Protonated heterocyclic derivatives of cyclopropane and cyclopropanone: classical species, alternate sites, and ring fragmentation

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Abstract: A computational study has been performed for protonated oxygen- or nitrogen-containing heterocyclic derivatives of cyclopropane and cyclopropanone. We have searched for the most stable conformations of the protonated species using density functional theory with the B3LYP functional and the 6-31G(2df,p) basis set. More accurate enthalpy values were obtained from G4 calculations. Proton affinities and gas-phase basicities were accordingly derived.

Key words: protonated cyclopropane and cyclopropanone derivatives, enthalpy, Gibbs energy, proton affinity, gas-phase basicity, QTAIM analysis.

Résumé : Nous avons réalisé une étude de modélisation sur des dérivés hétérocycliques protonés du cyclopropane ou de la cyclopropanone contenant un atome d'oxygène ou d'azote. Nous avons recherché les conformations les plus stables au moyen de la théorie de la fonctionnelle de la densité, en utilisant la fonctionnelle B3LYP et la base 6-31G(2df,p). La meilleure exactitude des valeurs d'enthalpie a été obtenue grâce aux calculs selon le modèle G4. De ces résultats ont été dérivées les affinités protoniques et les basicités en phase gazeuse. [Traduit par la Rédaction]

Mots-clés : dérivés protonés du cyclopropane et de la cyclopropanone, enthalpie, énergie de Gibbs, affinité protonique, basicité en phase gazeuse, théorie quantique des atomes dans les molécules.

Introduction

The structure and energetics of species with three-membered rings and the amide linkage have been actively studied by both the experimental and theoretical chemical communities. It is now acknowledged that measured enthalpy of formation data on species with three-membered rings of any type are simultaneously few in number¹ and reliability is occasionally suspect.² Likewise, measured proton affinities are almost totally absent for these species. Paralleling our recent publication,³ using cyclopropanone (**1**), aziridine (**2**), and oxirane (**3**) as archetypes, the assembled species for our current study are shown in Fig. 1: aziridine-2-one (also called α -lactam, **4**), oxirane-2-one (also called α -acetolactone, **5**), 1,2-diaziridine-3-one (**6**), 1,2-dioxirane-3-one (also called carbon trioxide, **7**), 1,2-oxaziridine-3-one (**8**), cyclopropane-1,2-dione (**9**), aziridine-2,3-dione (also called oximide, **10**), and oxirane-2,3-dione (also called oxalic anhydride, **11**); we recently also studied the associated enol tautomers such as the two rotamers of 2-hydroxycyclopropenol (**9a**) corresponding to cyclopropane-1,2-dione (**9**).³ An additional feature of interest is the site of protonation — nearly all of the neutral species have two or more such sites, e.g., the nitrogen and oxygen of aziridine-2-one (**4**). How can the proton affinity of each site be separately ascertained and understood? There is additionally also the possibility of ring rupturing and fragmentation upon protonation, e.g., is 2-hydroxyallyl cation not a plausible product of protonating cyclopropanone (**1**)? Computational theory ameliorates the paucity of experimental infor-

mation of energetics, structure, and any post-protonation reaction chemistry. The current study reports our computational findings for these and related neutral and protonated species where we have used the G4 method.⁴ Very good agreement is shown between the results from calculational theory and experimental proton affinity measurements where the latter is available for comparison. A QTAIM analysis^{5–7} was also performed with the electron density generated at the B3LYP/6-311++G(2d,2p) level of theory. The current investigation interrelates all of these studies and aids in their understanding and utility.

Computational details

In this study, we have used density functional theory with the B3LYP^{8,9} functional and the 6-31G(2df,p) basis set (level of theory used in the geometry optimization in the G4 method⁴) to search for the most stable conformations of the protonated derivatives of oxygen- and nitrogen-containing cyclopropanes and cyclopropanones. Vibrational frequency calculations were performed to characterize the stationary points found on the potential energy surface as minima or transition state structures. Calculations have also been carried out at the G4⁴ level of theory for the most stable conformations of each species. All calculations were performed with Gaussian 09.¹⁰

A QTAIM analysis^{5–7} was carried using the AIMAll¹¹ software, with the electron density generated at the B3LYP/6-311++G(2d,2p)

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Fig. 1. Studied cyclopropane and cyclopropanone derivatives.

level of theory. This analysis focuses on the properties at the bond critical points (denoted as r_b) of the electron density, $\rho(r)$, the Laplacian topology of the electronic density, $\nabla^2\rho(r)$, and selected atomic properties such as atomic populations, $N(\Omega)$, and atomic energy, $E(\Omega)$. The accuracy achieved in the calculation of the QTAIM atomic properties was checked through of sum of $N(\Omega)$ and $E(\Omega)$ on all atoms of the molecule. These values for each molecule reproduce total electron populations and electronic molecular energies, respectively. Another parameter corresponds to the values of the integrated Laplacian in each atomic basin, $L(\Omega)$. Ideally, this last parameter should be close to zero.

Results and discussion

Structure and energetics of protonated cyclopropane and cyclopropanone species

In previous work, we have searched for the most stable conformation of the corresponding neutral heterocyclic cyclopropane and cyclopropanones (see Fig. 1) at the B3LYP/6-31G(2df,p) level of theory.³ In this work, we have searched for the most stable conformations of oxygen and nitrogen protonated cyclopropane and cyclopropanone derivatives at the same level of theory.

In Table 1, we present the protonation site (see Fig. 2 for the atom numbering scheme), the description of the protonated species formed, symmetry point group used in calculations, the B3LYP/6-31G(2df,p) calculated absolute electronic energies (i.e., no zero-point energy and thermal corrections), and absolute enthalpies and Gibbs energies at $T = 298.15$ K.

The most stable conformations found for the protonated cyclopropane derivatives are shown in Fig. 3 where we include protonated cyclopropanone itself, as there is but one "hetero" atom on the three-membered ring.

From protonation of the oxygen atom of cyclopropanone, the closed-ring 1-hydroxycyclopropyl cation is formed. This cation was found to be more stable than the ring-opened 2-hydroxyallyl cation ($\text{CH}_2\text{C}^+(\text{OH})\text{CH}_2$) by $\Delta H = 2.9$ kJ mol⁻¹ at the B3LYP/6-31G(2df,p) level of theory. The barrier for going from the 1-hydroxycyclopropyl cation to the 2-hydroxyallyl cation is $\Delta E = 4.4$ kJ mol⁻¹ (difference

of B3LYP/6-31G(2df,p) electronic energies of transition state and 1-hydroxycyclopropyl cation). There is hesitancy in comparing these cations with the nominally related deprotonated neutrals, the highly strained but otherwise normal cyclopropanone, and the non-Kekulé biradical (both singlet and triplet) oxyallyl.

N-protonated aziridine presents a C_{2v} symmetry point group. The two hydrogen atoms bonded to the nitrogen atom are out of the plane of the ring, one on each side. This species is an altogether normal protonated secondary amine.

From protonation of the oxygen atom of oxirane, the closed-ring oxiranium cation is formed (C_s symmetry point group). The geometry around the oxygen atom was found to be pyramidal, with the hydrogen atom being 77° out of the plane of the ring. The planar conformation obtained imposing a C_{2v} symmetry point group has one imaginary frequency (transition state structure). The calculated barrier to oxygen inversion is 64 kJ mol⁻¹ (difference of B3LYP/6-31G(2df,p) electronic energies of transition state and pyramidal structure). Protonated oxirane is recognizable as a dialkyloxonium ion, and like the parent H_3O^+ ,¹² it is pyramidal. That aziridine has a much higher inversion barrier than ammonia provides isoelectronic reasoning support for the observation that protonated oxirane has a much higher inversion barrier than the hydronium ion.

The most stable conformations found for the protonated cyclopropanone derivatives are shown in Fig. 4. In the geometry optimization of the N-protonated form of aziridine-2-one (4), the starting closed ring opens via C–N bond cleavage and the formed species, nominally $\text{H}_2\text{NCH}_2\text{CO}^+$, splits into two fragments, CH_2NH_2^+ and CO. This is in agreement with previous studies reported in the literature where a variety of $\text{C}_2\text{H}_4\text{NO}^+$ isomers were examined and it was concluded that N-protonated aziridine-2-one (4) is not an energy minimum on the potential energy surface and attempts to minimize it lead to dissociation products.^{13,14} Also, Lengyel et al.¹⁵ reported that strong acids with a negative pK_a decarbonylate substituted aziridinones to give immonium salts (we also recognize C- and N-substituted $\text{H}_2\text{NCH}_2\text{CO}^+$ ions from mass spectrometric studies of peptides, in particular the so-called "b-ions", cf. Yalcin et al.¹⁶ and Harrison¹⁷). This is in agreement with previous studies reported for protonated aziridine.

From protonating the oxygen atom of 4, two species can be formed, 4OH_{anti} and 4O_{syn} (see Fig. 4). The 4OH_{anti} conformation was found to be more stable than 4O_{syn} by about 6 kJ mol⁻¹, in agreement with a computational study at HF/6-31G(d) reported in the literature.¹⁸ In both oxygen-protonated species, the hydrogen atom bonded to nitrogen is in the plane of the ring (sum of the bond angles at nitrogen is 360°), in contrast with what happens in 4 where the sum of the bond angles at nitrogen is 306° (planarizing the nitrogen in amides (or nominally acylamines) such as aziridine-2-one is plausibly less energetically beneficial than in the corresponding oxygen-protonated ion as found in the cation).^{19,20} Morgan and Greenberg²¹ predicted the chemical shifts for the NMR of two nitrogen- and oxygen-protonated alkylated aziridine-2-ones within the context of the alternative protonated forms of strained amides.

In the case of oxirane-2-one (5), when the O_2 oxygen atom of 5 is protonated, the ring opens and the HOCH_2CO^+ species is formed (see Fig. 4, $5\text{O}_2\text{H}$). Protonating the oxygen atom O_4 , two species can be formed, $5\text{O}_4\text{H}_{\text{anti}}$ and $5\text{O}_4\text{H}_{\text{syn}}$. The $5\text{O}_4\text{H}_{\text{syn}}$ conformation was found to be more stable than $5\text{O}_4\text{H}_{\text{anti}}$ by about 4 kJ mol⁻¹. Ruttink et al.²² used the G2 method to study the methoxycarbonyl cation and various isomers including $5\text{O}_2\text{H}$, $5\text{O}_4\text{H}_{\text{syn}}$ and $5\text{O}_4\text{H}_{\text{anti}}$. The G2-predicted relative energetic stability of the three species, $5\text{O}_2\text{H} > 5\text{O}_4\text{H}_{\text{syn}} > 5\text{O}_4\text{H}_{\text{anti}}$, is in agreement with the one found in this study. It is plausible that an $\alpha\text{-OH}$ offers a carbenium ion less stabilization than an $\alpha\text{-NH}_2$ and so the $[\text{HOCH}_2\text{-CO}]^+$ bond is stronger than in $[\text{H}_2\text{NCH}_2\text{-CO}]^+$; it is not surprising that the former ion is more stable with regards to C–C bond cleavage than the latter and indeed does not fragment

Protonated species	Protonation site ^a	Description of species formed ^a	Symmetry point group	$E_{\text{B3LYP/6-31 G(2df,p)}}(\text{hartree})^b$	$H_{\text{B3LYP/6-31 G(2df,p)}}(\text{hartree})^b$	$G_{\text{B3LYP/6-31 G(2df,p)}}(\text{hartree})^b$
Cyclopropanone (1)	O	Ring-closed (1-hydroxycyclopropyl cation, 1OH)	C _s	−192.211171	−192.132982	−192.165537
		Ring-opened (2-hydroxyallyl cation)	C _s	−192.210166	−192.131866	−192.165281
Aziridine (2)	N	Ring-closed/ 2NH	C _{2v}	−134.298100	−134.209356	−134.237314
Oxirane (3)	O	Ring-closed O pyramidal/ 3OH	C _s	−154.110602	−154.036068	−154.064722
		Ring-closed O planar (transition state)	C _{2v}	−154.086182		
Aziridine-2-one (4)	O ₄	H <i>anti</i> to N/ 4OHanti	C ₁	−208.268919	−208.200725	−208.231920
	O ₄	H <i>syn</i> to N/ 4OHsyn	C ₁	−208.266757	−208.198746	−208.229953
	N	Splits into CH ₂ NH ₂ ⁺ and CO ^c		−208.305881	−208.239423	−208.287995
Oxirane-2-one (5)	O ₂	Ring-opened/ 5O₂H	C ₁	−228.142451	−228.087215	−228.119270
	O ₄	H <i>syn</i> to O ₂ / 5O₄Hsyn	C _s	−228.122362	−228.066849	−228.097403
	O ₄	H <i>anti</i> to O ₂ / 5O₄Hanti	C _s	−228.120893	−228.065205	−228.095701
1,2-Diaziridine-3-one (6)	N	Ring-opened/ 6NH	C _s	−224.310728	−224.253459	−224.285071
	O	Ring-closed/ 6OH	C ₁	−224.261169	−224.205811	−224.236367
1,2-Dioxirane-3-one (7)	O ₂	Ring-opened/ 7O₂H	C ₁	−263.934004	−263.903345	−263.935763
	O ₄	Ring-closed/ 7O₄H	C _s	−263.922373	−263.891923	−263.922038
1,2-Oxaziridine-3-one (8)	O ₃	Ring-opened/ 8O₃H	C ₁	−244.135409	−244.091507	−244.122905
	N	Ring-opened/ 8NH	C ₁	−244.129544	−244.085389	−244.117232
	O ₄	H <i>anti</i> to N/ 8O₄Hanti	C ₁	−244.102963	−244.060053	−244.090404
	O ₄	H <i>syn</i> to N/ 8O₄Hsyn	C ₁	−244.101236	−244.058278	−244.088624
Cyclopropane-1,2-dione (9)	O	Ring-opened, H <i>anti</i> to O/ 9OH	C ₁	−266.244792	−266.183983	−266.218186
	O	Ring-closed, H <i>syn</i> to O (transition state)	C ₁	−266.170345		
Syn-2-hydroxycyclopropenone (9a)	O ₄	H <i>anti</i> to O ₅ / 9aO₄Hanti	C ₁	−266.237453	−266.175060	−266.207713
	O ₄	H <i>syn</i> to O ₅ / 9aO₄Hsyn	C _{2v}	−266.234989	−266.172689	−266.204748
	O ₅	9aO₅H	C ₁	−266.151958	−266.092333	−266.127147
Aziridine-2,3-dione (10)	O	H <i>syn</i> to N/ 10O₄Hsyn	C _s	−282.280412	−282.231233	−282.264785
	O	H <i>anti</i> to N/ 10O₄Hanti	C _s	−282.261834	−282.212595	−282.245549
	N	Splits into NH ₂ CO ⁺ and CO ^c		−282.306436	−282.259712	−282.310196
Oxirane-2,3-dione (11)	O ₄	H <i>anti</i> to O ₂ / 11O₄Hanti		−302.186615	−302.151931	−302.187702
	O ₄	H <i>syn</i> to O ₂ / 11OH	C _s	−302.153953	−302.116882	−302.150657
	O ₂	11OH	C _s	−302.153956	−302.116883	−302.150662

^cSummed values of E (H or G) for the two separate fragments.

A diagram of a triangle with vertices labeled X_2 , X_3 , and O_4 . The edges are labeled 1, 2, and 3 respectively. The edge between X_2 and X_3 is labeled 2. The edge between X_2 and O_4 is labeled 1. The edge between X_3 and O_4 is labeled 3.

X₃ = NH, O, CH₂ or CO where the carbonyl oxygen when present is numbered O₅.

From protonation of the oxygen O₄ atom of **9a**, two conformers can be found, **9aO₄Hsyn** and **9aO₄Hanti**. This last one was found

Fig. 4. B3LYP/6-31G(2df,p) optimized structure of protonated cyclopropanone derivatives.

to be more stable than the first by only 6 kJ mol⁻¹. Protonation of the O₅ atom leads to the least stable isomer, **9aO₅H**.

Protonation of the nitrogen atom of aziridine-2,3-dione (**10**) imposing a C_{2v} symmetry point group leads to a conformation with one imaginary frequency (transition state). Not imposing symmetry, the protonated species splits into two fragments, NH₂CO⁺ and CO. Considering the ion NH₂CO⁺, this species may be recognized as protonated HNCO. The proton affinity of HNCO, 753 kJ mol⁻¹,²⁵ (gas-phase basicity ΔG_{basicity} = 718.8 kJ mol⁻¹²⁵) is so much larger than that of CO (proton affinity (at carbon) = 594 kJ mol⁻¹²⁵ and ΔG_{basicity} (at carbon) = 562.8 kJ mol⁻¹²⁵) that it is not surprising that separated protonated HNCO and CO are seen upon nitrogen protonation of species **10**. That the dipole moment of CO is so close to zero also makes any complex of NH₂CO⁺ and CO but very weakly bound.

When the oxygen atom is protonated with the O–H bond *syn* to nitrogen, the ring opens and the C(OH)(NH)CO⁺ species is formed (see Fig. 4) (**10O₄Hsyn**). Protonating the oxygen atom with the O–H *anti* to nitrogen, the ring remains closed (**10O₄Hanti**).

In the case of oxirane-2,3-dione (**11**), protonating O₄ with the hydrogen atom in a *syn* conformation to O₂ or protonating O₂ leads to the same conformer, **11OH** (see Fig. 4). Protonating the O₂ atom imposing a C_{2v} symmetry leads to a conformer with one

imaginary frequency. Protonating O₄ with the hydrogen atom with an *anti* conformation to O₂, the closed ring opens and the formed species CO(OH)CO⁺ (it is **11OH** but with the OH in the other direction) and the complex **11O₄Hanti** is formed (see Fig. 4). The proton affinity of CO is higher than that of CO₂ (proton affinity = 540.5 kJ mol⁻¹²⁵ and ΔG_{basicity} = 515.8 kJ mol⁻¹²⁵) and that is why the H⁺ moves towards CO. The enthalpy of the reaction HCO⁺ + CO₂ → complex **11O₄Hanti** is –59.3 kJ mol⁻¹, which is in good agreement the experimental clustering energy for these species, –52.7 kJ mol⁻¹, from Hiraoka et al.²⁶

Calculated proton affinities and gas-phase basicities

Calculated G4 absolute enthalpies and Gibbs energies, at T = 298.15 K, calculated only for the most stable conformations found for the cyclopropane and cyclopropanone derivatives and their protonated species are given in Table S1 and Table S2, respectively, of the supplementary data (see Supplementary material section). From these calculation, we were able to calculate proton affinities and gas-phase basicities, which are presented in Table 2. In this table, we also provide existing experimental values for comparison, taken from the classic review of Hunter and Lias.²⁵ There are experimental data for the cyclopropane derivatives, aziridine (**2**) and oxirane (**3**), and there are no experimental data

Table 2. Protonation site and G4 calculated gas-phase proton affinities (PA) and basicities ($\Delta G_{\text{basicity}}$), at $T = 298.15$ K, for the cyclopropane and cyclopropanone derivatives.

Molecule	Protonation site ^a	PA (kJ mol ⁻¹)		$\Delta G_{\text{basicity}}$ (kJ mol ⁻¹)	
		G4	Exp. ²⁵	G4	Exp. ²⁵
Cyclopropanone (1)	O	772.4		746.3	
Aziridine (2)	N	908.6	905.5	875.1	872.5
Oxirane (3)	O	769.0	774.2	737.8	745.3
Aziridine-2-one (4)	O ₄ (anti to N)	802.5		772.4	
	O ₄ (syn to N)	797.5		767.5	
Oxirane-2-one (5)	O ₂	805.0		778.2	
	O ₄ (syn to O ₂)	735.4		704.6	
	O ₄ (anti to O ₂)	731.2		700.2	
1,2-Diaziridine-3-one (6)	N	851.5		825.0	
	O	726.2		696.9	
1,2-Dioxirane-3-one (7)	O ₂	634.1		610.7	
	O ₄	621.7		592.3	
1,2-Oxaziridine-3-one (8)	O ₃	759.3		731.0	
	N	738.2		711.1	
	O ₄ (anti to N)	682.9		651.9	
	O ₄ (syn to N)	678.4		647.7	
Cyclopropane-1,2-dione (9)	O	922.0		887.4	
Syn-2-hydroxycyclopropenone (9a)	O ₄ (anti to O ₅)	847.6		815.2	
	O ₄ (syn to O ₅)	842.0		808.1	
	O ₅	636.1		609.5	
Aziridine-2,3-dione (10)	O (syn to N)	800.9		770.9	
	O (anti to N)	732.9		701.3	
Oxirane-2,3-dione (11)	O ₄ (anti to O ₂)	886.5		863.8	
	O ₄ (syn to O ₂)	789.1		761.2	
	O ₂	789.1		761.2	

^aSee Fig. 2 for the numbering of the atoms.

regarding the cyclopropanone derivatives. The G4 estimates are in very good agreement with the existent experimental data.

QTAIM analysis

The topological analysis of the electron density, $\rho(\mathbf{r})$, and its Laplacian function, $\nabla^2\rho(\mathbf{r})$, has been made for the protonated cyclopropane and cyclopropanone derivatives. The results are reported in Tables 3 and 4 and Fig. 5.

In all cases when the O₄ atom is protonated (see Table 3), the C₁–O₄ interatomic distances are longer than a conventional C=O double bond (except in the 11O₄Hanti species) and slightly shorter than protonated acetone. In these cases, the C₁–O₄ interatomic distances range from 1.242 Å (in 7O₄H species) to 1.334 Å (in 9OH species), while the C–O interatomic distances are 1.209 and 1.379 Å in acetone and protonated acetone, respectively. Topological parameters enable us to characterize the double bond. In all protonated species studied here, $\rho(\mathbf{r}_b)$ and, in most cases, also ε at the bond critical point C₁–O₄ (see Table 3) are lower than the values found in the C=O double covalent bonds (i.e., $\rho(\mathbf{r}_b) = 0.4219$ au and $\varepsilon = 0.08$ in acetone). Moreover, the bond order n of the C–O bond has also been examined within the framework of QTAIM^{5–7} with the expression $n = \exp[A\rho(\mathbf{r}_b) - B]$, where $A = 5.1151$ and $B = 1.4616$. The bond order n denotes a decrease of the double bond character of the C₁–O₄ interatomic interaction. These results clearly show that protonation on O₄ lessens the bond order and thereby weakens the C₁–O₄ bond as befits the greater contribution of the resonance structure $>\text{C}^+-\text{OH}$ to the protonated species than $>\text{C}^+-\text{O}^-$ to the parent carbonyl species.

On the other hand, the C₁–O₄ bonds in 5O₂H, 6NH, 7O₂H, 8NH, and 8O₃H species and the C₃–O₅ bonds in 9OH, 10O₄Hsyn, 10O₄Hanti, 11OH, and 11O₄Hanti species are similar to the C≡O triple bond in diatomic CO. The C–O interatomic distances are around 1.1 Å and $\rho(\mathbf{r}_b)$ values are around 0.50 au. That is, these

Table 3. Interatomic distances and selected local topological properties of the electronic charge density distribution calculated at the position of the bond critical points of selected bond paths.

Species	Bond	d	$\rho(\mathbf{r}_b)$	$\nabla^2\rho(\mathbf{r}_b)$	ε	n
4OHanti	C ₁ –O ₄	1.273	0.3585	–0.6344	0.03	1.45
	O ₄ –H	0.974	0.3532	–2.7631	0.01	
4OHsyn	C ₁ –O ₄	1.271	0.3600	–0.6329	0.04	1.46
	O ₄ –H	0.976	0.3509	–2.7242	0.01	
5O ₂ H	C ₁ –O ₄	1.116	0.5124	0.5105	0.00	3.19
	O ₂ –H	0.969	0.3634	–2.7605	0.02	
5O ₄ Hsyn	C ₁ –O ₄	1.257	0.3742	–0.6432	0.06	1.57
	O ₄ –H	0.982	0.3427	–2.6902	0.01	
5O ₄ Hanti	C ₁ –O ₄	1.259	0.3725	–0.6381	0.06	1.56
	O ₄ –H	0.977	0.3475	–2.7433	0.01	
6NH	C ₁ –O ₄	1.132	0.4926	0.2875	0.04	2.88
	N ₂ –H	1.017	0.3444	–1.8195	0.05	
6OH	C ₁ –O ₄	1.257	0.3737	–0.6450	0.09	1.57
	O ₄ –H	0.979	0.3455	–2.7214	0.01	
7O ₂ H	C ₁ –O ₄	1.127	0.4961	0.3799	0.03	2.93
	O ₂ –H	0.985	0.3500	–2.7472	0.04	
7O ₄ H	C ₁ –O ₄	1.242	0.3922	–0.7598	0.13	1.72
	O ₄ –H	0.984	0.3345	–2.6778	0.01	
8NH	C ₁ –O ₄	1.129	0.4948	0.3014	0.02	2.91
	N ₂ –H	1.029	0.3403	–1.8513	0.05	
8O ₃ H	C ₁ –O ₄	1.132	0.4922	0.3193	0.04	2.87
	O ₃ –H	0.977	0.3584	–2.7523	0.04	
8O ₄ Hanti	C ₁ –O ₄	1.251	0.3821	–0.7198	0.11	1.64
	O ₄ –H	0.982	0.3396	–2.6899	0.01	
8O ₄ Hsyn	C ₁ –O ₄	1.251	0.3814	–0.7115	0.10	1.63
	O ₄ –H	0.980	0.3419	–2.7138	0.01	
9OH	C ₁ –O ₄	1.334	0.3209	–0.8544	0.16	1.20
	O ₄ –H	0.969	0.3594	–2.7620	0.02	
9aO ₄ Hanti	C ₃ –O ₅	1.123	0.5041	0.4292	0.01	3.06
	C ₁ –O ₄	1.281	0.3501	–0.6244	0.01	1.39
9aO ₄ Hsyn	C ₁ –O ₄	1.284	0.3480	–0.6238	0.01	1.38
	O ₄ –H	0.972	0.3571	–2.7649	0.01	
9aO ₅ H	C ₁ –O ₄	1.166	0.4580	–0.1241	0.06	2.41
	O ₅ –H	0.982	0.3459	–2.7719	0.02	
10O ₄ Hsyn	C ₁ –O ₄	1.314	0.3359	–0.8606	0.17	1.29
	O ₄ –H	0.973	0.3533	–2.7383	0.01	
10O ₄ Hanti	C ₃ –O ₅	1.117	0.5113	0.5227	0.00	3.17
	C ₁ –O ₄	1.266	0.3648	–0.6288	0.04	1.50
11OH	O ₄ –H	0.977	0.3476	–2.7417	0.01	
	C ₃ –O ₅	1.160	0.4652	–0.0692	0.11	2.50
11O ₄ Hanti	C ₁ –O ₄	1.291	0.3564	–0.8918	0.17	1.44
	O ₄ –H	0.980	0.3445	–2.7025	0.01	
11O ₄ Hanti	C ₃ –O ₅	1.114	0.5145	0.5760	0.00	3.22
	C ₁ –O ₄	1.181	0.4382	–0.3700	0.01	2.18
11O ₄ Hanti	O ₄ –H	1.470	0.0724	0.1468	0.00	
	C ₃ –O ₅	1.110	0.5220	0.5623	0.00	3.35

Note: See Fig. 2 for the numbering of the atoms. d , interatomic distances; $\rho(\mathbf{r}_b)$, electron density; $\nabla^2\rho(\mathbf{r}_b)$, Laplacian of the electron density; ε , ellipticity of the electron density; n , bond order. Distances in angstroms, $\rho(\mathbf{r}_b)$ and $\nabla^2\rho(\mathbf{r}_b)$ in atomic units, and ε and n dimensionless.

values are nearly the same as in CO (1.113 Å and 0.5001 au) and in protonated CO, i.e., HCO⁺ (1.107 Å and 0.5153 au).

In all cases when oxygen/nitrogen atoms are protonated, the O–H/N–H interatomic distances are on the same order of magnitude of that of a conventional O–H/N–H bond (about 0.95 and 1.02 Å, respectively). Topological parameters reveal (see Table 3) that O–H/N–H interactions are within the shared-shell regime ($\rho(\mathbf{r}_b)$ relatively high and $\nabla^2\rho(\mathbf{r}_b) < 0$). In other words, according to QTAIM, an O–H/N–H covalent bond is formed as a result of the protonation of an oxygen/nitrogen atom.

The $L(\mathbf{r}) = -1/4\nabla^2\rho(\mathbf{r})$ function shows the regions of the space where $\rho(\mathbf{r})$ is locally concentrated ($L(\mathbf{r}) > 0$) or depleted ($L(\mathbf{r}) < 0$).^{5–7} In a previous work, we have used this function to show that triplet

Table 4. Total electronic energy of molecule, atomic energy, and atomic electronic population on protonation site for the protonated cyclopropanone species and cyclopropanone derivatives isolated (in parentheses).

Molecule	Protonation site	Electronic energy		
		$E(\Omega_{\text{Total}})$	$E(\Omega_{\text{Atomic}})$	$N(\Omega)$
Aziridine-2-one (4)	O ₄ (anti to N)/4OHanti	-207.5427 (-207.2264)	-75.6629 (-75.6335)	9.0759 (9.1046)
	O ₄ (syn to N)/4OHsyn	-207.5396 (-207.2264)	-75.6634 (-75.6335)	9.0745 (9.1046)
Oxirane-2-one (5)	O ₂ /5O ₂ H	-227.3981 (-227.0978)	-75.5201 (-75.5042)	8.9929 (8.8878)
	O ₄ (syn to O ₂)/5O ₄ Hsyn	-227.3909 (-227.0978)	-75.6958 (-75.6551)	9.0765 (9.1041)
	O ₄ (anti to O ₂)/5O ₄ Hanti	-227.3885 (-227.0978)	-75.6924 (-75.6551)	9.0723 (9.1041)
1,2-Diaziridine-3-one (6)	N/6NH	-223.5750 (-223.2574)	-54.7122 (-54.8063)	7.5559 (7.6489)
	O/6OH	-223.5495 (-223.2574)	-75.6913 (-75.6559)	9.0734 (9.1002)
1,2-Dioxirane-3-one (7)	O ₂ /7O ₂ H	-263.1941 (-262.9566)	-75.1200 (-75.2914)	8.3533 (8.5077)
	O ₄ /7O ₄ H	-263.2008 (-262.9566)	-75.7136 (-75.6861)	9.0731 (9.0935)
1,2-Oxaziridine-3-one (8)	O ₃ /8O ₃ H	-243.3943 (-243.1163)	-75.2458 (-75.4019)	8.5696 (8.6964)
	N ₂ /8NH	-243.3917 (-243.1163)	-54.6228 (-54.7150)	7.3678 (7.4694)
	O ₄ (anti to N)/8O ₄ Hanti	-243.3875 (-243.1163)	-75.7038 (-75.6721)	9.0770 (9.1021)
Cyclopropane-1,2-dione (9) syn-2-Hydroxycyclopropenone (9a)	O/9OH	-265.3413 (-264.9957)	-75.5861 (-75.6188)	9.0490 (9.0290)
	O ₄ (anti to O ₅)/9aO ₄ Hanti	-265.3538 (-265.0245)	-75.6416 (-75.6205)	9.0776 (9.1346)
	O ₄ (syn to O ₅)/9aO ₄ Hsyn	-265.3528 (-265.0245)	-75.6389 (-75.6205)	9.0725 (9.1346)
	O ₅ /9aO ₅ H	-265.2725 (-265.0245)	-75.5936 (-75.5904)	9.0616 (9.0902)
Aziridine-2,3-dione (10)	O (syn to N)/10O ₄ Hsyn	-281.3875 (-281.0916)	-75.6343 (-75.6533)	9.0650 (9.0945)
	O (anti to N)/10O ₄ Hanti	-281.3773 (-281.0916)	-75.6766 (-75.6533)	9.0738 (9.0945)
Oxirane-2,3-dione (11)	O ₄ (syn to O ₂)/11OH	-301.2514 (-300.9550)	-75.6708 (-75.6698)	9.0629 (9.0580)
	O ₄ (anti to O ₂)/11O ₄ Hanti	-301.2575 (-300.9550)	-75.6853 (-75.6698)	9.1249 (9.0580)

Note: See Fig. 2 for the numbering of the atoms; all values in atomic units.

Fig. 5. Molecular graph and nonbonded maxima of the $L(\mathbf{r})$ function (critical points (3,-3) in $L(\mathbf{r})$) for the 1,2-oxaziridine-3-one molecule. The red dots indicate the preferred protonation sites. Color in online version only.

vinyl nitrene has lone pairs available to interact electrostatically with a Lewis acid to form a Lewis adduct.²⁷ With this in mind, we wanted to check if the preferred protonation sites can be predicted through the localization of the nonbonded maxima of the $L(\mathbf{r})$ function (critical points (3,-3) in $L(\mathbf{r})$). The critical points (3,-3) correspond in number and position to the electron pairs defined by the Lewis and VSEPR model and correspond to zones where an electrophilic attack can occur.²⁸ Figure 5 shows the critical points (3,-3) in $L(\mathbf{r})$ and molecular graph for 1,2-oxaziridine-3-one (5). In this figure, it can clearly be observed the preferred protonation sites through the local charge concentration (lump – critical point (3,-3) in $L(\mathbf{r})$) in the valence shell charge concentration of the nitrogen and oxygen atoms.

The valence shell charge concentration of O₄ exhibits two nonbonded maxima (see the red dots in Fig. 5). The endocyclic oxygen atom has two sites of protonation, while the endocyclic nitrogen atom has a single site of protonation. These results agree with species formed upon protonation. That is, when the O₄ is protonated, 8O₄Hanti and 8O₄Hsyn species are formed and when the O₃ is protonated, 8O₃H species is formed, while when the N₂ is protonated, 8NH species is formed. Similar situations are observed in all other cyclopropanone derivatives.

The integration of electron density on the atomic basins of the protonation site provides a useful tool for analyzing charge redistribution that occurs as a result of protonation. Table 4 reports the total electronic energy of the molecule, atomic electronic energy, and electronic population.

In all cases, it is observed that the total electronic energy of the protonated cyclopropanone derivatives is greater in magnitude than that of the isolated neutral molecule. That is to say, the protonated cyclopropanone derivatives are more stable than the nonprotonated species. Moreover, in most cases, the heteroatom being protonated is stabilized (except in 6NH, 7O₂H, 8NH, 8O₃H, 9OH, and 10O₄Hsyn species).

The protonation of the molecules causes a decrease of the electronic population of the protonated atom (see Table 4), except when the O₂ atom of 5, the oxygen atom of 9, and the O₄ (syn and anti to O₂) atom of 11 are protonated.

The QTAIM results suggest. (1) Protonation on O₄ weakens the C₁-O₄ bond. Moreover, the C₁-O₄ bonds in 5O₂H, 6NH, 7O₂H, 8NH, and 8O₃H species and the C₃-O₅ bond in 9OH, 10O₄Hsyn, 10O₄Hanti, 11OH, and 11O₄Hanti species are similar to the C≡O triple bond in diatomic CO. (2) When a nitrogen or oxygen atom is protonated, a N-H/O-H covalent bond is formed. In addition, the cyclopropanone derivative species are less stable than their protonated counterparts. (3) The topological analysis of the $L(\mathbf{r})$ function reveals that the localization of the nonbonded maxima (critical points (3,-3) in $L(\mathbf{r})$) correspond in number and position to the electron pairs defined by the Lewis structures and VSEPR model and are the preferred protonation sites.

Supplementary material

Supplementary material is available with the article through the journal Web site at <http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2015-0029>.

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