PAPER

Base initiated depolymerization of polycarbonates to epoxide and carbon dioxide co-monomers: a computational study†

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High-accuracy CBS-QB3(+) calculations were used to obtain the free energy barriers for several polycarbonates of interest to undergo alkoxide back-biting to give the corresponding epoxide and carbon dioxide. Free energy barriers to epoxide formation were modest for most polymeric alkoxides (12.7–17.4 kcal mol^{-1}), and they were higher than for the same starting material to give cyclic carbonate (10.7–14.6 kcal mol^{-1}). Poly(cyclopentene carbonate) differs: epoxide formation has a lower free energy barrier (13.3 kcal mol^{-1}) than cyclic carbonate formation (19.9 kcal mol^{-1}). These results explain why poly(cyclopentene carbonate) depolymerizes to cyclopentene oxide when treated with a strong base, whereas propylene and styrene polycarbonates depolymerize to their respective cyclic carbonates. Recycling *via* regeneration of the monomer represents the ideal method for producing material of the highest quality.

Introduction

The increasing levels of carbon dioxide in the atmosphere are of great concern due to carbon dioxide's role as a greenhouse gas. A multi-pronged effort to address this problem likely includes technologies such as carbon capture and storage (CCS),[1] whereby carbon dioxide is extracted from point sources (mainly flue gases), then sequestered indefinitely in appropriate reservoirs such as disused oil wells. Aside from sequestration, carbon dioxide is a cheap, abundant, non-toxic gas that can be utilized in three broad ways: (1) as-is in the form of a propellant, solvent, blowing agent, *etc.*; (2) as a C_1 feedstock for further chemical transformation; (3) as a biological feedstock in the bio-production of desirable chemicals or fuels.[2] In regards to its use as a chemical feedstock, 10% of CO_2 emissions are attributed to the production of chemical products. Aresta suggests that if carbon dioxide were fully utilized as a chemical feedstock, a 7% saving in CO_2 emissions might be realized.[3]

Carbon dioxide and epoxides react to give polymers and cyclic carbonates (Scheme 1). The former have been commercialized as burnable binders and packaging material,[4–6] while the latter are used as green solvents.[7–9]

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†Electronic supplementary information (ESI) available: ^{1}H NMR spectra of the depolymerization product of poly(propylene carbonate) and poly(styrene carbonate). Calculated C–O lengths and O–C–O angles at the alkoxides' transition states to epoxide formation. See DOI: 10.1039/c3gc40475g

Scheme 1 Carbon dioxide and epoxides react to give polymers (left) and cyclic carbonates (right).

Extensive mechanistic studies of the metal-catalyzed reaction between carbon dioxide and different epoxides to give polymers or cyclic carbonates have been carried out.[9–22] Polymer growth is often accompanied by cyclic carbonate formation as the anionic growing polymer chain (metal-bound or metal-free) undergoes alkoxide or carbonate back-biting, leading to the loss of one repeat unit, and the formation of one equivalent of cyclic carbonate.[20,23,24] Complementary to experimental reports by ourselves and others, we have recently performed a computational study on the thermodynamics of the enchainment reaction, and the reaction barriers of both the metal-free back-biting reactions.[25]

In that article, we reported that the metal-free carbonate and alkoxide back-biting reactions had free energy barriers of 18–25 kcal mol^{-1} and 10–14 kcal mol^{-1}, respectively. In contrast, where a (salen)Cr(III) catalyst were used, the analogous metal-bound degradation reaction of poly(cyclohexene carbonate) had higher activation energies, 32 kcal mol^{-1} [26] and 25 kcal mol^{-1} [23] respectively. The theoretical results indicate that back-biting requires more energy when metal-bound, helping to explain the success of contemporary catalysts for the polymerization reaction that have tethered onium

cations.[19] These onium cations prevent the growing polymer chain from dissociating fully, thus avoiding metal-free degradation.[20,27]

Herein, we present the reaction barriers of another degradation pathway that causes these polycarbonates to revert to the epoxide and carbon dioxide co-monomers. Such a depolymerization reaction is particularly attractive in the context of recycling plastic waste:[28] by returning the waste polymer to monomer indistinguishable to raw material in an energy-undemanding process, the original polymer can be recreated with no compromise as to its physical properties.

The results will be discussed in the context of the carbonate- and alkoxide-backbiting reactions that yield cyclic carbonate. These computational results will also be used to rationalize experimental observations with regard to the degradation of poly(*trans*-cyclopentene carbonate). They emphasize that poly(*trans*-cyclopentene carbonate)'s behavior sets it apart from other members of this class of polycarbonates.

Results and discussion

The motivation for the investigation undertaken herein was an interesting experimental observation.[29] That is, when treated with sodium bis(trimethylsilyl)amide, a strong base, hydroxy-terminated poly(*trans*-cyclopentene carbonate) was degraded to a mixture of cyclopentene oxide and *cis*-cyclopentene carbonate. However, upon performing the same reaction in the presence of carbon dioxide, only *cis*-cyclopentene carbonate was obtained (Scheme 2).

Formation of the epoxide indicated that the alkoxide had undergone an intramolecular nucleophilic substitution, displacing a carbonate-terminated polymer represented by a methyl carbonate anion (Scheme 3). This reaction is akin to the formation of an epoxide by the deprotonation of a chlorohydrin.
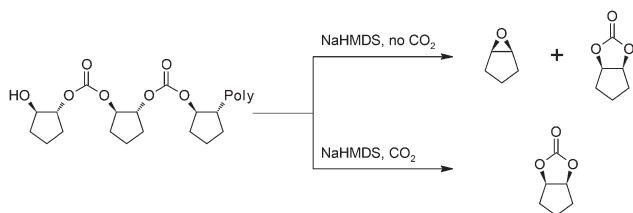
Scheme 2 Behavior of hydroxy-terminated poly(*trans*-cyclopentene carbonate) when treated with a strong base, with and without added carbon dioxide.
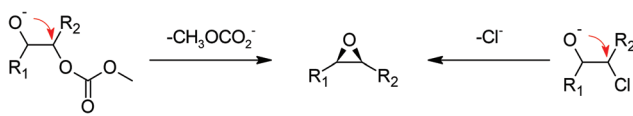
Scheme 3 Intramolecular nucleophilic substitution reactions leading to an epoxide. Methine attack occurs where $R_2 \neq H$ and methylene attack occurs where $R_2 = H$.

Reaction barriers for the alkoxide back-biting reaction to give epoxide

In this study, we considered a free alkoxide anion generated by the complete deprotonation of a hydroxy-terminated polymer, solvated by tetrahydrofuran. This approach allowed us to evaluate barriers to epoxide formation that are uncomplicated by ion pairing, and by the equilibrium that arises when the alcohol is deprotonated by a poorer base.[24]

At the transition state, the appropriate carbon–oxygen bonds are ~2.0 Å in length, significantly greater than the typical C–O length of 1.42 Å.[30] To yield epoxides, the alkoxide oxygen is only two bonds away from the carbon center undergoing substitution; the O–C–O angles of 148–157° are significantly distorted (Table S1†). For the oxetane-forming reaction, the alkoxide oxygen is three bonds away, permitting an O–C–O angle of 175° that is close to the idealized 180°.

The free energy barriers for the alkoxide back-biting reaction to yield epoxides were computed (Table 1) in advance of experimental kinetic data. The trends previously reported for carbonate back-biting reactions to give cyclic carbonates[25] were also observed for the current system that yields epoxides, and they are consistent with S_N2-type reactions in general:[31]

(1) There is a higher barrier to reaction at the methine position than at the methylene position; this is a steric effect (entries 2 and 4; see Scheme 3).

(2) In some cases, there is a lower barrier to reaction at the methylene position, compared with the alkoxide derived from ethylene carbonate (entries 3 and 5). For the case of carbonate back-biting, we showed that this lowering was due to favorable interactions between the pendant group and the carbon atom undergoing substitution. Such interactions are less obvious for the cases we have studied here.

(3) The reactivity trends mentioned above are not observed for the alkoxides derived from styrene carbonate. The p_π electrons on the phenyl pendant group delocalize onto the empty

Table 1 Relative free energies (in kcal mol^{-1}) of the species involved in alkoxide back-biting to give the corresponding epoxide[a]

No.	Parent carbonate	Open-chain alkoxide	Transition state	Epoxide + methyl carbonate
1	EC	0.0	14.6	−16.7
2	PC-1	0.0	14.9	−19.1
3	PC-2	0.0	12.7	−18.8
4	1ClPC	0.0	17.4	−15.7
5	2ClPC	0.0	13.7	−14.2
6	SC-1	0.0	14.5	−18.0
7	SC-2	0.0	15.4	−14.0
8	CPC	0.0	13.3	−20.6
9	CHC	0.0	15.6	−17.1
10	TMC	0.0	20.7	−19.6

[a] Open chain alkoxide derived from ethylene carbonate (hereafter abbreviated EC) = $^-$OCH$_2$CH$_2$OCO$_2$CH$_3$. PC = propylene carbonate; ClPC = chloropropylene carbonate; SC = styrene carbonate; CPC = cyclopentene carbonate; CHC = cyclohexene carbonate; TMC = trimethylene carbonate. -1 and -2 denote alkoxide attack at the methine or methylene positions, respectively. The convention used here is consistent with that used in our last report on this topic.[24]
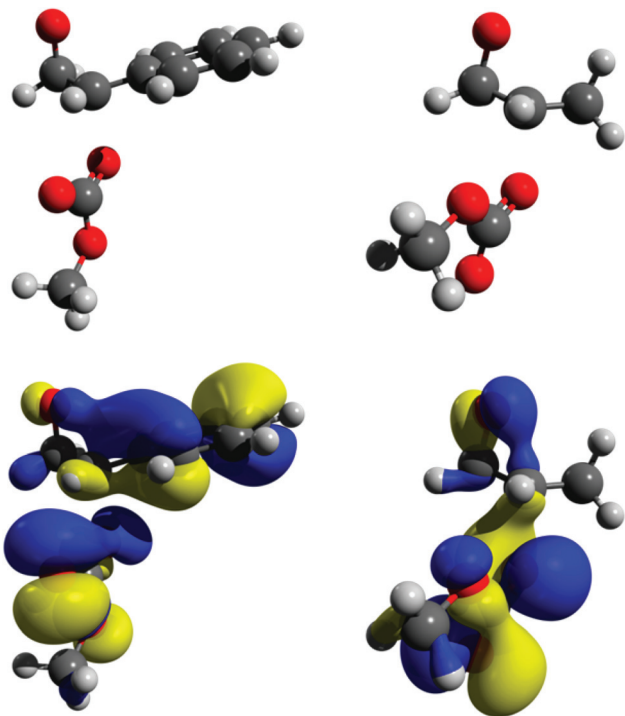
Fig. 1 HOMO-3 of the alkoxides derived from styrene carbonate (left) and propylene carbonate (right) at the transition state to epoxide formation (methine attack). The filled p_π electrons on the phenyl pendant group are delocalized into the empty p orbital on the carbon undergoing substitution, stabilizing the transition state, and lowering the barrier for reaction (left). The methyl pendant group provides no such stabilizing interaction (right).

p orbital of the carbon undergoing substitution, thereby reducing the barrier to reaction (entry 6 and Fig. 1).

The alkoxide derived from trimethylene carbonate (entry 10) has an unusually high free energy barrier to ring closure (20.7 kcal mol^{-1}), compared with that derived from ethylene carbonate (14.6 kcal mol^{-1}, entry 1), even though the ring strain energies for cyclobutane and cyclopropane are approximately the same (26.2 and 27.6 kcal mol^{-1}, respectively).[31] An extended discussion of this topic is beyond the scope of this article, but we do note that at the transition state, the substituents on two carbons are eclipsed for the alkoxide derived from trimethylene carbonate, whereas such an arrangement is absent in the alkoxide derived from ethylene carbonate (Fig. 2). When allowed to relax, the alkoxide derived from trimethylene carbonate is able to extend and relieve such strain. From a different perspective, more conformational change is needed for trimethylene carbonate's alkoxide to attain the transition state to cyclic ether formation, compared with ethylene carbonate's. Similar attempts were made to rationalize the free energy barriers for cyclopentene and cyclohexene carbonate-derived alkoxides to form the corresponding epoxides, but no straightforward explanation was found for their differing reactivity.

The data in Table 1 indicate that the epoxide-forming reactions are exergonic, which may seem surprising given the strain present in the three-membered cyclic ethers. However,
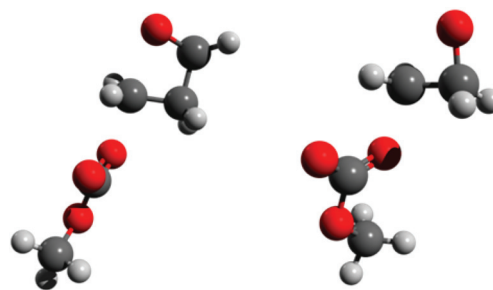

Fig. 2 At the transition state to cyclic ether formation, the substituents on the two carbons of the alkoxide derived from trimethylene carbonate are eclipsed, whereas that is not the case for the alkoxide derived from ethylene carbonate. This may help explain why the former's free energy barrier to cyclic ether formation is 6.1 kcal mol^{-1} higher.

the methyl carbonate leaving anion is expected to be a poor nucleophile. Consequently, it has a very high free energy barrier to cause the epoxide to undergo ring-opening. Note that the methyl carbonate anion and the epoxide are considered as separate species rather than as a product complex, so the $T\Delta S$ component of free energy is overestimated by approximately 10 kcal mol^{-1}.

### Alkoxide back-biting reactions to give epoxide *vs.* cyclic carbonate

For a given alkoxide, epoxide formation has a higher barrier than cyclic carbonate formation (Table 2). The barrier to cyclic carbonate formation was previously found to be the energy required for the polymeric alkoxide (represented by a methoxide anion) to dissociate from the tetrahedral intermediate. Formation of the tetrahedral intermediate is barrierless, in comparison.[25] The alkoxide derived from cyclopentene carbonate is an anomaly, and it will be discussed *vide infra*.

Because epoxide formation has a higher barrier than cyclic carbonate formation, it follows that cyclic carbonate formation should dominate. Indeed, no trace of the corresponding

**Table 2** Free energy barriers (in kcal mol^{-1}) for both alkoxide back-biting reactions

No.	Parent carbonate	Epoxide formation	Cyclic carbonate formation[24]
1	EC	14.6	11.6
2	PC-1	14.9	11.8
3	PC-2	12.7	11.8
4	ClPC-1	17.4	12.4
5	ClPC-2	13.7	12.4
6	SC-1	14.5	10.7
7	SC-2	15.4	10.7
8	CPC[a]	13.3	19.9[b]
9	CHC[a]	15.6	14.6
10	TMC	20.7	15.8[c]

[a] The oxygen and the methyl carbonate substituents of the alkoxide anion are mutually *trans*, as they would appear in the polymer. The epoxide will have a *cis* configuration, whereas the cyclic carbonate formed will have a *trans* configuration. [b] Overall barrier from the open chain alkoxide, through the tetrahedral intermediate to the cyclic carbonate + methyl carbonate anion. [c] Not previously published.
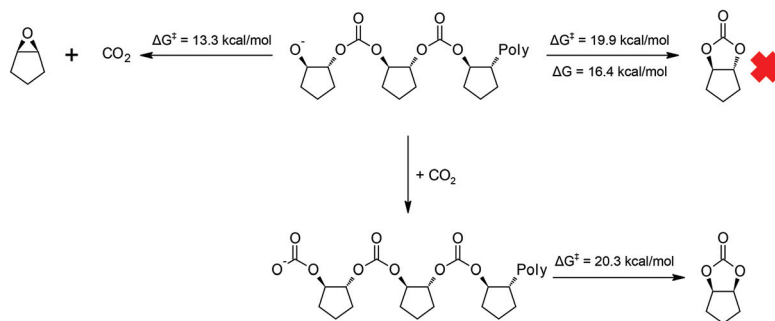
Scheme 4 The possible degradation routes available for poly(*trans*-cyclopentene carbonate). Free energy barriers are noted.

epoxide was observed when propylene and styrene polycarbonates were treated with base (Fig. S1†). Furthermore, sequential epoxide formation steps generate carbon dioxide. An equilibrium between polymeric alkoxide (left) and carbonate (right) exists:

$$Poly\text{-}O^- + CO_2 \rightleftharpoons Poly\text{-}OCO_2^- \qquad (1)$$
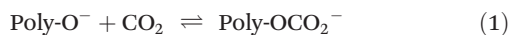
This equilibrium reduces the concentration of free alkoxide that is required for epoxide formation. With that said, this equilibrium cannot be used to exclude epoxide formation outright since the alkoxide derived from cyclopentene carbonate is able to form appreciable amounts of epoxide in a closed system.

It remains of great interest to depolymerize polycarbonates to recover the starting epoxides. Recycling the co-monomers allows the production of new polycarbonates no different from virgin polymer, superior to current recycling efforts that blend recovered polymer with fresh material to give a product with inferior physical properties. Cyclic carbonates formation may be avoided by conducting the base-initiated degradation reaction under a mild vacuum. By removing any carbon dioxide formed, carbonate back-biting (to cyclic carbonate) can be excluded, and epoxide formation will be able to compete with cyclic carbonate formation.

Understanding poly(*trans*-cyclopentene carbonate)

At this point, we return to the poly(*trans*-cyclopentene carbonate) story that inspired this line of inquiry: Absent added carbon dioxide, poly(*trans*-cyclopentene carbonate) degrades to a mixture of cyclopentene oxide and *cis*-cyclopentene carbonate. In a carbon dioxide atmosphere, *cis*-cyclopentene carbonate is the only product.

cis-Cyclopentene carbonate has a low free energy barrier to formation (9.9 kcal mol^{-1}) *via* alkoxide back-biting of poly(*cis*-cyclopentene carbonate), but the polymer is of a *trans* configuration.[25] Unlike the other open chain alkoxides, the alkoxide derived from *trans*-cyclopentene carbonate is lower in free energy than the tetrahedral intermediate leading to cyclic carbonate formation. This tetrahedral intermediate is, in turn, lower in free energy than the *trans*-cyclopentene carbonate + methoxide product complex, and this was attributed to angle strain. Rather than a 10–15 kcal mol^{-1} free energy barrier for

Table 3 Relative enthalpies (in kcal mol^{-1}, CBS-QB3) of the different conformations of cyclopentene carbonate and trithiocarbonate

Conformation	Cyclopentene carbonate	Cyclopentene trithiocarbonate
cis-Boat	0.0	0.0
cis-Chair	2.5	0.1
trans	19.2	5.0

the loss of the polymeric alkoxide (modeled as methoxide), the overall free energy barrier for cyclopentene carbonate to undergo alkoxide back-biting is 19.9 kcal mol^{-1},[25] significantly higher than the free energy barrier for epoxide formation (13.3 kcal mol^{-1}).

The great disparity between these two free energy barriers helps explains why no *trans*-cyclopentene carbonate (the product of alkoxide back-biting) is produced (Scheme 4).[29] Additionally, *trans*-fused five-membered cyclic rings are unstable relative to *cis*-fused isomers due to their strained geometries (Table 3), and this statement is generally true.[32] Replacing oxygen with sulfur leads to less strain due to the C–S bond (~1.83 Å) being longer than C–O bonds (1.44 Å), and *trans*-cyclopentene trithiocarbonate is well known.[32,33]

To explain the formation of *cis*-cyclopentene carbonate, the polymeric alkoxide is rapidly converted to carbonate in the presence of carbon dioxide (*e.g.* from epoxide-forming reactions).[34] The polymeric carbonate product back-bites, giving rise to the *cis*-cyclopentene carbonate that is observed experimentally. Given significant amounts of carbon dioxide, negligible free alkoxide should exist. Carbonate back-biting is the only possibility, making *cis*-cyclopentene carbonate the sole product.[29]

Concluding remarks

Beyond the established carbonate and alkoxide back-biting routes, an additional degradation mode for cyclic carbonates has been described, and the computational results presented have explained experimental observations well. This epoxide-forming degradation is only observed for poly(*trans*-cyclopentene carbonate) without added carbon dioxide, because its free energy barrier is lower than the free energy barrier to cyclic

carbonate formation *via* alkoxide back-biting. In all other cases examined, cyclic carbonate is the sole product because epoxide formation has a higher barrier for reaction, and because epoxide formation gives rise to polymeric carbonates that undergo carbonate back-biting.

Nevertheless, epoxide formation reactions have small barriers, and this pathway may be competitive if carbon dioxide were continually removed. The base initiated degradation can therefore serve as a low energy route to recycle waste polycarbonate to fresh polymer.

Computational methods

All calculations were performed using the Gaussian 09 suite.[35] Geometries were fully optimized using the B3LYP functional[36–38] and the Pople-style 6-311+G(2d,d,p) basis set.[39–41] Molecular orbitals were visualized at this level as well. The Integral Equation Formalism Polarization Continuum Model (IEFPCM) calculation with radii and non-electrostatic terms for Truhlar and coworkers' SMD solvation model[42] was used with tetrahydrofuran as the prototypical solvent throughout.

All local minima and saddle points were verified by their calculated vibrational frequencies (zero and one imaginary frequencies respectively), except for one example noted in the text. The saddle points found were confirmed to be the correct ones by visualizing the imaginary vibrational modes with AGUI[43] and Avogadro.[44] No attempts were made to locate global energy minima of the structures studied.

To be consistent with our previous work,[25] the enthalpies and free energies of the various species at their stationary points were obtained using CBS-QB3(+) calculations:[45] B3LYP/6-311+G(2d,d,p) reference geometries and frequencies were read-in, and the CBS-QB3[46,47] calculation proceeded directly to the third step (CCSD(T)/6-31+G(d′)) using the CBS-QB3 (StartMP2) keyword in Gaussian 09. The scale factor for the zero-point energies was not changed from the 0.99 pre-defined by CBS-QB3.

Experimental methods

Degradation of polycarbonates with base

15 mg of propylene, styrene and cyclopentene polycarbonates were charged into separate J. Young-sealed NMR tubes. 0.4 mL of a stock solution of sodium bis(trimethylsilyl)amide in toluene-d_8 (11 mM) was added to each NMR tube. The solutions were heated to 110 °C for 16 hours, and the NMR spectra were recorded.

Notes

The authors declare no competing financial interest.

Note added after first publication

This article replaces the version published on the 19th April 2013, which contained errors in Table 2.

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