PERKIN 2

Ring strain energy and enthalpy of formation of oxiranone: an *ab initio* theoretical determination

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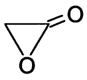
The enthalpy of formation $\Delta H^\circ_{f,298}$ for oxiranone is estimated as −190 ± 10 kJ mol^{-1} by means of *ab initio* molecular orbital calculations at the QCISD(T)=full/6-311G(2df,p)//MP2=full/6-311G(d,p) level of theory, corresponding to a conventional ring strain energy of 169 kJ mol^{-1}. The QCISD(T) calculated enthalpy of formation of cyclopropanone is 6.3 kJ mol^{-1}. The oxiranone ring is probably slightly less strained than the cyclopropanone ring.

Introduction

Oxiranones (α-lactones) are very unstable and highly reactive intermediates which are difficult to isolate; they polymerise readily to polyesters and undergo decarbonylations, even at low temperature.[1] The parent oxiranone **1** was reported in a matrix isolation study of the reaction of methylene with carbon dioxide,[2] and other species have recently been formed by carboxylation of substituted carbenes in low-temperature matrices.[3,4] They may be generated by photodecarboxylation of malonyl peroxides[5] or by epoxidation of ketenes.[6] Only two species, **2** and **3**, with electron withdrawing[7] and, additionally, bulky[8] substituents have any stability at room temperature. Oxiranones have been postulated as transient intermediates in a variety of reactions,[9] perhaps most notably in the alkaline hydrolysis of α-halocarboxylates in dilute solution[10] and most recently in the gas-phase pyrolysis of α-chlorocarboxylic acids.[11]



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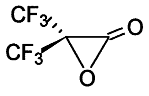

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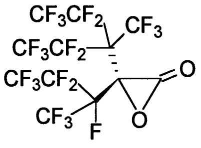

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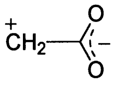
It has been suggested[6] that the extreme reactivity of oxiranones is due to their ease of ring-opening to a zwitterionic form **4**. Theoretical studies employing the semiempirical INDO[12] and MINDO/3[13] molecular orbital (MO) methods both found the cyclic structure **1** to be of lower energy than ring-opened forms. However, no minimum-energy structure corresponding to a closed-shell acyclic zwitterion **4** was found at the HF/3-21G* level of *ab initio* MO theory; high-energy zwitterionic structures in which the methylene and carboxylate moieties were coplanar disintegrated spontaneously to CH_2 and CO_2, whereas those in which these groups were mutually perpendicular collapsed to the cyclic oxiranone.[14] Configuration interaction (CI) calculations, involving single and double excitations selected by perturbation theory, and extrapolation to the full CI limit, for various electronic states of the acetoxyl diradical **5**, in both planar and perpendicular geometries, were all found to be at least 147 kJ mol^{-1} higher in energy than the oxiranone **1**.[14]



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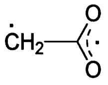

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Our interest in the thermochemistry of oxiranones was aroused by the suggestion put forward in a recent experimental study that the spontaneous and acid-catalysed hydrolyses of the *p*-nitrophenyl glycoside of *N*-acetylneuraminic acid occur by means of a transition state involving intramolecular nucleophilic assistance by the neighbouring carboxylate group, even though this mechanism might lead to formation of a highly strained α-lactone intermediate.[15] The precedent for this suggestion is the classical work, following Ingold, on nucleophilic substitutions of α-halocarboxylates:[16] the observations of retained stereochemical configuration and lack of dependence on hydroxide ion concentration in the reaction of α-bromopropionate anion with dilute sodium hydroxide may be explained by the intermediacy of an α-lactone.[10] How strained is such a species, and how likely is it to be formed as a reaction intermediate?

To answer the question 'What is the strain energy of an α-lactone?' requires knowledge of either the enthalpy of formation or the enthalpy change for a suitable isodesmic process involving a three-membered heterocycle of known strain energy. The only value available in the literature[17] appeared to be a bond-additivity estimate of the enthalpy of formation for the parent oxiranone **1** of dubious validity. The purpose of this paper is to present the results of high-level *ab initio* MO calculations for the enthalpy of formation and the ring strain energy of oxiranone; results for oxirane and cyclopropanone are also presented. First, the conventional ring strain energy of oxiranone is estimated by means of an isodesmic relation to oxirane **7**. Secondly, the enthalpy of formation of oxiranone is estimated by means of isodesmic relations both to oxirane and to cyclopropanone **10**. Thirdly, the enthalpies of formation of **1**, **7** and **10** are each evaluated directly from computed atomization energies. Finally, comparison is made between the ring strain energies of oxiranone and cyclopropanone. These ring strain energies should be of value in mechanistic discussions involving possible α-lactone intermediates.

Computational methods

All calculations were carried out using the GAUSSIAN92 and 94 series of programs.[18,19] Full geometry optimizations were performed at the second-order Møller–Plesset (MP2) level using the 6-311G(d,p) basis with all MOs being active (MP2=full). Hartree–Fock [HF/6-31G(d,p)] harmonic vibrational frequency calculations were used to obtain zero-point and thermal energy corrections at 298 K. Single-point energies were evaluated using fourth-order Møller–Plesset (MP4SDTQ) theory including single, double, triple and quadruple excitations but with inactive core MOs (frozen-core, MP4=fc) and also quadratic configuration interaction [QCISD(T)] including single and

Table 1 Calculated total energies, vibrational zero-point and thermal energies (E_{zp} and E_{th}/kJ mol^{-1}) and standard enthalpies of formation and of reaction ($\Delta H^\circ_{f,298}$ and $\Delta H^\circ_{r,298}$/kJ mol^{-1}) for the isodesmic reaction (1)

	HF/6-31G(d,p)			MP2/6-311G(d,p)	MP4/6-311G(2df,p)		
Structure	Total energy/ hartree[a]	E_{zp}[b]/ kJ mol^{-1}	E_{th}/ kJ mol^{-1}	Total energy/ hartree	Total energy/ hartree	$\Delta H^\circ_{f,298}$/ kJ mol^{-1}	Expt.
1	−226.570 24	110	9	−227.365 21	−227.458 68	−210	
6	−232.160 58	383	18	−233.110 87			−252.1 ± 0.8[d]
7	−152.874 07	163	8	−153.453 99	−153.522 78	−62	−52.6 ± 0.6[e]
8	−305.889 50	332	18	−307.045 98			−444.9 ± 0.7[f]
$\Delta H^\circ_{r,298}$[c]/ kJ mol^{-1}	−85			−61			

[a] 1 hartree = 2625 kJ mol^{-1}. [b] Unscaled vibrational zero-point energy. [c] Evaluated using zero-point energies scaled × 0.89. [d] Ref. 23. [e] Ref. 24. [f] Ref. 21.

Table 2 Calculated total energies, vibrational zero-point and thermal energies (E_{zp} and E_{th}/kJ mol^{-1}) and standard enthalpies of formation and of reaction ($\Delta H^\circ_{f,298}$ and $\Delta H^\circ_{r,298}$/kJ mol^{-1}) for the isodesmic reaction (2)

	HF/6-31G(d,p)			MP2/6-311G(d,p)	MP4/6-311G(2df,p)		
Structure	Total energy/ hartree[a]	E_{zp}[b]/ kJ mol^{-1}	E_{th}/ kJ mol^{-1}	Total energy/ hartree	Total energy/ hartree	$\Delta H^\circ_{f,298}$/ kJ mol^{-1}	Expt.
1	−226.570 24	110	9	−227.365 21	−227.458 68	−210	
9	−231.010 91	315	17	−231.938 55			−240.8 ± 0.6[d]
10	−190.733 26	173	10	−191.465 39	−191.545 21	−7	15.9 ± 4.2[e]
11	−266.846 53	253	15	−267.827 38			−410.0 ± 0.8[d]
$\Delta H^\circ_{r,298}$[c]/ kJ mol^{-1}	4			29			

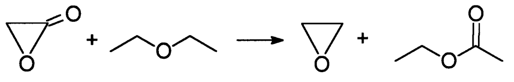
[a] 1 hartree = 2625 kJ mol^{-1}. [b] Unscaled vibrational zero-point energy. [c] Evaluated using zero-point energies scaled × 0.89. [d] Ref. 25. [e] Ref. 26.

double excitations together with a perturbative treatment of triple excitations and with all orbitals active; these calculations employed the 6-311G(2df,p) basis.

Results and discussion

Oxiranone ring strain energy from isodesmic relation to oxirane

The conventional ring strain energy of a cyclic compound is obtained as the difference between the enthalpy of atomization estimated from a group-additivity scheme for a strain-free molecule and the actual observed enthalpy of atomization for the compound.[20,21] The accepted value[22] for the conventional ring strain energy of oxirane **7** is 114 kJ mol^{-1}, very similar to that for cyclopropane (115 kJ mol^{-1}). The strain energy of oxiranone **1** relative to that of oxirane **7** may be evaluated as the enthalpy change $\Delta H^\circ_{r,298}$ for the isodesmic reaction (1), which



(1)

1 **6** **7** **8**

may be quantified by use of the energetic contributions listed in Table 1. [An isodesmic relation is a formal equilibrium in which the number of each different type of bond is conserved. The energy change for eqn. (1), therefore, is simply a measure of the relative preference for the carbonyl group to be located in a cyclic or acyclic ester.] At the MP2/6-311G(d,p) level of theory this quantity is −61 kJ mol^{-1}. The conventional ring strain energy of oxiranone may therefore be estimated by this means as 114 + 61 = 175 kJ mol^{-1}.

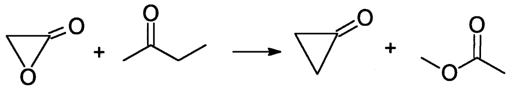
Oxiranone enthalpy of formation from isodesmic relations to oxirane and cyclopropanone

Combining the computed value of $\Delta H^\circ_{r,298}$ for the isodesmic reaction (1) with experimental enthalpies of formation for diethyl ether **6**,[23] oxirane **7**[24] and ethyl acetate **8**[21] allows the enthalpy of formation for oxiranone **1** to be evaluated.

$$\Delta H^\circ_{f,298}(\mathbf{1}) = \Delta H^\circ_{f,298}(\mathbf{7}) + \Delta H^\circ_{f,298}(\mathbf{8}) - \Delta H^\circ_{f,298}(\mathbf{6}) - \Delta H^\circ_{r,298} = (-52.6 \pm 0.6) + (-444.9 \pm 0.7) - (-252.1 \pm 0.8) - (-61.0) = -184\ \text{kJ mol}^{-1} \quad (1)$$

The scheme used by Liebman and Greenberg[17] to estimate the enthalpy of formation of oxiranone (as −130 kJ mol^{-1}) is equivalent to the isodesmic reaction (2), in which the molecular strain is considered relative to that of cyclopropanone **10**. [The energy change for eqn. (2) is a measure of the relative preference for the ether oxygen to be located in a cyclic or acyclic ester.] The enthalpy change $\Delta H^\circ_{r,298}$ for reaction (2) may be quantified by use of the energetic contributions listed in Table 2. At the MP2/6-311G(d,p) level of theory this quantity is 29 kJ mol^{-1}. Combining the computed value of $\Delta H^\circ_{r,298}$ for the isodesmic reaction (2) with experimental enthalpies of formation for butan-2-one **9**,[25] cyclopropanone **10**[26] and methyl acetate **11**[25] allows the enthalpy of formation for oxiranone **1** to be evaluated.

$$\Delta H^\circ_{f,298}(\mathbf{1}) = \Delta H^\circ_{f,298}(\mathbf{10}) + \Delta H^\circ_{f,298}(\mathbf{11}) - \Delta H^\circ_{f,298}(\mathbf{9}) - \Delta H^\circ_{r,298} = (16 \pm 4) + (-410.0 \pm 0.8) - (-240.8 \pm 0.6) - (29.2) = -182\ \text{kJ mol}^{-1} \quad (2)$$



(2)

1 **9** **10** **11**

The two isodesmic schemes yield computed estimates for the enthalpy of formation of oxiranone which are identical within the errors of the experimental $\Delta H^\circ_{f,298}$ values employed. It should be noted, however, that there remains a yet unquantified error associated with the choice of the MP2/6-311G(d,p) theoretical method. [The more reliable QCISD(T)=full/6-311G(2df,p) method (see below) could not be employed for the larger species **6**, **8**, **9** and **11** (containing more than four carbon or oxygen atoms) involved in the isodesmic relations (1) and (2), owing to lack of sufficient computational resources.] In Liebman and Greenberg's scheme,[17] the quantity which is here identified as $\Delta H^\circ_{r,298}$(reaction 2) was replaced by a 'π resonance energy' whose value (−46 kJ mol^{-1}) was taken to be equal to the π conjugation energy of acetamide.[27] Since this value differs in both sign and magnitude from our computed value of $\Delta H^\circ_{r,298}$(reaction 2) = +29 kJ mol^{-1}, it is not surprising that

Table 3 Calculated total energies and standard enthalpies of formation (kJ mol^{-1}) for selected species

	MP4SDTQ=fc/6-311G(2df,p)// MP2=full/6-31G(d,p)		QCISD(T)=full/6-311G(2df,p)// MP2=full/6-31G(d,p)		
Structure	Total energy/ hartree[a]	$\Delta H°_{f,298}$/ kJ mol^{-1}	Total energy/ hartree	$\Delta H°_{f,298}$/ kJ mol^{-1}	Expt. $\Delta H°_{f,298}$/ kJ mol^{-1}
1	−227.458 68	−210	−227.536 96	−190	
7	−153.522 79	−59.0	−153.585 19	−54.4	−52.6 ± 0.6[b]
10	−191.545 21	−6.7	−191.627 30	6.3	16 ± 4[c]
C	−37.775 44		−37.796 42		
O	−74.965 54		−74.986 01		
H	−0.499 81		−0.499 81		
H_2	−1.167 73		−1.168 32		

[a] 1 hartree = 2625 kJ mol^{-1}. [b] Ref. 24. [c] Ref. 26.

Liebman and Greenberg's estimate for $\Delta H°_{f,298}(\mathbf{1})$ is considerably different from our MP/6-311G(d,p) derived value of −184 kJ mol^{-1}.

Enthalpies of formation from computed atomization energies: oxirane, cyclopropanone and oxiranone

Although it is not computationally feasible to evaluate the energy changes for the isodesmic reactions (1) and (2) using a theoretical method of any significantly greater accuracy than that used above, it is possible to perform more sophisticated calculations upon the individual species of interest **1**, **7** and **10** (containing only three or four carbon or oxygen atoms), as follows. Oxirane **7** and cyclopropanone **10** are considered first, since these are the 'standards' used in the alternative isodesmic schemes.

Oxirane. Enthalpies of formation may be calculated directly using a previously described procedure[28,29] which has been shown to be accurate to *ca.* ±10 kJ mol^{-1}. This method may be illustrated step by step using oxirane (for which the experimental value[24] of $\Delta H°_{f,298} = -52.6 \pm 0.6$ kJ mol^{-1} is reliably established) as the working example.

(*i*) The atomization energy is determined at the MP4(fc)/6-311G(2df,p)//MP2(full)/6-311G(d,p) level for reaction (3) (energies from Table 3).

$$C_2H_4O \longrightarrow 2C + O + 4H \qquad (3)$$
$$\Delta E_{atom}(7) = 1.007\,13 \text{ hartree}$$

(*ii*) Since this reaction is non-isogyric (C and O atoms each have two unpaired electron spins and atomic H has one), 10H are added to the left-hand side and are balanced on the right-hand side by $5H_2$, to yield the isogyric reaction (4). Use of the MP4(fc)/6-311G(2df,p) energies for C, O, H and H_2 (Table 3) then leads to a corrected atomization energy.

$$C_2H_4O + 6H \longrightarrow 2C + O + 5H_2 \qquad (4)$$
$$\text{corrected } \Delta E_{atom}(7) = 0.166\,57 \text{ hartree}$$

(*iii*) The exact dissociation energy[30] for $5H_2$ (5 × 0.174 47 hartree) is added, giving a value for $\Sigma D_e(7) = 1.038\,92$ hartree (2728 kJ mol^{-1}).

(*iv*) The zero-point vibrational energy of C_2H_4O [HF/6-31G(d,p), Table 1, scaled by 0.89] is subtracted to give $\Sigma D_0(7) = 2583$ kJ mol^{-1}.

(*v*) Using the experimental enthalpies of formation of atoms at 0 K (C, 711; O, 247; H, 216 kJ mol^{-1}),[31] the standard enthalpy of formation of oxirane at 0 K is obtained from eqn. (5).

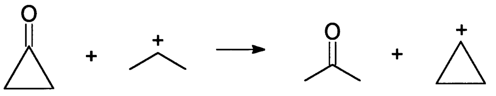
$$\Delta H°_{f,0}(7) = \Delta H°_{f,0}(C) + \Delta H°_{f,0}(H) + \Delta H°_{f,0}(O) - \Sigma D_0\,(C_2H_4O)$$
$$2 \times 711 + 4 \times 216 + 247 - 2583$$
$$= -50 \text{ kJ mol}^{-1} \qquad (5)$$

(*vi*) Thermal corrections are added, using standard heat capacities for the elements in their standard states[32] and theoretical values from Table 3 to give $\Delta H°_{f,298}(7, \text{MP4}) = -59$ kJ mol^{-1}.

This MP4-derived value compares reasonably well with the experimental value[24] of −52.6 ± 0.6 kJ mol^{-1}, given the estimated error of ±10 kJ mol^{-1} in enthalpies of formation computed in this manner.[28] Use of the yet more reliable (but also more expensive!) QCISD(T)=full/6-311G(2df,p)//MP2=full/6-311G(2df,p) energies[29] (Table 3) in place of the MP4 energies, within the procedure laid out in steps (*i*) to (*iv*) above, yields a still better calculated result of $\Delta H°_{f,298}(7, \text{QCI}) = -54$ kJ mol^{-1}.

Cyclopropanone. The same procedures applied to cyclopropanone **10** yield MP4 and QCI calculated values for its enthalpy of formation: $\Delta H°_{f,298}(\mathbf{10}, \text{MP4}) = -6.7$ kJ mol^{-1} and $\Delta H°_{f,298}(\mathbf{10}, \text{QCI}) = +6.3$ kJ mol^{-1}.

Unfortunately, it is not possible to choose between these two computed values simply by appeal to available experimental data, since published estimates for the enthalpy of formation of cyclopropanone vary between *ca.* −12 and +21 kJ mol^{-1}. At the lower end of this range are Liebman and Greenberg's estimates[27] which, however, are unlikely to be reliable in view of their implicit assumption that the enthalpies of reaction for the isodesmic processes (6) and (7) are zero.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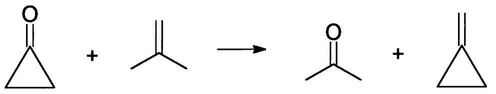
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The value of 16 ± 4 kJ mol^{-1}, adopted in the above discussion of isodesmic reaction (2), was obtained by Thomas and co-workers[26] from measurements of the appearance potential for the $C_2H_4^+$ ion formed from cyclopropanone by electron impact in a mass spectrometer. Evaluation of $\Delta H°_{f,298}(\mathbf{10})$ by this method requires a known value for $\Delta H°_{f,298}(C_2H_4 + CO)$; use of more recent thermochemical data,[31] together with the appearance potential (9.69 eV) of Thomas and co-workers,[26] yields a value for $\Delta H°_{f,298}(\mathbf{10})$ of 21 kJ mol^{-1} rather than 16 kJ mol^{-1}. Note that any excess of internal energy might have yielded an overestimated appearance potential; however, correction for this possible source of experimental error would lead to a still larger value for $\Delta H°_{f,298}(\mathbf{10})$. [It may also be noted that the accuracy of ±0.03 eV claimed for the appearance potential measurement seems optimistic for mid-1970s equipment; ±0.1 eV (±10 kJ mol^{-1}) may be more likely.]

McLafferty and co-workers[33] calculated the enthalpy difference between cyclopropanone and propenal as 76 kJ mol^{-1} at the MP4/6-31G(d)//HF/6-31G(d) level with a scaled HF/6-31G(d) zero-point energy correction; taking the enthalpy of formation of propenal[31] as −77 kJ mol^{-1} yielded a value for $\Delta H°_{f,298}(\mathbf{10})$ of −1 kJ mol^{-1}. Our present MP4 calculations use a considerably larger basis set than was employed by these workers, and should therefore lead to more reliable results.

McKee and Radom[34] employed the G2 theoretical procedure to compute $\Delta H^{o}_{f,298}(\mathbf{10}) = 17.5$ kJ mol^{-1}, but also calculated $\Delta H^{o}_{f,298}$(propenal) = -67.6 kJ mol^{-1}, as compared with the literature value[31] of -77 kJ mol^{-1}, the latter result suggests the possibility of larger errors for molecules of this size with G2 theory than the average error of less than 4 kJ mol^{-1} claimed for atomization energies over its test set of smaller molecules.[35] If the G2 value for $\Delta H^{o}_{f,298}$(propenal) is overestimated by 9 or 10 kJ mol^{-1}, then our calculated value for $\Delta H^{o}_{f,298}(\mathbf{10}$, QCI) = 6.3 kJ mol^{-1} may be quite close to the true enthalpy of formation for cyclopropanone.

Use of the QCI calculated value for $\Delta H^{o}_{f,298}(\mathbf{10}) = 6.3$ kJ mol^{-1} in the isodesmic relation (2) in place of the literature value of 16 kJ mol^{-1} leads to an MP2 estimate for the enthalpy of formation of oxiranone equal to -192 kJ mol^{-1} (see below).

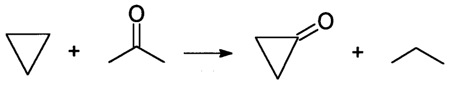
Oxiranone. The same procedures applied to oxiranone **1** yields MP4 and QCI calculated values (Table 3) for its enthalpy of formation: $\Delta H^{o}_{f,298}(\mathbf{1}$, MP4) = -210 kJ mol^{-1} and $\Delta H^{o}_{f,298}(\mathbf{1}$, QCI) = -190 kJ mol^{-1}

As for oxirane and cyclopropane, the MP4 method also predicts a more negative enthalpy of formation for oxiranone than does the QCISD(T) method. Since the latter method leads to very good agreement with experiment for oxirane and, as argued above, may be rather close to the true value for cyclopropanone, we suggest a best estimate for $\Delta H^{o}_{f,298}$(oxiranone) = -190 ± 10 kJ mol^{-1}. This value is in fair agreement with those obtained from the isodesmic relations (1) and (2) at the MP2 level but contrasts with the bond-additivity estimate of -130 kJ mol^{-1} previously reported by Liebman and Greenberg.[17] Although it would be desirable to employ the QCISD(T) method with the isodesmic relations (1) and (2), in practice the computations involved at this level for diethyl ether **6**, ethyl acetate **8**, butan-2-one **9**, and methyl acetate **11** are beyond our present resources. Nonetheless, the measure of agreement between the results obtained from these different approaches is such that we propose that our *ab initio* value for $\Delta H^{o}_{f,298}$(oxiranone) = -190 ± 10 kJ mol^{-1} should now be adopted in preference to the previous estimate in the literature.[17]

Comparison of ring strain energies for oxiranone and cyclopropanone

The enthalpy change for isodesmic reaction (1) determined using the present QCISD(T) value for $\Delta H^{o}_{f,298}$(oxiranone) together with the experimental values for **6–8** noted above, is -55 kJ mol^{-1}, the MP2 value noted above (-61 kJ mol^{-1}) is in reasonable agreement. The negative of this quantity represents the additional strain introduced into the three-membered heterocyclic oxirane ring due to replacement of a methylene group (sp^3 carbon) by a carbonyl group (sp^2 carbon). The QCISD(T) estimate for the conventional ring strain energy of oxiranone is therefore 114 + 55 = 169 kJ mol^{-1}. How does this extra increment of strain compare with that arising from the corresponding replacement in the three-membered carbocyclic cyclopropane ring? This question may be answered by consideration of the enthalpy change for the isodesmic reaction (8), evaluated using the QCISD(T) value for $\Delta H^{o}_{f,298}$(cyclopropanone) together with the experimental values[25] for cyclopropane **12**, acetone **13** and propane **14**:

$$\Delta H^{o}_{r,298}(\text{reaction 8}) = \\ \Delta H^{o}_{f,298}(\mathbf{10}) + \Delta H^{o}_{f,298}(\mathbf{14}) - \Delta H^{o}_{f,298}(\mathbf{12}) - \Delta H^{o}_{f,298}(\mathbf{13}) = \\ (6.3) + (-104.5 \pm 0.3) - (53.3 \pm 0.5) - (-217.2 \pm 0.4) = \\ +66 \text{ kJ mol}^{-1}$$



(8)

12 **13** **10** **14**

(Use of pentan-3-one and pentane in place of acetone and propane, respectively, yields a very similar result, $\Delta H^{o}_{r,298} = +65$ kJ mol^{-1}.) Bearing in mind that the QCISD(T) value for the enthalpy of formation for cyclopropanone is lower by 10 kJ mol^{-1} than the experimental value of Thomas and coworkers,[26] adoption of any higher value for this quantity in the isodesmic relation (8) would lead to a further increased estimate for the additional strain energy of cyclopropanone over cyclopropane. This would suggest that replacement of CH$_2$ by C=O in a three-membered ring involves an increase in strain energy for oxirane ⟶ oxiranone which is certainly not larger—and is very likely to be smaller—than for cyclopropane ⟶ cyclopropanone. Since the conventional ring strain energy of cyclopropane is 115 kJ mol^{-1}, that of cyclopropanone may therefore be estimated as 181 kJ mol^{-1}. Like oxiranone, cyclopropanone is a highly strained molecule and very reactive; it may be formed by reaction of diazomethane with ketene at low temperature, but it is not stable at room temperature.[36,37] Cyclopropanones are known intermediates in, for example, Favorksii rearrangements. Oxiranones, although elusive species, would seem to be (if anything) slightly less strained than cyclopropanones and may therefore be no less likely to occur as reaction intermediates, albeit transiently.

Conclusions

Ab initio molecular orbital calculations at the QCISD(t)=full/6-311G(2df,p)//MP2=full/6-311G(d,p) level of theory provide a best estimate for the enthalpy of formation $\Delta H^{o}_{f,298}$ for oxiranone of -190 ± 10 kJ mol^{-1}, corresponding to a conventional ring strain energy of 169 kJ mol^{-1}. In the absence of an experimental determination, this computed value is to be preferred over the previous bond additivity estimate. The oxiranone ring is probably slightly less strained than the cyclopropanone ring.

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