Oxiranones: α-lactones or zwitterions? Insights from calculated electron density distribution analysis

Giuseppe D. Ruggiero and Ian H. Williams *

Department of Chemistry, University of Bath, Bath, UK BA2 7AY.
E-mail: i.h.williams@bath.ac.uk

Electron density distributions for oxiranone and hydroxyoxiranone have been analysed *in vacuo* [MP2/6-31+G(d,p)] and in water [SCI-PCM/MP2/6-31+G(d,p)//HF/6-31+G(d,p)] and compared with those for cyclopropane, cyclopropanone, and oxirane. Oxiranone possesses a ring critical point *in vacuo*, and may be considered as an α-lactone with considerable ionic character in the endocyclic C_α–O_n bond. In water, oxiranone has neither a ring critical point nor a bond critical point for C_α–O_n, and may be considered as a zwitterion, whose carboxylate group has a net charge of −0.63. Geometrically, however, the molecule still possesses an acute-angled three-membered ring with a $C_\alpha CO_n$ angle of only 69°. Electronically, hydroxyoxiranone is acyclic and zwitterionic even *in vacuo*, but geometrically it still looks like an α-lactone.

Introduction

Recent experimental work in our laboratory has provided clear evidence for the intermediacy of α-lactones in the addition of HOBr to the disodium salts of dimethylmaleate and dimethylfumarate in aqueous solution.[1] α-Lactones are very unstable, highly reactive species, whose instability is thought to be due to the possibility of facile ring opening to a zwitterion.[2] The intermediate implicated in hydrolysis of α-halocarboxylates with retention of configuration has been described as a zwitterion,[3] an α-lactone,[4] or an α-lactone possessing much ionic character.[5]

An exocyclic double bond raises the ring strain energy of a three-membered ring (3MR).[6] On the basis of measured enthalpies of combustion,[7] the strain energy of methylenecyclopropane is ∼56 kJ mol⁻¹ greater than that of cyclopropane **1**. We have estimated[8] cyclopropanone **2** to be more strained by about 66 kJ mol⁻¹ than cyclopropane, and calculated oxiranone **4** to have a ring strain energy 55 kJ mol⁻¹ greater than that of oxirane **3**. On the basis of MP2/6-311++G(d,p) calculations, we concluded[9] that the intermediate was best described as an α-lactone, but that the transition structure (for halide elimination from an α-halocarboxylate) leading to the intermediate possessed substantial charge separation and a significant degree of covalency in the bond between C_α and the endocyclic oxygen O_n. There is no doubt that structure **4** is the preferred configuration for oxiranone, although of course there are other isomers of lower energy on the global potential surface for $C_2H_2O_2$. A zwitterionic structure **5** in which the methylene and carboxylate moieties are coplanar disintegrates spontaneously to CH_2 and CO_2, whereas structure **6**, in which these groups are mutually perpendicular, collapses to **4**.[8] 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 **7** in both planar and perpendicular geometries, were all found to be at least 147 kJ mol⁻¹ higher in energy than **4**.[10]

We also considered hydroxyoxiranone **8** as a model for a possible intermediate in the hydrolysis of glycosides of *N*-acetyl-α-D-neuraminic acid.[11] Our QCISD(t)=full/6-311++G(2df,p)//MP2=full/6-311++G(d,p) calculations led to an estimate of 104 kJ mol⁻¹ for the conventional ring strain energy of **8**, 65 kJ mol⁻¹ less than that of **4**. Furthermore, the ring-closed

α-lactone structure **8** was predicted to be 21 kJ mol⁻¹ lower in energy than the ring-opened zwitterion (*cf.* **5**) in aqueous solution by means of the isodensity surface polarized continuum model, IPCM-MP2(fc)/6-31+G(d). However, the stabilizing influence of the hydroxy substituent in **8** resulted in a curiously long C_α–O_n bond (extended by 0.035 Å relative to **4**) and an increasing degree of planarity about C_α, consistent with resonance stabilization of the hydroxyoxiranone, as indicated in Scheme 1.
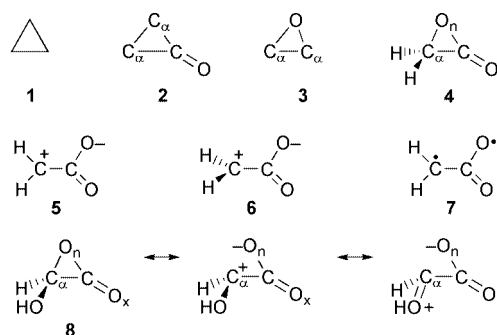
Scheme 1

The nature of the endocyclic C_α–O_n bond and the charge distribution in α-lactones is therefore a subject of considerable topical interest. In this paper we address this question by means of Bader's quantum theory of atoms in molecules[12] (AIM) to compute the topological characteristics of the electron density distributions for oxiranone and hydroxyoxiranone *in vacuo* and in water. In order to facilitate comparisons, we have also considered cyclopropane, cyclopropanone and oxirane in this study. In addition, we compute relaxed stretching force constants for the bonds of oxirane, oxiranone and hydroxyoxiranone *in vacuo* as a measure of bond stiffness.

Methods

All calculations were carried out using the Gaussian 94 program.[13] Full geometry optimisations for structures *in vacuo* were performed using the 6-31+G(d,p) basis set with both Hartree–Fock (HF) and second-order Møller–Plesset (MP2)

Table 1 Calculated total energies[a]

	Vacuum		Water (SCI-PCM)	
	HF/6-31+G(d,p)	MP2/6-31+G(d,p)	HF/6-31+G(d,p)	MP2/6-31+G(d,p)[b]
Cyclopropane, **1**	−117.071002	−117.503207	−117.072144	−117.503993
Cyclopropanone, **2**	−190.735657	−191.325978	−190.746440	−191.329836
Oxirane, **3**	−152.876471	−153.346287	−152.884272	−153.349314
Oxiranone, **4**	−226.570261	−227.205337	−226.587392	−227.208238
gauche-Hydroxyoxiranone, **8**	−301.433783	−302.252983	−301.460374	−302.261256

[a] Energies in hartrees (E_h); $1\ E_h = 2625$ kJ mol^{-1}. [b] Single-point energy: MP2/6-31+G(d,p)//HF/6-31+G(d,p).

methods. The effects of aqueous solvation were determined by means of a self-consistent isodensity polarised continuum model (SCI-PCM)[14] with a relative permittivity of 78.36 for water; geometry optimisation was carried out at the HF/6-31+G(d,p) level, and single-point MP2/6-31+G(d,p) energies were then calculated for these structures.

Analysis of electron density distributions, both *in vacuo* and in water, was carried out at the MP2 level using the AIMPAC[15] suite of programs. The line of maximal density joining two nuclei in the equilibrium geometry of a structure is a bond path; the minimum along this line is a bond critical point (BCP), a first-order saddle point in the electron density. A second-order saddle point defines a ring critical point (RCP). The values of the electron density ρ, its Laplacian $\nabla^2\rho$, and its ellipticity ε at a BCP are diagnostic of the type of bonding. The ellipticity is a measure of the anisotropy of the electron density in directions perpendicular to the bond path at a BCP, and the Laplacian measures the local concentration ($\nabla^2\rho < 0$) or depletion ($\nabla^2\rho > 0$) of electronic charge. The bond path is often longer than the conventional straight-line bond drawn between the nuclei.[16] The angle between the tangents to the bond paths at a nucleus defines the bond-path angle; the difference Δ_{ang} between this and the geometrical bond angle provides a useful indicator of ring strain.

Second derivatives were computed at the MP2/6-31+G(d,p) level *in vacuo* and were transformed from Cartesian coordinates to non-redundant internal coordinates, which comprised a subset of bond stretches, angle bends, and torsions. Inversion of the nonsingular matrix of internal valence coordinates yielded the compliance constant matrix, the reciprocal of the diagonal elements of which are relaxed force constants.[17] The latter are unambiguously defined, and therefore physically meaningful, even in the presence of local or cyclic redundancies among the valence coordinates, as demonstrated in an earlier study of dioxiranone.[18]

Results and discussion

The energies of structures **1**–**4** and **8** optimised *in vacuo* and in water are given in Table 1, selected geometrical parameters in Table 2, AIM charges in Table 3, and relaxed force constants in Table 4. Fig. 1 shows the BCPs and RCPs in the plane of the 3MR for each species, together with electron density (ρ), Laplacians (in parentheses) and ellipticities [in square brackets].

Cyclopropane

In vacuo each C–C bond has a BCP, the ring possesses an RCP, and Δ_{ang} is 16.1°. At the BCP, ρ is large and $\nabla^2\rho$ is negative, as is typical of a single covalent bond.[12] In water these values are a little larger, and Δ_{ang} is increased to 18.2°. In both media the value of ρ at the RCP is significantly less than at the BCP. As expected, each carbon atom has only a very small charge.

Cyclopropanone

In vacuo each bond has a BCP, there is an RCP, and the values of ρ and $\nabla^2\rho$ for the ring bonds are typical of covalent bonds.
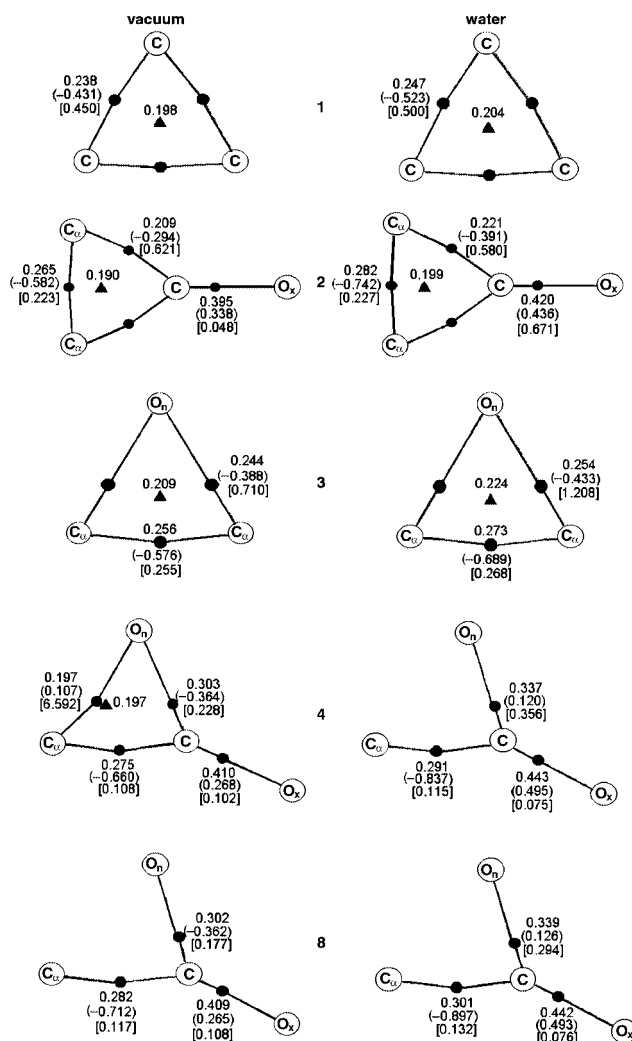

Fig. 1 Bond critical points (●) and ring critical points (▲) for cyclopropane **1**, cyclopropanone **2**, oxirane **3**, oxiranone **4**, and hydroxyoxiranone **8** from MP2/6-31+G* calculations *in vacuo* and in SCI-PCM water, together with electron densities (ρ/e au^{-3}), Laplacians ($\nabla^2\rho$/e a$_o^{-5}$, in parentheses) and ellipticities [ε, in square brackets]. (1 e au$^{-3} = 1.081 \times 10^{12}$ C m^{-3}; 1 e a$_o^{-5} = 3.8611 \times 10^{32}$ cm^{-5}).

The main point to note is the positive value of $\nabla^2\rho$ at the BCP for C=O$_x$, characteristic of a carbonyl double bond. The AIM charges on the atoms of the carbonyl group (C = 1.04, O$_x$ = −1.11) suggest a very polar bond. At 20.5°, the value of Δ_{ang} at C$_a$ is larger than for cyclopropane, and increases to 23° in water, suggesting a more strained ring.

Oxirane

As for cyclopropane, there is a significant difference between the value of ρ at the RCP (0.209) and at either the C$_a$–O$_n$ BCP (0.244) or the C$_a$–C$_a$ BCP (0.256). The differences Δ_{ang} at C$_a$ (10.3°) and at O$_n$ (13.2°) in oxirane are less than in cyclo-

Table 2 Calculated bond and bond-path lengths, and bond and bond-path angles[a]

	Bond	Vacuum Bond length/Å	Vacuum Bond-path length/Å	Angle	Vacuum Bond angle/°	Vacuum Bond-path angle/°	Water Bond length/Å	Water Bond-path length/Å	Water Bond angle/°	Water Bond-path angle/°
Cyclopropane	C–C	1.507	1.514	CCC	60.0	76.1	1.500	1.508	60.0	78.2
Cyclopropanone	C_α–C_α	1.471	1.484	$CC_\alpha C_\alpha$	64.8	85.3	1.456	1.472	64.9	87.9
	C_α–C	1.577	1.581	$C_\alpha CC_\alpha$	57.6	76.0	1.561	1.567	57.6	78.4
	$C{=}O_x$	1.218	1.218				1.188	1.188		
Oxirane	C_α–C_α	1.468	1.484	$OC_\alpha C_\alpha$	59.5	69.8	1.451	1.473	59.1	70.2
	C_α–O_n	1.446	1.449	$C_\alpha OC_\alpha$	61.0	74.2	1.412	1.415	61.9	75.0
Oxiranone	C_α–C	1.450	1.471	$O_n C_\alpha C$	53.2	33.9	1.429	1.456	52.4	
	C_α–O_n	1.567	1.624	$C_\alpha CO_n$	67.9	77.9	1.501	NBCP	68.7	
	C–O_n	1.346	1.352	$C_\alpha O_n C$	59.6	62.1	1.296	1.299	58.9	80.3
	$C{=}O_x$	1.204	1.204				1.178	1.179		
gauche-Hydroxyoxiranone	C_α–C	1.450	1.470	$O_n C_\alpha C$	52.7		1.433	1.462	51.9	
	C_α–O_n	1.572	NBCP	$C_\alpha CO_n$	68.7	79.3	1.519	NBCP	66.7	81.3
	C–O_n	1.346	1.349	$C_\alpha O_n C$	58.6		1.294	1.296	61.4	
	$C{=}O_x$	1.205	1.205				1.179	1.179		

[a] NBCP = no bond critical point.

Table 3 AIM atomic charges (|e|)

	Atom	Vacuum	Water
Cyclopropane	C	+0.02	+0.09
Cyclopropanone	C_α	−0.03	+0.06
	C	+1.04	+1.18
	O_x	−1.11	−1.37
Oxirane	C_α	+0.43	+0.62
	O_n	−0.91	−1.21
Oxiranone	C_α	+0.29	+0.47
	O_n	−0.91	−1.23
	C	+1.65	+2.00
	O_x	−1.15	−1.40
gauche-Hydroxyoxiranone	C_α	+0.87	+1.15
	O_n	−0.91	−1.24
	C	+1.67	+2.02
	O_x	−1.15	−1.40

Table 4 Relaxed stretching force constants (mdyn Å^{-1})

	C_α–C	C_α–O_n	C–O_n	$C{=}O_x$
Oxirane	5.64	3.91	3.91	
Oxiranone	5.54	2.55	5.30	13.59
gauche-Hydroxyoxiranone	5.61	1.54	5.20	13.38

propane. All the BCPs have negative Laplacians, indicating the covalent character of the bonding, and the C_α–O_n bond has a large ellipticity (0.710). Solvation increases the values of ρ, $\nabla^2\rho$ and ε at the critical points. The relaxed force constant for stretching the C_α–O_n bond is smaller than for the C_α–C_α bond (3.91 vs. 5.64 mdyn Å^{-1}) but is nonetheless typical of a covalent bond between carbon and oxygen.

Oxiranone

The C_α–O_n bond in vacuo is unusually long (1.567 Å) and the value of Δ_{ang} at C_α is negative (−19.3°), implying that the bond path bows inwards. The Laplacian is positive at the BCP for this bond, indicative of a closed shell, ionic interaction,[12] but this BCP lies very close to the RCP, which shares essentially the same value of ρ (0.197). Coalescence of an RCP and a BCP causes opening of a ring: the positive curvature of ρ at the RCP annihilates the in-plane negative curvature at the BCP to yield zero curvature, characteristic of an unstable critical point. The decrease in magnitude of negative curvature of ρ at the BCP and its eventual disappearance lead to a dramatic increase in the ellipticity of the bond being broken, becoming infinite at the point of coalescence; thus, a structure possessing a bond with an unusually high value of ε is potentially unstable.[19] The C_α–O_n bond has a very large ε (6.592) at the BCP. There is a nearly flat-bottomed trough in the distribution of electron density linking this BCP and RCP. The C_α–C and C–O_n bonds resemble the C_α–C_α and C_α–O_n bonds of oxirane, although with smaller values of ε, and the $C{=}O_x$ bond resembles the carbonyl bond of cyclopropanone. The charge separation between C and O_x is larger than in cyclopropanone, but it is smaller between C_α (0.29) and O_n (−0.91) than in oxirane (0.43 and −0.91). In vacuo, oxiranone may be considered as an α-lactone with a closed-ring (just!) but with ionic character between the C_α and O_n atoms. The relaxed force constant for stretching C_α–O_n in oxiranone is less than for the corresponding bond in oxirane (2.55 vs. 3.91 mdyn Å^{-1}) indicating a smaller restoring force for deformation of this bond.

In water, the C_α–O_n bond length is a reasonable value for an endocyclic bond: however, there is no BCP between these atoms! Solvation causes migration of the RCP along the trough to coalesce with the BCP, yielding an acyclic structure. Since there is no bond between the C_α and O_n atoms, oxiranone in water is perhaps best described as a zwitterion; however, the degree of charge separation between the C_α and O_n atoms is

actually slightly less than in oxirane. The Laplacian at the C–O_n BCP changes from a negative value *in vacuo* to a positive value in water, indicating double-bond character as expected for a carboxylate moiety. The net charges on the O_n–C–O_x and C_aH_2 groups of oxiranone in water are −0.63 and +0.63 respectively; the latter value is only very slightly greater than the net charge (+0.61) on each of the C_aH_2 groups of oxirane in water. Furthermore, the three bond angles O_nC_aC, C_aCO_n and C_aO_nC are all ≤69°, so that the structure is not at all open, despite lacking an RCP and a C_a–O_n BCP according to the Bader analysis; geometrically the structure still resembles a cyclic species.

Hydroxyoxiranone

Although the *anti* conformer is slightly lower in energy (5 kJ mol⁻¹), the *gauche* conformer of the exocyclic C_a–OH bond is considered here. The stability of 3MRs is enhanced by surface delocalisation of σ-electrons; σ-electron-withdrawing substituents remove electrons from the surface orbital and thereby destabilise a ring, but σ-electron-donating substituents push electrons into a 3MR and thus increase ring stability. The electron-donating HO group of hydroxyoxiranone preferentially stabilises the positive charge at C_a (0.87) to such an extent that no C_a–O_n BCP or RCP exists, even *in vacuo*. Hydroxyoxiranone has a quasi-cyclic zwitterion structure rather than an α-lactone structure, and consequently significantly lower strain energy. However, the three bond angles O_nC_aC, C_aCO_n and C_aO_nC are all ≤69°, so from a geometrical point of view one might still say that the molecule possesses a 3MR, even though electronically this is not present. The relaxed force constants for stretching the C_a–C, C–O_n and C=O_x bonds are very similar in value to those for oxiranone itself. The value for C_a–O_n is even smaller (1.54 *vs.* 2.55 mdyn Å⁻¹) than in oxiranone, but it does indicate that there is still a restoring force for extending or compressing the distance between this pair of atoms. Is this interaction a "bond"? Although there is no BCP in hydroxyoxiranone, it is still possible to determine the values of ρ and $\nabla^2\rho$ in this species at approximately the point where the BCP in oxiranone is located. The computed electron density of 0.193 e au⁻³ at this point is essentially the same value as for the nearly coalescing BCP and RCP in oxiranone. However, the value of −0.059 e a_o^{-5} for the Laplacian is not characteristic of either a shared interaction (covalent bond) or a typical closed-shell interaction (ionic bond).

Solvation increases the zwitterionic character relative to the vacuum. Both the C–O_n and C=O_x BCPs have positive Laplacians for hydroxyoxiranone in water, indicative of a double bond within a carboxylate group, and the net charge on the O_n–C–O_x group is −0.62. Again, the bond angles O_nC_aC, C_aCO_n and C_aO_nC are all acute, so geometrically the molecule still possesses a 3MR, even though electronically it does not. In our earlier work we found that HO-substituted structure **5**, in which the plane of the carboxylate group was essentially perpendicular to the plane of the carbocation centre at C_a, was 21 kJ mol⁻¹ lower in energy than the totally planar open zwitterion structure (*cf.* **6**) at the IPCM-MP2/6-31+G(d) level.[11]

Is oxiranone an α-lactone or not?

Kenyon suggested the intermediacy of an α-lactone to account for the retention of configuration in the deamination of alanine[20a] and the reaction of α-tosyloxypropionate with LiCl,[20b] drawing cyclic structures with (apparently) a single bond for C_a–O_n (in our present notation). Winstein also suggested that an α-lactone was involved in solvolysis of α-bromopropionate,[21] but then denied that this term implied a completely covalent species.[5a] Instead he reasoned that "considering the ionic character of a usual carbon–oxygen bond and allowing for the effects of resonance within the carboxylate ion group and of ring strain, one arrives at the conclusion that

there is a very large ionic character to the new carbon–oxygen bond in the intermediate."[5a]

Hughes and Ingold shunned the term α-lactone, apparently on the grounds that unpolymerised α-lactones were completely unknown, in contrast to β-lactones, which were well known.[3] They described a zwitterionic species[3,22] (although they called it a betaine) in which the charges were "probably not quite integral"[22b] and that would have a canonical structure "in which the charges are neutralised at the cost of producing septets, which maintain a tetrahedral character in the orbitals."[3,22b] Ingold considered that the α-carboxylate group established a "rather long, somewhat weak, essentially electrostatic bond"[23a] by interaction with the adjacent carbocationic centre, and that "its access is too limited stereochemically to allow it to form a strong bond: it forms a weak bond, probably somewhat long and thus of largely electrostatic character".[23b]

The quantum theory of atoms in molecules suggests that oxiranone *in vacuo* is an α-lactone possessing ionic character. Geometrically it contains a 3MR, although topological analysis of the electron density distribution reveals the presence of a distinct RCP to be marginal. The positive value of $\nabla^2\rho$ at the BCP for the C_a–O_n bond indicates ionic character rather than a covalent bond. In water, the electron density distribution shows neither a RCP nor a BCP for C_a–O_n. Bader asserts that the presence of a bond path is a necessary and sufficient condition for the existence of a bond between a pair of atoms,[12] although not everyone would agree with this as an adequate definition of a chemical bond. Thus, according to Bader's criteria, oxiranone in aqueous solution would possess neither a ring nor a C_a–O_n bond. What is clear from the present study is that C_a–O_n is different from the covalent bonds found in analogous cyclic molecules. Geometrically the molecule still possesses a 3MR with three acute angles; in particular, the C_aCO_n angle is only 69°. The carboxylate group has a net charge of −0.63, suggesting oxiranone has substantial zwitterionic character in water, but this group is able to approach closely to C_a, with the C_aCO_n angle distorting by about 50° from its value in α-chloroacetic acid.[9] There is nothing to suggest that there is "limited stereochemical access" of the carboxylate group towards C_a (*pace* Ingold). Indeed, the relaxed stretching force constant indicates that there is a significant (although rather weak) restoring force for distortion of the C_a–O_n "bond", consistent with there being no tendency for the "ring" to spring open spontaneously. The theoretical results do seem to accord quite well with Winstein's description of an α-lactone with considerable ionic character.

Conclusion

Oxiranone, either *in vacuo* or in water, may be fairly considered as an α-lactone with substantial ionic character, but it is also fair to consider it as a zwitterion, provided it is understood that geometrically it contains a three-membered ring, even though electronically it does not. Thus both the descriptions of Winstein and of Hughes and Ingold contain complementary aspects of truth, while neither provides a full account of this most interesting reactive species.

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