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The standard molar enthalpy of formation of 2,3-diphenylcycloprop-2-en-1-one

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The standard molar enthalpies of combustion and sublimation for 2,3-diphenylcycloprop-2-en-1-one ($C_{15}H_{10}O$) at 298.15 K have been redetermined. The experimental values: $\Delta_f H^\circ_m(C_{15}H_{10}O, cr) = (198.03 \pm 1.96)\ kJ \cdot mol^{-1}$ and $\Delta^g_{cr} H^\circ_m(C_{15}H_{10}O) = (119.7 \pm 8)\ kJ \cdot mol^{-1}$ yield a value for $\Delta_f H^\circ_m(C_{15}H_{10}O, g) = (317.7 \pm 8.2)\ kJ \cdot mol^{-1}$. If one assumes a ring strain in cycloprop-2-en-1-one of 280 $kJ \cdot mol^{-1}$, then the resonance stabilization in the three-membered ring is 88 $kJ \cdot mol^{-1}$. This indicates substantial ground-state aromatic stabilization in this molecule.

1. Introduction

Simple Hückel-type molecular-orbital calculations performed in 1959 indicated(1) that cyclopropenone should be resonance stabilized by at least 1.36β and the diphenyl derative by 6.16β (β is the Hückel molecular-orbital-calculation resonance integral). Since then, both compounds have been synthesized by a number of groups, notably that of Breslow and coworkers.(2,3) 2,3-Diphenylcycloprop-2-en-1-one has been shown to be remarkably stable(3) but decomposes to diphenylacetylene and carbon monoxide at temperatures greater than 423 K. It was therefore surprising that a thermochemical study by Hopkins, Bostwick, and Alexander(4) appeared to show that "when the resonance energy of the two phenyl substituents is accounted

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for, the cyclopropenone system is found to have the largest strain energy of any three-membered alicyclic compound." Greenberg *et al.*,(5) in an *ab initio* calculation using the 4–31G basis set and appropriate isodesmic equations which minimize errors in strain due to the basis set used, indicated a value about 170 kJ · mol^{-1} lower than Hopkins *et al.*'s value. It was therefore decided to reexamine the thermochemistry of 2,3-diphenylcycloprop-2-en-1-one using a carefully prepared sample and the Bartlesville rotary-bomb calorimeter. In addition, the enthalpy of sublimation of this relatively non-volatile solid has been redetermined.

2. Experimental

2,3-Diphenylcycloprop-2-en-1-one (Aldrich) was recrystallized five times from spectral-grade cyclohexane and stored in a desiccator. Prior to the combustion series, it was gently heated under high vacuum to remove the last traces of cyclohexane solvent and any hydrate that might have formed. The combustion sample was pelleted and stored in a dry glovebox under nitrogen.

Carbon-dioxide analysis was performed on the combustion products following the combustion calorimetry. Although quantitative carbon-dioxide analysis does not indicate the presence of isomeric impurity, it does indicate whether the materials are dry and free from all but isomeric material. The mass of carbon-dioxide recovered for 2,3-diphenylcycloprop-2-en-1-one was (99.925 ± 0.034) per cent of theoretical (mean and standard deviation for seven of the combustion experiments in the series).

H.p.l.c. analysis of the calorimetric sample failed to show any impurity. Mass-spectroscopic analysis gave a mass peak corresponding to $C_6H_5C{\equiv}CC_6H_5$ rather than the molecular ion. Evidently CO was eliminated under the conditions necessary to obtain the mass spectrum.

National Bureau of Standards sample 39i benzoic acid was used for calibration. Its specific energy of combustion is $-(26434 \pm 3)$ J · g^{-1} under certificate conditions. Conversion to standard states(6) gives $-(26413 \pm 3.01)$ J · g^{-1} for $\Delta_c U^\circ_m/M$, the specific energy of the idealized combustion reaction. For the cotton-thread fuse, empirical formula $CH_{1.774}O_{0.887}$, $\Delta_c U^\circ_m/M = -16945$ J · g^{-1}. Seven benzoic-acid calibration experiments interspersed among the 2,3-diphenylcycloprop-2-en-1-one combustions gave ε(calor) = (16759.22 ± 0.67) J · K^{-1} (mean and standard deviation of the mean) for the energy equivalent of the calorimetric system.

The rotating-bomb calorimeter BMR II,(7) and platinum-lined bomb PT–3b(8) of internal volume 0.349_4 dm^3, have been described. Experimental measurements of the energy of combustion followed procedures already described.(9) The bomb was not rotated. Water (1 cm^3) was added to the bomb, and the bomb was flushed and charged to 3.04 MPa with pure oxygen. Nitric acid was not formed in any of the combustions. Each experiment was started at 296.15 K and, because of the mass of sample chosen, the final temperatures were nearly 298.15 K.

The experimental results are based on 1970 relative atomic masses.(10) This set was used for consistency with the values used by CODATA in their recent recommendations of key values in thermodynamics.(11) For calculations of sample masses, conversion of the energy of the actual bomb process to that of the isothermal bomb process, and reduction to standard states,⁽⁶⁾ the values 1.32 and 1.10 $g \cdot cm^{-3}$ were used for density; 1.209 and 1.5 (estimated) $J \cdot K^{-1} \cdot g^{-1}$ for the specific heat capacity at constant pressure; and −0.00012 and −0.00015 (estimated) $m^3 \cdot kg^{-1}$ for $(\partial u/\partial p)_T$ for benzoic acid and 2,3-diphenylcycloprop-2-en-1-one, respectively.

Vapor-pressure measurements were conducted in an apparatus previously described by the process of head-space analysis.⁽¹³,¹⁴⁾ The method consists of allowing the vapor of a sample at T_1 to reach a steady state with a ballast tank maintained at T_2 where $T_2 > T_1$, isolation of the ballast tank, followed by an indirect analysis of its contents. Modifications to this apparatus to accommodate 2,3-diphenylcycloprop-2-en-1-one included a 12 dm^3 ballast tank to replace the previous one and 10 mm Teflon stopcocks. Previous work had demonstrated that vapor pressures down to 0.1 Pa could be measured reliably by this technique. Below this pressure, contributions of adsorbed substrate on the glass surface become significant and plots of the logarithm of vapor pressure against $1/T$ showed significant curvature. Subsequent work⁽¹⁵⁾ has shown, however, that the rate at which the adsorbed material is collected is approximately tenfold slower than for collection of material in the vapor state. By carefully controlling the collection period, quantitative transfer (>98 per cent) of the vapor can be achieved with only minor contributions from adsorbed substrate and linearity of plots of the logarithm of vapor pressure against $1/T$ can be achieved down to 0.01 Pa. By repeating the collection sequence for an equivalent time, an estimate of the contribution of desorbed substrate can be obtained. Correction for the contribution of adsorbed material has permitted the measurement of vapor pressures down into the 1×10^{-3} Pa range.

3. Results

Results of a typical combustion experiment are summarized in table 1. It is impractical to list summaries for all experiments, but values of $\Delta_c U_m^\circ/M$, the specific

TABLE 1. Summary of a typical combustion experiment at 298.15 K [a]

m'(DPCP)/g [b]	0.913819
m''(fuse)/g	0.002528
$n^i(H_2O)$/mol	0.05535
Δt_c/K	1.99120
ε(calor)($-\Delta t_c$)/J	−33371.0
ε(cont)($-\Delta t_c$)/J [c]	−37.0
ΔU(ign)/J	0.8
$\Delta U_w/J$ [d]	21.9
$-m''\Delta_c u^\circ$(fuse)/J	42.8
$m'\Delta_c u^\circ$(DPCP)/J	−33342.5
$\Delta_c u^\circ$(DPCP)/(kJ·g^{-1})	−36.4870

[a] The symbols and abbreviations of this table are those of reference 2.

[b] DPCP = 2,3-diphenylcycloprop-2-en-1-one.

[c] $\varepsilon^i(\text{cont})(t_i - 298.15\ \text{K}) + \varepsilon^f(\text{cont})(298.15\ \text{K} - t_f - \Delta t_{corr})$.

[d] Items 81 to 85, 87 to 90, 93 and 94 of the computation form of reference 2.

TABLE 2. Summary of experimental results: values of $\Delta_c u^\circ$ for reaction (1) at 298.15 K

$\Delta_c u^\circ/(\text{kJ}\cdot\text{g}^{-1})$:	-36.4688, -36.4746, -36.4914, -36.4958, -36.4870, -36.4783, -36.4859, -36.4972
$\langle\Delta_c u^\circ\rangle/(\text{kJ}\cdot\text{g}^{-1})$:	-36.4849 ± 0.0036[a]

[a] Standard deviation of the mean.

energy of the idealized combustion reaction, for all experiments are given in table 2. The combustion reaction for 2,3-diphenylcycloprop-2-en-1-one is represented by the equation:

$$C_{15}H_{10}O(\text{cr}) + 17O_2(\text{g}) = 15CO_2(\text{g}) + 5H_2O(\text{l}). \qquad (1)$$

Derived values of the standard molar energy of combustion $\Delta_c U^\circ_m$, the standard molar enthalpy of combustion $\Delta_c H^\circ_m$, the standard molar enthalpy of sublimation $\Delta^g_{cr} H^\circ_m$, and the corresponding molar enthalpies of formation $\Delta_f H^\circ_m$, for both crystalline and gaseous phases of 2,3-diphenylcycloprop-2-en-1-one are given in table 3. The uncertainties in table 3 are twice the standard deviations of the means and include the uncertainties in the determined energies of combustion of all the materials used. The values$^{(11)}$ $\Delta_f H^\circ_m(CO_2, \text{g}) = -(393.51 \pm 0.13)\ \text{kJ}\cdot\text{mol}^{-1}$ and $\Delta_f H^\circ_m(H_2O, \text{l}) = -(285.830 \pm 0.042)\ \text{kJ}\cdot\text{mol}^{-1}$ were used to derive the enthalpies of formation.

The vapor pressure of 2,3-diphenylcycloprop-2-en-1-one was measured in the temperature range 353 to 378 K and varied from 0.1 to 0.01 Pa. Equilibration of the vapor pressure in the sample compartment with the ballast tank was experimentally demonstrated to require 600 s. A similar period was necessary for transfer of the vapor from the ballast tank to the collection trap. Consequently, each vapor-pressure measurement required 600 s for equilibration with the ballast tank and 1200 s for collection. Vapor pressures were measured at seven temperatures; an average of four measurements were made at each temperature. Vapor pressures are reported in table 4 and figure 1. The uncertainties associated with each measurement are standard deviations. Error bars in $1/T$ represent the uncertainty associated with a temperature control of the sample chamber of ±0.4 K. Since the vapor pressures measured for 2,3-diphenylcycloprop-2-en-1-one are in the 0.01 Pa range, corrections for the contributions of adsorbed substrate were not necessary to

TABLE 3. Derived molar values for 2,3-diphenylcycloprop-2-en-1-one at 298.15 K

$\Delta_c U^\circ_m(C_{15}H_{10}O, \text{cr}) = -(7524.87 \pm 1.82)\ \text{kJ}\cdot\text{mol}^{-1}$ [a]

$\Delta_c H^\circ_m(C_{15}H_{10}O, \text{cr}) = -(7529.83 \pm 1.82)\ \text{kJ}\cdot\text{mol}^{-1}$ [a]

$\Delta_f H^\circ_m(C_{15}H_{10}O, \text{cr}) = (198.03 \pm 1.96)\ \text{kJ}\cdot\text{mol}^{-1}$

$\Delta^g_c H^\circ_m(C_{15}H_{10}O, \text{cr}) = (119.7 \pm 8)\ \text{kJ}\cdot\text{mol}^{-1}$

$\Delta_f H^\circ_m(C_{15}H_{10}O, \text{g}) = (317.7 \pm 8.2)\ \text{kJ}\cdot\text{mol}^{-1}$

[a] Relates to reaction (1).

TABLE 4. Experimental vapor pressures p^{s} with standard deviations of 2,3-diphenylcycloprop-2-en-1-one

p^{s}/Pa	$(T/\mathrm{K}) \pm 0.4$	p^{s}/Pa	$(T/\mathrm{K}) \pm 0.4$
0.0328 ± 0.0040	353.6	0.188 ± 0.039	369.0
0.0566 ± 0.0130	357.0	0.299 ± 0.040	373.2
0.0878 ± 0.0130	361.4	0.465 ± 0.020	377.8
0.126 ± 0.024	365.2		

achieve linearity and the effect of these corrections on the molar enthalpy of vaporization $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}$ was small, increasing the slope by 4 kJ · mol^{-1}. The results reported in figure 1 are corrected for the contributions of adsorbed substrate and thus are a more accurate measurement of the true vapor pressure and the molar enthalpy of sublimation $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}$ of 2,3-diphenylcycloprop-2-en-1-one at these temperatures.

Quantitative analysis of each 2,3-diphenylcycloprop-2-en-1-one sample was done by u.v. spectroscopy, recording the absorbance at 297 nm in acetonitrile. A Beckman Acta MV1 spectrometer was used for these measurements.

In order to ensure that traces of the 2,3-diphenylcycloprop-2-en-1-one hydrate, which has been reported to be more volatile,(4) did not interfere with the vapor-pressure measurements, approximately 5 to 10 per cent of the sample was sublimed in the apparatus prior to use. A least-squares treatment of the results gave a molar enthalpy of sublimation of (119.7 ± 8.0) kJ · mol^{-1} and an intercept corresponding to 1.81×10^{10} MPa. The correlation coefficient was 0.9982.

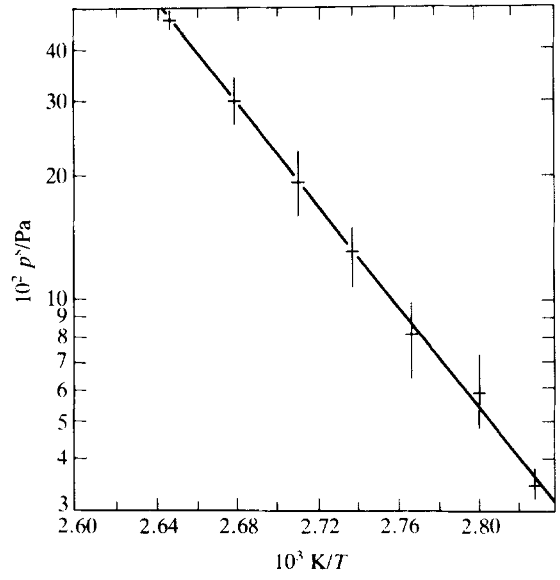
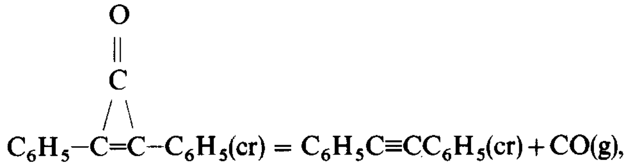


FIGURE 1. The vapor pressure plotted on a logarithmic scale against $1/T$ for 2,3-diphenylcycloprop-2-en-1-one.

4. Discussion

There is a large discrepancy between the published specific energy of combustion of 2,3-diphenylcycloprop-2-en-1-one: $-(37518 \pm 17)\ \text{J}\cdot\text{g}^{-1}$ of Hopkins, Bostwick, and Alexander(4) and the result obtained here: $-(36484.9 \pm 3.6)\ \text{J}\cdot\text{g}^{-1}$. A possible reason for the discrepancy might have been the presence of diphenylethyne in the Hopkins *et al.* sample. Diphenylethyne has a specific energy of combustion of $-40645\ \text{J}\cdot\text{g}^{-1}$,(12) and is known to be the decomposition product of 2,3-diphenylcycloprop-2-en-1-one at 423 K. The impurity would have had to be present to the extent of 0.25 mole per cent to explain the noted discrepancy.

It is also interesting to note that the decomposition reaction:



$$\overset{\displaystyle O}{\overset{\|}{\overset{\displaystyle C}{\overset{/\ \backslash}{C_6H_5{-}C{=}C{-}C_6H_5}}}}(\text{cr}) = C_6H_5C{\equiv}CC_6H_5(\text{cr}) + \text{CO}(\text{g}), \qquad (2)$$

is almost thermoneutral with $\Delta_r H_m^\circ = (3.9 \pm 2.3)\ \text{kJ}\cdot\text{mol}^{-1}$.

Application of Benson group increments leads to a value of $126\ \text{kJ}\cdot\text{mol}^{-1}$ for $\Delta_f H_m^\circ$ of hypothetical gaseous 2,3-diphenylcycloprop-2-en-1-one lacking strain and resonance stabilization in the three-membered ring.(5) If one assumes a ring-strain energy of $280\ \text{kJ}\cdot\text{mol}^{-1}$,(12) then the cyclopropenone resonance stabilization is $88\ \text{kJ}\cdot\text{mol}^{-1}$. The magnitude of this value supports the general view of cyclopropenone as an aromatic molecule having significant ground-state stabilization.

NOTE ADDED AFTER SUBMISSION

Following submission of this work, a paper(16) appeared in which the enthalpy of decarbonylation of 2,3-diphenylcycloprop-2-en-1-one was measured by photo-acoustic calorimetry. Use of the published value: $\Delta_f H_m^\circ(\text{diphenylethyne, cr}) = 312.4\ \text{kJ}\cdot\text{mol}^{-1}$,(17) with a recent value: $\Delta_{cr}^{g} H_m^\circ = 90\ \text{kJ}\cdot\text{mol}^{-1}$,(18) yields a value of $\Delta_f H_m^\circ(C_{14}H_{10}, \text{g})$ that is $28\ \text{kJ}\cdot\text{mol}^{-1}$ lower than the value estimated for this molecule in the above paper.(16) Combination of this experimental result with the published(16) enthalpy of decarbonylation yields a value for $\Delta_f H_m^\circ(C_{15}H_{10}O, \text{g})$ of $(333.2 \pm 17)\ \text{kJ}\cdot\text{mol}^{-1}$, assuming that differential enthalpies of solvation in benzene are negligible for reactants and products. This value is in agreement with the value reported in the present paper.

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