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Heats of Hydrogenation of the Cis and Trans Isomers of Cyclooctene[1]

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Strain in organic molecules has long been of interest, and there are diverse ways of measuring its effect upon physical and chemical properties. With the advent of the powerful force field method for determining molecular structures and energies,[3] strained molecules have become a testing ground for those interested in this area of chemistry. The largest and most complete body of data available on the energies of molecules is to be found in the heats of formation of hydrocarbons.[4] These are ordinarily determined by measurement of heats of combustion. Since heats of combustion are large numbers and are measured relative to the elements, for which the heats of combustion are also large numbers, the experimental determination of the heat of formation of a compound involves a relatively small difference between two large numbers, and the experimental measurements must be of very high accuracy in order to secure heat of formation data which are of only moderate accuracy. This problem has long been recognized, and one solution is to measure the energy difference between two species in which one is interested, which is usually a much smaller quantity. In the case of unsaturated hydrocarbons, this is in principle easy. Heats of hydrogenation can be measured for alkenes and related compounds, and the heats of formation of the corresponding alkanes are usually known. Hence, the heat of hydrogenation can be determined directly to rather high accuracy, and the heat of formation can usually be obtained for the alkene with an accuracy approaching that which is available for the alkane. In practice there are some problems with experimental heats of hydrogenation. These can be determined in the gas phase, and this was the method used by Kistiakowsky in his classical investigations.[5] For experimental convenience, subsequent measurements have usually been made in acetic acid solution. This presents some interpretive difficulty. The experimental technique used by Turner[6] in his extensive studies on the heats of hydrogenation of alkenes is such that in order to convert his data to gas-phase numbers, one needs to know the heats of solvation of the alkanes obtained in acetic acid solution. These numbers are positive and often quite sizable since solvation of the hydrocarbon disrupts the liquid structure of the acetic acid. The heats of solvation are not usually known.

Recently, a technique for measuring heats of hydrogenation of unsaturated hydrocarbons in hexane solution at room temperature was developed.[7,8] The experimental technique is such that the directly measured number differs from the gas phase value only to the extent that the thermodynamic states of the reactant and product in very dilute hexane solution differ from the thermodynamic states of the gaseous product and reactant. We argue that the absence of differential intermolecular interactive forces makes this difference negligibly small. Hence, the values obtained pertain (to a very good approximation) to the actual molecular quantity desired, uncomplicated by solvation effects.

The cyclooctenes are a case of special interest in several ways. First, the heat of hydrogenation of *cis*-cyclooctene itself is known in the gas phase[5] and in acetic acid solution,[6] and these values can be compared with the value in hexane. More importantly, the trans isomer is a highly strained molecule, in which there is a bending (or rehybridization) deformation about the double bond.[9–11] Molecules with this deformation are scarce, hence the heat of hydrogenation of this compound is of interest. Since the heat of formation of cyclooctane is accurately known,[4] the heats of hydrogenation give us the heats of formation for these compounds.

Finally, there has been some question as to the structure of *trans*-cyclooctene.[9–12] The initial independently proposed structures arrived at from electron diffraction[11] and by molecular mechanics calculations[10] differed with respect to the stable conformation. More recent electron diffraction results[12] have borne out the calculations rather than the original electron diffraction results. We feel it is especially important that the energy of this molecule, as well as its structure, be accurately calculated by any force field which is going to be useful for strained alkenes.

We recently reported[13] a new force field (MM2) which utilized low-order torsional terms as a key feature and which was shown to work extremely well for calculation of the structures and energies of saturated hydrocarbons.[13,14] In extending this force field to alkenes, we noticed that we were not able to reproduce very well the heat of formation of *trans*-cyclooctene, as estimated from the heat of hydrogenation in acetic acid by Turner.[6] Our calculated structure was 2–3 kcal/mol more strained than Turner's heat of hydrogenation indicated.

It was concluded that it would be worthwhile to remeasure the heats of hydrogenation of the cyclooctenes in a hexane solvent so as to avoid the solvation problem. In addition, we now have available better criteria for determining the purity of the compounds than were available to Turner, and finally, we are now aware of the fact that *trans*-cyclooctene polymerizes to some extent upon distillation, and presumably also upon simply standing at room temperature. The purity of the samples was established by gas chromatography.

The heats of hydrogenation were determined, and the data are summarized in Table I. Indeed, the *cis*-cyclooctene value

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Table I. Heats of Hydrogenation ($-\Delta H_{H_2}$, kcal/mol)[a] for the Cyclooctenes

Cis	*Trans*	Solvent	Ref
22.98 ± 0.10	32.24 ± 0.21	Acetic acid	6
23.53 ± 0.04	–	Gas phase	5
23.04 ± 0.17	34.41 ± 0.43	Hexane	This work

[a] Under Turner's conditions in acetic acid, the magnitude of the heat of hydrogenation will be smaller than the gas-phase value by the heat of solvation of cyclooctane in acetic acid (about 0.4 kcal/mol). Kistiakowsky's measurements were at 82 °C, and heats of hydrogenation are generally slightly greater in magnitude at elevated temperatures.

is quite comparable with earlier values, as anticipated. The *trans*-cyclooctene value is approximately 2 kcal greater in magnitude than that reported by Turner. The difference is attributed in part to solvation but mainly to sample purity, as discussed above. The predictive value of the force field calculations is again borne out. From the heat of hydrogenation obtained herein, we can estimate the heats of formation and strain energies of the cyclooctenes. Taking the heat of formation of cyclooctane[4a] as −29.73 ± 0.28, we obtain $H_f°$ values for the gas phase at 25 °C, as: trans, +4.68 ± 0.71 kcal/mol, and cis, −6.69 ± 0.45 kcal/mol. An independent literature value[4a] gives: cis, −6.45 ± 0.30 kcal/mol.

The calculated inherent strain energies[3a] for cyclooctane, and *cis*- and *trans*-cyclooctene are respectively 14.15, 10.36, and 21.99 kcal/mol.[13] While these numbers are quantitatively different from earlier values, the interpretation is the same, namely that cyclooctane contains considerable strain from van der Waals repulsion and unfavorable torsion, which is partly relieved in *cis*-cyclooctene. The *trans*-cyclooctene, on the other hand, contains a large amount of bending and twisting strain about the double bond.

Experimental Section

The apparatus and technique used for the heat of hydrogenation measurements has been previously described.[8] 1-Hexane was used as the standard (H_{H_2} = −30.00[4b] kcal/mol). Samples of compound, 0.15–0.30 g, were weighed to ±0.01 mg and made up to volume with hexane. Forty-microliter aliquots were added to the hydrogenation vessel, which contained the Pd/C catalyst suspended in hexane.

cis-Cyclooctene was purchased from Columbia Carbon Co., Princeton, N.J., and was distilled. GLC showed it to be quite pure (SE 30 capillary column). The trans isomer was furnished by Dr. R. Bach, and had been prepared by elimination from the 1,2-diol. It was shipped in pentane. The pentane was removed by distillation and the *trans*-cyclooctene was distilled. A polymeric residue remained. This sample of *trans*-cyclooctene was shown by GLC not to contain any detectable amount of the cis isomer. It did contain 1.8 ± 0.5% pentane, which was allowed for in calculation of the heat of hydrogenation.

The *trans*-cyclooctene sample described above was both used as described and partly redistilled (to give a second sample), which now was found by GLC to contain 0.45 ± 0.15% pentane. The heat of hydrogenation was also measured with this sample. Uncertainties in Table I are 95% confidence limits on nine replicate samples plus an estimated uncertainty on the correction due to pentane in the trans sample.

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Registry No.—*cis*-Cyclooctene, 931-87-3; *trans*-cyclooctene, 931-89-5.

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Reaction of Methyl and *tert*-Butyl Hypochlorite with Cyclopentadiene

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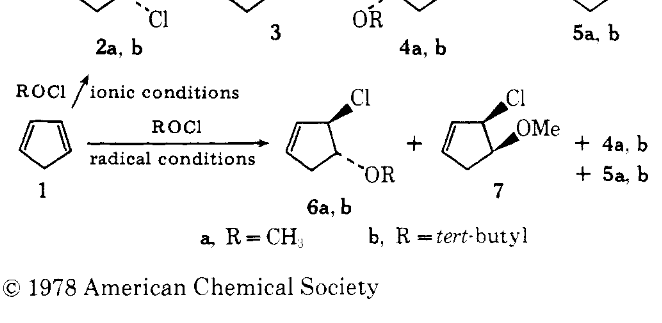
Recently, we reported studies on the ionic and radical addition of methyl hypochlorite to acyclic, conjugated dienes.[1] In order to examine the stereochemistry of this reaction, we decided to explore the addition of alkyl hypochlorites to cyclopentadiene (1). The reaction of 1 with *tert*-butyl hypochlorite has been reported[2] but without identification of the stereoisomers and without a discrimination between ionic and radical addition mechanisms.

The products obtained from 1 and methyl and *tert*-butyl hypochlorite are identified in Scheme I. The ratios of products obtained under ionic and radical conditions are listed in Tables I and II, respectively. Both of the hypochlorites give a rapid radical reaction (molecule-induced homolysis) with the

Scheme I



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