

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 systems 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_{chair} agrees well with observed rates of cyclopropyl-assisted solvolysis in rigid 3-bicyclo[3.1.0]hexyl systems.

Extensive NMR,¹⁻¹³ UV,¹⁴ far-IR,^{15,16} Raman,¹⁷ and microwave¹⁸⁻²³ 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 conformations²⁴⁻²⁶ 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

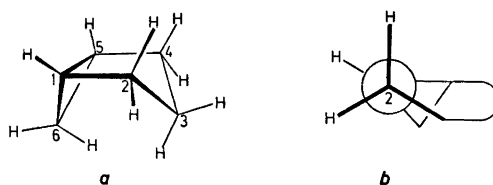
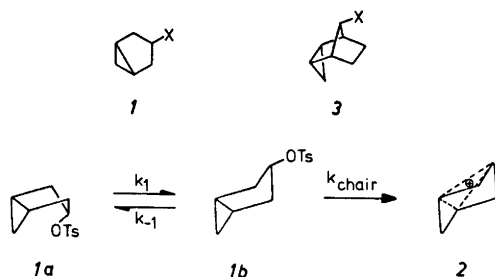


Fig. 1. (a) Boat-like conformation of bicyclo[3.1.0]hexane and (b) Newman-projection of the C(1)–C(2) bond.

spectroscopic studies on bicyclo[3.1.0]hexane^{16,21} 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^{4,29} (*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*-nitrobenzoate).³⁰⁻³² In order to explain the low rate of solvolysis of *1* Winstein *et al.*^{4,7,33} 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*).



Winstein *et al.*^{4,7} (*cf.* also Refs. 34, 35, and 36) have assumed an equilibrium between the boat and the chair conformations with a low value of the equilibrium constant $K = k_1/k_{-1}$. Furthermore, they assumed that the equilibrium between *1a* and *1b* is maintained during the process. From these assumptions an expression for the over-all reaction rate was derived in terms of the equilibrium constant and k_{chair} ,

$$k_{\text{obs}} = K(1 + K)^{-1}k_{\text{chair}} \approx Kk_{\text{chair}}$$

The second assumption would by necessity demand that k_{chair} is small compared to k_{-1} . However, k_{chair} should be relatively large and should correspond to the rate constants of cyclopropyl-assisted solvolysis in related rigid systems.^{35,36} The use of a steady-state approximation for the concentration of the chair conformation (*1b*) would give the more correct result

$$k_{\text{obs}} = K(1 + k_{\text{chair}}/k_{-1})^{-1}k_{\text{chair}}$$

The angle $180^\circ - \angle(\text{C}_1\text{C}_2\text{C}_3\text{C}_4) - (\text{C}_2\text{C}_3\text{C}_4)$ is denoted by ϕ . Positive values of ϕ correspond to the boat conformation and negative values to the chair conformation. In the systems hitherto investigated, the angle ϕ at equilibrium varies from approximately 20° ²² up to 40° .¹⁸⁻²¹ A bulky substituent at the *cis*-3-position might possibly cause a smaller equilibrium angle. It is also of interest to note that the vibrational potential curves obtained from far-IR^{15,16,22} and Raman¹⁷ spectra of bicyclo[3.1.0]hexane and some related compounds give indications of a stable chair conformation only in the case of 6-oxabicyclo[3.1.0]hexane. In this molecule a stable chair conformation might possibly occur at approximately 13 kJ mol^{-1} above the ground-state of the boat conformation.

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 ϕ .²² In higher vibrational states the large amplitude of the ring-bending motion will cause the molecule to pass through a chair-like conformation, with ϕ less than approximately -20° , 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^{16,22} 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 (*1*) 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_{obs} , in terms of k_{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

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

in which ν is the fundamental ring-bending vibration frequency.

The product $nh\nu (=E_n - (1/2)h\nu)$ 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, ΔE , 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,¹⁶ 3-oxabicyclo[3.1.0]hexane,¹⁶ 6-oxabicyclo[3.1.0]hexane,^{15,16} 3,6-dioxabicyclo[3.1.0]hexane,¹⁶ and 3-bicyclo[3.1.0]hexanone.²²

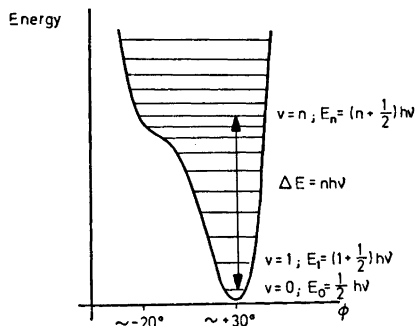


Fig. 2. A typical ring-bending potential function for a bicyclo[3.1.0]hexyl system.

ability for a molecule to be in a state $j \geq n$ can then be calculated to be somewhere between 4×10^{-4} and 5×10^{-3} at 25°C.

When the molecule is in an excited state, $j \geq n$, the ring-bending vibration is of large amplitude between boat and chair forms as previously discussed. The probability of a chair conformation, $P(\text{chair})$, will thus be smaller than $P(j \geq n)$. Since the vibrational amplitude is not well established at higher vibrational levels, $P(\text{chair})$ is difficult to determine. However, any reasonable assumption will reduce the derived value of $P(j \geq n)$ by at least a factor of 5 to 10. Accordingly, we find the total probability of the molecule being in a chair-like conformation to lie between 4×10^{-5} and 1×10^{-3} . These values can be regarded as limits for the "equilibrium constant" K .

The ratio $k_{\text{obs}}/k_{\text{chair}}$ is equal to $[Ib]/([Ia] + [Ib]) = [Ib]/[Ia]$. The chair conformation (*Ib*) will react faster than equilibrium can be attained. As long as k_{-1} is unknown it is, however, reasonable to adopt the approximation of Winstein *et al.*^{4,7} that the ratio $[Ib]/[Ia]$ does not differ very much from that at equilibrium. From the known values²⁹ $\Delta H^\ddagger = 101 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -21 \text{ J K}^{-1} \text{ mol}^{-1}$ we may calculate $k_{\text{obs}} = 1.1 \times 10^{-6} \text{ s}^{-1}$ at 25°C. Finally, from the value of $P(\text{chair})$ calculated above, we get $k_{\text{chair}} = 0.001$ 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 ϕ (e.g. 3, 4 and 5) show high values for the rate of solvolysis.^{29-32,34,35,37,38} 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 ϕ .

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.^a

Temp. of solvolysis (°C)	$k_{1b, \text{calc}}/k_1 \times 10^{-4}$	$k_3/k_1 \times 10^{-4}$	$k_4/k_1 \times 10^{-4}$	$k_5/k_1 \times 10^{-4}$
25 ^b	0.1–2.5	—	0.11	—
100 ^c	0.03–0.5	36	—	1.2

^a In this table k_1 refers to the observed rate constant of solvolysis for compound 1, k_3 is the observed rate constant for compound 3, etc. $k_{1b, \text{calc}}$ is equal to the calculated value of k_{chair} .^b In AcOH. ^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.

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