Ultrasonic Relaxation in Substituted 1,3-Dioxans

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THE concept of rotational isomerism is now basic in theories covering large areas of chemistry particularly the conformational analysis of alicyclic, acyclic, and heterocyclic molecules. In the last class of compounds there is much less experimental information available on their stereochemistry than in alicyclic or acyclic systems. For instance, in the 1,3-dioxans most of the published work on structural determination has involved n.m.r.[1] and dipole-moment[2,3] measurements. Here we illustrate the potential of the ultrasonic absorption technique in an unfamiliar role as an aid to the structural assignment of some heterocyclic molecules[4] in conjunction with other physical methods. Basically, ultrasonic absorption is a relaxation method used in the study of kinetics of fast reactions and we have applied this technique to some derivatives of 1,3-dioxan.

Using a pulse apparatus operating in the frequency range 15—105 MHz. we have observed an ultrasonic relaxation at ~50° in 4-methyl- and 4-phenyl-1,3-dioxan both in the pure liquid and also in 50% (v/v) solutions in *p*-xylene. We found no evidence of a relaxation in pure 1,3-dioxan over the temperature range 20—70°.

For a single relaxation the quantity α/f^2 decreases with increasing frequency in accordance with the equation:—

$$\alpha/f^2 = [A/(1 + (f/f_{\mathrm{c}})^2)] + B$$

where α is the sound absorption coefficient at frequency f, A is a relaxation parameter, f_{c} is the relaxation frequency, and B represents contributions to α/f^2 from "classical" viscosity and any other relaxation processes having a relaxation frequency much higher than f_{c}. The relaxation parameters for 4-methyl- and 4-phenyl-1,3-dioxan are as follows:

	$10^{17}A$ (sec.^{2} cm.$^{-1}$)	$10^{17}B$ (sec.^{2} cm.$^{-1}$)	f_{c} (MHz.)
4-Methyl-1,3-dioxan (pure liquid)	2377	71	7·8
p-Xylene solution	1077	82	8·0
4-Phenyl-1,3-dioxan (pure liquid)	610	93	10·7
p-Xylene solution	303	80	10·9

These values are consistent with a single relaxation process. The occurrence of an ultrasonic relaxation in pure liquids may be due to any of the following causes: (i) viscous relaxation; (ii) vibrational relaxation; (iii) equilibria between associated and single molecules; or (iv) conformational changes.

Mechanisms (i)—(iii) are all intermolecular in nature and therefore the relaxation times, and hence the relaxation frequency, will be a function of dilution. On the other hand, conformational change in a molecule is an intramolecular process and the relaxation frequency should be the same for the solution as that of the pure liquid.[5] The relaxation frequencies of both pure 4-methyl- and 4-phenyl-1,3-dioxan are sensibly the same as those of their respective solutions, thus showing that the observed single ultrasonic relaxation can be attributed to a perturbation of an equilibrium between two conformers of the molecule. This equilibrium may be between any two of the possible extreme forms; chair, boat, twist, half-boat, *etc.*, or between the axial and equatorial isomers of any of these forms, *i.e.*, where the alkyl or aryl substituents are in an axial or equatorial position.

The relaxation frequency for a conformational change is characteristic of the particular system. For example, the data listed below show the approximate relaxation frequencies[5] at room temperature for the following conformational changes:

C–C bonds in ethanes	15—300 MHz
C–O bonds in esters	500 kHz—5 MHz
C–O bond in vinyl ethers	300 MHz
C–N bond in amines	20—60 MHz
Axial–equatorial chair forms in substituted cyclohexanes	150 kHz

On this basis we would expect that an equilibrium between any two of the extreme forms; boat, chair, twist, *etc.*, would result in an ultrasonic relaxation both in 1,3-dioxan and in its derivatives. However, if the relaxation is due to an equatorial ⇌ axial equilibrium only the 4-methyl and 4-phenyl derivatives will give rise to an active ultrasonic relaxation. The axial and equatorial hydrogen atoms of the two preferred chair conformers[2,3] of 1,3-dioxan have the same energy since during inversion one hydrogen rotates from an equatorial to an axial position whilst the other geminal hydrogen rotates from an axial to an equatorial position.

The chair form is energetically more stable in these systems and consequently we attribute the relaxation observed with substituted 1,3-dioxans to an equilibrium between the axial and equatorial conformers of this form.

We are extending the present acoustic measurements to cover a wide temperature range in order to study the kinetics of the ring inversion process in these compounds.

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