The Thermochemistry of Diphenylcyclopropenone. Strain vs. Delocalization Energy

Harry P. Hopkins, Jr.,* David Bostwick, and C. J. Alexander

Contribution from the Department of Chemistry, Georgia State University, Atlanta, Georgia 30303. *Received May 9, 1975*

Abstract: The standard enthalpy of formation, ΔH_f^0(g), for gaseous diphenylcyclopropenone has been determined from bomb calorimetric and vapor pressure measurements. This value is compared to several ΔH_f^0(g) estimated from empirical bond energy schemes. The difference between the calculated and experimental values indicates that diphenylcyclopropenone has a strain energy of at least 78 kcal mol^{-1}.

Alicyclic compounds containing the strained cyclopropane ring have fascinated chemists for many years because of the remarkable chemical and physical properties of the three-membered ring.[1,2] The parent hydrocarbon has been estimated[3] to possess a ring strain of nearly 27 kcal mol^{-1}, whereas the introduction of a double bond in the cyclopropane ring has been reported[4] to virtually double the empirical strain energy. Cyclopropanone was considered[5] for many years to be too unstable to isolate because of excessive ring strain, but this compound has recently been prepared[6] and characterized.[7] In view of these results a three-membered ring possessing a double bond in the ring and a carbonyl group directly attached to the remaining ring carbon would be expected to be a highly strained alicyclic compound. However, simple Huckel type molecular orbital calculations performed in 1959 indicated[8] that cyclopropenone should be resonance stabilized by at least 1.36β and the diphenyl derivative by 6.16β. The latter compound was subsequently synthesized during the same year by independent routes by Breslow and co-workers[9] and in Volpin's laboratory.[10] Since that time numerous derivatives of cyclopropenone have been reported[11] in the literature, with the parent hydrocarbon recently being prepared and characterized by Breslow and co-workers. The disubstituted (phenyl and alkyl) cyclopropenones have been shown[12,1] to be remarkably stable, e.g., diphenylcyclopropenone decomposes thermally above 150 °C almost exclusively to carbon monoxide and diphenylacetylene. However, the appropriate thermochemical data needed to evaluate the strain and/or delocalization energy for the cyclopropenone system are not available.

In order to obtain a value for the gaseous enthalpy of formation for diphenylcyclopropenone, a series of bomb calorimetric and vapor pressure measurements were performed on this compound. The thermochemical data have been compared to the appropriate values calculated from several literature bond energy schemes to yield an estimate of the strain and delocalization effects in diphenylcyclopropenone. When the resonance energy of the two phenyl substituents is accounted for, the cyclopropenone system is found to have the largest strain energy of any three-membered alicyclic compound.

Experimental Section

Diphenylcyclopropenone was prepared by the procedure of Breslow et al.[12] After recrystallizations from cyclohexane the melting point, infrared spectra, and NMR spectra were found to be identical with the literature values. Additional recrystallizations were needed before reproducible bomb calorimetry data could be obtained. The samples used in the vapor pressure studies were vacuum sublimed immediately before being used.

The bomb calorimetric experiments were performed in a modified Parr system.[13] In the calorimetric measurements the combustion was initiated below 25 °C so that the midpoint of the reaction was near 25 °C.

The vapor pressures were determined by the Knudsen cell method with a procedure and system previously described.[13] Reproducible vapor pressure measurements were difficult to obtain because of the presence of a minute quantity of impurity with an appreciably higher vapor pressure. This impurity was presumably the hydrate[14] of cyclopropenone which formed on the surface of the particles, since the samples always had a sharp melting point (119 °C) and spectral characteristics which were consistent with literature values. Reproducible vapor pressures were obtained after the samples were exposed to the high vacuum for several hours.

Results and Discussion

The bomb calorimetric data for five reproducible experiments on solid diphenylcyclopropenone are shown in Table I. The average heat of combustion per gram, 8967.0 ± 4.0 cal g^{-1}, yields $\Delta E_{\text{comb}}^0(\text{s}) = -1849.4 \pm 0.9$ kcal mol^{-1} which can be converted in the standard way to $\Delta H_{\text{comb}}^0(\text{s}) = -1850.6$ kcal mol^{-1}.

Vapor pressure measurements were performed at 5° intervals between 50 and 70 °C, with the final values listed in Table II being the average of at least five reproducible determinations. A least-squares procedure was employed to provide a linear representation of log P vs. the inverse of temperature (T^{-1}). The derived equation for the experimental data is log $P(\text{Torr}) = 17.9688 - 7378.27(T\ °\text{K})^{-1}$ with a correlation coefficient of 0.998. The enthalpy of vaporization determined from this equation in the standard way is $\Delta H_{\text{vap}} = 33.8 \pm 1.0$ kcal mol^{-1} which is used without correction as the standard enthalpy of vaporization, ΔH_{vap}^0.

Combining ΔH_{vap}^0 with the combustion data, the standard enthalpy change for

$$C_{15}H_{10}O(g) + 17O_2(g) \rightarrow 15CO_2(g) + 5H_2O(l)$$

is $\Delta H_{\text{comb}}^0(\text{g}) = -1884.4$ kcal mol^{-1}. A value for the standard enthalpy of formation for gaseous diphenylcyclopropenone was calculated from $\Delta H_{\text{comb}}^0(\text{g})$ and the enthalpies of formation[15] for CO_2(g) and H_2O(l) in the usual manner to be $\Delta H_f^0(\text{g}) = 132.0$ kcal mol^{-1}. This result can now be compared with the corresponding values estimated from modern thermochemical-structural relationships[16,17] to yield an empirical energy difference for the cyclopropenone ring system which is the sum of delocalization and strain effects.

When the Klages[17,18] method based on a consistent set of bond contributions to $\Delta H_{\text{comb}}^0(\text{g})$ is applied to diphenylcyclopropenone, the estimated value of $\Delta H_{\text{comb}}^0(\text{g})$ is -1858.1 kcal mol^{-1}. An alternative procedure developed by Franklin[17,19] utilizing structural group contributions provides an estimated value of $\Delta H_{\text{comb}}^0(\text{g}) = -1860.4$ kcal mol^{-1} if the correction for the presence of a three-mem-

Table I. Bomb Calorimetric Results for Diphenylcyclopropenone (Solid) at 25 °C

Mass, g	Q_t,[a] cal	Q_i,[b] cal	Q_{HNO_3},[c] cal	Q_{Corr}[d]	Q_{Corr}/g
0.8117	7318.5	20.9	14.5	7283.0	8972.6
0.8807	7930.3	15.9	15.2	7899.2	8969.2
0.7396	6663.1	20.9	13.6	6628.6	8962.5
0.7897	7104.4	14.7	13.7	7076.0	8960.3
0.7506	6763.2	17.5	12.7	6733.0	8970.2
					Av = 8967.0 ± 4.4 cal

[a] Total heat evolved during combustion. [b] Heat due to fuse wire. [c] Heat effect attributable to formation of nitric acid determined from titration. [d] Corrected heat of combustion.

Table II. Vapor Pressure Data for Diphenylcyclopropenone

T, °C	P, $\times 10^5$ Torr
50.0	1.34
55.0	3.07
60.0	6.68
65.0	15.9
70.0	27.2

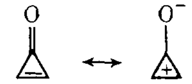
bered ring is deleted. Since these estimations are virtually identical, an average value of −1859.7 kcal mol^{-1} will be employed in subsequent calculations. The difference, E, between the calculated and experimental enthalpy of combustion is +24.6 kcal mol^{-1} which would conventionally be considered, because of the positive sign, to be the strain energy for the diphenylcyclopropenone molecule. However, this difference can be thought of as the sum of at least four terms which are defined here as: (1) the resonance stabilization, E_R, due to the phenyl groups; (2) the strain energy effects, E_S, of the three-membered ring; (3) the delocalization energy attributable to the cyclopropenone system, E_d; and (4) any effects due to the interaction of the phenyl groups with the three-membered ring, E_i. The first term, E_R, can be estimated by attributing 36 kcal mol^{-1} of resonance energy to each phenyl group, since this is the resonance energy obtained for benzene from either the Klages[17] or Franklin[17] thermochemical estimation scheme. Now assuming that all terms are additive

$$E_S + E_d + E_i = 96.6 \text{ kcal mol}^{-1}$$

Since E_S is opposite in sign to E_d and E_i, a minimum strain energy of at least 97 kcal mol^{-1} is obtained by this method. Furthermore, simple molecular orbital calculations[8] estimate $E_d + E_i$ to be 2.16β,[20] which would imply according to this method additional strain energy above the minimum E_S to be present in the cyclopropenone ring system.[21]

Recently, more sophisticated approaches to the formulation of thermochemical-structural relationships have appeared in the literature.[16] The Laidler method seems to be the most appropriate for diphenylcyclopropenone, since a phenyl group contribution plus mutual interaction effects between bonds and groups are an integral part of the scheme. However, two choices for the parameter for the formal singles bonds within the cyclopropyl ring are possible. A similar ambiguity exists for the carbon-carbon bonds attaching the phenyl group to the cyclopropyl ring. Since in both cases the two choices are similar in magnitude, the average values[22] will be employed in the calculations. Now with this assumption, the ΔH_f^0(g) for diphenylcyclopropenone is calculated from the recommended Laidler values of Cox and Pilcher[16] as $2E(C_6H_5-) + E(C{=}C) + E(C{=}O) + 2E(C_{co}-C_d) + 2E(C_d-C_b) = 51.12 + 37.9 - 13.28 - 13.86 - 8.08 = 53.8$ kcal mol^{-1}. When this value is combined with the experiment ΔH_f^0(g), the sum of $E_S + E_d + E_i$ is estimated to be 78.2 kcal mol^{-1}.

The sum of $E_S + E_d + E_i$ is estimated to be in the range of 78-97 kcal mol^{-1} from empirical thermochemical-structure relationships. If $E_d + E_i$ is negligible, even the lower estimate of 78 kcal mol^{-1} would be the largest empirical strain energy reported for a simple alicyclic molecule.[21] It is reasonable to expect that additional strain is present since $E_d + E_i$ is predicted to be nonzero. Apparently cyclopropenone is substantially more strained than cyclopropene (52.6 kcal mol^{-1})[4] and at least as strained as the bicyclobutane (68.2 kcal mol^{-1}) or benzocyclopropene (68 kcal mol^{-1}).[24] The introduction of the carbonyl group onto the three-membered ring has increased the strain by an amount which has not been compensated for by the delocalization predicted by the simple resonance theory often applied to cyclopropenone.



It is interesting to compare this result with the conclusion of Flygare, Benson, Oda, and Breslow[25] that according to a magnetic criterion based on magnetic susceptibility anisotropies "aromaticity" cannot be detected in cyclopropenone.

In view of the above discussion it is remarkable that the disubstituted cyclopropenones are thermally stable, decomposition occurring only above 150 °C. The products of the decomposition are primarily carbon monoxide and diphenylacetylene, but some dimer is obtained. The kinetic stability of diphenylcyclopropenone relative to the expulsion of carbon monoxide is predicted from an application of the Woodward-Hoffmann[26] orbital symmetry conservation rules; i.e., the process is the reverse of a forbidden 2 + 2 cycloaddition.

Acknowledgment. We are grateful for the partial support of the Research Corporation for this work.

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mum E_S value obtained in our analysis could actually be lower by several kcal mol^{-1}.

(22) From ref 16, $E(C_{co}–C_d) = (E(C_{co}–C) + E(C_d–C))/2 = (-9.23 - 4.62)/2 = -6.93$; $E(C_d–C_b) = (E(C_d–C) + E(C_b–C))/2 = (-4.62 - 3.46)/2 = -4.04$.

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Transfer Hydrogenation in the Presence of a Homogeneous Rhodium Catalyst

C. Masters,* A. A. Kiffen, and J. P. Visser

Contribution from Shell Research B.V., Koninklijke/Shell-Laboratorium, Amsterdam, The Netherlands. *Received January 27, 1975*

Abstract: Complexes formed by addition of a tertiary phosphine to a solution of tetra(cyclooctene)di-μ-chloro-dirhodium(I) in 1,4-dioxane function as active catalysts for the transfer of hydrogen from the dioxane to a suitable olefin. The catalytic activity is dependent upon the nature of the tertiary phosphine ligand, with trialkylphosphines giving rise to the most active catalysts. The preferred tertiary phosphine to rhodium ratio is 2 and any deviation from this ratio results, except with triphenylphosphine, in a marked decrease in catalytic activity. A range of olefins is shown to be effective as hydrogen acceptors. Of the aliphatic olefins tested cyclopentene was the most effective and of the aromatic olefins, styrene. Several substrates other than 1,4-dioxane were tested as hydrogen donors, but none of them was capable of matching the activity of this compound. Transfer of hydrogen between the organic groups of the tertiary phosphine ligands and the cyclopentene is shown to occur during the transfer-hydrogenation reaction although this appears to be incidental to the main reactions. The kinetics of the hydrogen-transfer reaction between 1,4-dioxane and cyclopentene catalyzed by either the $RhCl(PPh_3)_3$ or Rh_2Cl_2(cyclooctene)$_4$-4PEt_3 system are reported. Although the reaction is at first sight first order in cyclopentene, the observed first-order rate constant is not independent of the initial cyclopentene concentration, $[C]_0$, but decreases as $[C]_0$ increases. It is proposed that the apparent first-order dependence on cyclopentene is due to a competitive inhibition step involving reversible complex formation between either 1,4-dioxene (product) or cyclopentene and the catalyst. It is suggested that the nonintegral order in catalyst, 0.73 ± 0.04 for Rh_2Cl_2(cyclooctene)$_4$-4PEt_3 and 0.85 ± 0.04 for $RhCl(PPh_3)_3$, is due to the rhodium complex being present, to a small extent, as a dimeric species. With $RhCl(PPh_3)_3$ as catalyst, dioxane-solvated chloro-bridged dimeric rhodium complexes of the type $Rh_2Cl_2(PPh_3)_4 \cdot x$(dioxane), where $x = 1–2$, were isolated from the reaction mixture.

Interactions between a carbon-hydrogen bond and a metal center in both heterogeneous[1] and homogeneous[2] systems are currently the subject of much study. The finding that $RhCl(PPh_3)_3$ catalyzes the transfer of hydrogen from the saturated ether 1,4-dioxane to cyclopentene[3] prompted us, in view of our interest in reactions occurring at a saturated C–H bond,[4,5] to investigate this reaction in some detail.

Some months after we had completed our study Nishiguchi and Fukuzumi reported[6] in detail on the $RhCl(PPh_3)_3$-catalyzed transfer-hydrogenation reaction. Our results differ considerably from theirs and, we believe, shed more light on this interesting, and potentially important reaction.

Results

(a) Catalyst Modifications. In studying (i) the importance of the tertiary phosphine to rhodium ratio, and (ii) the effect of the nature of the tertiary phosphine ligand on the catalytic activity, we have made use of the fact that in the tetra(cyclooctene)di-μ-chloro-dirhodium(I)–tertiary phosphine system[7,8] the cyclooctene ligands are easily replaced, and the chloro bridge is readily split, by tertiary phosphines.

(i) **Variation of the Tertiary Phosphine to Rhodium Ratio.** Under standard conditions (see Experimental Section) we varied the tertiary phosphine:rhodium ratio. It can be seen from the results given in Table I that when L = PPh_3 the catalytic activity increases with the L:Rh ratio, reaching a maximum at ca. 3. In agreement with the result reported by Nishiguchi et al.,[6] we find that adding more triphenylphosphine has no measurable effect on the performance of the catalyst. However, with the other tertiary phosphines tested a maximum catalytic activity is observed with a L:Rh ratio of 2:1 and addition of more tertiary phosphine results in a decrease in activity. At Rh:L ratios below 1:2 the solution did not, under the reaction conditions, remain homogeneous but deposited rhodium metal.

The decrease in activity in the presence of excess tertiary phosphine indicates that, with the exception of triphenylphosphine,[6] the tertiary phosphines can effectively compete with solvent dioxane for vacant coordination sites on the rhodium. The observation that the decrease is more marked for the dialkylphenylphosphines than for the diphenylalkylphosphine ligands may reflect the stronger bonding properties of the former.

(ii) **Variation of the Tertiary Phosphine Ligand.** The data we obtained using a wide range of tertiary phosphine ligands, in an attempt to understand some of the factors influencing the catalytic activity, are summarized in Table II.

The first five results in this table show that, whereas electron-withdrawing substituents (i.e., F) in the aromatic ring of the triarylphosphine ligand cause a marked decrease in activity, electron-donating substituents (i.e., CH_3) cause a slight increase. With this in mind we investigated catalyst systems involving more basic, electron-releasing, tertiary phosphine ligands.

The remaining data in Table II show that for the mixed arylalkylphosphines replacement of phenyl by either ethyl or propyl leads to an increase in activity. Similarly triethyl-,