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Kinetics of Carbenium Ion Additions to Methylenecycloalkanes: Cycloalkyl Cation Stabilities Are Not Predominantly Controlled by Strain

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Kinetic investigations of the reactions of the (*p*-anisyl)phenylcarbenium tetrachloroborate (1 BCl_4^-) with methylenecycloalkanes (ring size 3–12 and 15) have been performed. The second-order rate constants correlate with the solvolysis rates of the corresponding cycloalkyl derivatives, though none of the ring carbons is rehybridized in the rate-determining step (electrophilic attack of 1 at the CC double bond). A simple explanation for the observed rate effects cannot be given, and it is claimed that the common rationalization of cycloalkyl solvolysis rates by differences of internal strain has to be modified.

Introduction

In 1952, Brown reported the solvolysis rate constants of 1-chloro-1-methylcycloalkanes to be strongly dependent on ring size (Figure 1).[1] The reactivity maxima for the five- and eight-membered rings and the reactivity minimum for the six-membered ring were explained by the change of internal strain during rehybridization of a ring carbon from sp^3 to sp^2. This interpretation seemed to be widely accepted, when Pock and Mayr reported competition experiments which showed that methylenecyclopentane is 50 times more reactive toward diarylcarbenium ions than methylenecyclohexane.[2] The reactivity order of the addition reactions was thus similar to that observed for cycloalkyl solvolyses, though none of the ring carbons is rehybridized in the rate-determining step. In order to examine whether the coincidence of relative rates for these three compounds is accidental or whether there is a general relationship between these two types of reaction, we have now investigated the reactivities of an extended series of methylenecycloalkanes (ring size 3–12, 15) toward the (*p*-anisyl)phenylcarbenium ion [(p-$MeOC_6H_4$)$PhCH^+$] which has previously been used as a reference electrophile for comparing nucleophilicities of alkenes.[3–6]

Methods

p-Methoxybenzhydryl chloride is completely ionized when added to a solution of BCl_3 in CH_2Cl_2 and gives a colored solution of 1 BCl_4^-, as described previously.[3] This solution is completely decolorized upon addition of the methylenecycloalkanes **R3–R15**, and the second-order rate constants for these reactions, which proceed via rate determining attack of 1 at the methylenecycloalkanes (Scheme 1), can be determined photometrically as described before.[3]

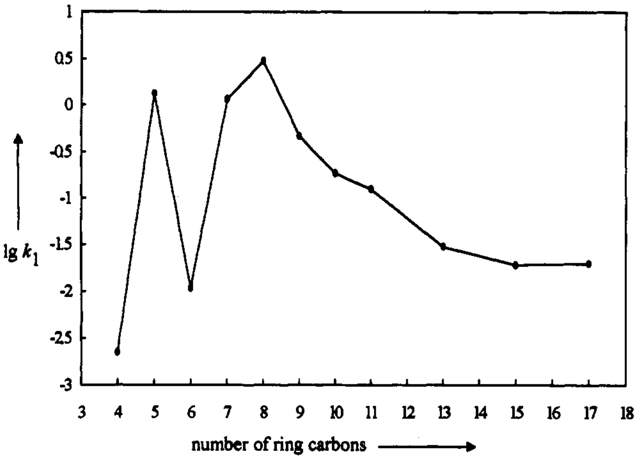

Figure 1. Effect of ring size on the solvolysis rates of 1-chloro-1-methylcycloalkanes (80% aqueous EtOH, 25 °C).[1]

Results

Product studies show that the adducts **P4–P15** are produced in almost quantitative yield when the methylenecycloalkanes **R4–R15** are combined with 1 BCl_4^- in dichloromethane at −78 °C. A full characterization of the products is given in the supplementary material. In analogy to the corresponding solvolytic reactions, a ring-opening reaction[7] takes place when methylenecyclopropane (**R3**) is attacked by the carbenium ion 1, and the allylic chloride **P3** is isolated instead of a cyclopropyl derivative.

The rate constants determined in this work (Table 1, Figure 2), which show reactivity maxima for the five- and eight-membered ring, are in qualitative agreement with the reactivity pattern observed for solvolysis reactions of 1-chloro-1-methylcycloalkanes in 80% ethanol (Figure 1). Table 2 shows that the directly measured rate constants are in good agreement with the results of competition

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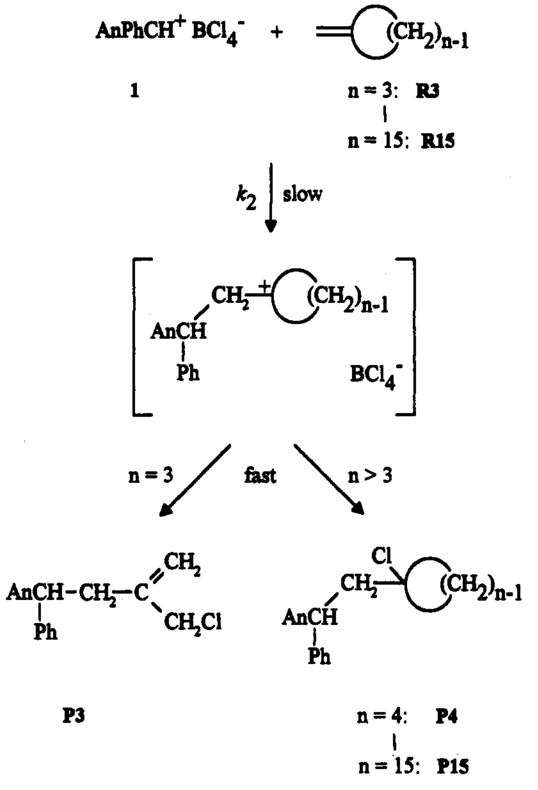
Table 1. Rate Constants (−70 °C) and Activation Parameters for the Reactions of (p-Anisyl)phenylcarbenium Tetrachloroborate with Methylenecycloalkanes in CH_2Cl_2

alkene	k_2, L mol^{-1} s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J mol^{-1} K^{-1}	T, °C
R3	0.12			−70
R4	40.1	20.6 ± 0.3	−110 ± 1	−70 to −20
R5	1750	11.6 ± 0.4	−123 ± 2	−70 to −20
R6	46.9	19.8 ± 0.1	−112 ± 1	−70 to −20
R7	425	14.2 ± 0.1	−121 ± 1	−70 to −20
R8	5085	11.2 ± 0.3	−116 ± 2	−80 to −50
R9	1598	10.7 ± 0.1	−128 ± 1	−70 to −30
R10	2260	11.7 ± 0.3	−120 ± 1	−70 to −30
R11	783	12.0 ± 0.2	−127 ± 1	−70 to −30
R12	133	12.5 ± 0.3	−139 ± 1	−70 to −20
R15	88.4	16.7 ± 0.1	−122 ± 1	−70 to −20
2-methyl-1-pentene	25.8	19.5 ± 1.2	−119 ± 6	−70 to −30

Scheme 1



experiments performed with the bis(p-methylphenyl)carbenium ion (Tol_2CH^+) several years ago.[2]

Discussion

Table 1 shows that the observed reactivity order reflects a complex interplay between enthalpic and entropic effects. For the methylenecycloalkanes with $n = 4$–7, both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are variable, but the differences in $\Delta H^{\ddagger}$ are more pronounced. In contrast, the reactivity differences of the medium-size rings ($n = 8$–12) are predominantly due to entropic effects. We do not have an explanation for the regular alternation of $\Delta S^{\ddagger}$ for $n = 4$–11 (Figure 3).

While comparison of the plots shown in Figures 1 and 2 suggests a close relationship between solvolysis rates of cycloalkyl derivatives and addition rates to methylenecycloalkanes, the correlation in Figure 4 is only of moderate quality ($r = 0.89$). We stress this point since plots as shown in Figures 1 and 2 have often been employed for comparing cycloalkane reactivities.

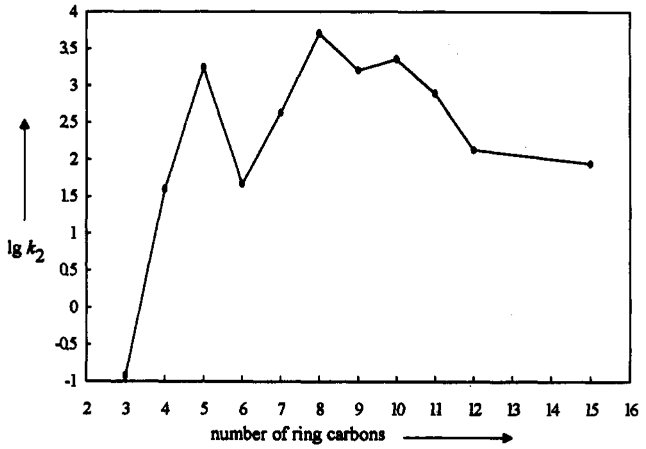
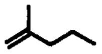
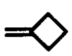
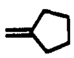
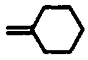


Figure 2. Second-order rate constants for the reactions of methylenecycloalkanes with 1 BCl_4^- as a function of ring size (CH_2Cl_2, −70 °C).

Table 2

	k_{rel}[a] (Tol_2CH^+)	k_{rel}[b] ($AnPhCH^+$)
	1.00	1.00
	1.86	1.54
	95.1	67.8
	1.91	1.81

[a] From competition experiments, ref 2. [b] Direct rate measurements, this work.

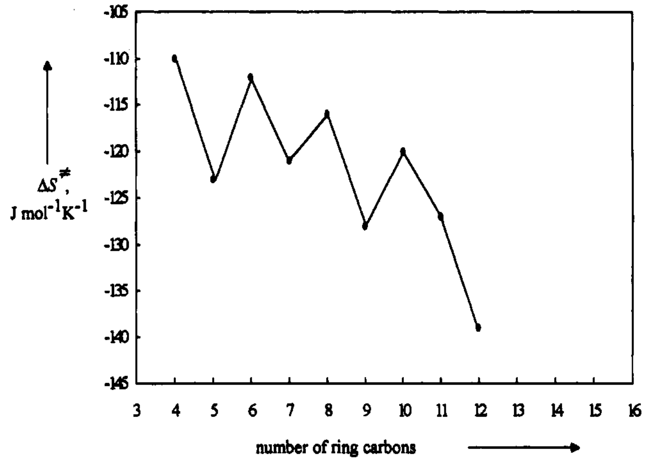


Figure 3. Activation entropy for the reactions of 1 BCl_4^- with methylenecycloalkanes as a function of ring size.

Since changes of strain had been suggested to account for the different rates of cycloalkyl solvolyses, one has to consider whether changes of strain can also account for the different reactivities of the methylenecycloalkanes. As discussed in the Introduction, this explanation appeared improbable to us since in the rate-determining step of the addition reaction the hybridization of the ring carbons is not altered.

In order to exclude the possibility that rehybridization of the exocyclic carbon was responsible for the different reaction rates of methylenecycloalkanes, we have performed force field calculations (PIMM88)[8] of the methylenecycloalkanes R4–R10 and the corresponding 1-meth-

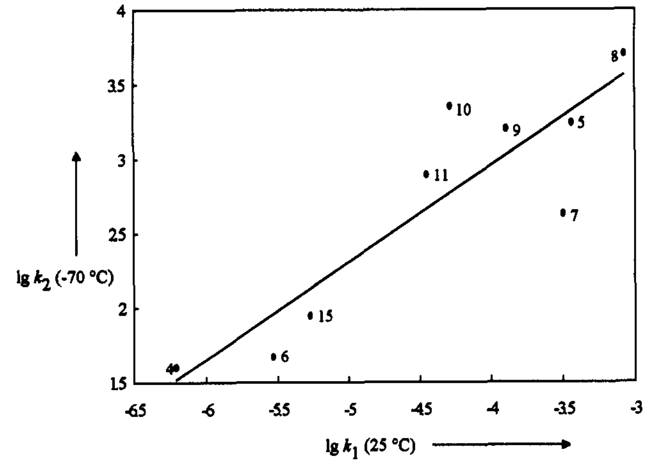


Figure 4. Correlation between the rate constants of the addition of 1 BCl_4^- to methylenecycloalkanes (CH_2Cl_2, −70 °C) and the solvolysis rate constants of 1-chloro-1-methylcycloalkanes (80% aqueous EtOH, 25 °C)[1] [$m = 0.65$, $r = 0.89$].

ylcycloalkyl cations assuming the same force constants for the sp^2-hybridized ring carbon in methylenecycloalkanes and in methylcycloalkyl cations. While protonation was calculated to cause identical enthalpy changes for the compounds with $n = 6$–10, the protonations of methylenecyclopentane **R5** and methylenecyclobutane **R4** were calculated to be 4 and 10 kJ·mol^{-1} less exothermic, respectively. Thus, as intuitively expected, no correlation between methylenecycloalkane reactivities and calculated changes of strain between methylenecycloalkanes and their protonated analogues was found.[9]

There is also no correlation between the calculated ionization potentials (MINDO/3 and AM1) of **R5**–**R8** and the reaction rates of **R5**–**R8** toward **1**, in accord with previous observations that the rates of carbenium additions toward alkenes do not correlate with the ionization potentials of the olefins.[2,4,6]

We had observed a good correlation between the reactivities of alkenes, dienes, and allylsilanes toward benzhydryl cations and the solvolysis rates of those alkyl chlorides that give the same types of carbenium intermediates,[4,10] however, and concluded that the relative reactivities of π-systems toward benzhydryl cations are controlled by the relative stabilities of the carbenium ions produced during electrophilic attack. By analogy, we now infer that the relative reactivities of the methylenecycloalkanes also reflect the relative stabilities of the corresponding cycloalkyl cations. For 1-ferrocenylcycloalkyl cations, a relationship between solvolysis rates and thermodynamic stabilities of the carbenium ions had been demonstrated by Ortaggi (Figure 5).[11]

The correlation between the rates of electrophilic additions to methylenecycloalkanes and cycloalkyl solvolysis rates (Figure 4) raises the question whether the differences in solvolysis rates are really caused by variable changes of strain and not by the same factors that control the relative reactivities of the methylenecycloalkanes.

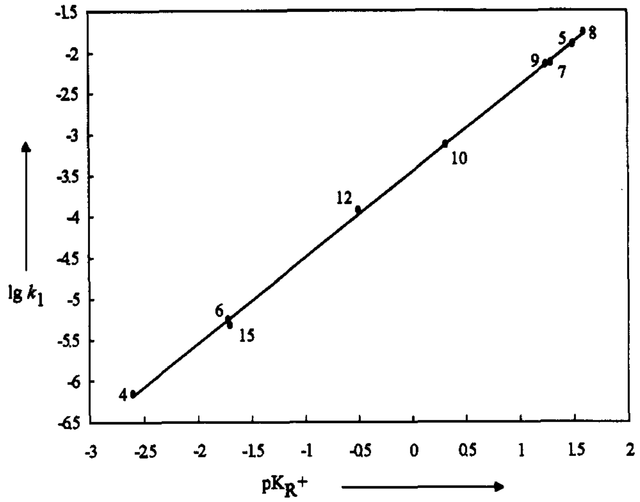
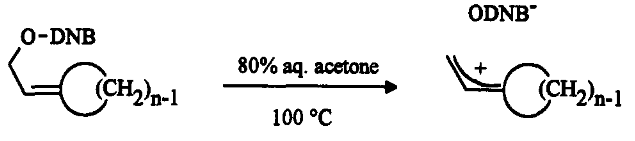


Figure 5. Correlation between the rates of the solvolyses of ferrocenyl cycloalkylacetates (aqueous H_2SO_4, 25 °C) and the pK_{R^+} values of the corresponding carbocations[11] [$m = 1.05$, $r = 0.999$].

Scheme 2



n	4	5	6	7
k_{rel}	1.0	13.7	2.7	5.3

Already in 1956 the limitations of the I-strain theory have been stressed by Brown, when the poor correlation between the ethanolysis rates of 1-methylcycloalkyl chlorides and the rates of BH_4^- reductions of cycloalkanones was noted.[13–15]

Another important argument against the dominating role of strain was Richey's report that the solvolysis rates of the allyl dinitrobenzoates depicted in Scheme 2 show a similar dependence on ring size as the cycloalkyl solvolyses, though none of the ring carbons becomes rehybridized in the rate-determining step.[12]

In spite of these discrepancies, the application of the I-strain theory has been continued,[16] and force field calculations even seemed to provide a quantitative basis for this theory. Schneider reported that cycloalkyl tosylate solvolyses in trifluoroethanol (TFE) and hexafluoro-2-propanol (HFIP), but not in ethanol, correlate with the calculated differences in strain energy.[17–19] Remarkably,

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(9) One of the reviewers has questioned the appropriateness of force field calculations to explain small differences of reactivity. This point is well taken, but it also questions the significance of the correlations in Figures 6 and 7 which provide the basis for the I-strain theory of cycloalkyl solvolyses. It does not affect the essential conclusions of this work, however, which are exclusively based on correlations between experimental data (Figure 4).

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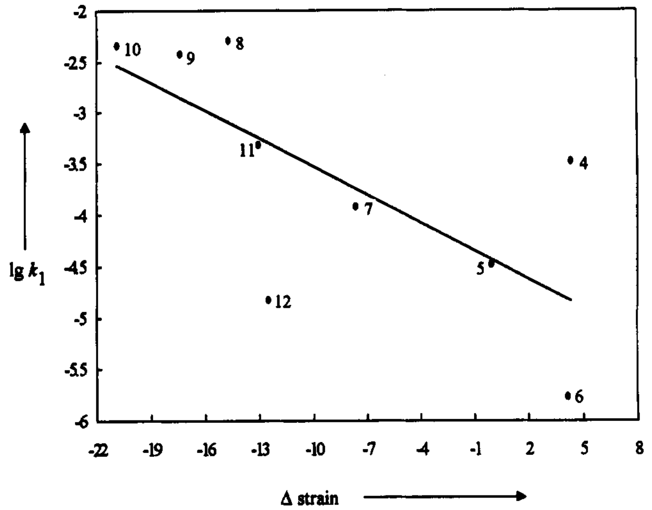

Figure 6. Correlation between the solvolysis rate constants of cycloalkyl tosylates (TFE, 25 °C)[18] and the differences in strain energies (cycloalkanones–methylcycloalkanes),[19] kJ/mol [$(2.303RT)m = -0.52$, $r = 0.70$].

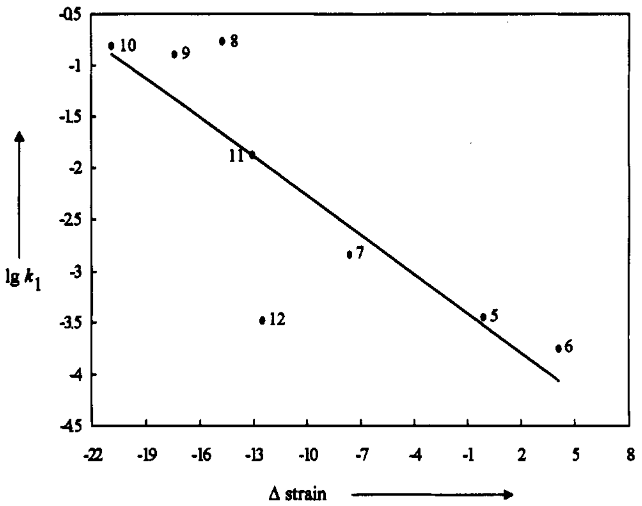

Figure 7. Correlation between the solvolysis rate constants of cycloalkyl tosylates (HFIP, 25 °C) and the differences in strain energies (cycloalkanones–methylcycloalkanes),[19] kJ/mol [$(2.303RT)m = -0.72$, $r = 0.84$].

the unusual high reactivity of the cyclopentyl compound, the starting point of Brown's qualitative I-strain theory, has not been observed in the fluorinated alcohols. This is surprising, since in solvolyses (80% acetone) of 1-(arylcycloalkyl)-*p*-nitrobenzoates (ring size 4–8) reactivity maxima have also been found for the five- and eight-membered rings,[20] though for these compounds nucleophilic solvent participation cannot play a dominant role.

Correlations of high quality between rates of cycloalkyl solvolyses and differences in strain ($r = 0.96$, 7 points, TFE;[18] $r = 0.96$, 7 points, HFIP[19]) have been obtained when certain ring systems were eliminated. Figures 6 and 7 show, however, that the correlations give r values of 0.70 (9 points, TFE) and 0.84 (8 points, HFIP) when all available data are considered. These correlations are, therefore, worse than the correlation between solvolysis rate constants and the rates of electrophilic additions to methylenecycloalkanes (Figure 4) which are not controlled by strain (see also ref 9).

Strain effects may, therefore, account for part of the reactivity differences of cycloalkyl derivatives, but other factors (e.g., ring size dependent hyperconjugative effects or transannular hydride bridging[14,21]) that stabilize the intermediate cycloalkyl cations must be at least equally important.

Conclusion

While the correlation between strain effects and rate as well as equilibrium constants for nucleophile additions to cycloalkanones is well substantiated,[22,23] variable strain effects are not the *major* reason for the differences of cycloalkyl solvolysis rates. The correlation between cycloalkyl solvolysis rates and electrophilic additions to methylenecycloalkanes (Figure 4) stresses the importance of electronic effects. Since a complex interplay of enthalpic and entropic factors was found to be responsible for the relative reactivities of methylenecycloalkanes, an analysis of cycloalkyl solvolyses that is based solely on strain enthalpies appears to be too simplistic.

Experimental Section

Details of the kinetic procedure and preparation of the carbenium ion precursors have been published elsewhere.[3] The methylenecycloalkanes have been synthesized from the cycloalkanones according to a modified procedure of Takai (for details see supplementary material).[24]

Addition Products P3–P15. Three equiv of **R3–R15** was added dropwise to a colored solution of 1 equiv of 1 BCl_4^- in CH_2Cl_2 (100 mL) at −78 °C. The mixture was allowed to stand at −78 °C until it was completely decolorized (approximately 2 h). The mixture was washed with concentrated hydrochloric acid and dried over $MgSO_4$. The solvent was evaporated, and the remaining colorless oil was filtered over neutral alumina before recrystallization from EtOH.

Acknowledgment. We thank Prof. A. Maercker for bringing this problem to our attention, Monika Deters for experimental assistance, Prof. H.-J. Schneider for critical comments, Prof. H. J. Lindner for providing his force field programs, and the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie for financial support.

Supplementary Material Available: Data tables containing concentrations, rate constants, and activation parameters of the kinetic experiments, experimental procedures for **R7–R15**, and full characterization of **R7–R15** and **P3–P15** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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