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Thermochemistry of conjugation of simple cyclopropane derivatives

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RICHARD FUCHS, JOHN H. HALLMAN, and MICHAEL O. PERLMAN. Can. J. Chem. 60, 1832 (1982).

Heats of vaporization of cyclopropyl cyanide and cyclopropylbenzene have been measured by vaporization calorimetry, and combined with liquid state heats of formation to give gaseous state heats of formation. When these compounds, cyclopropane, 1,1-dimethylcyclopropane, and cyclopropylamine are involved in (hypothetical) isodesmic reactions with ethane to give the isopropyl derivative and propane, the enthalpies of reaction are -116.0 ± 1.3 kJ mol⁻¹, except for cyclopropylbenzene (-103.7 kJ mol⁻¹). The latter is less exothermic, in part, because of slight steric destabilization of the product, isopropylbenzene, but mainly due to 8 kJ mol⁻¹ stabilization of cyclopropylbenzene, which is the only of these cyclopropyl derivatives showing appreciable thermochemical stabilization.

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Faisant appel à la calorimétrie de vaporisation, on a mesuré les chaleurs de vaporisation du cyanure de cyclopropyle et du cyclopropylbenzène et on les a combinées aux chaleurs de formation à l'état liquide pour obtenir les chaleurs de formation à l'état gazeux. Quand ces composés: le cyclopropane, le diméthyl-1,1 cyclopropane et la cyclopropylamine sont impliqués dans des réactions isodesmiques (hypothétiques) avec l'éthane pour conduire au dérivé isopropylique et au propane, les enthalpies de réaction sont de $-116,0 \pm 0.3$ kJ mol⁻¹, sauf pour le cyclopropylbenzène (-103,7 kJ mol⁻¹). Ce dernier est moins exothermique, en partie à cause de la légère déstabilisation stérique du produit, l'isopropylbenzène, mais principalement à cause de la stabilisation de 8 kJ mol⁻¹ cyclopropylbenzène, qui est le seul de ces dérivés cyclopropyles à montrer une stabilisation thermochimique appréciable.

There is a growing feeling among theorists that molecular parameters can be more accurately calculated than measured. The results of a calculation may indeed be closer to the "truth" than the corresponding experimental measurement, but the significance of the calculation may be limited by our inability to establish error limits accurately by experiment. It is therefore of the utmost importance that the best possible experimental measurements be performed. The alternative is devolution of chemistry from an experimentally verifiable science to the status of a religion, based on articles of nondemonstrable faith.

When a group, X, is substituted into a molecule, Y—H, we may consider the interactions between Y and X in the resulting molecule, Y—X, which lead to alteration in spectra, bond lengths, etc. But the most significant question is whether special interactions between X and Y lead to a *thermochemically demonstrable decrease in the energy of* Y-X relative to reasonable models.

For many years data have been presented suggestive of "double bond character" of the cyclopropane ring (1), but evidence for significant conjugation is strongest for cationic reaction intermediates (2) and excited states, rather than for the ground states of neutral cyclopropane derivatives. We have recently completed a decade of substantial theoretical interest in conjugative interactions of the cyclopropane ring. Variation in ring bond lengths with the nature of the attached group have been examined (3-8), and often indicate substantial substituent-ring conjugation (3-7). Hoffmann (9) attributed the stabilization of norcaradienes by cyano and phenyl substituents (relative to the isomeric cycloheptatrienes) to π -type cyclopropane-substituent conjugation. Ab initio calculations by Hehre (10) predicted a 13.4-14.6 kJ mol⁻¹ stabilization of vinylcyclopropane. Dill, Greenberg, and Liebman (11) recently made extensive calculations on small ring and bicyclic systems with a variety of substituents. They predict the following stabilizations of cyclopropane by substituents: CH₃, 10.0 kJ mol⁻¹; CN, 24.3 kJ mol⁻¹; and NH₂, 12.1 kJ mol⁻¹; but note that STO-3G calculations appear to overestimate stabilizations. It has been suggested (11) that stabilization or destabilization results not only from the ring-substituent bond character, but also from an increase or decrease in ring strain. It is the sum of these factors which is calculated, and is experimentally measurable.

What of the experimental thermochemical data previously available? We note several problems. (a) The data are few. (b) Some "experimental" values of gaseous state heats of formation ($\Delta H_f^0(g)$) are based on estimated heats of vaporization (11) (methylcyclopropane). (c) Some $\Delta H_g^0(g)$ values are based on defective values of ΔH_v^0 (12) (cyclopropyl cyanide).

It is the objective of the present study to provide $\Delta H_f^0(g)$ data of sufficient accuracy that a critical assessment of cyclopropane-substituent thermo-

0008-4042/82/141832-04\$01.00/0

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chemical stabilization can be made. We will examine the results by two methods. The first involves the (hypothetical) isodesmic reaction (13), or group separation method, as recently modified (11, 14):

$$X \xrightarrow{+3CH_3CH_3} \xrightarrow{\Delta H_r} 2CH_3CH_2CH_3 + CH_3 - CH_2CH_3$$

where $\Delta H_r = 2\Delta H_f^{0}(g) (\mathbf{C}) + \Delta H_f^{0}(g) (\mathbf{D}) - \Delta H_f^{0}(g)$ (A) $- 3\Delta H_f^{0}(g)$ (B). The reaction is exothermic due to the ring strain in (A), and $-\Delta H_r$ is the strain energy. ΔH_r will be the same where X = H and all other nonconjugating substituents, but ΔH_r will be less exothermic when a stabilizing interaction of X and the ring occurs, or more exothermic if (A) is destabilized.

The second method we term the metathetical relationship. Here substituents are exchanged by conjugating and equivalent, but nonconjugating systems:



(B) can be the 2-propyl, cyclopentyl, or cyclohexyl derivative, with Y = H or other nonconjugating substituent, and $\Delta H_{\rm m} = \Delta H_{\rm f}^{0}({\rm g})$ (C) + $\Delta H_{\rm f}^{0}({\rm g})$ (D) - $\Delta H_{\rm f}^{0}({\rm g})$ (A) - $\Delta H_{\rm f}^{0}({\rm g})$ (B). The reaction is thermoneutral if (A) is unstabilized, endothermic if (A) is stabilized, and exothermic if (A) is destabilized.

Experimental

The technique and apparatus for measurement of calorimetric heats of vaporization (15) have been considerably changed in the present study, but the results with test substances are in excellent agreement with our earlier work, and with the best literature values (16). The vaporization calorimeter is again a coiled tube embedded in a copper disc heat sink fitted with a thermistor and heater, and enclosed in a vacuum jacketed solution calorimeter. The coiled tube is 0.476 cm (3/16 in.) od nickel tubing rather than copper, and the inlet and outlet stopcocks are Hamilton valves made of Teflon and Kel-F. Nitrogen flow is established by a low range digital mass flow controller (0-10 cc/min, Porter Instrument Co.). Vacuum below 1.3 kPa (10 Torr) is furnished by a vacuum pump, and by an aspirator with a drying column at higher pressures. Well dried 100 µL samples are introduced volumetrically (microliter syringe, constant stroke adapter), and the mass of separate samples is determined with a semimicro balance, using air buoyancy corrections. A major change from our earlier procedure (15) is introduction of the sample into the (25.00°C) calorimeter at a temperature at which no net heating or cooling effect occurs in the absence of vaporization. Surprisingly, these conditions are met with the sample and syringe jacket at $22.00\pm$

0.01°C, and the 30 cm Teflon needle (air) temperature at 23.00 \pm 0.05°C. We presume that the delivered sample is warmed by frictional heating and by handling of the needle. The previously used heat capacity correction for the sample is, therefore, no longer required. The validity of this procedure is verified not only by the excellent agreement of measured ΔH_v^0 values of test substances with literature values, but also by the observation that nonvolatile samples (hexadecane introduced under conditions suitable for the evaporation of hexane) produce random temperature changes no greater than $1-2 \times 10^{-4}$ K. We have also observed that the overall cycle of closing the exit stopcock to the vacuum system, refilling the calorimeter with dried nitrogen or air to atmospheric pressure, opening the entrance stopcock to the atmosphere for 30s (the time required for sample introduction) and reestablishment of the original nitrogen flow and vacuum produces negligible change ($< 1 \times 10^{-4}$ K) in the calorimeter temperature.

Sample evaporation occurs over a 14-20 min period, and the cooling effect is periodically compensated by short (8 or 10 s) heating periods (total 75-175 s), such that temperature excursions of 0.06-0.08 K occur symmetrically about the equilibrium temperature of the calorimeter. When no further evaporation cooling occurs, the block is brought to the original temperature $(\pm 1 \times 10^{-4} \text{ K})$. The calorimeter temperature is monitored for an additional 4 min to establish that the final and initial equilibrium temperatures are identical. The temperature measurement system consists of a thermistor (2000 Ω) imbedded in the copper heat sink, as the unknown resistance of a Wheatstone bridge, the output of which is displayed on a digital multimeter (Keithley 177, 19.999 mV full scale). The multimeter analog output is plotted on a potentiometer recorder. The heating system consists of a Type RN55C metal film resistor (822.8 Ω), a timed constant current source (17) with an output of 19.85 mA, and monitored by a digital milliammeter, and an adjustable interval timer based on the 555 integrated circuit. Operation of the vaporization calorimeter was verified by measurements of compounds with well established values of ΔH_v^0 (16, 18): pentane, $26.61 \pm 0.09 \,\text{kJ}\,\text{mol}^{-1}$ (reported, 26.74 ± 0.21); hexane, 31.54 ± 0.18 (31.55 ± 0.04); octane, 41.44 ± 0.07 (41.51 ± 0.04); butanenitrile, 39.22 ± 0.11 (39.29 ± 0.08); butyl acetate, $43.66 \pm$ $0.09 (43.60 \pm 0.21)$; and isopropylbenzene, $45.12 \pm 0.02 (45.15)$ ± 0.04).

Cyclopropyl cyanide (Fluka) and cyclopropylbenzene (Aldrich) were fractionally distilled. Purity was established by gas chromatography (99.90% and 99.70%, respectively), using a Shimadzu Mini 2 gc with a glass lined system, a $30 \text{ m} \times 0.25 \text{ mm}$ id SE-30 silica capillary column, and a Hewlett-Packard 3390A integrator.

Results and discussion

Heats of vaporization and gaseous heats of formation

The standard heat of vaporization at 25°C of cyclopropyl cyanide (the mean of six determinations) is 41.94 \pm 0.11 kJ mol⁻¹. A previously reported value based on vapor pressure measurements (12) is 39.8 \pm 0.4 kJ mol⁻¹. However, a number of ΔH_v^0 values published in this article appear to be considerably too low (by 12 kJ mol⁻¹ for ethyl benzoate, 8.3 kJ mol⁻¹ for cyclohexyl cyanide, etc.).

We are unaware of any previous ΔH_v^0 measurements on cyclopropylbenzene. The mean of our four determinations is 50.22 ± 0.10 kJ mol⁻¹ where the indicated uncertainty is twice the standard deviation.

Based on the liquid state heats of formation (16) of cyclopropyl cyanide (140.8 \pm 0.7 kJ mol⁻¹), and of cyclopropylbenzene (100.5 \pm 1.0 kJ mol⁻¹) one may derive gaseous state heats of formation of 182.7 \pm 0.7 kJ mol⁻¹ and 150.7 \pm 1.0 kJ mol⁻¹, respectively, where $\Delta H_f^0(g) = \Delta H_f^0(1) + \Delta H_v^0$. Other values of $\Delta H_f^0(g)$ below are taken from the Pedley–Rylance Tables (16).

Enthalpies of isodesmic reactions

The following are isodesmic reactions of cyclopropane and the four simply substituted cyclopropane derivatives for which *experimental* values of $\Delta H_f^0(\mathbf{g})$ are now known. The values are in kJ mol⁻¹.



The mean of the first four heats of reaction is $-116.0 \pm 1.3 \text{ kJ mol}^{-1}$ (-27.7 $\pm 0.4 \text{ kcal/mol}$). Only the reaction of cyclopropylamine differs from the mean value by more than the experimental uncertainty; the difference is only 0.6 kJ mol⁻¹ (0.1 kcal/mol) larger than the uncertainty, and is of doubtful significance. By contrast, the reaction of cyclopropylbenzene is 12.3 kJ mol⁻¹ less exothermic than the mean of the other four reactions. Of this, 4.4 kJ mol⁻¹ results from steric strain in the product isopropylbenzene (the isodesmic reaction of isopropylbenzene with ethane to give isobutane and neopentane is more exothermic by this amount than the corresponding reactions of benzene, toluene, and ethylbenzene). The remaining 7.9 kJ mol⁻¹ results from conjugative stabilization in cyclopropylbenzene.

Enthalpies of metathetical reactions

An alternative but related method of detecting thermochemically significant interactions involves metathetical reactions. Exchange of substituents between two nonconjugated systems should be thermally neutral ($\Delta H = 0$), but destruction of a conjugated molecule leads to an endothermic reaction.

$$\bigvee_{CH_3}^{CH_3} + CH_3 \longrightarrow C - CH_3 \xrightarrow{0.0 \text{ kJ mol}^{-1}}_{Me_2 \text{ exchange}}$$

$$\bigvee_{CH_3}^{CH_3} + CH_3 \longrightarrow C - CH_3 \xrightarrow{CH_3}_{Harrow}$$

The other four cyclopropane derivatives can be similarly involved in metathetical reactions: cyclopropyl cyanide (CN, H exchanged for Me₂), ΔH $= 1.0 \pm 1.6$; cyclopropane, 1.4 ± 1.4 ; cyclopropylamine, -1.6 ± 1.5 ; and cyclopropylbenzene, 12.5 \pm 1.9 kJ mol⁻¹. The first four reactions have enthalpies which, essentially within the uncertainty limits, are zero. This again demonstrates that no stabilizing interactions occur in cyclopropyl cyanide, 1,1-dimethylcyclopropane, and cyclopropylamine, which are not also present in (unconjugated) cyclopropane. Similar conclusions would be drawn if cyclopropane substituents were exchanged with cyclopentane. Data for cyclopentane derivatives are less available and have larger uncertainties than the data for propane derivatives used above. The enthalpy of reaction of cyclopropylbenzene (12.5 kJ mol⁻¹) is in excellent agreement with the results of the isodesmic reaction, and indicates 8.1 kJ mol⁻¹ stabilization of cyclopropylbenzene.

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Conclusions

Studies of cyclopropane derivatives (3–7, 9–11) experimentally and by calculations have generally indicated appreciable ring-substituent interactions, and substantial stabilization has been predicted for many of the substituted compounds relative to unsubstituted cyclopropane. An exception is 1,1-dibromo-*trans*-2,3-diphenylcyclopropane (8), where the phenyl-cyclopropane interaction is apparently not strong enough to require a conjugating conformation in the crystal structure. However, *trans*-2-(*p*-nitrophenyl)cyclopropyl methyl ketone (19), the only unhindered cyclopropylbenzene derivative of known crystal structure, has the rings very close to the bisected (conjugated) conformation.

Many of the conclusions of previous studies regarding the stabilization of cyclopropane derivatives cannot be confirmed by the present experimental thermochemical measurements. Perhaps compounds such as cyclopropyl cyanide have a substituent-ring stabilizing π interaction of 5–10 kJ mol⁻¹, together with destabilization of other orbitals and increased ring strain amounting to 4–9 kJ mol⁻¹. If this were the case, the very small net stabilization might not be observed thermochemically. We feel it is presently unwise to use calculations, structural data, and other nonthermochemical information to draw quantitative thermochemical conclusions about small effects.

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Acknowledgements

Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, and to The Robert A. Welch Foundation (Grant E-136) for additional support.

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