

in methanol to afford 1-phenyl-1-methoxycyclohexane (**2**), via the 1-phenylcyclohexyl carbocation.^{10,11} Extrapolation of the double-reciprocal plot of the quantum yield of formation of **2** vs. $[\text{H}_2\text{SO}_4]$, after correction for $^3\text{Ph}_2\text{CO}$ quenching by H_2SO_4 and for the small (2.2%) inefficiency of conversion of the carbocation to ether,¹⁹ affords $\phi_{\text{form}} = 0.36 \pm 0.01$ (2σ)²⁰ and thus a value of 44.7 ± 5 kcal/mol for E_{c-t} . The sum of the amplitude factors, $\phi_1 + \phi_2 + \phi_3$, equals unity, indicating all the photon energy is recovered as heat within experimental error. Results in cyclohexane are almost identical. However, the inability to measure ϕ_{form} in aprotic solvent prevents a computation of E_{c-t} in cyclohexane.

The values of E_T and E_{c-t} are the first experimental measurements of the relaxed energy of a short-lived twisted alkene triplet²¹ and of the heat of geometric isomerization to the most strained cycloalkene known, respectively. The E_T value of 56 ± 3.4 kcal/mol is but slightly lower than the expected²² spectroscopic triplet energy of 60 kcal/mol. We believe that this corresponds to partial relaxation (i.e., $<90^\circ$ rotation) of the triplet.¹⁹ Therefore, the triplet surface is nearly flat, similar to the trans to perpendicular region for stilbene triplet.²³

The energy E_{c-t} of 44.7 kcal/mol is remarkably close to the prediction of molecular mechanics (MM) for *trans*-cyclohexene ($E_{c-t} = 42.4$ kcal/mol).²⁴ Given the $\Delta H_f(c-1) = -4.0 \pm 1.6$ kcal/mol²⁵ and the strain energy $E_s(c-1) = 1.2$ kcal/mol,²⁶ then $\Delta H_f(t-1) = 41 \pm 5$ kcal/mol and $E_s(t-1) = 46 \pm 5$ kcal/mol. We note the structural prediction by MM of substantially pyramidalized vinyl carbons in these and related compounds.^{4,24} The implications of this for the chemistry of *trans*-cyclohexenes and for dynamics on the ground-state surface will be discussed in a future report.

In conclusion, we have demonstrated the applicability of time-resolved photoacoustic calorimetry to the study of alkene ground and triplet surfaces. Further studies should allow a wealth of thermochemical information on relaxed olefin triplets and strained ground-state isomers.

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Registry No. 1-Phenylcyclohexene, 771-98-2.

(19) To be elaborated in a full paper.

(20) Bonneau and Herran¹⁷ report 0.34 ± 0.07 by a less extensive series of measurements by the same technique. We gratefully acknowledge helpful discussions with Dr. Bonneau.

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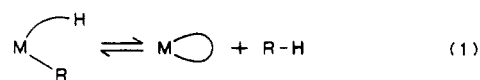
Intramolecular vs. Intermolecular Alkyl C-H Bond Activation. Complete Thermodynamic and Kinetic Parameters for a Reversible Cyclometalation

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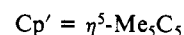
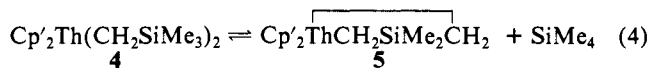
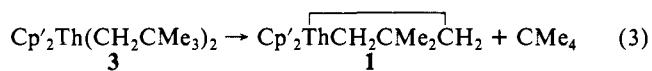
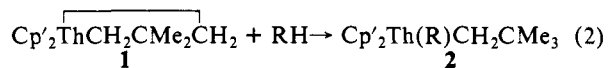
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Despite the widespread occurrence of intramolecular C-H activating^{1,2} cyclometalation processes³ (eq 1) and the possibility



that they may enjoy an "intramolecular advantage"^{4,5} over competing intermolecular processes, relevant comparative thermodynamic (ΔH , ΔS) and kinetic (ΔH^\ddagger , ΔS^\ddagger) information is surprisingly sparse. For one rhodium system, Jones and Feher⁶ showed that an intramolecular process enjoyed a slight thermodynamic (only ΔG° could be measured) advantage but also a slight kinetic disadvantage (only in ΔH^\ddagger). We recently reported kinetic/mechanistic studies of intermolecular alkane activation⁷ and closely related intramolecular cyclometalation⁸ at thorium centers (eq 2-4). C-H scission was found to be rate-limiting, and



thermochemical data (ΔH)⁹ suggest that eq 3 and 4 are entropically driven. We now report that the reversibility of eq 4 can be rendered observable, presenting a unique opportunity to quantify, in toto, thermodynamic and kinetic aspects of the in-

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Table I. Summary of Rate and Equilibrium Data for Eq 4^a

k_{fwd} , s ⁻¹	k_{rev} , M ⁻¹ s ⁻¹	K , M	ΔG , kcal mol ⁻¹ ^b	T , K
1.75 (7) × 10 ⁻⁶	4.49 (22) × 10 ⁻⁷	3.91 (4)	-0.91	333.15
5.27 (25) × 10 ⁻⁶	1.08 (5) × 10 ⁻⁶	4.90 (7)	-1.1	343.15
1.45 (5) × 10 ⁻⁵	2.36 (2) × 10 ⁻⁶	6.23 (21)	-1.3	353.15
3.43 (3) × 10 ⁻⁵	5.01 (3) × 10 ⁻⁶	6.85 (16)	-1.4	363.15
7.36 (3) × 10 ⁻⁵	8.76 (20) × 10 ⁻⁵	8.39 (16)	-1.6	373.15

^a Values in parentheses are estimated standard deviations.^b Standard state concentration is 1.0 mol L⁻¹.¹²

tramolecular cyclometalation process vis-à-vis its intermolecular microscopic reverse.

Table I and Figure 1 summarize the results obtained by monitoring the relaxation to equilibrium of eq 4, starting with 5 and large quantities of SiMe₄.¹⁰ As implied by our earlier measurements of thoracyclobutane ring strain,⁹ we find that the intramolecular metalation is indeed driven by the production of entropy. The present analysis yields $\Delta H = 4.6$ (3)¹³ kcal mol⁻¹, in excellent agreement with our earlier calorimetric⁹ measurements of Th-C bond enthalpies which indicated that $\Delta H = 4.5$ (1.6) kcal mol⁻¹. Most noteworthy is the present result of $\Delta S = +16.6$ (5) eu, which is significantly less than anticipated by the usual physical models for such systems. For example, estimates based only on the increase in translational entropy from forming a new particle, comparable in mass to SiMe₄, suggest that ΔS for eq 4 could be as large as ca. 33 eu.¹⁴

Not only is ΔS for eq 4 less than might be anticipated from the approximate increase in translational entropy, but it also appears to differ significantly from ΔS for eq 3. Here, calorimetric measurements indicate that $\Delta H = 7.0$ (1.5) kcal mol⁻¹.⁹ Combining this result with the present observation that eq 3 is irreversible ($K > 75.1$ M) in neat neopentane at 60 °C,¹⁵ we estimate that ΔS must be ≥ 29 eu for eq 3. It is therefore evident that factors in addition to simple translational entropy contribute significantly to differences in ΔS for these cyclometalation processes. These factors for eq 3 and 4 could include differences in internal rotational entropy (arguable from solid-state structural^{16,17}

(10) These results¹¹ were obtained by monitoring the Cp' ¹H NMR signals of samples of Cp'₂ThCH₂SiMe₂CH₂ as they relaxed to equilibrium (eq 4) in 2–5 M solutions of SiMe₄ in C₆D₁₂. Spectra were recorded at appropriate intervals to afford data that could be fit via a least-squares algorithm to an integrated rate expression containing values for the forward and reverse rate constants. Equilibrium constants determined from the composition of the system at equilibrium and from the ratio of the rate constants agreed to within experimental limits. The values reported in Table I are ratios of rate constants. Least-squares fits resulted in r values ($r = [\sum(f_{\text{calcd}} - f_{\text{obsd}})^2 / \sum(f_{\text{obsd}})^2]^{1/2}$, where f is the extent of reaction) that ranged from 0.25% to 4.6%; the average $r = 2.8\%$. Two samples were prepared at each temperature, each with a different, precisely measured, concentration of SiMe₄. Corrections were applied for changes in volume due to temperature. The estimated standard deviations for rate constants are based on the range observed for the two measurements at each temperature. No sample required more than 1% of the total SiMe₄ present to reach equilibrium, so pseudo-first-order conditions hold for all experiments. All entropy and enthalpy values employ a 1.0 mol L⁻¹ standard state.¹²

(11) We note the agreement between data in Figure 1 and ΔH^*_{fwd} and ΔS^*_{fwd} , independently derived from a smaller data base in a different type of experiment.⁹

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(14) (a) This estimate is from the equation for translational entropy in an ideal gas (cf., the Sackur–Tetrode equation).^{14b} In applying this equation to an ideal solution, we take 1.0 L as the volume occupied by 1 mol of SiMe₄, to be consistent with a 1.0 mol L⁻¹ standard state. This reduces the calculated ΔS by 6 eu relative to a gaseous standard state of 1 atm. Estimates of ΔS for eq 3 and 4 are approximately equal. (b) McQuarrie, D. A. *Statistical Mechanics*; Harper & Row Publishers: New York, 1976; Chapters 5–8, pp 56, 86. (c) Comparable results are obtained in a treatment which also includes qualitative estimates of the changes in rotational and vibrational entropy.^{5b}

(15) At 60 °C, [CMe₄] = 7.51 M in neat neopentane.¹⁶ If our limit of detection is [Cp'₂ThCH₂CMe₂CH₂]/[Cp'₂Th(CH₂CMe₃)₂] = 10, a conservative estimate, then $K_{\text{eq}} \geq 75.1$ M which means $\Delta G \leq -2.86$ kcal mol⁻¹. Using $\Delta H = +7.0$ kcal mol⁻¹ from ref 9, then $\Delta S \geq 29$ eu. Ample time⁸ was allowed for equilibration.

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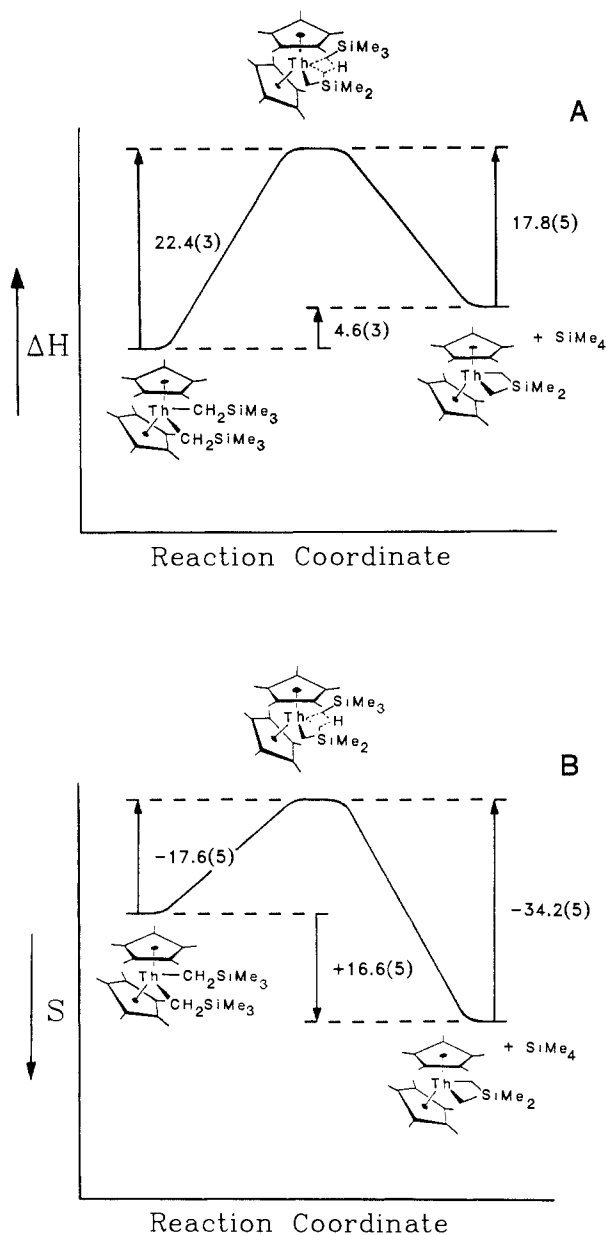


Figure 1. (A) Schematic reaction coordinate for eq 4 showing the change in enthalpy¹⁰ on going from thorium dialkyl through the transition state to the cyclometalated product. Enthalpy is increasing in the upward direction and all values are given in kilocalories per mole. (B) Schematic reaction coordinate for eq 4 showing the changes in entropy¹⁰ on going from thorium dialkyl through the transition state to the cyclometalated product. Entropy is increasing in the downward direction so that the change in entropy on going to the transition state is "uphill". All values are given in entropy units.

and bond enthalpy data⁹) as well as in bond stretching force constants and entropies of solution.

As can be seen in Figure 1, the present results also afford a kinetic picture of the intra- vs. intermolecular C–H activation pathways. We find that $\Delta H^*_{\text{rev}} = +17.8$ (5) kcal mol⁻¹ and, as demanded by ΔH , $\Delta H^*_{\text{fwd}} - \Delta H^*_{\text{rev}} = 4.6$ (5) kcal mol⁻¹. As noted previously,⁸ ΔS^*_{fwd} is surprisingly negative (although not unprecedented¹⁸) for an intramolecular process. Nevertheless, we now find that ΔS^*_{rev} is considerably more negative, reasonably

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reflecting the additional entropic cost of bringing two particles together¹⁸ and demonstrating that any intramolecular kinetic advantage resides in ΔS^\ddagger .

The present results provide a fairly detailed thermodynamic/kinetic picture of the reaction coordinate for eq 4. As found by Jones and Feher, the intramolecularly metalated product is thermodynamically more stable than the corresponding intermolecular product under the reaction conditions—for eq 4 because $T\Delta S > \Delta H > 0$. In addition, this study quantitates the change in entropy on releasing an alkyl silane from (or conversely for incorporating an alkyl silane into) a metal complex. This change in entropy, although smaller¹⁹ than predicted by simple physical models, is sufficient to drive the cyclometalation reaction and to overcome the ring strain in the product. As is the case for chelate ring formation,²⁰ the change in entropy upon cyclometalation is likely a complex composite of a number of factors.

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(19) Had we chosen neat alkyl silane as the standard state, ΔS would have been even smaller ($\Delta S_{\text{neat}} = \Delta S_{1M} - R \ln (C_{\text{neat}}/C_{1M}) = \Delta S_{1M} - 4.0$ eu, where C_{neat} and C_{1M} are concentrations).^{12b}

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"Diffusion-Controlled" Unimolecular Reactions and the Lifetime of a Strong Acid in Water

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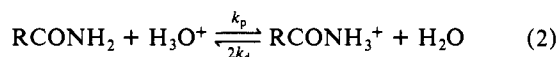
There is considerable uncertainty about the rate constant for a "diffusion-controlled" unimolecular reaction. For a bimolecular reaction the encounter rate can be calculated¹ in good agreement with experimental values.² When one of the reactants is the solvent, it does not need to diffuse to the other reactant, since it is already there. Consequently the reaction becomes formally first order. Several models have been proposed to treat this situation. In the most widely accepted, the reaction rate is considered to be limited by translational diffusion of two products, A and B, from each other. The rate constant is given³ by eq 1, where D

$$k = 4\pi Dr/V \quad (1)$$

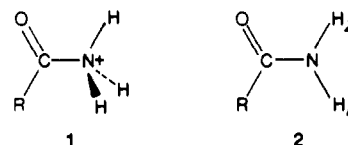
is the sum of the diffusion constants of A and B, r is the sum of their radii, and V is the volume of a spherical shell on the surface of one of the reactants. This leads to $k = 10^{10}$ or 10^{11} s⁻¹,⁴ but the value is too sensitive to the values assumed for r and V . An alternative model⁵ considers the rate to be limited by a rotational reorientation. From dielectric relaxation of the solvent the rate constant can then be estimated as 10^8 - 10^{12} s⁻¹. The simplest model⁶ is to multiply the second-order encounter rate constant

by the concentration of solvent or by an estimated "effective molarity" of solvent. This gives estimates for k ranging from 10^{10} to 10^{12} s⁻¹. Experimental values for proton-transfer reactions of HClO₄,⁷ H₃O⁺,⁸ OH⁻,⁸ and electronically excited 1-naphthol⁹ with solvent H₂O are 4.35×10^{13} , 6×10^{11} , 1.6×10^{11} , and 2.1×10^{10} s⁻¹, respectively. The first value is unreliable,¹⁰ since hydrogen-bond formation ("nonreactive" motion along the reaction coordinate) also broadens Raman lines, and the latter cases do not involve strongly exergonic proton transfers, required² for diffusion control. We now report that the rate constant for deprotonation of the strong acid RCONH₃⁺ is 6×10^{10} s⁻¹.

This first-order rate constant is $2k_d$, obtainable from the kinetics of acid-catalyzed proton exchange in primary amides (eq 2). (The



factor of 2 arises because there are two acidic protons in the preferred conformer, **1**, of the intermediate.) It is essential to use



a primary amide, **2**, with protons H_E and H_Z whose rates of exchange, k_E and k_Z , can be measured separately.¹¹ From Scheme I (eq 3, 4, and 7) of ref 11 it follows that $k_p[\text{H}_3\text{O}^+] = 2k_E - 1/2k_Z$. For acrylamide (**2**, R = CH₂=CH) at pH 1.9, $k_E = 49$ s⁻¹ and $k_Z = 33$ s⁻¹, so $k_p = 6.5 \times 10^3$ M⁻¹ s⁻¹. If $K_a (=2k_d/k_p)$, the acidity constant of RCONH₃⁺, were known, it would then be possible to evaluate k_d . From the thermodynamics of hydrolysis of acyltrialkylammonium ions, pK_a has been estimated¹² as -7.6, and this leads¹³ to $k_d \sim 10^{11}$ s⁻¹. However, this estimate has been criticized¹⁴ for neglecting solvation effects on RCONH₃⁺, and a pK_a of -1.8 (for methacrylamide) was proposed instead, corresponding to $k_d \sim 10^5$ s⁻¹. This is not obviously wrong, since proton transfer is often retarded¹³ when it is accompanied by electronic reorganization.

We have sought a more direct determination of $2k_d$. Fortunately this is possible because deprotonation of **1** competes¹¹ with rotation about its C-N single bond, and $2k_r$, the rate constant of this latter process, can be estimated independently. From Scheme I (eq 3, 4, and 7) of ref 11 it follows that $k_E/k_Z = 1 + k_d/2k_r$, so $k_d/k_r = 0.97$ for acrylamide.

For many years k_r was also uncertain. Rotation was assumed¹¹ to be fast, by analogy to methyl rotors on a double bond, where the rotational barrier is 1-2 kcal/mol,¹⁵ varying only slightly with substitution. The barrier in **1** itself is unknown, but two MO calculations¹⁶ on HCONH₃⁺ (**1**, R = H) give barriers of 1.3 and 1.08 kcal/mol. This latter is quite close^{16b} to the value of 1.14 kcal/mol calculated for HCOCH₃ with the same STO-3G basis. Therefore we might expect the barrier in **1** (R = CH₂=CH) to be 1.2 kcal/mol, as in the isoelectronic ketone.¹⁷ However, this estimate neglects solvation, and it is quite possible that solvation and hydrogen bonding greatly retard the rotation.¹⁸ Nevertheless, the rotational correlation time of aqueous NH₄⁺ was recently

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