å and $\theta = 154°$ for the ($x = 5$, p → s) process. At the semiempirical AM1 level,[55] $d = 1.41$, 1.35, 1.32, and 1.31 Å and $\theta = 99°$, 125°, 145°, and 158° were obtained for the symmetrical (p → p) cases for $x = 3-6$, respectively;[56] this group[55] attributed most of the increased barriers for $x = 3$ and 4 to the compression of θ. Thus, in all cases, θ is larger than the C−C−C angle in the corresponding carbocycle model, while d is shorter than the C−C distance. Specifically for $x = 5$,[3] **1**, while chairlike, has the migrating H only 3−5° out of the plane defined by the four C_α and C_β carbons; that is, it is less puckered than the normal chair conformation in this region. Hence, the geometrical mapping of **1** onto the model **2** is less than perfect.

Dependence of Computed Kinetic Parameters on *x*. Calculated values of the threshold energy E_0[3,16] or the Arrhenius activation energy E_∞[5] ($E_\infty = E_0 + T\langle \Delta C_v^\ddagger \rangle + RT$) for shifts in unbranched radicals are listed in Table 1 along with the differences $\Delta E = E_{1,x} - E_{1,5}$ for $x = 2-5$.[57] The good correspondence of these computed ΔE values as a function of x with the strain enthalpies of the (x+1)-carbocycle models gives more comprehensive and consistent support for the carbocycle model than do the more scattered experimental data, especially for $x = 2$ and 3 (Figures 3 and 4). However, a counter-example is the calculated $E_0 = 15.1$ kcal mol^{-1} for the 1,6-shift of (2-methyl-1-hexyl → 2-methyl-6-hexyl),[3b,60] which, with the authors conventions for bimolecular analogues, leads to $\Delta H°_{\text{strain}}$(cycloheptane) = 0 rather than ∼6 kcal mol^{-1}.

For a variety of examples from Lendvay and co-workers,[3] including prim, sec, and tert centers (albeit also in branched systems; see below), the average calculated A values were $10^{12.86}$, $10^{12.54}$, $10^{11.96}$, $10^{11.53}$, and $10^{11.15}$ s^{-1} for $x = 2-6$, respectively; thus the average decrease in A for unit increase in x was 2.7-fold, notably less than the factor of ∼10-fold used in previous estimates based on changes in $\Delta S^\ddagger$ for loss of free rotors.[1,2] This might suggest that the decrease in $\Delta S^\ddagger$ with increasing x from this source is somewhat offset by increasing conformational flexibility of **1** as the ring size increases. However, in contrast, the computed recommendations for A values at 773 K for the (p → p) shift from Green and co-workers[5] of $10^{13.48}$, $10^{12.81}$, $10^{11.50}$, and $10^{10.57}$ s^{-1} for $x = 2-5$, respectively, do lead to an almost 10-fold decrease for unit increase in x. The spread in A factors is even greater for the hybrid recommendations of Curran and co-workers,[17] almost a 100-fold decrease in A for unit increase in x.

Dependence of Computed Kinetic Parameters on Reaction Class for Constant *x*. To compare activation barriers between shifts with the same x but in different reaction classes, we define $\Delta E_{\text{ij,kl}} = E(\text{i} \rightarrow \text{j}) - E(\text{k} \rightarrow \text{l})$, where i−l are permuted among p, s, and t. As illustrated above, the experimental data in Figures 1−4 are too limited in structural variation and precision to make reliable comparisons. First, the E_∞ values for the thermoneutral (p → p), (s → s), and (t → t) cases for a given x should be identical if simple Evans−Polanyi behavior pertains or should decrease modestly if a "prim-tert electronic acceleration" (see above) pertains. Two $\Delta E_{\text{pp,ss}}$ values can be extracted from the calculated E_0 values of Lendvay and co-workers[3] (although there are additional spectator substituents present; see below): for $x = 2$, $\Delta E_{\text{pp,ss}} = 2.8$ or 2.7 kcal mol^{-1} for (5-methyl-3-hexyl → 5-methyl-4-hexyl)[60] or (5-methyl-2-hexyl → 5-methyl-3-hexyl), as compared to (ethyl → ethyl); and for $x = 3$, $\Delta E_{\text{pp,ss}} = 2.6$ kcal mol^{-1} for (5-methyl-2-hexyl → 5-methyl-4-hexyl), as compared to (1-propyl → 1-propyl). The recommendations from Green and co-workers[5] for E_∞ give values of $\Delta E_{\text{pp,ss}}$ and $\Delta E_{\text{ss,tt}}$ = 0.9 and −0.9 kcal mol^{-1} for $x = 2$, 0.6, and 1.6 kcal mol^{-1} for $x = 3$, and −0.4 and 4.1 kcal mol^{-1} for $x = 4$. While clearly the latter do not present a uniform pattern, there may indeed be a trend suggested by these computational studies for a "prim-tert electronic acceleration", as for the bimolecular analogues. Second, based on the currently accepted stability differences of 2.8 and 2.0 kcal mol^{-1} between prim, sec, and tert radicals[52,61] and if simple Evans−Polanyi behavior pertained with $\alpha = 0.5$, the successive E_∞ values for the increasingly exothermic (p → p), (p → s), and (p → t) classes for a given x might be expected to decrease by 1.4 and 1.0 kcal mol^{-1}. In comparison, Lendvay and co-workers[3] obtained $\Delta E_{\text{pp,pt}} = 5.1$ kcal mol^{-1} for (5-methyl-1-pentyl → 5-methyl-5-pentyl) ($x = 5$) as compared to (1-pentyl → 1-pentyl) and 4.6 kcal mol^{-1} for (2-methyl-1-pentyl → 2-methyl-2-pentyl) ($x = 2$) as compared to (ethyl → ethyl). Similarly, values of $\Delta E_{\text{pp,ps}}$ ranged from 2.5 to 3.4 kcal mol^{-1} for $x = 2-4$ for those cases least likely to have been perturbed by spectator substituents (see below). The values of $\Delta E_{\text{pp,ps}}$ and $\Delta E_{\text{ps,pt}}$ recommended by Green and co-workers[5] are 2.7 and 2.7 kcal mol^{-1} for $x = 2$, 2.2 and 2.3 kcal mol^{-1} for $x = 3$, and 2.5 and 2.3 kcal mol^{-1} for $x = 4$. Because all of these ΔE values

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[54] Toh, J. S.-S.; Huang, D. M.; Lovell, P. A.; Gilbert, R. G. *Polymer* **2001**, *42*, 1915.

[55] Huang, X. L.; Dannenberg, J. J. *J. Org. Chem.* **1991**, *56*, 5421.

[56] For unsymmetrical shifts, the high-level calculations show that the migrating H is slightly closer to the carbon that carries more alkyl substituents, in accord with the Hammond principle.

[57] A single-example high-level calculation gave $E_0 = 39.0$ kcal mol^{-1} for $x = 2$ in 1-propyl (ref 58), and modified semi-empirical BEBO calculations have also been applied to estimate barrier heights as a function of x (ref 59).

[58] Galland, N. G.; Caralp, F.; Hannachhi, Y.; Bergeat, A.; Loison, J. C. *J. Phys. Chem. A* **2003**, *107*, 5419.

[59] Simon, P.; Valko, L. *Chem. Phys.* **1987**, *117*, 219. Valko, L.; Simon, P. *Chem. Phys.* **1985**, *99*, 447.

[60] Non-systematic radical names are occasionally used to emphasize the change in substitution pattern being highlighted.

[61] The differences calculated by Lendvay and coworkers (ref 3) are somewhat smaller.

are larger than expected from simple Evans−Polanyi behavior, some support for a "prim-tert electronic acceleration" may again exist.

Computed Dependence on Spectator Substituents. Lendvay and co-workers[3] suggested from their calculations of E_0 that there is a general accelerating effect of spectator alkyl substituents that are not on the reaction centers. They ascribed this to comparatively lower ring strain in the alkylated transition states, although they had no independent source to estimate the relevant strain enthalpies. A case that allows the closest comparison, that is, a reaction pair with the same x in the same reaction class with and without a spectator substituent, is the 1.7 kcal mol^{-1} decrease from (1-propyl → 1-propyl) to (2-butyl-1-propyl → 2-butyl-1-propyl) ($x = 3$).

Results and Discussion

Applications of the carbocyclic model in the literature have involved only the strain enthalpies of the unsubstituted cycloalkanes (**2** with $R = R' = H$) and hence are strictly applicable only to the (p → p) class of 1,x-shifts in unadorned 1-alkyl radicals, although most of the experimental data (see above) apply to the (p → s) class for which the exact carbocycle models should be methylcycloalkanes. To anticipate extending the model to more highly alkylated radicals, either at the radical centers or on intervening carbons, we note that, while the major sources of strain in unsubstituted cycloalkanes as compared to open-chain alkanes are usually considered to be distortions of bond angles and H−H eclipsing, alkyl substituents could lead to additional unfavorable nonbonded interactions both in the carbocycle (e.g., 1,3-diaxial interactions in cyclohexane) and in the radical (e.g., gauche interactions). We construct a more formal definition by comparing the 1,x-shift in a target radical with that in a reference radical:

$$R^{\bullet}_{\text{target}} \rightarrow \mathbf{1}_{\text{target}}\ (\rightarrow R^{\bullet\prime}_{\text{target}}) \qquad E = E_{\text{target}} \tag{4}$$

$$R^{\bullet}_{\text{ref}} \rightarrow \mathbf{1}_{\text{ref}}\ (\rightarrow R^{\bullet\prime}_{\text{ref}}) \qquad E = E_{\text{ref}} \tag{5}$$

and formulating the formal difference reaction:

$$R^{\bullet}_{\text{target}} + \mathbf{1}_{\text{ref}} \rightarrow R^{\bullet}_{\text{ref}} + \mathbf{1}_{\text{target}} \qquad \Delta E = E_{\text{target}} - E_{\text{ref}} \tag{6}$$

Analogously, we compare the formal conversion of each radical to the appropriate carbocycle **2**:

$$R^{\bullet}_{\text{target}} + \text{CH} \rightarrow \mathbf{2}_{\text{target}} \qquad \Delta H_{\text{insert,target}} \tag{7}$$

$$R^{\bullet}_{\text{ref}} + \text{CH} \rightarrow \mathbf{2}_{\text{ref}} \qquad \Delta H_{\text{insert,ref}} \tag{8}$$

and formulate the formal difference reaction:

$$R^{\bullet}_{\text{target}} + \mathbf{2}_{\text{ref}} \rightarrow R^{\bullet}_{\text{ref}} + \mathbf{2}_{\text{target}} \qquad \Delta H_{\text{rel}} = \Delta H_{\text{insert,target}} - \Delta H_{\text{insert,ref}} \tag{9}$$

The simplest hypothesis of the model is that carbocycle **2** can be taken as a stand-in for transition state **1** with respect to strain effects that result from variations in x. Thus, $\Delta E \approx \Delta H_{\text{rel}}$, and determining ΔH_{rel} requires no kinetic input because it can be calculated from the $\Delta_f H°$ values of $R^{\bullet}_{\text{target}}$, $\mathbf{2}_{\text{ref}}$, $R^{\bullet}_{\text{ref}}$, and $\mathbf{2}_{\text{target}}$.

This formulation does not, however, consider more subtle nonsteric effects. In particular, if either of the reactions ($R^{\bullet}_{\text{target}} \rightarrow R^{\bullet\prime}_{\text{target}}$) or ($R^{\bullet}_{\text{ref}} \rightarrow R^{\bullet\prime}_{\text{ref}}$) is not thermoneutral, the nonzero $\Delta H°_{\text{rxn}}$ should be reflected directly in the energy level of **1** but not of **2**; in other words, the product radicals $R^{\bullet\prime}_{\text{target}}$ and $R^{\bullet\prime}_{\text{ref}}$, whose stabilities are incipient in **1**, do not appear in this formal definition of ΔH_{rel}. To isolate strain effects as much as possible from thermochemical and other effects, a more stringent definition of ΔH_{rel} would appear useful in which we demand that its defining reaction (9) be rigorously homodesmotic, that is, that the carbon atom types (primary through quaternary) and connectivity be the same on each side of the equation and that $R^{\bullet}_{\text{target}}$ and $R^{\bullet}_{\text{ref}}$ be in the same radical class. Also, if $R^{\bullet\prime}_{\text{target}}$ and $R^{\bullet\prime}_{\text{ref}}$ are not in this class, they at least should be mutually in the same class; in other words, reactions (4) and (5) should be comparably exo-/endothermic so that effects of $\Delta H°_{\text{rxn}}$ on E will largely cancel.

Because experimental $\Delta_f H°$ values for most of the radicals and carbocycles of interest are not available, the molecular mechanics approach, which is sensitive to strain,[62a] was used to estimate them. The MMX program that is parametrized for radicals was used[62b] with the GMMX search routine to systematically identify conformers. Note that MMX-derived $\Delta_f H°$ values for radicals[62c] and carbocycles are Boltzmann-weighted averages for all identified minima that are ≤3 kcal mol^{-1} above the global minimum, and therefore ΔH_{rel} is not exactly comparable to computational values of E or ΔE that typically refer only to global minima.[16,63]

Effects of *x* for Each Reaction Class. We progressively substituted 1−4 methyl groups at the radical-bearing carbons to give the complete set of shift reactions with x varied from 2 to 6 and both the starting and the final radical class varied from prim to tert. Compare first ΔH_{rel} for the unsubstituted (p → p) class for $x = 2$, 3, 4, and 6, referenced to $x = 5$, that is, the usual model in the literature. In this case, experimental $\Delta_f H°$ values are available, both for the radicals (based on those for the *n*-alkanes[64] with the assumption that $D°$(prim-C−H) is independent of chain length) and for the carbocycles.[64] These lead to $\Delta H_{\text{rel}} = 27.2$, 25.8, 6.2, and 6.0 for $x = 2$, 3, 4, and 6, respectively, in good agreement as expected with the conventional cycloalkane strain enthalpies (Table 1) because there should be minimal "strain" in the prim radicals involved. The corresponding values from the MMX simulations are 24.3, 25.5, 5.7, and 6.9 kcal mol^{-1}. These small differences presumably represent the particular potential functions and parametrization for calculation of $\Delta_f H°$ used in MMX; however, these should largely cancel when values from MMX are used consistently.

The corresponding dependences of ΔH_{rel} on x for the other thermoneutral and exothermic shift reactions, each referenced to $x = 5$ for the same reaction class, are listed in Table 2; for example, for $x = 4$ for the (p → t) class, the homodesmotic defining reaction (9) is (4-methyl-1-pentyl + 1,1-dimethylcy-

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[62] (a) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemistry Society: Washington, DC, 1982. Cramer, C. J. *Essentials of Computational Chemistry: Theories and Models*; Wiley: Chichester, West Sussex, 2004. (b) PC Model, 9.00.0, Serena Software, Bloomington, IN. Gajewski, J. J.; Gilbert, K. E.; McKelvey J. *Adv. Mol. Model.* **1990**, *2*, 65. (c) Because MMX overestimates the stability of alkyl radicals, correction factors of 3.3, 5.1, and 6.6 kcal mol^{-1} were applied to prim, sec, and tert radicals, respectively, to bring the resulting $D°$(C−H) values for representative "unstrained" C_4−C_7 radicals to average values of 101.0, 98.2, and 96.2 kcal mol^{-1} (ref 52), respectively.

[63] Pacansky, J.; Waltman, R. J.; Barnes, L. A. *J. Phys. Chem.* **1993**, *97*, 10694.

[64] Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics, Internet Version 2006, (http://www.hbcpnetbase.com)*; Taylor and Francis: Boca Raton, FL, 2006.

TABLE 2. Dependence of ΔH_{rel} (kcal mol^{-1}) on *x* for Each Reaction Class[a]

x	(p → p)[b]	(p → s)	(p → t)	(s → s) (cis)	(s → s) (trans)	(s → t)	(t → t)
2	24.3	26.3	24.0	28.3	25.1	25.5	21.4
3	25.5	25.0	23.2	24.6	23.0	23.0	18.7
4	5.7	5.6	4.6	5.4	4.1	4.6	1.1
6	6.9	7.4	7.1	7.8	6.4	7.6	6.7

[a] Each value is referenced to $x = 5$ for that reaction class. [b] Values based on literature $\Delta_f H°$ data are 27.2, 25.8, 6.2, and 6.0.

clohexane → 5-methyl-1-hexyl + 1,1-dimethylcyclopentane). While all of the columns reveal some modest differences from the (p → p) class as a function of *x*, a discontinuity occurs for the (t → t) class for $x = 2$, 3, and 4 (but not 6) whose ΔH_{rel} values are notably lower. Hence, the reactivity scale is predicted to be compressed specifically for this class, either by facilitation of the shift for $x = 2-4$ or inhibition for $x = 5$ and 6.

Effects of Reaction Class for Each *x*. To resolve these options for the absolute reactivity change, comparisons are required among the thermoneutral (p → p), (s → s),[65] and (t → t) classes for each *x* ("across the rows" of Table 2). However, determining ΔH_{rel} for a given reaction class and *x* with use of the (p → p) class at the same *x* as the reference would violate the stringent homodesmotic condition because not only would the defining reaction (9) involve conversion of a sec or tert to a prim radical but also a change in the number of tertiary and quaternary carbons. We label such non-homodesmotic values as "ΔH_{rel}" and propose its approximate dissection into $\Delta H_{non-strain}$ and ΔH_{strain}. Here, $\Delta H_{non-strain}$ accounts for changes in radical class and in carbon atom types and connectivity and is estimated from group additivity without any correction terms for ring strain or gauche interactions,[1,12] "ΔH_{rel}" is derived from the MMX simulations as above,[66] and $\Delta H_{strain} \equiv$ "ΔH_{rel}" $- \Delta H_{non-strain}$ then becomes the approximated analogue of a properly homodesmotic ΔH_{rel} that focuses on the difference in strain. Consider as a specific example the (t → t) as compared to the (p → p) class for $x = 4$, for which the defining reaction (9) is (2,5-dimethyl-2-hexyl + cyclopentane → 1-butyl + 1,1,3,3-tetramethylcyclopentane); "ΔH_{rel}" $= -0.7$ from MMX, $\Delta H_{non-strain} = -1.0$ from group additivity, and hence $\Delta H_{strain} = +0.3$ kcal mol^{-1}. Because both the MMX and the group additivity parametrizations have been adjusted to give a contribution of +4.8 for the conversion of a tert to prim radical,[66] the other contribution to $\Delta H_{non-strain}$ from the changes in carbon connectivity must be -5.8 kcal mol^{-1}.[67] Contrast this with the (t → t) as compared to the (p → p) class for $x = 5$, for which the defining reaction (9) is (2,6-dimethyl-2-heptyl + cyclohexane → 1-pentyl + 1,1,3,3-tetramethylcyclohexane). Because $\Delta H_{non-strain}$ is obtained by group additivity by simply adding 1 $C(C)_2(H)_2$ contribution to each species, it remains at -1.0, but "ΔH_{rel}" from MMX increases from -0.7 to $+3.9$ and hence ΔH_{strain} increases from $+0.3$ to $+4.9$ kcal mol^{-1}. The collected ΔH_{strain} values are shown in Table 3 for the thermoneutral reaction classes. While the effects of reaction class are rather small for $x = 3$ and 4,[68] they are larger for $x = 5$ and 6, in particular the significantly positive values for the (t → t) class. Hence, these simulations predict a non-trivial increase in *E*[69] for this class, which indeed then constitutes a "prim-tert steric deceleration" for $x = 5$ and 6.

TABLE 3. Dependence of ΔH_{strain} (kcal mol^{-1}) on Thermoneutral Reaction Classes for each *x*[a]

x	(s → s) (cis)	(s → s) (trans)	(t → t)
2	4.6	3.1	2.0
3	−0.3	−0.1	−1.9
4	0.3	0.7	0.3
5	0.5	2.4	4.9
6	1.5	1.9	4.8

[a] The value for each reaction class is referenced to the (p → p) class for the given *x*.

These contrasting effects of *x* suggest that, as compared to the open-chain starting radicals, the cyclobutane and cyclopentane models are better able to accommodate the strain introduced by four terminal methyl groups than are cyclohexane and cycloheptane. Geometrical considerations can rationalize this result. Unfavorable end-to-end methyl−methyl interactions in the open-chain radicals should, if anything, decrease as *x* increases, but obligatory 1,3-interactions occur in all of the cycloalkanes, reaching a maximum for the (t → t) cases for which a "diaxial-like" methyl−methyl contact becomes unavoidable. As the rings from cyclobutane upward become larger and more puckered, the distance of this contact actually decreases. From MMX simulations, the closest methyl−methyl distance in 1,1,3,3-tetramethylcycloalkanes is 3.91 and 3.85 Å in the cyclobutane and cyclopentane, but only 3.39 and 3.38 Å in the cyclohexane and cycloheptane. Hence, this particularly unfavorable 1,3-diaxial-like methyl−methyl interaction is maximized in the larger rings. This effect can be illustrated by the MMX-estimated $\Delta H°$ values for the homodesmotic reactions (cyclo-C_n + 1,1,3,3-tetramethylcyclo-C_6 → cyclo-C_6 + 1,1,3,3-tetramethylcyclo-C_n) of -7.3, -4.6, and -0.2 kcal mol^{-1} for $n = 4$, 5, and 7, respectively. Note that the notably larger value of ΔH_{strain} for the (s →s)(trans) than the (s →s)(cis) class for $x = 5$ correlates with the fact that *cis*-1,3-dimethylcyclohexane can have both methyl groups equatorial but the trans isomer is forced to have one axial.[65]

As already noted, there are unfortunately no experimental data to test whether this prediction of some "prim-tert steric deceleration" for $x = 5$ and 6 that arises from considerations of

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(65) For the (s → s) class for which cis and trans isomers of **1** and **2** exist, we assume reaction will proceed largely through the more favorable stereochemistry, which simulations indicate is the cis.

(66) The $\Delta_f H°$ parameters for alkyl radical centers in both the MMX simulations (ref 62c) and the group additivity calculations (refs 12 and 52) were adjusted to reproduce the same $D°$(C−H) values for small alkanes.

(67) That the latter value is reasonable is indicated by the fact that group additivity gives $\Delta H° = -5.7$ kcal mol^{-1} for the analogous non-radical formal reaction (2,5-dimethylhexane + cyclopentane → butane + 1,1,3,3-tetramethylcyclopentane). As a simpler example of the stabilizing effect of quaternary centers, consider the formal reaction (2 isopentane → pentane + neopentane) for which $\Delta H° = -1.8$ kcal mol^{-1} (ref 64).

(68) We record but do not attempt to specifically rationalize the pattern for $x = 2$ because of the unusual C−C bonding in cyclopropane and possible ambiguities in the simulations for this case.

(69) For order-of-magnitude orientation, ΔE values of 2 and 4 kcal mol^{-1} would correspond at 500 °C to rate decelerations of 4- and 14-fold. Note that our discussion of the carbocyclic model is limited to considerations of *E*. There may well also be subtle steric effects on *A* factors, but we refrain from estimates of entropies, in particular because of the difficulties in dealing with hindered methyl rotations and configurational entropy differences (ref 7b).

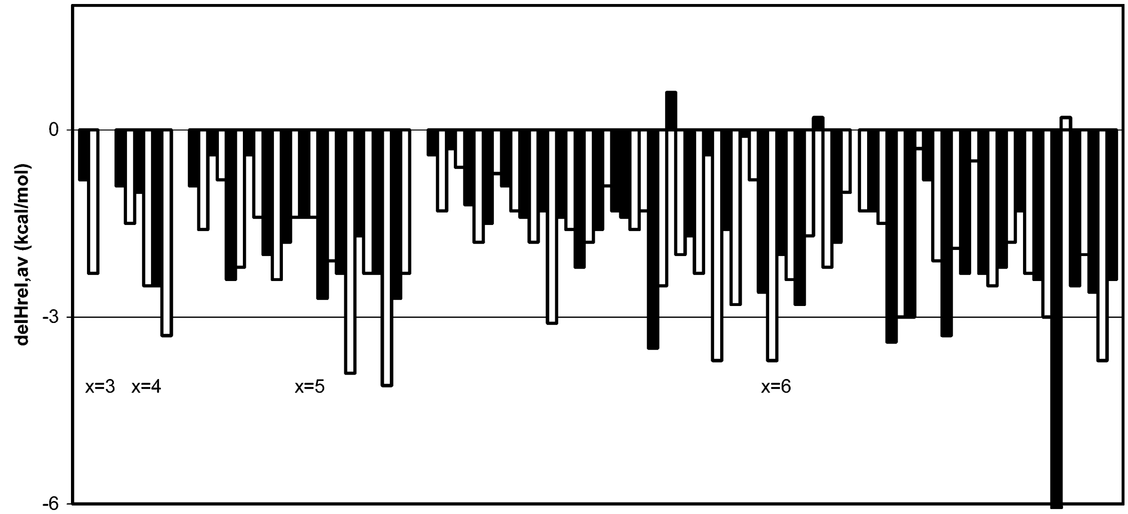

FIGURE 5. ΔH_{rel} (kcal mol^{-1}) as a function of increasing methylation of internal carbons in the (p → p) class for $x = 3-6$, each referenced to the unsubstituted (p → p) case for the given value of x. For reactions that are not fully symmetrical, the average ΔH_{rel} is shown. The bars representing ΔH_{rel} are alternating solid and open simply for clarity of presentation. The specific reaction represented by each bar is given in Table S1. The apparent gap in the $x = 6$ set is a zero value.

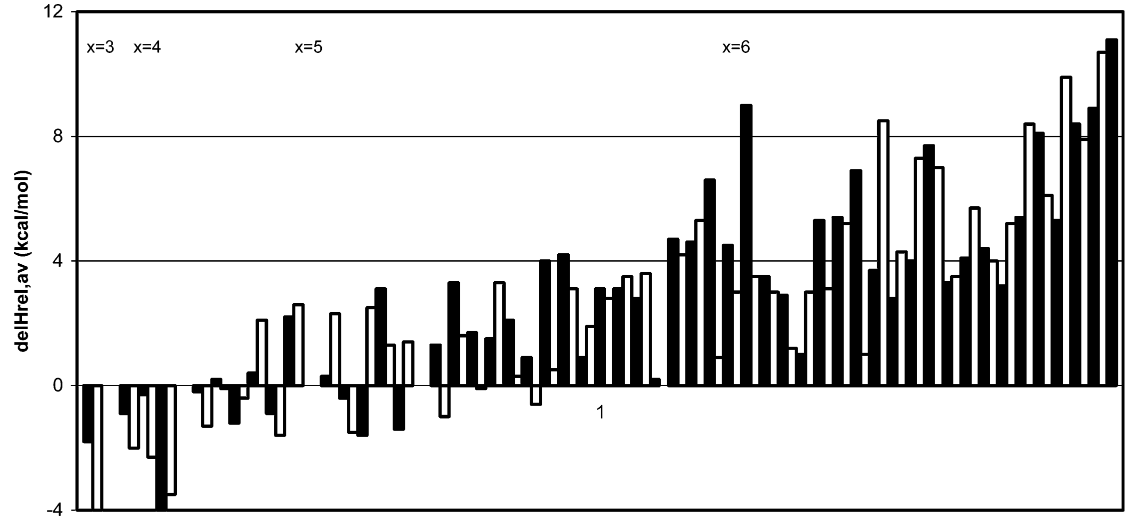

FIGURE 6. ΔH_{rel} (kcal mol^{-1}) as a function of increasing methylation of internal carbons in the (t → t) class for $x = 3-6$, each referenced to the unsubstituted (t → t) case for the given value of x. For reactions that are not fully symmetrical, the average ΔH_{rel} is shown. The bars representing ΔH_{rel} are alternating solid and open simply for clarity of presentation. The specific reaction represented by each bar is given in Table S2. The apparent gaps in the $x = 5$ and 6 sets are zero values.

2 is actually manifested in **1**. The computational recommendations from Green and co-workers[5] give $E(\mathrm{p} \rightarrow \mathrm{p}) \approx E(\mathrm{s} \rightarrow \mathrm{s}) \geq E(\mathrm{t} \rightarrow \mathrm{t})$ for $x = 3$ and $E(\mathrm{p} \rightarrow \mathrm{p}) \approx E(\mathrm{s} \rightarrow \mathrm{s}) > E(\mathrm{t} \rightarrow \mathrm{t})$ for $x = 4$, but parallel computations to test for a reversal of this order for the discriminating cases for $x = 5$ and 6 were not presented. The computational results of Lendvay and co-workers[3] include $[E(\mathrm{p} \rightarrow \mathrm{p}) - E(\mathrm{p} \rightarrow \mathrm{t})] = 5.1$ kcal mol^{-1} for $x = 5$ (the latter value may have used a larger basis set[3,16]), a value larger than the computed exothermicity for the (p → t) case and hence counter to any steric deceleration. Semiempirical AM1 theory has been applied to all radical classes,[9] and values of $[\Delta H^{\ddagger}(\mathrm{t} \rightarrow \mathrm{t}) - \Delta H^{\ddagger}(\mathrm{p} \rightarrow \mathrm{p})] = -0.8, -0.3, +1.3$, and $+2.5$ kcal mol^{-1} were obtained for $x = 2-5$, respectively. This calculated order does reproduce the predicted trend with increasing x; however, we remain skeptical because this less rigorous computational method overestimated $\Delta H^{\circ}_{\mathrm{rxn}}$ by a factor of ~2 for the exothermic (p → s), (s → t), and (p → t) cases. In summary, the available data do not allow a clear decision whether the prediction of some "prim-tert steric deceleration" for $x = 5$ and 6 is real or an artifact of the carbocyclic model, that is, that **2** does not represent **1** well at a more discriminating level.

Effects of Spectator Methyl Substituents on the Internal Carbons. Consider next the set of reversible shift reactions (4) and (−4) for the (p → p) class generated by progressive substitution of methyl groups on the non-radical-bearing carbons. All possible positional and stereochemical[70] permutations of adding from 1 to $(2x - 4)$ methyl groups to the $(x - 2)$ internal carbons of $\mathrm{CH_3(CH_2)}_{x-2}\mathrm{CH_2}^{\bullet}$ were considered. For each $x = 3-6$, the unadorned (p → p) case was used as the reference for that x value. The defining reactions (9) for ΔH_{rel} in either direction are properly homodesmotic because only prim radicals

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[70] The stereochemical descriptors for chiral centers in radicals assign a prim radical center as lower priority than a methyl group; that is, the unpaired electron is considered as a phantom atom of atomic number zero.

are involved and the carbon atom types and connectivities remain unchanged. However, the derived ΔH_{rel} values are not identical because the simulated $\Delta_f H°$ values of the isomeric radicals with differing substitution patterns with respect to the radical site vary slightly. The values displayed in Figure 5 are the averages of the forward and reverse reactions. Radicals with 1 methyl substituent at C_{x-1} have diastereotopic methyl groups from which shift may occur, and the stereoisomeric transition states and carbocycle models are both shown; that with the more negative ΔH_{rel} value should be preferred. The stereochemistry of the carbocycle model involved for other cases where isomers are possible is shown in Table S1. The overwhelming majority of shifts in Figure 5 (2 of 2 for $x = 3$, 6 of 6 for $x = 4$, 24 of 24 for $x = 5$, and 72 of 75 for $x = 6$) have $\Delta H_{\mathrm{rel}} < 0$. The grand average values were −1.6, −2.0, −2.0, and −1.8 kcal mol^{-1} for $x = 3-6$, respectively. Although one may deduce a weak trend for ΔH_{rel} to become more negative as the degree of internal substitution increases, "scatter" dominates and each case must be considered individually. In summary, the MMX simulations suggest that the carbocycle ring is almost always better able to accommodate strain effects from internal spectator methyl groups than is the open-chain starting radical, and hence a decrease in E is predicted as compared to the unsubstituted (p → p) case. This prediction is reminiscent of the Thorpe−Ingold kinetic effect in which alkyl substituents facilitate ring-closure reactions.[71] As noted above, such an effect was inferred from their calculations by Lendvay and co-workers.[3]

Effects of the identical sequence of methyl substitution for the other extreme of the (t → t) class are shown in Figure 6. For $x = 3$ and 4, ΔH_{rel} remained negative, as for the (p → p) class. However, as x increased for this class, the values became increasingly positive such that for $x = 6$ they were predominantly positive, predictive of further steric inhibition of the already sterically challenged (t → t) class. For the highly methylated (and admittedly rarely to be encountered) cases for $x = 6$, ΔH_{rel} values approached and exceeded 10 kcal mol^{-1}. The sharp difference in behaviors shown in Figures 5 and 6 indicates that, whereas the larger cycloalkanes are better able to accommodate spectator methyl substituents than are the open-chain radicals for the (p → p) class for which three adjacent carbons in the cycloalkane remain unsubstituted, the opposite is true for the (t → t) class for which only one carbon in the cycloalkane remains unsubstituted.

Structural Comparison of 1, 2, and 3. Modeling the structure of transition state **1** by carbocycle **2** is, of course, an approximation. We have already noted that the geometries do not fully superimpose. In addition, the bending and stretching potentials for the C−H−C unit in **1** would not be the same as for the $C-CH_2-C$ unit in **2**.[72] While the calculated C−H distance in **1** is shorter than a C−C single bond in **2**, the calculated C−H−C angle in **1** is larger than the corresponding C−C−C angle in **2** (see above). As a result, most of the calculated 1,3 C−C distances in **1** (1.49, 2.22, 2.53, and 2.63 Å, respectively, for $x = 2-5$[3]) are slightly larger than the MMX-estimated ones in **2** (1.51, 2.14, 2.40−2.46, and 2.53 Å). In addition for $x = 5$, the lesser puckering calculated for **1**[3] than for cyclohexane would allow the especially sterically demanding 1,3-diaxial substituents to move somewhat farther away from each other. Hence, carbocycle **2** may overemphasize this particularly important long-range steric repulsion. Because it is likely the major contributor to the predicted "prim-tert steric decleration" for the (t → t) class for $x = 5$ and 6, the magnitude of the latter (Table 3) may be exaggerated by the inexact superposition of **1** and **2**. On the other hand, as noted above, the distance between 1,3-"diaxial-like" substituents in the "bent" **1** will clearly be shorter than the corresponding distance that could contribute to destabilizing "gauche-like" interactions in the linear **3** for a bimolecular (t → t) hydrogen transfer. Hence, it seems probable to expect a greater contribution from "prim-tert steric deceleration" in the intramolecular shifts, especially for $x = 5$ and 6, than in the bimolecular analogues. Quantitative resolution must await further data.

Conclusions

A central feature of the carbocyclic model for the transition state of the intramolecular 1,x-hydrogen shift in alkyl radicals is that the value of $(E_{1,x} - E_{1,5})$ should quantitatively parallel the classical strain enthalpy of the (x+1)-carbocycle as compared to the "strain-free" cyclohexane. For the (p → p) class, the model can be implemented with strain enthalpies based on well-known $\Delta_f H°$ data. The predictions conform well to recent high-level ab initio calculations for $x = 2-4$, as compared to $x = 5$. For $x = 4$, they also conform to experimental data, largely for the (p → s) rather than (p → p) class, but data for $x = 2$ and 3 remain seriously scattered.

We have extended the model to methyl-substituted systems with $\Delta_f H°$ values based on molecular mechanics simulations. A number of more subtle predictions are made for addition of substituents, both at the reaction sites and as spectator groups on the chain. (1) In contrast with bimolecular hydrogen transfer for which there appears to be a "prim-tert electronic acceleration", some "prim-tert steric deceleration" is predicted specifically for $x = 5$ and 6 in which E, especially for the (t → t) class, is increased rather than decreased as compared to the analogous (p → p) class. There are unfortunately no experimental or computational data to test this prediction. (2) Shift reactions in the (p → p) class for all x are predicted to have E decreased by spectator substituents as compared to the unadorned (p → p) parent, an example of the Thorpe−Ingold effect. Again there are no relevant data, but calculations may support it. (3) In contrast, shift reactions in the (t → t) class for $x = 6$ are predicted to have E increased by spectator substituents as compared to the unadorned (and already decelerated) (t → t) parent. We find neither data nor calculations to test this prediction. Hence, most of the predictions herein must await experimental and/or computational testing.

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Supporting Information Available: Tables S1 and S2 listing the specific reactions associated with each bar in Figures 5 and 6. This material is available free of charge via the Internet at http://pubs.acs.org.

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[71] For leading references, see ref 19.

[72] The dependence of the energy of **1** on the C−H−C angle is discussed in ref 55.