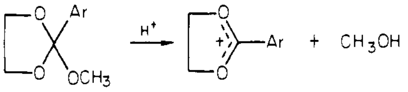
orthocyclopropanecarboxylate (see Table II for a listing of the relevant rate constants); indeed a change in rate-determining step cannot occur unless $k^{3}{}_{H^+}$ is less than $k^{1}{}_{H^+}$.

Other factors must be operative, and one of these could be the ring-opening nature of stage 3 in most of these cases. There is evidence that the exocyclic group is lost first in the hydrolysis of monocylic ortho esters such as 2-aryl-2-methoxy-1,3-dioxolanes (eq 10)[2b,7a] and that gives this reaction, and therefore stage 1, the


(10)

entropic advantage afforded by incipient generation of two particles from one. Stage 3, on the other hand, is a ring-opening process (see eq 7 and 8) from which this entropic benefit is absent because the two separating parts of the molecule are still held together by the remaining ring atoms. Effects of this kind have been observed, for example, in the hydrolysis of cyclic acetals and ketals, which react more slowly than do the corresponding acyclic substrates; the retardation, moreover, appears largely as a more negative entropy of activation.[16]

This factor, of course, cannot operate to slow the rate of stage 3 for acylic ortho esters such as the first three entries in Table II, and it is significant, therefore, that the ratio of $k^{+}{}_{H^+}$ to $k^{1}{}_{H^+}$ for each of these substrates is greater than that for its similarly substituted cyclic counterpart, e.g., $k^{+}{}_{H^+}/k^{1}{}_{H^+} = 270$ for trimethyl orthoformate whereas this ratio is only 6.9 for 2-methoxy-1,3-dioxolane. Another factor must be functioning here, and that could be an initial state effect which lowers the free energy of the hydrogen ortho ester reactant of stage 3 and thus slows the rate of reaction in this way. For example, hydrogen ortho esters, because of their hydroxy functional groups, will be better solvated than ortho esters themselves in the aqueous medium used for these reactions, and this additional stabilization will add an increment to the free energy of activation for reactions of hydrogen ortho esters which will be absent from that for the ortho esters. This solvation effect should be relatively more important for hydrogen ortho esters with large hydrophobic substituents such as aryl or cyclopropyl at their *pro*-acyl carbon atoms than for substrates with small groups such as hydrogen at this position, and it is significant, therefore, that the $k^{+}{}_{H^3}/k^{1}{}_{H^3}$ ratio drops from hydrogen through methyl to cyclopropyl (and aryl) substituents along both the acyclic and cyclic series listed in Table II.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada and the donors of the Petroleum Research Fund, administered by the Americal Chemical Society, for their financial support of this work.

Registry No. 2, 54917-76-9; **3**, 1445-45-0; **4**, 20006-56-8; **5**, 19798-71-1; HCl, 7647-01-0; H^+, 12408-02-5; H_3PO_4, 7664-38-2; $H_2PO_4^-$, 14066-20-7; $HC(OCH_3)_3$, 149-73-5; 2-methoxy-1,3-dioxolane, 19693-75-5.

Supplementary Material Available: Tables of rate constants (5 pages). Ordering information is given on any current masthead page.

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The Strain Energy of Diphenylcyclopropenone: A Reexamination

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Contribution from the Department of Chemical Engineering and Chemistry, New Jersey Institute of Technology, Newark, New Jersey 07102, and the Department of Chemistry, University of Maryland Baltimore County, Catonsville, Maryland 21228. *Received March 24, 1983*

Abstract: The published value for $\Delta H_f°(g)$ of diphenylcyclopropenone and its attendant strain energy have been reinvestigated. Conceptual and calculational schemes indicate that the published value is too high by as much as 50 kcal/mol. Preliminary heat of combustion studies support this conclusion. On the basis of isodesmic equations employing the 4-31G and 6-31G* basis sets, significant aromatic stabilization is found in cyclopropenone.

Almost 25 years of cyclopropenone chemistry[1-5] have failed to decide the issue of whether or not this molecule is, in fact, the smallest neutral aromatic specie. The stabilities of derivatives (e.g. diphenylcyclopropenone is thermally stable to 130 °C)[1-5] and their high dipole moments (ca. 4.7-5.1 D[5]), low infrared carbonyl frequencies (1640 cm^{-1} which may be compared with 1815 cm^{-1} for cyclopropanone), and low pK_b values[5] have all been cited as proof for aromatic stabilization. Gas-phase structural studies of cyclopropene, cyclopropanone, and cyclopropenone[6] suggest a lengthening of the carbonyl bond and a shortening of C_1–C_2 compatible with extensive π delocalization. Similar parameters have been found for solid-state diphenylcyclopropenone hydrate.[7] Admittedly primitive, Hückel calculations obtain a resonance stabilization of 1.36β in cyclopropenone,[8] which may be compared with values of 2β in benzene, 0.96β in methylenecyclopropene, and 0.47β in 1,3-butadiene. Using the criterion of resonance energy per π electron (REPE), Hess and Schaad concluded that cyclopropenone is aromatic while tropone is not.[9]

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Similar conclusions were reached by Aihara.[10] Ab initio molecular orbital calculations using the double-ζ basis set led Hase et al. to conclude that cyclopropenone has 37 kcal/mol more resonance stabilization than cyclopropene, but 9.5 kcal/mol less than benzene.[11] Herndon has recently interpreted photoelectron spectra and concluded that the resonance stabilization in cyclopropenone is 23.2 kcal/mol while that in tropone is 10.8 kcal/mol.[12]

In contrast, Tobey rationalized the high dipole moments of cyclopropenones as well as NMR and UV spectral data without recourse to aromaticity.[13] Another potential argument against cyclopropenone aromaticity was advanced by Benson, Flygare, Oda, and Breslow,[14] using the criterion of magnetic susceptibility anisotropy. They concluded that "by the magnetic criterion 'aromaticity' cannot be detected, although aromaticity in cyclopropenone is suggested by its other chemical and physical properties". Most striking, however, is a published experimental calorimetric study of diphenylcyclopropenone that indicates total destabilization in this molecule to be in the range 78–97 kcal/mol.[15] This total destabilization can be attributed to ring strain if π delocalization and the accompanying resonance stabilization in the three-membered ring are zero. If the resonance stabilization is not zero, then the strain energy should be even greater. The authors of this work[15] conclude that cyclopropenone is not aromatic.

The above-cited strain energies appear to be anomalously high, and the purpose of the present paper is to demonstrate that they are markedly incorrect. The arguments advanced in this paper will employ Benson group incremental schemes associated with known strain energies of related molecules, extended basis set ab initio molecular orbital calculations coupled with experimental calorimetric data, and preliminary calorimetric data for diphenylcyclopropenone. After establishing a better value for the total destabilization energy, the question of aromatic stabilization will be reexamined.

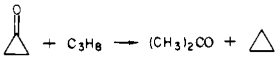
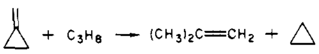
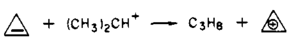
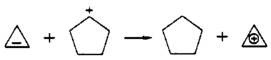
Calculational Technique

Where geometry-optimized calculational data were not available from the literature, ab initio molecular orbital calculations were performed by using the GAUSSIAN 70 program series[16] and the 4-31G basis set.[17] The structures employed for 3,3-cyclopropenediol and 1,1-cyclopropanediol, potential ketone hydrates, were derived by combining the structural parameters (STO-3G level) of methanediol[18] with those of cyclopropene[19] and cyclopropane,[19] respectively.

Experimental Section

Diphenylcyclopropenone (Aldrich, 98%) was recrystallized twice from spectral grade cyclohexane. It was then placed in a vacuum sublimator for ca. 6 h at 100–110 °C and 0.1–0.5 mmHg. Material collected on the cold finger was the monohydrate.[7] The remaining material formed a white crystalline cake sitting on top of some slightly yellow crystals. The white crystalline material (mp 118–120 °C) was stored in a desiccator until the combustion experiment. Bomb calorimetry was performed by using a Parr 1241 adiabatic oxygen bond calorimeter equipped with the Parr Master Control, Parr automated Bucket Filling System, and Parr Water Heater and Water Cooler.

Table I. Extended Basis Set Ab Initio Results Compared to Experimental Data for Reaction of Compounds Related to Cyclopropenone[a]

	reaction	calcd ΔE		ΔH_r°
		4-31G	6-31G*	
(1)		−18.7		−18.0
(2)		−10.5	−9.9	−14.2
(3)		−65.5	−69.5	−60.5[b]
(4)		−35.7	−41.9	−25.2
(5)				−25.9[c]

[a] Values for ΔH_f and 4-31G total energies are taken from Table I, ref 23; 6-31G* data are from ref 18. Energy and enthalpy changes are in kcal/mol. [b] The experimental value for the cyclopropyl cation is somewhat uncertain due to its ready rearrangement to allyl cation. The value assumed here is further discussed in Table I, ref 23. The fact that the discrepancies between calculation and experiment in eq 4 and 5 are similar lends support to the derived value for the cyclopropyl cation. [c] Value for cyclopentyl cation derived from Aue and Bowers: Aue, D. H.; Bowers, M. T. "Gas-Phase Ion Chemistry"; Academic Press: New York, 1979; Vol. 2.

Caution: As others have noted,[7] diphenylcyclopropenone can cause extremely severe contact dermatitis in sensitive individuals.

Results and Discussion

It is useful to compare the reported experimental value of [ΔH_f°(g)] for diphenylcyclopropenone (132.0 kcal/mol)[15] with that calculated by using Benson's group increments.[20] One may combine group ΔH_f° values of −25.8 kcal/mol for $CO(C_d)_2$, assumed here to be equal to $CO(C_B)_2$, with the published values of 3.30 kcal/mol for $C_B(H)$ and 5.68 kcal/mol for $C_B(C_d)$, and an assumed value of 5.8 kcal/mol for $C_d(C_B)(CO)$ (compare $C_d(C)(CO)$, 7.5 kcal/mol, with $C_d(C)_2$, 10.34 kcal/mol, and $C_d(C_B)(C)$, 8.64 kcal/mol). The resulting hypothetical diphenylcyclopropenone has ΔH_f°(g) equal to 30.2 kcal/mol, which is almost 102 kcal/mol lower than the reported experimental value! While the assumptions made above may introduce errors of a few kcal/mol, the basic conclusion is clear. (No correction for repulsion between nonbonded phenyl groups is included since none are apparent from the published X-ray study[7] and, in any case, the enthalpy difference between cis and trans stilbene is only 4.2 kcal/mol.[21]) It is also worthwhile to note that the Benson group increments for $C_B(H)$ and $C_B(C_d)$ already take into account benzene's resonance stabilization.

The 102-kcal/mol total destabilization in diphenylcyclopropenone could be equated to ring strain if one assumes no resonance stabilization in the three-membered ring. Any resonance stabilization must increase the strain energy above 102 kcal/mol. What is a reasonable strain energy for cyclopropenone? Taking the strain energy of cyclopropene at 53.7 kcal/mol[20] and adding the difference in the strain energies of methylenecyclopropane (41 kcal/mol[20]) and cyclopropane (27.6 kcal/mol[20]) leads to a value of 67 kcal/mol. It is hard to imagine the strain energy of methylenecyclopropene differing from this by more than a few kcal/mol.

At this point it is useful to explore the predictions of extended basis set ab initio molecular orbital calculations applied to the problem at hand. The ability of the 4-31G and 6-31G* basis sets

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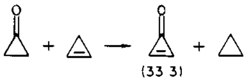
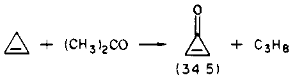
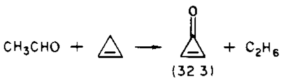
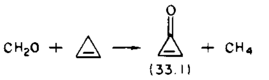
[21] Pedley, J. B.; Rylance, J. "Sussex-N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds"; University of Sussex: Sussex, England, 1977.

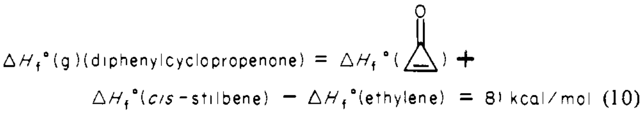
Table II. Use of Isodesmic Reactions Involving 4-31G and 6-31G* Data To Calculate ΔH_f°(g) of Cyclopropenone Using Known Values of ΔH_f°(g) for the Other Three Members of Each Equation (4-31G Data Employed)[a]

	reaction	ΔE (kcal/mol)	
		4-31G	6-31G*
(6)		−24.0	−27.6[b,c]
(7)		−5.3	
(8)		−14.4	−15.4[c]
(9)		−24.9	−25.5[c]

[a] Calculated energy changes are in kcal/mol; the calculated value of ΔH_f°(g) for cyclopropenone is listed under its structure in each equation. [b] A 6-31G* total energy of −119 724.8 kcal/mol (−190.72659 hartrees, using 627.73 kcal/mol·hartree) for cyclopropanone using its experimental geometry; Dr. James P. Snyder, personal communication. [c] The cyclopropenone value is obtained from Komornicki et al. [Kormornicki, A. K.; Dykstra, C. F.; Vincent, M. A.; Radom, L. *J. Am. Chem. Soc.* 1981, *103*, 1652] and is based upon their 6-31G** value. Since the difference between 6-31G** and 6-31G* values for two other two-hydrogen molecules, acetylene and vinylidene (compare data in this reference to those in ref 18), is 2.5 kcal/mol, the published 6-31G** value was so corrected.

to accurately predict the energies of isodesmic reactions 1–5 is shown by the data in Table I. It is known that 4-31G calculations do not quantitatively describe strain energies, but these problems largely disappear when energies are compared isodesmically.[22] The 6-31G* basis set handles strain adequately, correctly predicting the energy of the isomerization of cyclopropane to propene.[22]

In Table II, 4-31G and 6-31G* results are listed for isodesmic eq 6–9 involving cyclopropenone and other molecules for which ΔH_f°(g) data are available.[21,23] The calculated value for ΔH_f°(g) with use of these data is listed in parentheses under cyclopropenone in each equation of Table II. A value for ΔH_f°(g) of 33 kcal/mol is taken as the assumed value. If one now compares the derived value for cyclopropenone with the experimental values for ethylene and *cis*-stilbene, an estimated value for the correct ΔH_f°(g) of diphenylcyclopropenone is obtained (eq 10). This value is about



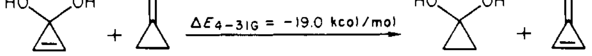
ΔHf°(g)(diphenylcyclopropenone) = ΔHf°( ) + ΔHf°(*cis*-stilbene) − ΔHf°(ethylene) = 81 kcal/mol (10)

51 kcal/mol lower than the published value, a conclusion that does not change qualitatively if one attempts relatively minor refinements of the estimation scheme.

Preliminary bomb calorimetry results have been obtained for diphenylcyclopropenone. The average of seven runs[24] indicates an enthalpy of combustion for the solid of 8749 ± 23 cal/g, which may be compared with the published value[15] of 8967.0 ± 4.4 cal/g. The discrepancy is 45 ± 5 kcal/mol and is consistent, in magnitude and direction, with the calculated energy difference. Presently, while more refined enthalpy of combustion and enthalpy of sublimation measurements are being made on diphenylcyclopropenone, they will not qualitatively affect out conclusion.

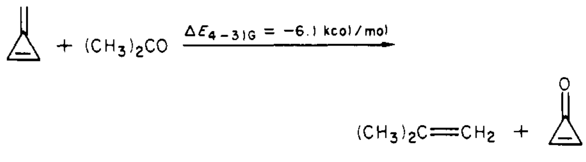
It is worthwhile to return to the question of resonance (aromatic?) stabilization in diphenylcyclopropenone. The hypothetical molecule, lacking strain as well as resonance stabilization in the three-membered ring, has ΔH_f° equal to about 30 kcal/mol. The approximate correct value is 81 kcal/mol. The apparent 51-kcal/mol total destabilization is the sum of ring strain, previously estimated at 67 kcal/mol, and resonance stabilization, thus calculated to be 16 kcal/mol. (If the strain is greater, so is resonance stabilization.) It is important to note, however, that the resonance stabilization of the cyclopropenone ring in diphenylcyclopropenone may well be less than that in the parent ring despite the fact that Hückel calculations predict the total resonance energy in this molecule to to 0.79β greater than in the sum of cyclopropenone and two benzenes.[8] Some evidence of this seems apparent from the photoelectron spectroscopic investigations of Schweig and co-workers.[25] In the present work, it is implicitly assumed that the three-membered-ring resonance stabilization in diphenylcyclopropenone is equal to that of the parent compound. If it is less, then the predicted value may be in even better agreement with the preliminary calorimetric data.

A resonance stabilization of 16 kcal/mol begins to "smell" aromatic. It is worthwhile to make comparisons using good calculational data in the absence of experimental data. For example, eq 6 in Table II has, to a first approximation, equal strain energies on both sides. The reaction's exothermicity might thus be simply equated to electronic delocalization and thus aromatic stabilization. Another comparison is made in eq 11.[26] However,



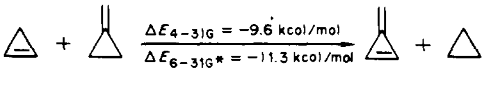
(11)

if one compares cyclopropenone to methylenecyclopropene (eq 12), the difference in resonance energies is significant, though not very great. However, according to both 4-31G and 6-13G*



(12)

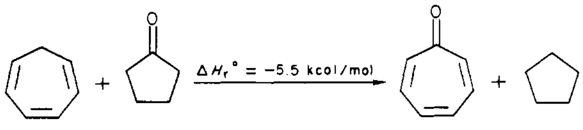
calculations there is significant resonance stabilization in methylenecyclopropene (eq 13). Thus, the difference between cyclopropenone and methylenecyclopropene may be more quantitative than qualitative. Although an even smaller resonance



(13)

energy difference was calculated by Hess and Schaad,[9] they made a qualitative distinction between aromatic cyclopropenone and nonaromatic methylenecyclopropene.

One can also briefly examine the next potentially aromatic annulenone. Tropone is nonaromatic from the standpoint of calorimetry.[27] Equation 14 indicates stabilization largely explicable in terms of enone resonance. In contrast, of course, the



(14)

corresponding ions, cyclopropenium and tropylium, have large resonance stabilization energies of 60 kcal/mol (eq 3, Table I) and 47 kcal/mol (eq 15),[28] respectively, reflecting the advantages

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[22] Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978; Chapter 1.

[23] Greenberg, A.; Liebman, J. F.; Dolbier, W. R., Jr.; Medinger, K. S.; Skancke, A. *Tetrahedron* **1983**, *38*, 1533–1538.

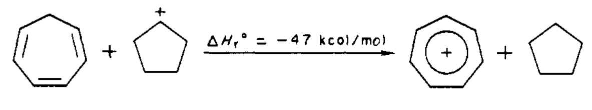
[24] Experimental values (n = 7) for ΔH_c(diphenylcyclopropenone) in cal/g: 8710.5, 8745.3, 8735.5, 8772.9, 8740.8, 8769.5, 8767.8.

[25] Muller, C.; Schweig, A.; Vermeer, H. *J. Am. Chem. Soc.* **1978**, *100*, 8056–8060.

[26] Calculated total energies (h): 3,3-cyclopropenediol, STO-3G −262.08459 and 4-31G −265.13841; 1,1-cyclopropanediol, STO-3G −263.34011 and 4-31G −266.37233.

[27] Jackson, W.; Hung, T. S.; Hopkins, H. P., Jr. *J. Chem. Thermodyn.* **1971**, *3*, 347–353.

of charge delocalization over charge separation in the annulenones.



(15)

Conclusions

The published experimental value for $\Delta H_f°(g)$ of diphenylcyclopropenone is too high by as much as 50 kcal/mol corresponding to a 2.5% error in the heat of combustion, possibly due to the presence of a small amount of impurity in the compound tested in the earlier work. More refined calorimetric measurements are in progress. The resonance stabilization in cyclopropenone appears to be in the range of 20 ± 5 kcal/mol. The value is about 6 kcal/mol greater than in methylenecyclopropene and lends support to the view that cyclopropenone has some ground-state aromatic stabilization.

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Registry No. Diphenylcyclopropenone, 886-38-4.

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(28) Greenberg, A.; Liebman, J. F. *J. Org. Chem.* **1982**, *47*, 2084–2088.

Kinetics of Ozonation. 1. Electron-Deficient Alkenes

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Abstract: Absolute rates of reaction of ozone with a series of alkenes bearing electron-withdrawing groups have been determined at several temperatures in CCl_4 by a stopped-flow technique. From these data, activation parameters have been calculated and range from those of tetrachloroethylene (E_a = 11 kcal/mol; log A(s^{-1}) = 6.0) to those of styrene (E_a = 3.1 kcal/mol; log A(s^{-1}) = 7.5) and 1-hexene (E_a = 2.4 kcal/mol; log A(s^{-1}) = 6.8). These results show that the ozonation of alkenes is quite sensitive to electronic effects, with electron-deficient alkenes reacting orders of magnitude slower than electron-rich alkenes. The rate of reaction of *trans*-1,2-dichloroethylene is about 25 times that of the cis or the 1,1 isomer, which is consistent with a 1,3-dipolar cycloaddition mechanism. Calculated entropies of activation also are consistent with this, but a general trend toward less negative entropies of activation with lower E_a suggests the possibility of a change in mechanism for more electron-rich alkenes.

Ozone is one of the most important toxins on a worldwide basis, responsible for lost work and illness to humans living in high-smog areas.[1-5] In order to model the reactivity patterns of ozone with the many potential targets in the lung, it is necessary to combine a knowledge of pulmonary physiology with the rate constants for the reactions of ozone with a wide range of biological molecules. Although the absolute rate constants for reaction of ozone with a large number of low molecular weight species have been measured in studies aimed at understanding the reactions that occur in gas-phase smog,[6-8] very few data are available for the reaction of typical organic and biological molecules with ozone in condensed phases. Therefore, we have begun a program to determine the absolute rate constants for reaction of ozone with major organic functional groups and with critical biological molecules and biopolymers.[9-12]

In this paper we report the rate constants for the halogenated olefins and other alkenes bearing electron-withdrawing groups. The rate constants at room temperature for the reactions of several of these compounds with ozone have been reported earlier, allowing a comparison of our data with literature values. However, few of the Arrhenius parameters have been previously reported, and we now provide those data.

Experimental Section

Purification of Carbon Tetrachloride. Carbon tetrachloride (Mallinckrodt, analytical reagent) was pretreated with a stream of ozone in oxygen for several hours at room temperature and then allowed to stand overnight. The solution was still blue after this time. After degassing under reduced pressure, no ozone or other peroxidic material reactive toward aqueous iodide remained in the carbon tetrachloride.

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