An Interpretation of Kinetic Data for Cyclopropyl-assisted Solvolysis in a 3-Bicyclo[3.1.0]hexyl System Using Spectroscopic Information

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Analysis of the kinetics of cyclopropyl-assisted solvolysis in a 3-bicyclo[3.1.0]hexyl system using far-IR and microwave spectroscopic information indicates that the reaction occurs in a highly excited vibrational state in which the molecule briefly has a chair-like conformation.

The cyclopropyl-assisted reaction may go through a possible intermediate trishomocyclopropenyl cation. The spectroscopic data give an estimated value for the relative rate of reaction for the chair conformation \(k_{\text{chair}}/k_{\text{obs}}\). The calculated \(k_{\text{chair}}\) agrees well with observed rates of cyclopropyl-assisted solvolysis in rigid 3-bicyclo[3.1.0]hexyl systems.

Extensive NMR, 1,4,12 UV, 1,14 far-IR, 15,16 Raman, 17 and microwave 18-22 spectroscopic investigations have shown that in bicyclo[3.1.0]hexane systems the most stable conformations are boat-like forms. X-Ray crystallographic structure determinations of a few bicyclo[3.1.0]hexane derivatives also show boat-like conformations 14-22 and additional support is given by dipole moment studies. 27 A knowledge of the conformations of bicyclo[3.1.0]hexane derivatives is important for the interpretation of kinetic data on rearrangement reactions 4,7,28 and of chiro-optical data provided by conjugated cyclopropyl chromophores in these systems. 14

In this communication we wish to discuss the significance of conformational changes for the kinetics of cyclopropyl-assisted solvolysis in 3-bicyclo[3.1.0]hexyl systems. This discussion is based on spectroscopic results and especially on recent far-IR and microwave spectroscopic studies on bicyclo[3.1.0]hexane 18,21 and some related compounds. 15-20,22,23

In bicyclo[3.1.0]hexane systems, in contrast to cyclohexane derivatives, the boat conformation leads to the preferred staggered arrangement of C(1) - C(2) and C(4) - C(5) bonds (cf. Fig. 1). In the chair conformation these bonds possess an eclipsed arrangement.

The rate of the cyclopropyl-assisted solvolysis of cis-3-bicyclo[3.1.0]hexyl tosylate 18 (1, \(X = p\)-toluenesulfonate, OTs) is very low compared with the rates of other cyclopropyl-assisted reactions, e.g. the solvolysis of the tricyclic homologue (3, \(X = p\)-nitrobenzozate). 20-22 In order to explain the low rate of solvolysis of 1, Weinstein et al. 4,7,28 suggested that cis-3-bicyclo[3.1.0]hexyl tosylate exists mainly in a boat-like conformation (1a) while the reaction takes place primarily from a chair-like conformation (1b) by a cyclopropyl-assisted ionization to form a trishomocyclopropenyl cation (2).

![Fig. 1.](image)
The ring-bending motion usually has a large amplitude even in the ground vibrational state. Amplitudes of vibration in different states of 3-bicyclo[3.1.0]hexanone have been estimated in terms of the angle $\phi$. In higher vibrational states the large amplitude of the ring-bending motion will cause the molecule to pass through a chair-like conformation, with $\phi$ less than approximately $-20^\circ$, for a short period in the vibrational cycle.

It is well-known that a vibration associated with a heavy group (large reduced mass) will result in a closer spacing of the vibrational levels than in one with a lighter group. Far-IR results$^{14,16}$ are in agreement with this conclusion. A heavy substituent on C(3), such as a p-toluenesulfonate group, will accordingly result in very low-lying vibrational states.

In the light of the discussion above we prefer to consider the ionization process of cis-3-bicyclo[3.1.0]hexyl tosylate (I) as occurring in a highly excited vibrational state in which the molecule for a short moment has a chair-like conformation. From these assumptions we can make a qualitative estimate of the rate of reaction, $k_{\text{obs}}$, in terms of $k_{\text{chair}}$.

The assisted solvolysis is possible only if the molecule is in or above a vibrational state $n$, which is the lowest state in which the molecule for a short moment can go over to a chair conformation. In order to simplify the calculation of the probability for a molecule to be in a state $j \geq n$, the potential function is approximated as a harmonic one. The probability is then

$$P(j \geq n) = \exp[-n\hbar\nu(RT)^{-1}]$$

in which $\nu$ is the fundamental ring-bending vibration frequency.

The product $n\hbar\nu = (E_n - (1/2)\hbar\nu)$ for several bicyclohexanes, calculated with $n$ as the first vibrational state above the inflection or the second minimum point of the potential curve (cf. Fig. 2), is relatively constant and varies only between 13 and 19 kJ mol$^{-1}$. This energy, $\Delta E$, can be considered as the energy above ground state of the lowest vibrational state in which a chair conformation occurs. The prob

$^*$ Bicyclo[3.1.0]hexane, 3-oxabicyclo[3.1.0]hexane, 6-oxabicyclo[3.1.0]hexane, 3,6-dioxabicyclo[3.1.0]hexane, and 3-bicyclo[3.1.0]hexanone.

Fig. 2. A typical ring-bending potential function for a bicyclo[3.1.0]hexyl system.

The ratio $k_{obs}/k_{chair}$ is equal to $[1b]/[1a] + [1b] = [1b]/[1a]$. The chair conformation (1b) will react faster than equilibrium can be attained. As long as $k_{-1}$ is unknown it is, however, reasonable to adopt the approximation of Wainstein et al.\textsuperscript{47} that the ratio $[1b]/[1a]$ does not differ very much from that at equilibrium. From the known values\textsuperscript{48} $\Delta H^\# = 101$ kJ mol$^{-1}$ and $\Delta S^\# = -21$ J K$^{-1}$ mol$^{-1}$ we may calculate $k_{obs} = 1.1 \times 10^{-4}$ s$^{-1}$ at 25°C. Finally, from the value of $P$ (chair) calculated above, we get $k_{chair} = 0.001$ to 0.03 s$^{-1}$.

The value 0.001 s$^{-1}$ of $k_{chair}$ can probably be regarded as a lower limit. A vibration of larger amplitude in a state of higher energy than that assumed, $n$, might be required for successful trapping of the molecule. In such a case the calculations above would give a higher value of $k_{chair}$.

Some rigid systems with quite large negative values of the angle $\phi$ (e.g. 3, 4 and 5) show high values for the rate of solvolysis.\textsuperscript{49,50} The solvolytic reactivities of these rigid systems can now be compared with the calculated rate of solvolysis from a chair conformation of 1 ($k_{chair}$). The relative rate for the chair conformation is of the same order of magnitude as those of the rigid systems 3, 4 and 5 as shown in Table 1. This interpretation is in agreement with the higher rate of solvolysis of the compound 3, which has a large negative value of the angle $\phi$.

This discussion has been concerned with the solvolysis of cis-3-bicyclo[3.1.0]hexyl tosylate.

| Table 1. Relative solvolysis rates of some 3-bicyclo[3.1.0]hexyl systems.\textsuperscript{a} |
|---|---|---|---|---|
|  | Temp. of solvolysis (°C) | $k_{ib}/k_1$ | $k_{a}/k_1$ | $k_{b}/k_1$ | $k_{c}/k_1$ |
|  | × 10$^{-4}$ | × 10$^{-4}$ | × 10$^{-4}$ | × 10$^{-4}$ |
| 1  | 25$^b$ | 0.1 - 2.5 | - | 0.11 | - |
|  | 100$^c$ | 0.03 - 0.5 | 36 | - | 1.2 |

\textsuperscript{a} In this table $k_1$ refers to the observed rate constant of solvolysis for compound 1, $k_2$ is the observed rate constant for compound 3, etc. $k_{ib, calc}$ is equal to the calculated value of $k_{chair}$.\textsuperscript{b} In AcOH. \textsuperscript{c} In 70% aqueous dioxane solvent.

It has been based on potential functions for the ring-bending of some bicyclo[3.1.0]hexane derivatives. The potential curve of the tosylate will, of course, be slightly different from those here. However, the same effects, ring-strain and H,H-interaction, will undoubtedly determine the vibrational potential of the tosylate as well. The spectroscopic results have been obtained from measurements in the gas-phase while the kinetic studies have been performed in the liquid phase. In spite of these shortcomings the agreement of the kinetic data calculated on the basis of spectroscopic results with data obtained from solvolysis experiments is surprisingly good.

REFERENCES


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