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Computational study of electrophilic addition to acrylate anion:cyclic halonium is the transition structure for degenerate rearrangement of α-lactones†

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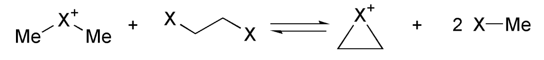
The cyclic chloronium or bromonium carboxylate obtained by addition of Cl^+ or Br^+ to acrylate anion is shown by PCM/B3LYP/6-31+G* calculations to be not an intermediate but a transition structure for interconversion of equivalent halomethyl oxiranones.

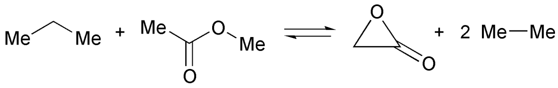
The intermediacy of a cyclic halonium cation[1] in electrophilic halogenation of many alkenes is widely accepted, although it is also recognised that a suitable substituent (*e.g.* aryl) may stabilise an open carbocation intermediate.[2] The stereochemistry of addition of aqueous bromine to the disodium salts of 2,3-dimethylmaleic acid and 2,3-dimethylfumaric acid was recently demonstrated[3] by X-ray crystallographic analysis of the product bromo-β-lactones to be *syn*, not *anti*. This result is most easily interpreted by a mechanism in which the initially formed bromonium ion is attacked intramolecularly by a carboxylate group to give an α-lactone intermediate which in turn is attacked by the second carboxylate group to form the β-lactone, with a second inversion of configuration.[3] As part of a programme of theoretical study related to aspects of this mechanism, we now present unexpected results for the simplest example of an alkene with a carboxylate substituent.

Geometry optimisation[4] using the B3LYP/6-31+G* level of density functional theory, together with the polarised continuum model (PCM) for aqueous solvation (ε = 78.4), yields cyclic chloronium and bromonium cations **1** derived formally by addition of Cl^+ or Br^+ to acrylic acid (Table 1). Analysis of the vibrational frequencies of these species reveals them to be true intermediates. In contrast, the analogous cyclic chloronium and bromonium species **2** (X = Cl, Br) from acrylate anion, which are neutral overall, each possess an imaginary frequency and thus correspond to first-order saddle points on their potential energy surfaces.‡ The reaction-coordinate vibrational mode shows a concerted motion of opening and closing the two three-membered rings, coupled with rotation about the C_α–CO_2^- bond. Following the intrinsic reaction coordinate downhill in both directions from these species leads in each case to a pair of equivalent halomethyloxiranones **3a** and **3b**, according to which of the oxygen atoms of the carboxylate group forms a bond to C_α. These α-lactones are themselves energy minima and would differ only in the labelling of the oxygen atoms, O and O*; in all other respects they are identical. Thus the cyclic halonium is the transition structure for degenerate rearrangement of the α-lactone; this identity process (which retains the stereochemical configuration at C_α) has a barrier of 71 kJ mol^{-1} for the chloromethyloxiranone and 85 kJ mol^{-1} for the bromomethyloxiranone.

At first sight this result is surprising. The ring strain energy of the parent ethene chloronium and bromonium cations **4** may be estimated (PCM/B3LYP/6-31+G*) from isodesmic relations [eqn. (1), X = Cl or Br] to be about 67 kJ mol^{-1} for each (Table 1). In contrast, the ring strain energy of the parent oxiranone **5** is much larger at 150 kJ mol^{-1} [eqn. (2)]. Why are the halomethyloxiranones so much lower in energy than the halonium carboxylates, despite apparently possessing about 83 kJ mol^{-1} more ring strain energy?



(1)



(2)

The answer lies with the even greater instability of the zwitterion $XC_\beta H_2$–$C_\alpha{}^+H$–CO_2^- (**6**, X = Cl or Br) which corresponds to a second-order saddle point with respect to rotation about both C–C bonds (Table 1). Formation of the cyclic halonium carboxylate species serves to stabilise the

Table 1 B3LYP/6-31+G* relative energies ΔE/kJ mol^{-1}, (total energies E/hartree), number n_i and [magnitude/cm^{-1}] of imaginary frequencies for optimised species in PCM water

Species	w.r.t.	X = Cl		X = Br	
		ΔE (or E)	n_i	ΔE (or E) n_i	
1	**2**	(−727.14521)	0	(−2838.68119)	0
2		(−726.70247)	1 [73*i*]	(−2838.23962)	1 [85*i*]
3	**2**	−70.9	0	−84.7	0
6	**2**	4.6	2 [200*i*,67*i*]	25.7	2 [179*i*,70*i*]
7	**4**	148.8	1 [414*i*]	188.1	1 [333*i*]
8	**5**	198.9	1 [1416*i*]		
eqn. (1)	Me_2X^+	XCH_2CH_2X	**4**	MeX	ΔE
X = Cl	(−539.69597)	(−999.12275)	(−538.56843)	(−500.11225)	67.7
X = Br	(−2651.31108)	(−5222.07692)	(−2650.09523)	(−2611.63354)	67.4
eqn. (2)	$MeCH_2Me$	$MeCO_2Me$	**5**	MeMe	ΔE
	(−119.14540)	(−268.40325)	(−227.83023)	(−79.83056)	150.4

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† Electronic supplementary information (ESI) available: Cartesian coordinates for optimised geometries. See http://www.rsc.org/suppdata/cc/b2/b200900e/

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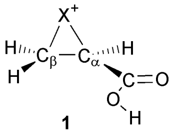

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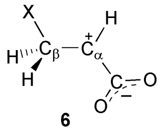

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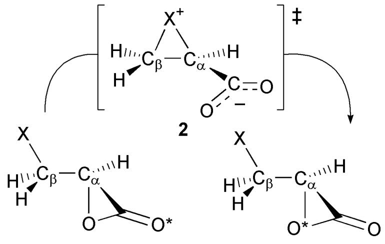
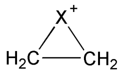


2

3a

3b



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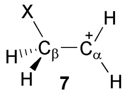

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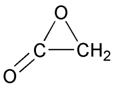

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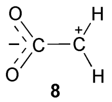

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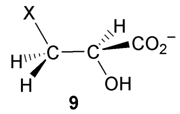

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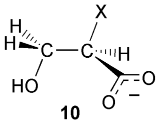

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carbocation centre at C_α, but not as effectively as formation of the halomethyloxiranone, since the former is still a zwitterion whereas the latter is formally a covalent species. Ring-closures of haloethyl cations (**7**, C–X bond coplanar with the carbocation centre) are exothermic by 67 (X = Cl) and 82 (X = Br) kJ mol^{-1}, but the unsubstituted zwitterion $H_2C^+–CO_2^-$ **8** is unstable with respect to oxiranone **5** by 199 kJ mol^{-1} (PCM/B3LYP/6-31+G*). The acyclic reference compounds employed in the isodesmic eqns. (1) and (2) are not entirely appropriate for consideration of the ring strain energies of the halonium carboxylates **2** and halomethyloxiranones **3** because they do not involve charge separation such as is present in the zwitterions **6**. Heterolytic opening of an α-lactone ring involves not only a favourable release of ring strain energy but also an unfavourable separation of positive and negative charges, even in solution.

Chlorination[5] and bromination[6] of undissociated acrylic acid and acrylate ester probably proceeds by means of a cyclic halonium ion intermediate; competition between Br^- and H_2O for the positively charged intermediate in bromination of ethyl acrylate in water leads to a predominance of dibromide product over bromohydrin.[6] Aqueous bromination of acrylate (and crotonate) anion is nearly 10^4 times faster than of undissociated acrylic (and crotonic) acid, and the overall uncharged intermediate shows much less preference towards nucleophilic attack by bromide anion.[6] The present computational study suggests that this latter intermediate is neither the bromonium carboxylate, nor the $BrC_\beta H_2–C_\alpha{}^+H–CO_2^-$ zwitterion, but is instead the bromomethyloxiranone. The literature does not appear to contain an experimental report of the regiochemistry of bromohydrin formation in the aqueous bromination of acrylate anion, but based upon the present theoretical study we predict that 3-bromo-2-hydroxypropanoate (**9**, X = Br) would predominate over 2-bromo-2-hydroxypropanoate (**10**, X = Br). The opposite regioselectivity would be expected for bromohydrin formation from undissociated acrylic acid or acrylate ester. Finally we note that treatment of 2-octenoic acid with biscollidinebromine(I) hexafluorophosphate in dichloromethane yields polymers that could result from the intermediacy of an α-lactone.[7]

We previously suggested[3] that the transient intermediacy of an α-lactone significantly affects the stereochemical course of a reaction involving a dicarboxylate in aqueous solution. We now suggest that a molecule containing a single carboxylate group adjacent to an atom that acquires significant electrophilic character during the course of a reaction may transiently adopt an α-lactone configuration.

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Notes and references

‡ Geometries optimised in PCM water (Electronic Supplementary Information†) differ very little from those optimised *in vacuo*, and the imaginary frequencies for the reaction coordinate modes of structures **2** (X = Cl and Br) differ by only 2 cm^{-1} from the gas-phase values. Intrinsic reaction coordinates are calculated *in vacuo*, as are vibrational frequencies presented in Table 1.

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