Stability of Novel Oxo- and Chloro-Substituted Trioxanes

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Abstract: The thermodynamic and kinetic stabilities of several novel substituted trioxanes have been explored computationally. Our calculations show that concerted ring opening provides the most likely path for dissociation to the building block molecules: CO_2, CH_2O, and CCl_2O. These studies indicate that *gem*-dichlorotrioxane ($C_3H_4O_3Cl_2$, **1**), tetrachlorotrioxane ($C_3H_2O_3Cl_4$, **7**), and trioxanone ($C_3H_4O_4$, **2**) should be kinetically stable and are likely candidates for synthesis.

Introduction

Only a few stable molecules with a cyclic C_3O_3 backbone are known. One of them is trioxane ($C_3H_6O_3$). Although trioxane is stable relative to three single formaldehyde molecules, electronegative substituents, such as chlorine and doubly bonded oxygen, apparently diminish the stability with respect to concerted ring opening. We are not aware of any of these molecules having been prepared, but our calculations, described below, predict that some are stable. Some of these substituted trioxanes may be of particular interest; e.g., compounds containing a dichlorinated carbon within the trioxane backbone probably decompose to phosgene. This could provide a convenient source of this highly useful but dangerous reagent. Also, one may speculate that the cyclic trimer of CO_2 is possibly the preferred form under very high pressure.

The latter molecule has received some interest recently. Bodor and Huang[1] carried out semiempirical AM1 calculations on its stability. However, they only considered the nonsymmetric radical dissociation mechanism that has a significantly higher barrier than concerted ring opening. Lewar[2] has recently carried out much higher level calculations (ab initio SCF and MP2 with the 6-31G* basis) for various polymers of CO_2. His transition state for the concerted dissociation of C_3O_6 has C_{3h} symmetry and a low barrier. We are not aware of any theoretical predictions concerning chlorine-substituted and other partially substituted trioxanes. However, bis(trichloromethyl) carbonate (or "triphosgene") is a known organic reagent[3] and is a structural isomer of the cyclic trimer of phosgene (**3**). The synthetic utility of "triphosgene" (**4**) is that it provides in situ phosgene. The cyclic trimer (**3**) is probably too unstable to be useful, but partially-chloro-substituted trioxanes may be potentially even better sources of in situ phosgene than "triphosgene".

Although synchronous ring opening preserves electron pairs and can thus be treated qualitatively at the Hartree−Fock level, electron correlation preferentially stabilizes the carbon−oxygen double bond and thus significantly influences the energetics of these dissociation reactions. It is also known that inclusion of electron correlation generally lowers reaction barriers even if no bond breaking is involved. Traditional configuration-based

correlation methods, though possible, are still quite expensive for some of these systems. Density functional methods are much more economical and are expected to be fairly accurate for the structures and energetics of these reactions.

The proton-catalyzed polymerization/depolymerization of trioxane in the liquid phase has been studied recently using density functional theory and molecular dynamics by Curioni et al.[4] The mechanism of this essentially thermoneutral reaction is very different from the uncatalyzed thermal decomposition of trioxane. Unfortunately, as discussed below, the exchange-correlation potential used for the dynamics simulation by Curioni et al. gives poor results for the energetics of the thermal decomposition reaction.

Computational Methods

Molecular energies, geometries, and vibrational frequencies have been determined using standard methods by the following programs: TX90[5] (constrained geometry optimizations), PQS[6] (DFT optimizations and single-point MP2), Gaussian94[7] (frequency calculations and MP2 optimizations), and Molpro97[8,9] (CCSD and CCSD(T) calculations). All stationary states have been checked at the density functional (DFT) level to confirm that true minima or first-order saddle points of the potential energy surface have been located. To minimize the cost of optimization, a multi-level procedure has been adopted for the transition states (TS). Points along the concerted dissociation reaction path were determined by incrementally stretching alternating carbon−oxygen

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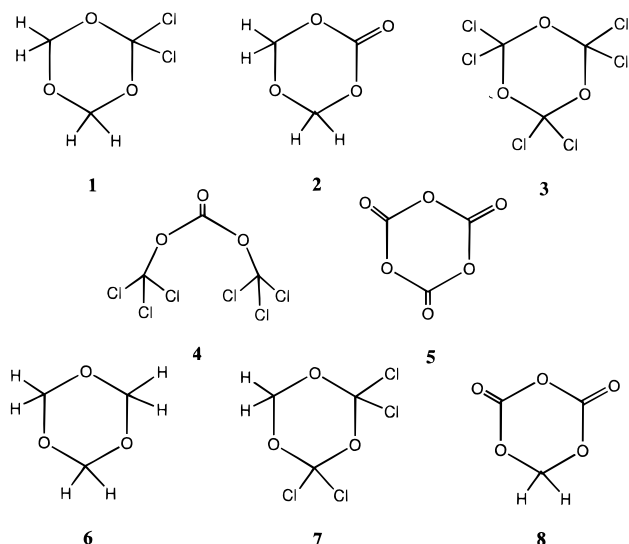
Figure 1. Molecular structures.

bonds of the backbone. The distorted structures were optimized at the RHF/3-21G* level by constraining the stretched bonds and optimizing all other coordinates. The maximum along this reaction path gave a good starting geometry for the TS, which was further refined at the B3-LYP[10]/6-31G* level by a full (unconstrained) transition state search. These geometries served as starting points for higher level optimizations. As a rough guide for evaluating the stabilities of metastable species, we calculated approximate half-lives by simple transition state theory using calculated rotational constants, 6-31G* B3-LYP harmonic frequencies, and the B3-LYP calculated barrier height.[11–13]

Calculating accurate reaction barriers is still a problem in quantum chemistry. We have carried out preliminary tests on the effects of the following variables: basis set, optimized geometry, and electron correlation for three representative molecules (trioxane (**6**), the cyclic trimer of carbon dioxide (**5**), and dichloro-substituted trioxane (**1**)).

Results and Discussions

Two series of molecules (see Figure 1 for structures) have been investigated to determine relative stabilities with respect to dissociation. Series 1 (comprised of molecules **6**, **1**, **7**, and **3**) is the systematic substitution of a pair of hydrogens at a given carbon in the C_3O_3 backbone of trioxane by a pair of chlorines. Series 2 (comprised of molecules **6**, **2**, **8**, and **5**) is the corresponding substitution by a doubly bonded oxygen. These series of molecules have been chosen because each can be viewed as a cyclic trimer composed of CO_2, CH_2O, and $COCl_2$ as monomer building blocks.

Effect of the Basis Set. Table 1 compares results obtained at different basis set levels for the three representative molecules. Relative DFT energies stabilize to within 4 kcal/mol of the basis set limit at the 6-311G** level. The 6-31G* basis is clearly inadequate for quantitative results for these reactions. For trioxane, we also explored a very large basis but the resulting change was insignificant. Traditional correlation methods, like MP2, are more sensitive to the basis set. Table 2 shows the basis set effect for the MP2 calculations. For correlated methods, these results indicate that the 6-311G** level approaches the basis set limit for the barrier but the heat of reaction is still improved by further basis set extension.

Table 1. Effect of the Basis Set on B3-LYP Calculated Reaction Energies (ΔH_{rxn}) and Barrier Heights (E_a)[a]

molecule		6-31G*	6-311G**	6-311G(2df,p)	basis limit[b]
$C_3O_3H_6$ (**6**)	ΔH_{rxn}	40.15	33.09	34.02	32.75
	E_a	47.00	42.77	43.35	43.59
C_3O_6 (**5**)	ΔH_{rxn}	−47.62	−62.15	−57.90	NA
	E_a	22.20	16.92	20.28	NA
$C_3H_4O_3Cl_2$ (**1**)	ΔH_{rxn}	23.70	16.58	17.10	NA
	E_a	38.76	34.10	35.43	NA

[a] All energies are given in kcal/mol without vibrational and rotational zero-point energy corrections. [b] Fully decontracted in the valence shell DZVP2 basis.[25]

Table 2. Effect of the Basis Set and Reoptimization on MP2 Calculated Reaction Energies (ΔH_{rxn}) and Barrier Heights (E_a) at DFT Optimized Geometries[a]

molecule		6-311G**	6-311G**[b]	6-311G (2df,p)	6-311+G (3df,3p)
$C_3O_3H_6$ (**6**)	ΔH_{rxn}	35.71	35.71	42.99	42.55
	E_a	54.00	54.19	53.97	53.57
C_3O_6 (**5**)	ΔH_{rxn}	−73.04	−73.59	−60.26	−61.90
	E_a	18.61	18.43	22.67	22.03

[a] All energies are given in kcal/mol without vibrational and rotational zero-point energy corrections. [b] Results from MP2 optimized structures.

Effect of Geometry. Table 2 also reports the reaction energy and barrier height calculated at the MP2 optimized geometry. These energy differences were very close (∼0.2 kcal/mol or less) to the MP2 single point results calculated at the B3-LYP optimized geometries, showing that DFT is adequate for the geometries.

Effect of Correlation Methods. Electron correlation preferentially stabilizes carbon−oxygen double bonds and further lowers the reaction barrier. Table 3 shows the energies calculated at the RHF and and various correlated levels of theory with the 6-311G** basis. The RHF results are provided mainly to demonstrate the magnitude of correlation effects. The other methods' results correlate well for reaction enthalpies and give us confidence that DFT provides a quantitatively correct picture of the equilibrium system. However, DFT underestimates activation energies with respect to the correlated methods. This indicates that for the transition state system DFT provides only a qualitatively correct picture which represents a lower limit for activation energies but which should still be a reasonable model for predicting molecular stability. The highest level of correlation we used (CCSD(T)) gives barrier heights which are close (within 3.5 kcal/mol) to the MP2 results.

Comparison with Experiment for Trioxane. The calculated reaction enthalpy for the dissociation of trioxane into three formaldehyde molecules can be compared with a ΔH_{rxn} derived from experimental data. Standard heats of formation (trioxane,[14] −111.32 ± 0.12 kcal/mol; formaldehyde,[15] −27.70 kcal/mol) were used to calculate the ΔH_{rxn} at 298 K, 28.22 kcal/mol. To compare with the calculated value, this ΔH_{rxn} was "cooled" by removal of the translational, rotational, and vibrational contributions to the partition function[16] to produce a value of 24.65 kcal/mol at 0 K. This is 3.74 kcal/mol higher than the B3-LYP value reported in Table 4. Our best calculated value for this quantity is obtained by correcting the large basis MP2 result (Table 2), 42.55 kcal/mol, for higher order correlation effects using the

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Table 3. Effect of Correlation Methods on Calculated Reaction Energies (ΔH_{rxn}) and Barrier Heights (E_a) at the 6-311G** Level[a]

molecule		RHF	B3-LYP	B3−PW91	MP2	CCSD	CCSD(T)
$C_3H_6O_3$ (**6**)	ΔH_{rxn}	30.28	33.09	40.50	35.71	34.29	33.87
	E_a	65.25	42.77	48.42	54.00	58.68	53.02
C_3O_6 (**5**)	ΔH_{rxn}	−68.73	−62.15	−66.49	−73.05	−64.05	−65.88
	E_a	35.08	16.92	19.73	18.61	26.78	22.48
$C_3H_4O_3Cl_2$ (**1**)	ΔH_{rxn}	21.12	16.58	23.91	21.63	NA	NA
	E_a	56.12	34.10	39.57	44.10	NA	NA

[a] All energies are given in kcal/mol without vibrational and rotational zero-point energy corrections.

Table 4. Reaction Series 1: Chloro-Substituted Trioxanes at the 6-311G** Level[a]

	ΔH_{rxn}			E_a			
molecule	B3-LYP	MP2	ΔZPE^b	B3-LYP	MP2	ΔZPE^c	half-life[d]
$C_3H_6O_3$ (**6**)	33.09	35.71	−12.18	42.77	54.00	−5.07	∞
$C_3H_4O_3Cl_2$ (**1**)	16.59	21.66	−9.60	34.10	44.10	−4.28	∞
$C_3H_2O_3Cl_4$ (**7**)	−8.73	0.75	−6.24	26.92	37.18	−2.72	5.7 hrs
$C_3O_3Cl_6$ (**3**)	−41.25	−26.96	−3.35	24.87	33.25	−2.40	23.9 min
$CCl_3O(CO)OCCl_3$ (**4**)	−27.53	−15.32	−5.30	NA	NA	NA	NA

[a] All energies are given in kcal/mol. All ZPEs were calculated using the 6-31G* basis. [b] Zero-point energy correction for the reaction energy (ΔE_{rxn}). [c] Zero-point energy correction for the barrier height (E_a). [d] Calculated at 298.15 K from the B3-LYP barriers.[11−13] As discussed in the text, B3-LYP DFT appears to underestimate the barrier heights, and thus these numbers are lower bounds.

difference ΔH_{rxn}(CCSD(T)−MP2), −1.84 kcal/mol, and adding the DFT zero-point correction, −12.18 kcal/mol, giving 28.5 kcal/mol. DFT and CCSD(T) corrected MP2 bracket the experimental value (24.65 kcal/mol). The "experimental" value may be somewhat affected by uncertainties in the calculated contributions of the large-amplitude vibrations which were treated at the harmonic level. This value is also sensitive to the heat of formation of formaldehyde; using the 1970 value of Fletcher and Pilcher,[17] −25.96 kcal/mol, gives a reaction enthalpy of 33.45 kcal/mol at 298 K, and 29.88 kcal/mol at 0 K. Curioni et al.[4] report −10.3 kcal/mol (after zero-point correction) with the Becke exchange, +22.7 kcal/mol with the Becke-Perdew exchange-correlation functional, and +26.3 kcal/mol at the MP2 level with a fairly large basis set. These values are in semiquantitative agreement with ours.

The quality of predicted activation energies can be evaluated by comparison with experimental results for trioxane. Aldridge et al.[18] found the Arrhenius parameter for the dissociation of trioxane to three formaldehyde molecules to be 50.920 ± 0.505 kcal/mol. This value agrees well with the shock tube value of Irdam and Kiefer,[20] 50 kcal/mol, and with the results of Hochgreb and Dryer,[21] obtained at higher temperatures, 47.5 ± 2.5 kcal/mol. The latter value is very close to older values for this quantity which are close to 47 kcal/mol.[22,23] Our MP2 calculated barrier of 48.94 kcal/mol is in fair agreement with the average of the experimental values, and with the calculated 51.2 kcal/mol of Aldridge et al., obtained using the bond-additivity corrected MP4 method.[19] The RRKM calculations of Irdam and Kiefer[20] suggest that the barrier is about 2.4 kcal/mol lower than the Arrhenius parameter.

The B3-LYP calculation significantly underestimates the barrier height, yielding a value of only 37.70 kcal/mol after zero-point correction. Our best ab initio estimate for the barrier in trioxane, obtained in the same way as the reaction enthalpy, is 47.52 kcal/mol after correcting for zero-point vibrations, which is somewhat lower than the experimental value. These differences indicate that DFT calculations probably underestimate the stability of the trimer molecules and that the reported reaction

enthalpies, activation energies, and predicted lifetimes represent lower limits to the actual values. The MP2 values should be more accurate. To err on the safe side, predicted lifetimes have been calculated from the B3-LYP barriers.

The Becke gradient-corrected exchange functional[24] used in the simulation of Curioni et al.[4] gives very poor results: with the 6-311G** basis set, it predicts three formaldehyde molecules 11.5 kcal/mol *more* stable than trioxane (before zero-point energy correction). By contrast, other methods (cf. Table 3) predict trioxane between 30 and 41 kcal/mol more stable (before zero-point correction). The experimental value of the difference in the electronic energies, obtained by subtracting the calculated zero-point correction, −12.2 kcal/mol (Table 4), from the calorimetric value, 24.65 kcal/mol, discussed above, gives 36.85 kcal/mol with trioxane more stable. Similarly, the vibrationless barrier to dissociation, experimentally in the neighborhood of 56 kcal/mol, is very low with the Becke exchange, only 17.4 kcal/mol. The large discrepancies with experiment show that the method used in ref 4 cannot be used to describe the thermal "unzipping" reaction of polyoxymethylene, which proceeds by a mechanism similar to the decomposition of 1,3,5-trioxane.

Stability of Chloro- and Oxo-Substituted Trioxanes. Tables 4 and 5 show reaction energies and activation energies for the respective series, separated into electronic and zero-point contributions. Since the 6-31G* basis is clearly inadequate to describe accurately the energetics of these systems, only the 6-311G** results are reported. Figures 2 and 3 show a qualitative visualization of the dissociation reaction profiles.

As electronegative substituents replace pairs of hydrogens on the trioxane backbone, stability decreases rapidly. The replacement of a pair of hydrogens on a single carbon by a pair of chlorines results in a destabilization by 22 kcal/mol per substitution. Substitution by a doubly bonded oxygen destabilizes the molecule by nearly 30 kcal/mol per substitution. One interesting trend is that the first substitution has a significantly less destabilizing effect than the two subsequent substitutions. In both series, the change in ΔH_{rxn} for the first step is about

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Table 5. Reaction Series 2: Oxo-Substituted Trioxanes at the 6-311G** Level[a]

molecule	ΔH_{rxn} B3-LYP	MP2	ΔZPE[b]	E_a B3-LYP	MP2	ΔZPE[c]	half-life[d]
$C_3H_6O_3$ (6)	33.09	35.71	−12.18	42.77	54.00	−5.07	∞
$C_3H_4O_4$ (2)	5.49	2.10	−9.58	32.83	40.01	−3.97	5.3 yrs
$C_3H_2O_5$ (8)	−24.35	−30.89	−7.04	23.87	28.17	−2.87	2.8 min
C_3O_6 (5)	−62.15	−73.04	−3.95	16.91	18.61	−2.37	41.0 ms

[a] All energies are given in kcal/mol. All ZPEs were calculated using the 6-31G* basis. [b] Zero-point energy correction for the reaction energy (ΔE_{rxn}). [c] Zero-point energy correction for the barrier height (E). [d] Calculated at 298.15 K from the B3-LYP barriers. As discussed in the text, B3-LYP DFT appears to underestimate the barrier heights, and thus these numbers are lower bounds.
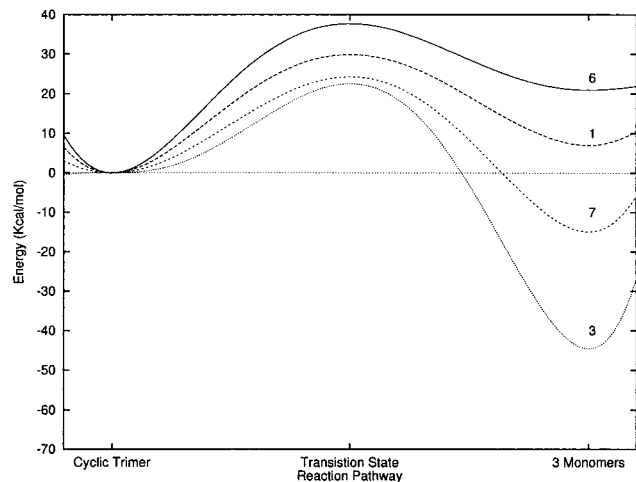
Figure 2. Reaction profiles for the dissociation of chlorinated trioxanes: **6**, trioxane (−CH_2−O−)$_3$; **1**, (−CCl_2−O−CH_2−O−CH_2−O−); **7**, (−CCl_2−O−CCl−O−CH_2−O−); and **3**, (−CCl_2−O−)$_3$.
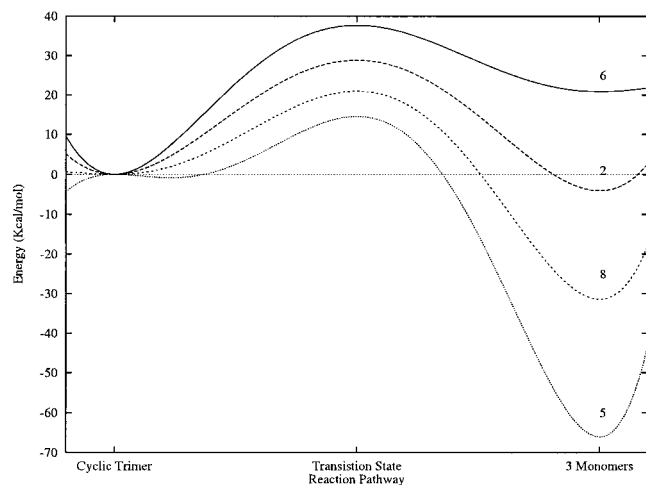
Figure 3. Reaction profiles for the dissociation of oxygenated trioxanes: **6**, trioxane (−CH_2−O−)$_3$; **2**, (−CO−O−CH_2−O−CH_2−O−); **8**, (−CO−O−CO−O−CH_2−O−); and **5**, (−CO−O−)$_3$.

70% that of the other steps. If the zero-point energy is added to the electronic energy, then only dichloro-substituted trioxane (**1**) joins trioxane as being thermodynamically stable. Bis-(trichloromethyl) carbonate (triphosgene) has a calculated B3-LYP ΔH_{rxn} with respect to three individual phosgene molecules of −32.8 kcal/mol, making it about 10 kcal/mol more thermodynamically stable than the cyclic trimer (**3**).

Activation energies have been calculated for each dissociation reaction based upon the optimized transition state. Calculated barrier heights, including zero-point corrections, range from 37.7

Table 6. Principal Symmetry Unique Structural Data of the C_3O_3 Backbone for the Equilibrium (EQ) and Transition (TS) States

molecule	state	symm	C−O [Å]	C−O−C [deg]	O−C−O [deg]
$C_3H_4O_3Cl_2$ (1)	EQ	C_s	1.3650	109.80	114.61
			1.3998	113.70	110.66
			1.4364	113.70	110.66
	TS	C_1	1.2150	102.57	111.44
			1.2375	105.20	112.83
			1.2724	110.93	116.81
			1.6793		
			1.8387		
			2.0229		
$C_3H_4O_4$ (2)	EQ	C_s	1.3584	108.72	117.02
			1.3945	120.37	111.28
			1.4335	120.37	111.28
	TS	C_1	1.2312	109.62	104.65
			1.2484	119.04	106.06
			1.2779	124.19	108.98
			1.7121		
			1.7616		
			2.0559		
$C_3O_3Cl_6$ (3)	EQ	C_{3v}	1.3899	119.75	113.22
	TS	C_3	1.2560	123.14	107.47
			1.7608		
C_3O_6 (5)	EQ	D_{3h}	1.3700	124.55	115.45
	TS	C_{3h}	1.2512	129.32	110.68
			1.6728		
$C_3H_6O_3$ (6)	EQ	C_{3v}[a]	1.4108	109.79	111.55
	TS	C_3	1.2517	107.05	110.31
			1.9263		
$C_3H_2O_3Cl_4$ (7)	EQ	C_s	1.3655	119.74	109.27
			1.3989	113.05	113.84
			1.4183	113.05	113.84
	TS	C_1	1.2373	102.43	115.10
			1.2412	105.70	116.65
			1.2879	112.21	120.42
			1.5527		
			1.7750		
			2.0690		
$C_3H_2O_5$ (8)	EQ	C_s	1.3494	122.98	110.68
			1.3884	115.22	114.06
			1.4178	115.22	114.06
	TS	C_1	1.2273	106.82	114.50
			1.2529	107.57	117.58
			1.2805	108.48	125.89
			1.5929		
			1.7965		
			1.8674		

[a] Distances in angstroms; angles in deg. Cf. the electron diffraction data of: Colmont, J. M. *J. Mol. Spectrosc.* **1980**, *80*, 166: C−O = 1.422 Å, C−O−C = 110.3°, O−C−O = 112.2°.

(**6**) to 14.5 kcal/mol (**5**) at the B3-LYP level, and from 48.9 (**6**) to 16.2 kcal/mol (**5**) at the MP2 level. As discussed above, the B3-LYP values are probably a lower bound to the actual barrier height. The barrier height of **2** (29.8 and 36.0 kcal/mol at the B3-LYP and MP2 levels) shows that this molecule should be moderately stable. Hexachlorotrioxane (**3**), 2,2,4,4-tetrachlorotrioxane (**7**), and trioxadione (**8**) have 21−24 kcal/mol barriers to dissociation at the B3-LYP level and 26−34 kcal/mol at the MP2 level and should be stable at low temperatures or perhaps even at room temperatures. The cyclic trimer of carbon dioxide (**5**) appears unlikely to be synthesizable owing to the very low barrier to dissociation. We hope that this study will encourage experimentalists to attempt to synthesize some of these previously unexplored molecules.

Posssibility of Radical Dissociation. We have carried out unrestricted density functional and SCF calculations on the radical dissociation mechnism for both trioxane and C_3O_6. The transition states in both cases are much higher than for the concerted pericyclic reaction. Therefore, it is unlikely that this

mechanism plays a significant role in the uncatalyzed decomposition of trioxane and its derivatives. Experimentally, there is strong evidence[22] that the thermal gas-phase decomposition of trioxane and its trimethyl derivative, paraldehyde, is homogeneous and unimolecular.

Table 6 shows the skeleton geometry parameters of both the equilibrium structures and the transitions states. The transition states are appreciably distorted in the asymmetrically substituted molecules but they are still qualitatively compatible with the concerted synchronous reaction mechanism. One should not attach too much weight to the unequal long C···O bond lengths of the transition states, as the energy surface is quite flat near the transition state.

Conclusion

1. DFT methods appear to describe reaction energies for equilibrium systems very well. However, they systematically, though not dramatically, underestimate reaction barrier heights.

2. It is virtually certain that the dissociation of trioxane and of electronegatively substituted trioxanes goes through a concerted transition state.

3. The unknown 1,1-dichlorotrixane (**1**) is predicted to be thermodynamically stable and may be useful as a solid source of phosgene. Trioxanone (**2**) and 1,1,3,3-tetrachlorotrioxane (**7**), both also unknown, are predicted to be slightly thermodynamically unstable but are expected to be kinetically stable and most likely can be prepared.

4. Hexachlorotrioxane (**3**) and trioxa-1,3-dione (**8**) are probably stable at low temperatures.

5. The cyclic trimer of carbon dioxide (**5**) is very unstable thermodynamically, and has a low barrier to dissociation. Therefore, it is unlikely that it can be prepared.