

Carbon Acidity. 54. Kinetic Acidities of Cycloalkenes with Lithium Cyclohexylamide^{1,2}

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Abstract: Deuterioprotonation exchange rates are reported for cycloalkenes compared to benzene and toluene with lithium cyclohexylamide-*N-d* in cyclohexylamine-*N,N-d*₂. Relative rates at 50 °C uncorrected for statistical effects follow: cycloheptene, 1; cyclopentene, 0.063; cyclohexene, 0.193; cyclooctene, 0.206; benzene, 0.505; toluene, 119. The kinetic acidities of the cycloalkenes are compared with several theoretical models that include LCAO-MO SCF calculations at the STO-3G level and are interpreted in terms of the C=C-C-H dihedral angle, ease of rehybridizing the reactive carbon, and the allylic CCC angle. No one simple model suffices to explain all of the cycloalkene relative rates. Cyclohexene and cycloheptene are deduced to have equilibrium pKs on the CsCHA scale (pK_{CsCHA}) in the range from 44 to 46. An important source of error in deuterioprotonation kinetics is pointed out and a procedure is derived to correct for this error.

Allylic conjugation has a long and important history in organic chemistry, yet relatively few studies have been made of the stabilities of allylic anions. The placement of the carbon acidity of the allylic hydrogen on Cram's MSAD scale, for example, is based on rather qualitative evidence.³ Relative stabilities of allylic anions have been studied by metalation reactions,⁴ but more frequently as kinetic intermediates in base-catalyzed proton exchange and olefin isomerization studies in liquid ammonia,⁵ *tert*-butyl alcohol,⁶ or dimethyl sulfoxide⁷⁻⁹ media. Several kinetic studies suggest the sensitivity of the relative stabilities of allylic anions to conformation^{7a,7b,9} and this aspect has received recent theoretical attention.¹⁰ Because of their more fixed frameworks, cycloalkenes are more suited than acyclic olefins for studying conformational effects on relative stabilities of allylic anions; that is, the kinetic acidities of cycloalkenes are especially useful in this context. Only limited studies of this type are currently available.

Schriesheim et al.^{7a,b} showed, for example, that isomerization of the exocyclic double bond in various methylenecycloalkanes with potassium *tert*-butoxide-dimethyl sulfoxide (Me₂SO) parallels the enolization reactivity of related cycloalkanones. More recently, Tjan, Steinberg, and de Boer⁹ studied double bond migration in ¹⁴C-labeled cycloalkenes and also in potassium *tert*-butoxide-Me₂SO, and found the reactivity order cycloheptene > cyclohexene > cyclopentene. We note, however, that the interpretation of relative kinetic acidities in Me₂SO media is frequently complicated by internal return phenomena.¹¹

As part of our continuing program in the study of carbon acidities we have measured isotope exchange reactivities of allylic hydrogens of several cycloalkenes in the lithium cyclohexylamide (LiCHA)-cyclohexylamine (CHA) system. Internal return has been shown to be generally less important in this system¹² and a similarity of transition states to related benzylic systems could provide the first reliable estimates of cycloalkene pKs.¹³ The kinetics was followed by the incorporation of deuterium into the cycloalkene from cyclohexylamine-*N,N-d*₂.

Experimental Section

Materials. MCB spectroquality benzene and Aldrich Gold Label cyclopentene were used without further purification. Matheson cyclohexene and Aldrich cyclopentene and cyclooctene were chromatographed on a 10-ft DOW 710-Chromosorb W GLC column. Cyclohexylamine-*N,N-d*₂ (CHA-*d*₂) was prepared as described previously.¹²

Lithium Cyclohexylamide-*N-d* (LiCHA-*d*). After removal of the hexane from 1.5 mL of 2.3 M *n*-butyllithium solution by vacuum

transfer, 10 mL of dry CHA-*d*₂ was transferred to the butyllithium (at -196 °C) on a vacuum line. After warming to room temperature, the CHA-*d*₂ was removed in vacuo leaving a white solid, to which 60-70 mL of dry CHA-*d*₂ was added. The formal LiCHA-*d* concentration was found to be 0.58 M by titration.

Kinetics. The kinetic solutions were prepared in a cylindrical flask fitted with stopcock and standard taper joint. All manipulations were performed on a vacuum line or in a glove box to scrupulously exclude air and moisture. The cylindrical flask was filled with 35 mL of CHA-*d*₂, and 5-10 mmol of each of the hydrocarbons was transferred in on the vacuum line after drying over 4A molecular sieves. After 16 mL of stock LiCHA-*d* solution was added, the reaction solution was thoroughly mixed and syringed in 4-mL aliquots into ten reaction bulbs fitted with long necks and stopcocks. The bulbs were sealed and submerged in a 50 °C constant temperature bath. Kinetic points were obtained by removing a bulb and quenching the reaction with 1 mL of water. The quenched solutions were worked up by addition to 1.5 mL of decalin and ~20 mL of ice, followed by extraction of the CHA with 5 mL of concentrated hydrochloric acid. The resulting decalin solution was washed with water and dried over anhydrous magnesium sulfate. The hydrocarbons were separated by preparative VPC on a 10-ft DOW 710-Chromosorb W column and collected in bent capillary tubes suspended in a dry ice-2-propanol bath. The amount of deuterium incorporation in each of the hydrocarbon samples was analyzed by several scans on a CEC-21-130 or MS 12 mass spectrometer at low voltage (5-6 eV).

Determination of Base Concentration. Aliquots of 4 mL each of kinetic solution were quenched with 1-2 mL of water. After removal of the amine and water in vacuo, 10 mL of 0.1 N HCl was added and the solution was back-titrated with 0.1 N NaOH solution to a phenolphthalein end point. As a result of care taken in excluding moisture and air by use of vacuum and glove-box techniques, only traces of catalytically inactive lithium hydroxide are produced by adventitious moisture and the total base titre is only slightly larger than the catalytically active base present.¹⁴ The effect of traces of moisture on the rate constants has been shown to be insignificant.¹⁵ Finally, the base concentration was corrected for the presence of catalytically inactive LiCHA dimers, trimers, etc. The concentration of active LiCHA monomer is related to the formal base concentration, *c*, by the following equation using model 2:¹⁶

$$c = [\text{monomer}] \exp(K[\text{monomer}]) \quad (1)$$

where $K = 500/\text{mol}$.

Analysis of Kinetic Data. A modified integrated rate equation arises from the pseudo-first-order kinetics of the problem:

$$\ln [(\% D_0)_t / (\% D_0)_0] = -kt \quad (2)$$

By following the disappearance of undeuterated substrate we avoid complications associated with subsequent exchange reactions that lead to multiple deuteration. Only the first exchange is thus kinetically significant and pseudo-first-order kinetics is anticipated. The program LSKIN1¹⁷ was used to evaluate the rate constants. However, all of the

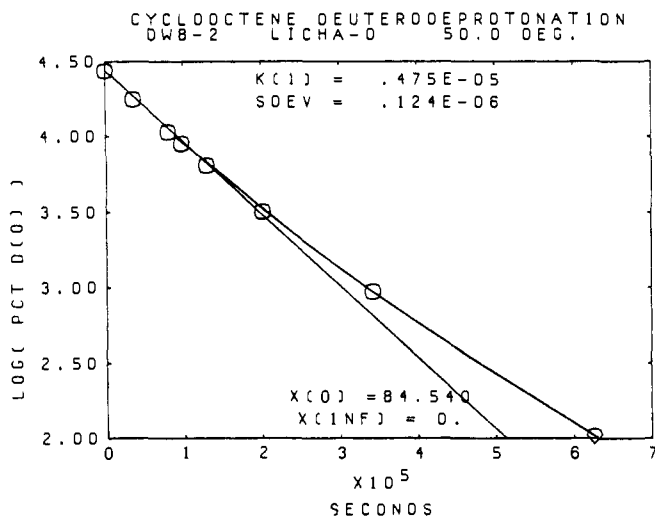


Figure 1. Example of simple pseudo-first-order behavior showing progressive deviation from linearity.

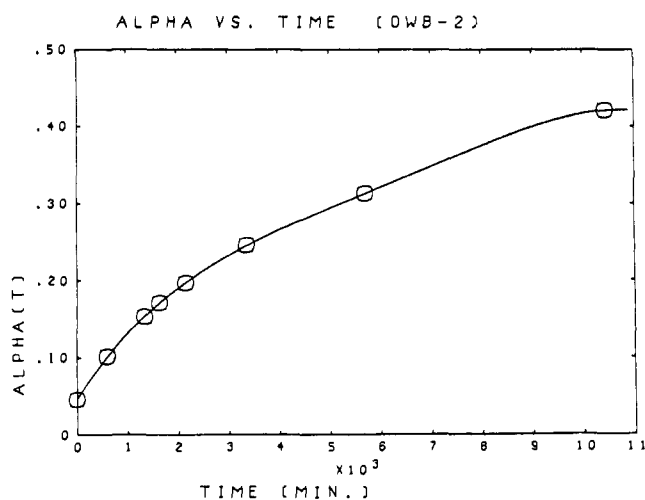
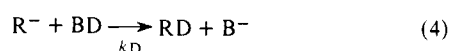
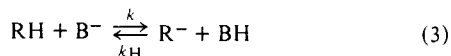


Figure 2. The 4th-order polynomial fitted to experimental points for α in kinetic run DWB-2.

kinetic plots from this simple treatment displayed systematic deviations from linearity after 2 half-lives of reaction. Figure 1 is an example of the typical behavior.

Serious errors in the rate constants (as large as 28%) result from such an oversimplified treatment. The method described above assumes that the deuterium pool in the solvent is infinite, whereas in reality the deuterium in the solvent changes by over 8% in a typical kinetic run. As the reaction progresses, the proton content in the solvent rises, and the probability increases that a proton removed will be replaced by another proton. With normal primary isotope effects, the resulting error can be especially serious. Although deuterio-deprotonation in deuterated solvents is a rather common experimental technique, this source of systematic error has apparently not been generally recognized. The following treatment produces a modified rate equation which corrects for this effect.

The equations for proton removal and deuterium incorporation



lead to a rate law equation for disappearance of undeuterated substrate:

$$-\frac{d[\text{RH}]}{dt} = k[\text{B}^-][\text{RH}] - k_{\text{H}}[\text{R}^-][\text{BH}] \quad (5)$$

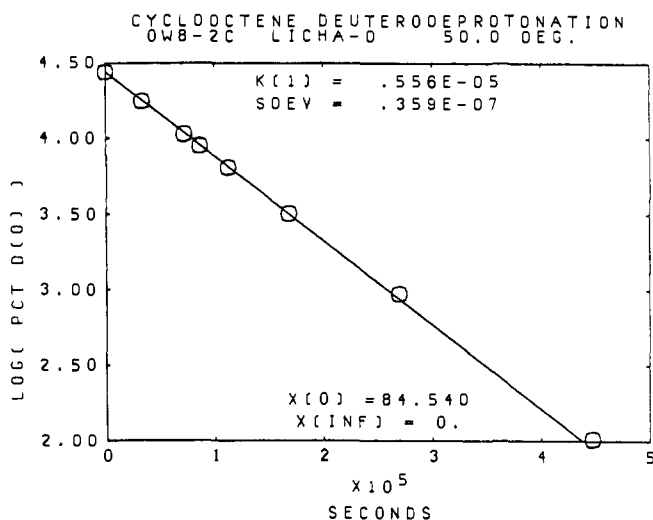


Figure 3. Examples of pseudo-first-order behavior after application of solvent correction.

Application of the steady-state approximation to the intermediate anion, R^- , yields

$$[\text{R}^-] = \frac{k[\text{B}^-][\text{RH}]}{k_{\text{H}}[\text{BH}] + k_{\text{D}}[\text{BD}]} \quad (6)$$

This may now be substituted into eq 5, and after rearrangement gives the expression

$$-d[\text{RH}]/dt = k[\text{B}^-][\text{RH}] \frac{1}{\lambda\rho + 1} \quad (7)$$

where $\lambda = k_{\text{H}}/k_{\text{D}}$ and $\rho = [\text{BH}]/[\text{BD}]$. Again considering that the base concentration is constant ($k' = k[\text{B}^-]$), eq 7 may be rewritten as

$$-d[\text{RH}]/dt = k'[\text{RH}](1 - \alpha) \quad (8)$$

where $\alpha = \lambda\rho/(\lambda\rho + 1)$. In this form, the equation may be integrated, yielding

$$\ln([\text{RH}]_0/[\text{RH}]_t) = k' \left(t - \int_0^t \alpha(t) dt \right) = k'\theta \quad (9)$$

Since ρ is changing throughout the course of the reaction, the correction factor to the simple first-order equation is not simply a constant. The integrand $\alpha(t)$ must, therefore, be numerically integrated for each time interval. The "corrected" time, θ , is then used for each of the kinetic points in a normal first-order treatment.

In the present case, the mass spectral peak data and the starting concentrations of CHA-d_2 and the olefins provide all of the information needed to obtain $\alpha(t)$. The constant λ is simply a primary isotope effect which has been assumed in our case to be 8. Although this isotope effect was not measured directly, it must be rather large in order to produce the observed deviations from first-order behavior. The value used is adopted from our work with toluene.¹² Reasonable variations in this value do not materially affect the final results. Finally, the ratio of hydrogen to deuterium in the solvent, ρ , can be obtained by the following equations:

$$[\text{BD}] = 2[\text{CHA-d}_2]f_0^{\text{D}} - \sum_g \sum_i f_{ig}^{\text{D}}[\text{R}_g\text{H}] \quad (10)$$

$$[\text{BH}] = 2[\text{CHA-d}_2](1 - f_0^{\text{D}}) + \sum_g \sum_i f_{ig}^{\text{D}}[\text{R}_g\text{H}] \quad (11)$$

where f_0^{D} is the fraction of deuterium in the solvent initially, f_{ig}^{D} is the fraction of olefin g with i deuteriums incorporated, and $[\text{R}_g\text{H}]$ is the starting concentration of olefin g . These equations permit evaluation of $\alpha(t)$ for all kinetic points. Although only the concentration of undeuterated substrate is required for application of the normal first-order expression, the concentrations of all deuterated species were required in order to evaluate the amount of protium in the deuterated solvent for use in the integral for the "corrected" time. In our work, $\alpha(t)$ and t from each kinetic run were fitted by least squares to a fourth-order polynomial (Figure 2). Integration of this equation provided the corrected time factors θ . The pseudo-first-order

Table I. Kinetic Conditions and Results (50 °C)

Compd	[CHA- <i>d</i> ₂] ₀	[RH] ₀	Formal [LiCHA- <i>d</i>]	Monomer [LiCHA- <i>d</i>] × 10 ³ from model 2 ^a	<i>k</i> _{exp} , s ⁻¹ × 10 ⁶ (initial) ^b	<i>k</i> ₁ , s ⁻¹ × 10 ⁶ (cor) ^c	% change in cor	<i>k</i> ₂ , mol ⁻¹ s ⁻¹ × 10 ⁴
Benzene ^d	8.325	0.116	0.0858	5.50	10.0 ± 0.1	11.2 ± 0.1	12	20.4
Cyclopentene ^d	8.325	0.134	0.0858	5.50	1.08 ₅ ± 0.02	1.31 ± 0.01	21	2.38
Cycloheptene ^d	8.325	0.122	0.0858	5.50	20.02 ± 0.5	22.2 ± 0.4	11	40.3
Cyclopentene ^e	8.169	0.175	0.166	6.48 ₅	1.41 ± 0.03	1.81 ± 0.02	28	2.79
Cyclohexene ^e	8.169	0.103	0.166	6.48 ₅	4.43 ± 0.09	5.22 ± 0.02	18	8.05
Cycloheptene ^e	8.169	0.104	0.166	6.48 ₅	24.6 ± 0.4	27.0 ± 0.1	10	41.6
Cyclooctene ^e	8.169	0.126	0.166	6.48 ₅	4.75 ± 0.1	5.56 ± 0.04	17	8.58
Benzene ^f	8.409	0.147	~0.028	3.9	5.7 ± 0.1	7.2 ± 0.2	27	
Toluene ^f	8.409	0.128	~0.028	3.9	1490 ± 40.	1700 ± 40.	14	

^a Reference 16. ^b Pseudo-first-order rate constant determined from the first few kinetic points before noticeable deviation from first-order behavior. ^c Corrected for depletion of deuterium from solvent, eq 9. ^d Run DWB1. ^e Run DWB2. ^f Run DWB5. The base titration in this run is not accurate.

approach, using θ instead of t , was then implemented with the program LSKINI.¹⁷

Application of the correction for deuterium depletion successfully eliminated the deviations from linearity in the kinetic plots. Linear plots resulted for all kinetic points involving up to 6 half-lives; Figure 3 is a typical example. Table I shows that the changes in the pseudo-first-order rate constants range from 10% to 28% depending on substrate and demonstrates that the correction is not trivial. In addition, the statistical quality of the results has been improved by the correction. The second-order rate constants for cycloheptene from two of the kinetic runs show agreement to within 3.2%.

Results and Discussion

Comparison with Other Reactions Involving Allyl Systems.

The relative rates of cycloalkene exchange found in the present work may be summarized as follows: C₅, 1; C₆, 3.1; C₇, 15.9; C₈, 3.3. The monotonic increase from C₅ to C₇ is reversed with cyclooctene, a rather unusual result which we will next explore. Only a few other systematic studies involving cycloalkenyl intermediates have been reported. Wiberg and Nakahira¹⁸ studied the formation of cycloalkenyl cation intermediates by solvolysis of the 3,5-dinitrobenzoates. Their results are compared to ours in Figure 4 and show no correlation at all. Both conformational and ring size effects may be involved. The substituted cycloalkenes may involve different conformational energies from the parent cycloalkenes. For example, greater eclipsing in the cyclopentenyl ester could account for at least part of its greater relative reactivity. The preference for a less reactive equatorial conformation could also contribute to establishing the series. Finally, the reduced angle of the cyclopentenyl cation and consequent aromatic cyclopropenyl cation character could also contribute (vide infra).

The base-catalyzed double bond isomerization studies of Tjan, Steinberg, and de Boer⁹ show the same order of reactivities as the present proton exchange reactions. Unfortunately, their series does not include cyclooctene so the reversal of a monotonic trend found in the present work cannot be compared. Although the trend for C₅, C₆, and C₇ is the same in both series, the actual relative rates differ. This difference could result from internal return differences or conformational differences in the two reactions; that is, the two reaction systems are clearly similar but not identical.

Conformational and Ring Size Effects. Several factors may be anticipated to contribute to the experimental reactivity order. The following effects may be expected to be of particular significance. (1) The C=C-C-H torsional angle; the more the C-H eclipses the adjacent p_r orbital, the greater the expected kinetic acidity. This factor was particularly emphasized by Tjan, Steinburg, and de Boer in interpreting their reactivity series.⁹ (2) The ease of rehybridization or coordination change to form the allylic anion. The conformational changes should

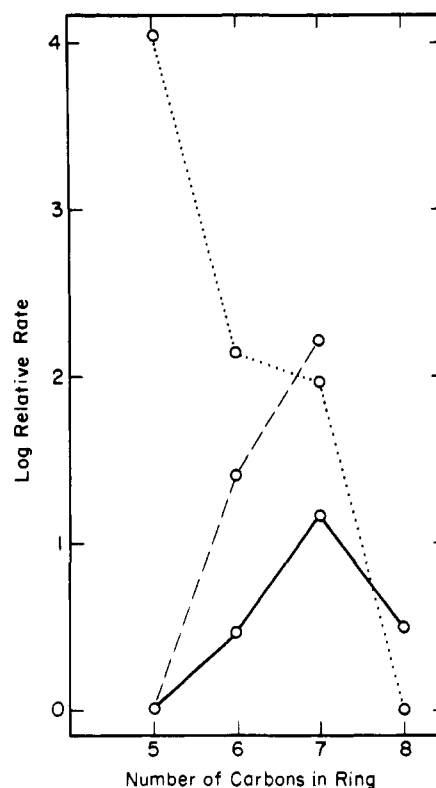


Figure 4. Comparison of several cycloalkenyl reactivities as a function of ring size: —, deuterium incorporation into cycloalkenes in CHA (this work); - - -, double bond isomerization with *t*-BuOK/Me₂SO (ref 9); ····, solvolysis of cycloalkenyl 3,5-dinitrobenzoates (ref 18).

be facilitated if the other CH and CC bonds in the allylic system already lie near the nodal plane of the π system in the starting olefin. (3) The magnitude of the C-C=C angle; our MO study¹⁰ gives a CCC bond angle in allyl anion of 132.5°, a value greater than that in normal alkenes. This factor should be particularly significant for smaller cycloalkenes. The last two factors are expected to be less serious in larger and more flexible systems.

In order to determine whether any one anticipated effect has a dominating importance that alone could account for the observed reactivity series, we now consider the results of some theoretical calculations. A complete theoretical treatment of the system is not practical. Instead, we considered several simplified models in which individual factors were isolated and emphasized. To facilitate this modeling a large body of geometrical data on the cycloalkenes is available. These structural data derive from NMR,¹⁹ IR-Raman,²⁰ microwave,^{21,22} and

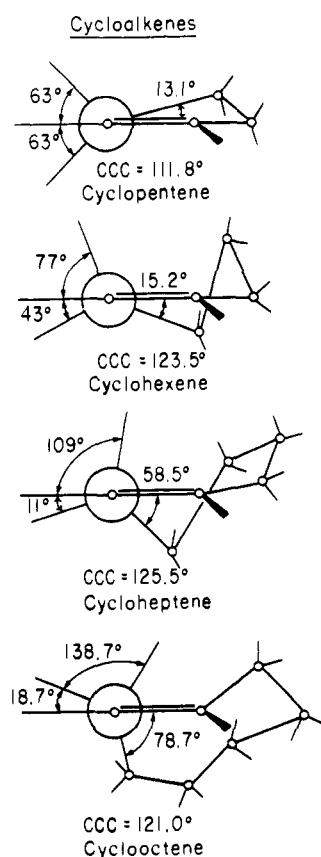
Table II. Geometries of Cycloalkenes and Propene Models^a

	CCC	α	β	γ
Cyclopentene	111.8° ^b (111.5° ^e , 111.0° ^f)	+63° ^c	-63° ^c	+13.1° ^{b,d} (13.0° ^{g,h})
Cyclohexene	123.5° ⁱ (124° ^{j,k}) (123.8° ^l)	+77° ^c (77.6° ^m)	-43° ^c (-42.4° ^m)	-15.2° ⁱ (-17.6° ^m)
Cycloheptene	125.5° ^b (124° ⁿ)	+109° ^c (107.8° ^m)	-11° ^c (-12.2° ^m)	-58.5° ^b (-72.2° ^m)
Cyclooctene	121° ^m (123° ^m)	+138.7° ^m (135° ^c)	+18.7° ^m (15° ^c)	-78.7° ^m (-83° ^b)

^a Values of angles used in calculations appear on the top line. Numbers in parentheses are other literature values. Plus sign means above nodal plane, minus means below (see Figure 5). Angles α , β , and γ are defined in Figure 6. ^b Reference 28. ^c Reference 19. ^d Calculated from ring pucker of 21.4° (ref 28). ^e Reference 21. ^f Reference 23. ^g Calculated from a ring pucker of 19° (ref 27). ^h Reference 27. ⁱ Reference 25. ^j Reference 30. ^k Reference 24. ^l Reference 22. ^m Reference 29. ⁿ Reference 20b.

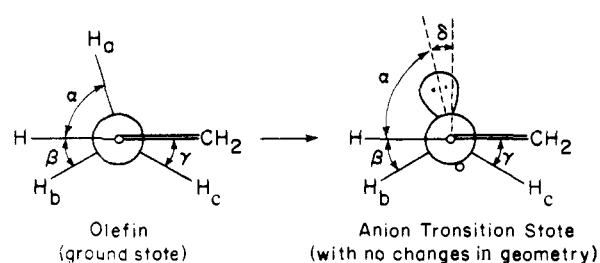
Table III. Total Energies and Energy Differences (Proton Affinities) (au) for Distorted Propenes and Propenyl Anions in Cycloalkene Conformations

	Propene fragment	Anion model I	Anion model II	Energy differences	
				Model I	Model II
Cyclopentene	-115.6411	-114.7899	-114.8088	0.8512	0.8323
Cyclohexene	-115.6580	-114.8195	-114.8259	0.8384	0.8320
Cycloheptene	-115.6525	-114.8153	-114.8272	0.8372	0.8253
Cyclooctene	-115.6561	-114.8015	-114.8237	0.8546	0.8325

**Figure 5.** Geometries used for cycloalkenes derived from force-field calculations (ref 27, 31).

electron diffraction²³⁻²⁵ studies, as well as force-field calculations.²⁶⁻³⁰ Some of the pertinent parameters are tabulated in Table II.

The first approach is based on an "early reaction" transition state. If we consider the transition state to be a small perturbation of the cycloalkene, we expect from the perturbation theory of a donor-acceptor reaction that the activation energy

**Figure 6.** Definitions of structural parameters for propylene and allyl anion to model cycloalkenyl systems.

should be related to the coefficient of the hydrogen being attacked in the lowest unoccupied MO (LUMO). Allinger's geometries^{27,31} (Figure 5) were used for CNDO/2 LCAO-SCF calculations³² of the cycloalkenes. The LUMO coefficients of the most favorable hydrogen for reaction are as follows: C₅, 0.244; C₆, 0.250; C₇, 0.215; C₈, 0.164. The corresponding reactivity order is C₆ > C₅ > C₇ > C₈. The trend with increasing ring size shows a reversal after C₆ rather than the experimental result of reversal after C₇.

We next consider transition state models based on complete proton transfer to form an allylic anion. CNDO calculations are known to be particularly inadequate in treating carbanions;³³ hence, we used ab initio SCF calculations at the STO-3G level³⁴ using the Gaussian 70 program.³⁵ Such calculations were not practical for the cycloalkenes and cycloalkenyl anions themselves so that the systems were modeled by propylene and allyl anion in appropriate geometries; that is, in this approach we consider a propylene distorted to conform to each cycloalkene in the allylic region of interest. Each such propylene is defined in terms of distortion of the methyl group with each hydrogen making a dihedral angle, α , β , and γ , as defined in Figure 6, and assigned the values of the corresponding cycloalkene summarized in Figure 5 and Table II. The model represents an improvement over that of the Dutch group⁹ by inclusion of the dihedral angle γ which corresponds to a C=C-C-C torsional angle in the cycloalkene. We next consider two models for the allylic anion. In model I the proton having a dihedral angle closest to 90° is removed with no other

geometric changes; the resulting pyramidal allylic anion corresponds approximately to an "early" transition state. Model II is a "rehybridized" planar anion with equal CC bonds taken as the mean of the single and double bond lengths and with the CCC angle of the starting olefin. The results of the calculations are summarized in Table III.

Neither model alone reflects the experimental pattern. In model I the calculated acidity order is $C_7 \sim C_6 > C_5 > C_8$. In model II, cyclopentene, cyclohexene, and cyclooctene are calculated to have comparable acidities with cycloheptene being much more acidic.

We conclude that all of the various effects expected to contribute significantly are indeed of comparable importance and that no one simple model is satisfactory.

Equilibrium Acidity of Cycloalkenes. Conversion of kinetic acidities to equilibrium acidities requires the establishment of a valid Brønsted linear free energy relationship. No such relationship has been established for systems closely related to cycloalkenes. The closest established correlation is that for arylmethyl systems such as toluene, diphenylmethane, etc.¹³ The Brønsted correlation between kinetic acidities toward LiCHA and equilibrium ion pair acidities with CsCHA (pK_{CsCHA})² has a slope of 0.314 and implies a transition state for proton transfer with a pyramidal carbon and only partial conjugation to the aryl π system. As discussed above, the allylic systems appear to involve a similar type of proton transfer transition state with LiCHA. We might expect, therefore, that the same correlation would apply to propylene itself. Experiments with propylene are currently in progress and will be reported subsequently. The cycloalkenes, however, involve reaction at an alkyl-substituted secondary position and are not expected to follow the same Brønsted relation. Ethylbenzene is 0.12 as reactive as toluene toward LiCHA³⁶ although the equilibrium acidities of both toward CsCHA are comparable.³⁷ We expect the methylene group of ethylbenzene to be a more appropriate reference for the methylene groups of cycloalkenes but, because of conformational restraints, it is unlikely that all of the cycloalkenes would fit a common Brønsted relation; that is, the analysis of the preceding section suggests that the equilibrium acidity order of the cycloalkenes is probably *not* the same as the kinetic acidity order. The varying C=C-C-H dihedral angle provides the greatest difficulty but should be of least importance in cyclohexene and cycloheptene for which these angles differ from 90° by 13 and 19°, respectively. The statistically corrected relative rates³⁸ follow: ethylbenzene, 1; cyclohexene, 0.020; cycloheptene, 0.10. This series was derived from the data in Table I for deuteriodeprotonation of toluene and cycloalkenes and the relative rate of ethylbenzene to toluene of 0.12 for protodeuteration.³⁶ Note the implied assumption that the isotope effects involved are the same for toluene and ethylbenzene. The pK_{CsCHA} of toluene is 41.2^{13,37} and that for ethylbenzene is expected to be about 40.9.³⁷ If the same Brønsted slope of 0.314 (vide supra) applies to conjugated methylene groups the pK_{CsCHA} values for cyclohexene and cycloheptene are then deduced to be about 46 and 44, respectively. Note that these values are higher than the pK_{CsCHA} value of 43 found previously for benzene³⁹ even though the cycloalkenes have kinetic acidities comparable to benzene (Table I). The discrepancy means that either the LiCHA exchange reactions have substantially different Brønsted correlations or that the pK_{CsCHA} values for cyclohexene and cycloheptene are approximately 43 and that the above comparison with ethylbenzene is incorrect. Another factor that has not been explored sufficiently in this connection is the possible

difference in ion pairs involved. The cesium salts of carbanions are all contact ion pairs whereas lithium apparently tends to form solvent-separated or loose ion pairs with delocalized carbanions and contact or tight ion pairs with localized carbanions.

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