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Ester Pyrolysis of Carbonates: Bis(benzene hydrate) Carbonate as Potential Precursor for Monomeric Carbonic Acid

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The twofold ester pyrolysis of carbonates, yielding monomeric carbonic acid, was investigated by computational methods. By comparison with CCSD(T)/cc-pVTZ//B3LYP/cc-pVTZ benchmark calculations, the M05-2X method was found to give the most accurate reaction enthalpies among the DFT methods employed. While the first ester pyrolysis of diethyl carbonate, (*E*)-bis(acetaldoxime) carbonate or di-*N*,*N*-dimethylhydroxylamine carbonate will yield the corresponding monocarbonates, these highly labile compounds are predicted to decay via alternative reaction channels that result in the formation of carbon dioxide. Due to competing O–O bond homolyis reactions, dialkyl diperoxycarbonates are predicted to afford at best moderate yields of monomeric carbonic acid upon flash vacuum pyrolysis. The carbonate derived from "benzene hydrate" (cyclohexa-2,4-dien-1-ol), however, is predicted to be an ideal precursor for monomeric carbonic acid, undergoing ester pyrolysis in a very facile reaction, with no competing bond homolysis processes.

Introduction

Carbonic acid (**1**, H_2CO_3), is inherently unstable towards decay into its anhydride, carbon dioxide, and water. It has been isolated at low temperature (180 K) as a neat crystalline substance.[1] The activation enthalpy for the unimolecular fragmentation of the isolated molecule has been predicted to be quite substantial ($\Delta H^{\ddagger}$ = 44 kcal mol^{-1}),[1b] which is due to the fact that the reaction involves a hydrogen transfer occurring via a four-membered-ring transition state. The presence of just one additional water molecule catalyzes the reaction and thus reduces the activation enthalpy to a much smaller value of $\Delta H^{\ddagger}$ = 16 kcal mol^{-1}.[1b] In the absence of water, carbonic acid is stable enough to be sublimed in vacuo. The stability of **1** in the gas phase is also demonstrated by neutralization-reionization mass spectrometry.[2] Another route to **1**, which may be relevant to its formation in extraterrestrial environments, is high-energy irradiation of water/CO_2 mixtures.[3] The saturation vapour pressures of monomeric **1** and the dimer of **1** have been estimated as 4×10^{-7} mbar (monomer) and 3×10^{-7} mbar (dimer) at T = 200 K.[1a] Obtaining a sample of monomeric **1** that does not already contain its dimer by simple sublimation of solid **1** therefore appears difficult, in particular as pulsed deposition methods used successfully for trapping pure monomeric carboxylic acids in argon matrices require far higher precursor vapour pressures.[4] In principle, however, matrix isolation spectroscopy, which involves the trapping of reactive molecules in solid noble gases at cryogenic temperatures, offers conditions that are perfectly suited for a detailed characterization of monomeric carbonic acid. Besides yielding the IR spectrum of monomeric **1**, such an experiment would also provide information about the mechanism of its dimerization and oligomerization. A successful matrix isolation experiment isolating free carbonic acid would require a stable, but thermolabile precursor molecule, that would be passed through an electrically heated hot tube followed by trapping of the pyrolysis products in solid inert argon. The goal of this contribution is to suggest precursor molecules that could successfully be used in the matrix isolation of **1**.

The ester pyrolysis reaction is an old method for generating C=C double bonds.[5] By heating (e.g.) ethyl acetate, transfer of a hydrogen atom from the methyl group of the ethyl substituent to the carbonyl oxygen atom takes place, yielding ethene and acetic acid. The reaction has to overcome a substantial activation enthalpy, which can be reduced by employing more labile esters such as xanthates (Čugaev elimination).[5] The ester pyrolysis is not a $\sigma_2s + \pi_2s + \pi_2s$ orbital-symmetry allowed fragmentation reaction because the orbital basis is orthogonal.[6] Concerted reactions of this type are termed pseudopericyclic.[7]

If single ethene elimination from ethyl acetate yields acetic acid, twofold ethene elimination from diethyl carbonate (**2**) should in principle yield carbonic acid (Scheme 1). On the radical cation surface, this reaction has indeed been used to generate the trihydroxycarbenium ion via consecutive elimination of a vinyl radical and ethene.[8] Its use on the closed-shell molecule, however, has not been reported yet. In this contribution, I present computational results on the twofold ester pyrolysis reaction of **2** and on a series of

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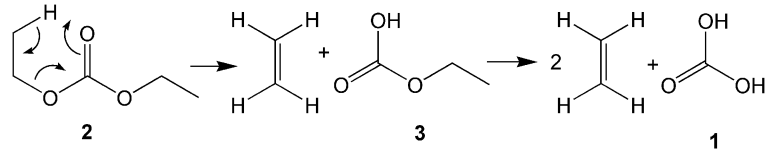


Scheme 1. Possible formation of carbonic acid (**1**) via twofold ester pyrolysis of diethyl carbonate (**2**).

related molecules, with the aim of presenting a potential target molecule for a pyrolytic precursor for monomeric carbonic acid.

Results and Discussion

Diethyl Carbonate

The ester pyrolysis of diethyl carbonate (**2**) was investigated at four different levels of theory, all with a cc-pVTZ basis set. In addition to the standard B3LYP and B3PW91 methods, the recent M05-2X method was utilized for optimization of stationary points [all including zero point energy (ZPE) correction]. Furthermore, CCSD(T)/cc-pVTZ//B3LYP/cc-pVTZ single point energies were calculated. The results are given in Figure 1 and Table 1.

To validate the DFT results they were compared to CCSD(T) single-point energy calculations performed on the cleavage of diethyl carbonate (**2**). This comparison reveals that all three DFT methods tested underestimate activation barriers. The M05-2X method is found to yield results best in agreement with the CCSD(T) single point energies.

The results presented in Table 1 and Figure 1 indicate that diethyl carbonate (**2**) is unlikely to be a suitable precursor for free carbonic acid (**1**). While the first ester pyrolysis reaction is predicted to proceed, albeit with a significant

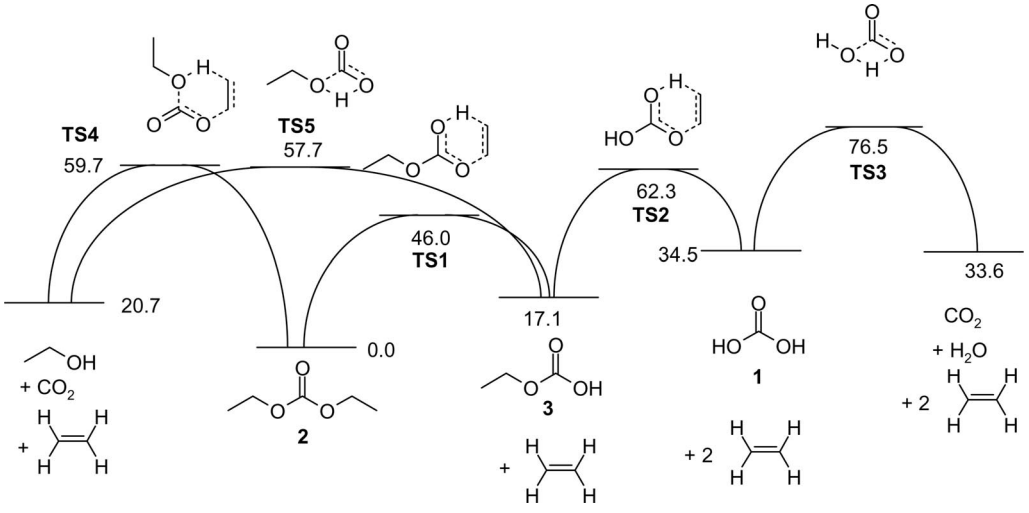
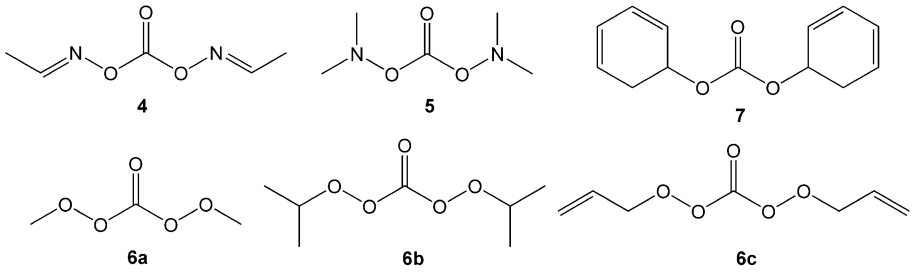


Figure 1. Thermal reaction pathways for cleavage of diethyl carbonate (**2**). Relative energies at $T = 0$ K relative to **2** (0 kcal mol^{-1}) as calculated by M05-2X/cc-pVTZ + ZPE. For the sake of simplicity, the additional ethylene molecules have been left away in the representations of the transition states.

Table 1. Relative energies (kcal mol^{-1}) at $T = 0$ K and entropies (cal mol^{-1} K^{-1}) for cleavage of **2**. The CCSD(T) values are referenced to **2** (0 kcal mol^{-1}). Energies calculated using DFT methods include a ZPE correction, whereas the CCSD(T)/cc-pVTZ//B3LYP/cc-pVTZ single point energies do not.

Stationary point	Relative energy (B3LYP)	Relative energy (B3PW91)	Relative energy (M05-2X)	Relative energy [CCSD(T)]	Entropy (M05-2X)
2	0.0	0.0	0.0	0.0	94.97
TS1	41.8	42.2	46.0	52.2	96.98
3 + C_2H_4	12.3	14.5	17.1	18.6	132.55
TS2 + C_2H_4	53.0	55.7	62.3	69.8	131.47
1 + 2 C_2H_4	24.9	29.3	34.5	37.4	167.30
TS3 + 2 C_2H_4	64.1	68.3	76.5	83.0	168.89
CO_2 + H_2O + 2 C_2H_4	17.9	24.1	33.6	35.3	200.49
TS4	54.3	55.8	59.7	65.8	93.66
C_2H_5OH + CO_2 + C_2H_4	8.1	12.1	20.7	20.0	168.24
TS5 + C_2H_4	50.0	51.8	57.7	62.1	133.30



barrier, ester pyrolysis of the resulting monoethyl carbonate (**3**) (via **TS2**) will not take place, even under gas-phase conditions precluding catalysis of its decomposition by water molecules. The competing 1,3-H shift to yield ethanol (via **TS5**) is predicted to be more favourable than formation of **1** via **TS2**, both kinetically and thermodynamically. Overall, the results presented are in agreement with a previous experimental study on diethyl carbonate pyrolysis, in which also ethene and carbon dioxide were found as products.[9]

If monomeric carbonic acid is to be made by twofold ester pyrolysis of carbonates, simple dialkyl carbonates are obviously unlikely to perform well. The following carbonates **4**–**7** all contain O–X (X = C, N, O) bonds that are weaker than the C–O bond of **2**.

(*E*)-Bis(acetaldoxime) Carbonate (4)

Twofold ester pyrolysis of **4** could potentially yield carbonic acid (**1**) along with two equivalents of acetonitrile. The relatively weak N–O bonds in **4** should facilitate both the primary and the secondary ester pyrolysis reactions. Figure 2 shows the results obtained at the M05-2X/cc-pVTZ + ZPE level of theory.

Inspection of Figure 2 shows that the primary objective of introducing the N–O bond in the carbonate, lowering of the barrier for ester pyrolysis, has been achieved. Moreover, the secondary ester pyrolysis of mono-(*E*)-acetaldoxime carbonate **8** is now predicted to show a barrier that is significantly smaller (31.6 kcal mol^{-1}) than the activation energy for the uncatalyzed decomposition of **1** (42.0 kcal mol^{-1}). Nevertheless, carbonate **4** is not predicted to be a suitable precursor molecule for **1**, because **8** can decompose via an alternative low-barrier (11.7 kcal mol^{-1}) pathway yielding acetaldehyde isoxime **9** and carbon dioxide. A similar situation is found for carbonate **5**, where dimethylamine *N*-oxide is formed in a very facile reaction. The results are shown in Figure S1 (see Supporting Information).

In order to prevent undesired reactions such as those yielding **9**, replacement of the nitrogen atoms present in **4** or **5** by oxygen atoms should prove beneficial, as the corresponding alcohol *O*-oxides would be high energy reactive intermediates.[10] For that reason, the peroxy carbonates **6a**–**c** were investigated by DFT calculations. The fact that diperoxycarbonates of this type are known to be free radical precursors[11] indicates that simple homolytic O–O cleavage also needs to be considered here. In addition to the M05-2X calculations, CCSD(T)/cc-pVTZ single point energy calculations based on B3LYP/cc-pVTZ geometries were performed for peroxy carbonate **6a**.

Peroxy Carbonates

For the diperoxy carbonates **6a**–**c**, the calculations predict a relatively low-barrier (34.4–37.0 kcal mol^{-1}) primary ester-pyrolysis reaction, yielding the peroxy monocarbonates **11a**–**c** plus a carbonyl compound (formaldehyde, acetone, or acrolein) (Figure 3). The energy required to break an O–O bond, with formation of an alkoxy radical and an

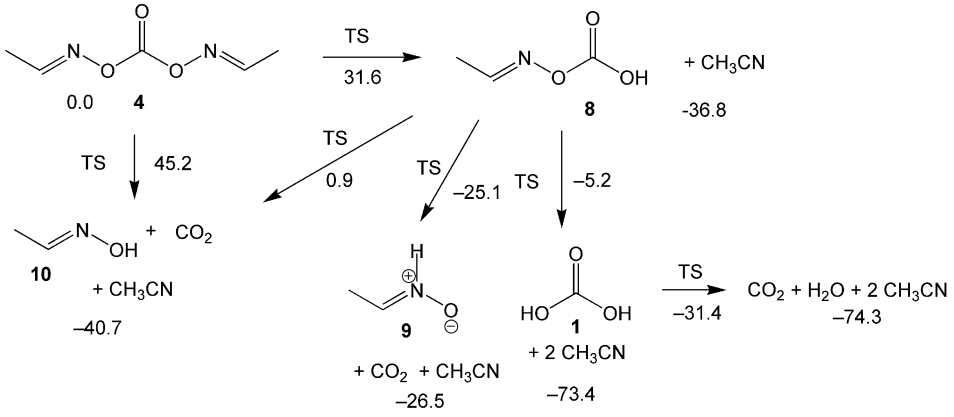


Figure 2. Thermal reaction pathways for cleavage of (*E*)-bis(acetaldoxime) carbonate (**4**). Energies at T = 0 K relative to **4** (0 kcal mol^{-1}) as calculated by M05-2X/cc-pVTZ + ZPE.

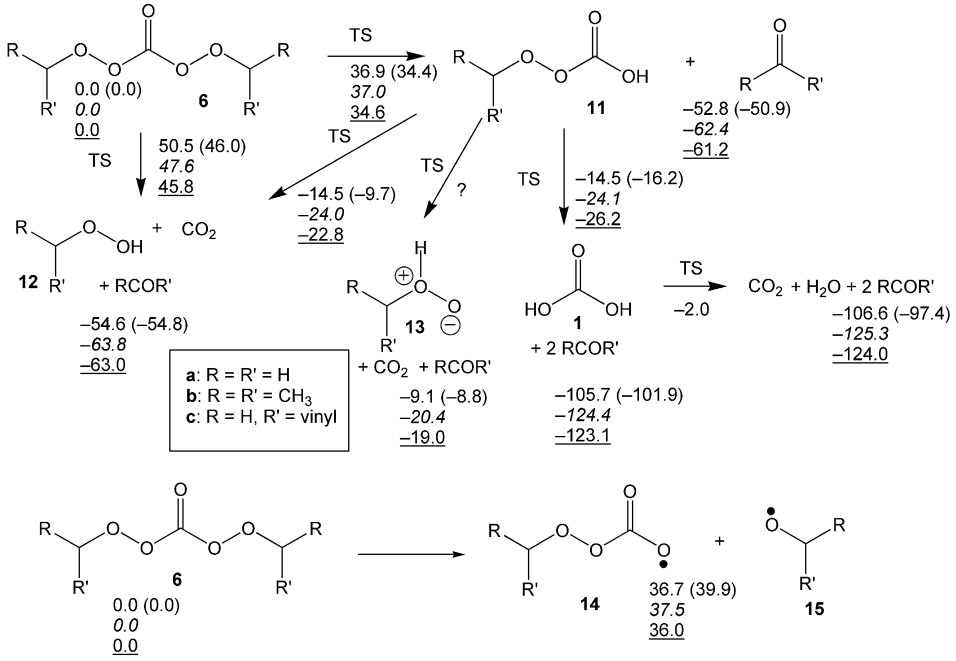


Figure 3. Thermal reaction pathways for cleavage of the peroxy carbonates **6a**–**6c**. Energies (at T = 0 K) relative to **6a**,**b**,**c** (0 kcal mol^{-1}), as calculated at the M05-2X/cc-pVTZ + ZPE level of theory [in brackets: CCSD(T)/cc-pVTZ//B3LYP/cc-pVTZ]. Top (normal font): **6a** (R = R′ = H). Middle (printed in *italics*): **6b** (R = R′ = CH_3). Bottom (underlined): **6c** (R = H, R′ = vinyl). The transition states leading to the alcohol *O*-oxides **13** could not be located.

alkylperoxycarbonyloxy radical, is similar to the activation energy of the primary ester pyrolysis reaction. In case of **6a**, the O–O bond-dissociation enthalpy (BDE) was calculated as BDE = 39.9 kcal mol^{-1} at the CCSD(T)cc-pVTZ//B3LYP/cc-pVTZ level of theory, or BDE = 38.1 kcal mol^{-1}, if calculated at the same level of theory using the isodesmic equation (1) and an O–O BDE for H_2O_2 of 50.3 ± 0.1 kcal mol^{-1}.[12,13] Both values are significantly higher than the activation barrier for the primary ester pyrolysis reaction (34.4 kcal mol^{-1}). Likewise, the O–O BDE of methyl monoperoxy carbonate **11a** is calculated as BDE = 41.7 kcal mol^{-1} if calculated directly at the same CCSD(T) level of theory, or as BDE = 39.8 kcal mol^{-1} if calculated using isodesmic Equation (2).

$$MeOOC(=O)OOMe + 2\ OH \rightarrow MeOOC(=O)O + MeO + H_2O_2 \quad (1)$$

$$MeOOC(=O)OH + 2\ OH \rightarrow HOC(=O)O + MeO + H_2O_2 \quad (2)$$

Depending on the temperature, the difference between the O–O BDE and the activation enthalpy for ester pyrolysis likely is comparable to or smaller than the entropic term, which also needs to be considered. In terms of entropy, the homolytic O–O cleavage likely is favoured over the competing ester pyrolysis reaction, as it does not involve a highly ordered cyclic transition state.

Based on the calculations, the ester-pyrolysis reaction is predicted to be faster than homolytic scission at least at low to moderate temperatures. At very high temperatures, the entropy term will prevail, and the homolytic scission of the O–O bond will become faster. I note that this is in contrast to results of previous experimental[14] and computational[15] work on the pyrolysis of simple peresters like *n*-butyl peroxyacetate, where the gas-phase pyrolysis was observed or predicted to result mostly in O–O scission. Nevertheless, the diperoxy carbonates **6** are not predicted to be the clean precursors to monomeric **1** that would be required for an in-depth investigation on the properties of this elusive species.

Bis(benzene hydrate) Carbonate (= Dicyclohexa-1,3-dien-1-yl Carbonate) (7)

Twofold ester pyrolysis of carbonate **7** would yield **1** along with two equivalents of benzene. Due to the particular stability of the latter pyrolysis product, the ester pyrolysis reaction of **7** can be anticipated to be particularly facile. DFT calculations (M05-2X/cc-pVTZ) indeed reveal this to be the case (Figure 4).

Both ester pyrolysis reactions of **7** are predicted to be exothermic, albeit less so than ester pyrolysis of the peroxy carbonates investigated. Of all substrates investigated, **7**/**16** are predicted to undergo ester pyrolysis most easily. At the same time, the C–O bond in **7** is not weak enough to make bond homolysis a problem to be considered. As there are no additional heteroatoms present that could accept a hydrogen atom, unwanted side reactions such as predicted for carbonates **4** and **5** also are no issue here. For that reason, carbonate **7** is expected to be an ideal precursor for monomeric **1**.

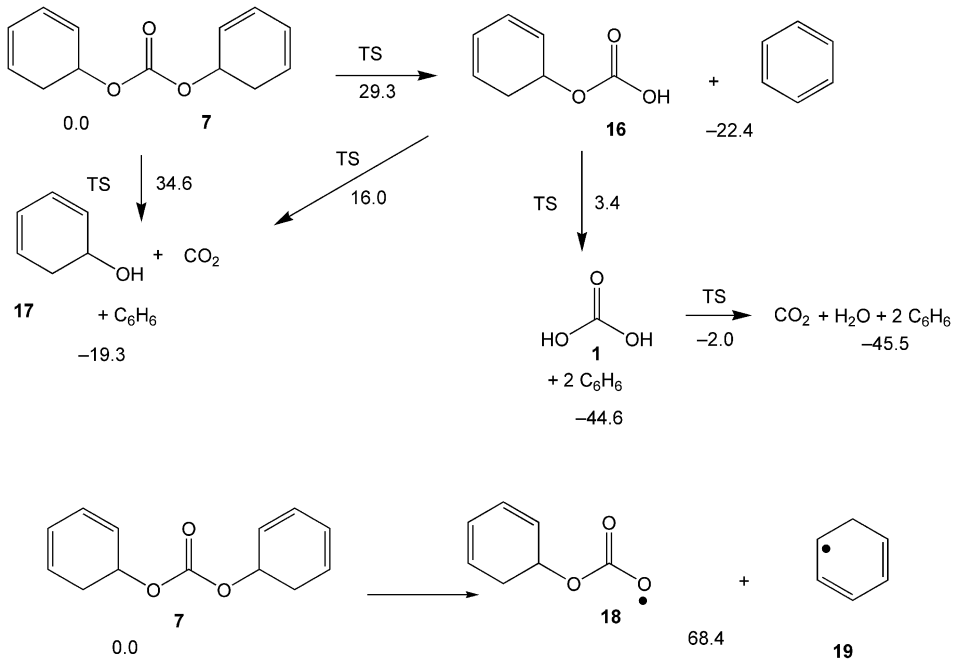


Figure 4. Thermal reaction pathways for cleavage of bis(benzene hydrate) carbonate (**7**). Energies (at $T = 0$ K, relative to **7** = 0 kcal mol^{-1}) as calculated by M05-2X/cc-pVTZ + ZPE.

Conclusions

According to high-level CCSD(T) calculations, carbonate **7** should represent a viable precursor molecule for the pyrolytic generation and matrix isolation of monomeric carbonic acid **1**. Among the DFT methods tested, the M05-2X method gives the best agreement with the CCSD(T) results. The current work also confirms that homolytic O–O scission will not be the only reaction pathway available to peresters of primary and secondary alcohols, and that the competing ester pyrolysis reaction will in some cases result in reduced free radical yields, e.g. in polymerization reactions.

Computational Methods

DFT calculations were performed using the Gaussian03 suite of programs.[16] CCSD(T) single-point energies were calculated employing ORCA software.[17] The DFT methods employed were the B3LYP[18] and the B3PW91[19] hybrid functionals as well as the M05-2X method by Truhlar and co-workers.[20] As basis set, the Dunning basis set cc-pVTZ was used throughout this work.[21] At the DFT levels of theory, all stationary points were fully optimized and characterized by a vibrational analysis. Calculations on open-shell species were performed using UHF wavefunctions. The computed energies provided in this work refer to $T = 0$ K, where there is no difference between total energy differences and enthalpy differences.

Supporting Information (see also the footnote on the first page of this article): Cartesian coordinates and energies of all stationary points calculated (Figure S1).

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