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Ring-Opening Reactions of Dioxetene, Oxetene, Dithiete, and Thiete

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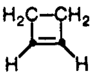
Abstract: A series of electrocyclic isomerizations related to the cyclobutene to butadiene reaction have been studied by ab initio theory. In addition to the cyclobutene isomerization, the ring-opening reactions of dioxetene, oxetene, dithiete, and thiete to *cis*-glyoxal, *cis*-acrolein, dithioglyoxal, and *cis*-thioacrolein have been examined. Structures and vibrational frequencies have been determined for reactants, transition states, and products with split-valence and split-valence plus polarization self-consistent field (SCF) methods. For the cyclobutene to butadiene, dioxetene to glyoxal, and oxetene to acrolein reactions, multiconfiguration SCF (MCSCF) geometries were optimized. The use of unrestricted Hartree-Fock natural orbitals (UHF-NO) to define the active space for complete active-space SCF (CASSCF) computations on the transition states was examined. MCSCF, configuration interaction (CISD), and Moller-Plesset perturbation theory (MP4SDTQ) methods were used to determine the activation barriers and reaction energies. Activation barriers decrease relative to the cyclobutene-butadiene reaction with heteroatom substitution. At the highest level of theory, dioxetene faces a barrier of less than 10 kcal·mol^{-1} to ring opening to glyoxal. The barrier for oxetene rearranging to *cis*-acrolein is predicted to be ~26 kcal·mol^{-1}, in good agreement with experiment. In light of recent controversy on the relative stabilities of dithiete and dithioglyoxal, the substantial barriers (20-27 kcal·mol^{-1}) for the opening of the sulfur-containing rings to the thioketone forms are noteworthy.

Introduction

The thermolysis of cyclobutene (**1**) leading to ring opening to butadiene is a prototypical example of a concerted reaction, which may be understood in terms of the Woodward-Hoffmann rules.[1,2]



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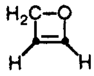

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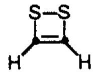

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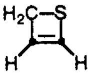

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An important early ab initio study of this reaction by Hsu et al.[3] was followed by a number of semiempirical studies.[4] To date, the most detailed ab initio theoretical examinations of the cyclobutene to butadiene reaction are the two-configuration SCF (TCSCF) work by Breulet and Schaefer[5] and the SCF and MP2 calculations of Rondan and Houk.[6] There has been no systematic survey of the ring opening of the heterosubstituted cyclobutenes: dioxetene (**2**), oxetene (**3**), dithiete (**4**), and thiete (**5**).

Dioxetene has been implicated as an intermediate in the reaction of a strained acetylene with molecular oxygen[7] and in the oxidation of acetylenes under elevated oxygen pressures.[8] A symmetry-based analysis of the interaction of molecular oxygen with acetylene[9a] has appeared. Recently 6-31G*, SCF, and MP2 calculations[9b] on the dioxetene to glyoxal reaction have been reported and indicate a barrier of ~11 kcal·mol^{-1} to the strongly exothermic (>75 kcal·mol^{-1}) ring opening. *cis*- and *trans*-glyoxal have been very thoroughly treated in ab initio studies[10] but not the ring-opening reaction transition-state structure. *cis*-Glyoxal recently has been fairly well characterized experimentally.[11,12] An STO-3G study[13] indicated that dioxetene was 26 kcal·mol^{-1} less stable than glyoxal.

Oxetene has been synthesized and characterized by NMR and IR, and the energetics of its electrocyclic ring opening have been studied.[14,15] A MINDO/3 study[16] gave an enthalpy of activation of 30.7 kcal·mol^{-1} for oxetene isomerization. An early ab initio study[17] of the oxetene to acrolein conversion estimated a barrier of ~1 eV. *cis*- and *trans*-acrolein have been studied often theoretically[18] but without reference to the oxetene form. *cis*-Acrolein's structure has been deduced from microwave spectroscopy,[19] and some of its fundamental vibrations are known.[20]

A model of the molecular structure for dithiete has been proposed that is compatible with its measured rotational constants.[21] The photoelectron spectrum of dithiete was determined,[22] and very recently, with the aid of ab initio calculations, its vibrational spectrum in an Ar matrix has been assigned.[23] *trans*-Dithioglyoxal and dithiete are known to lie close in energy.[23-25] *cis*-Dithioglyoxal has been predicted to adopt a C_2 gauche structure, which is ~5 kcal·mol^{-1} higher than the trans isomer.[25] Given that dithiete and the dithioglyoxals have been reliably predicted to lie very close in energy, it is surprising that prior to the present study the only work on their interconversion is the semiempirical study of Calzaferri and Gleiter.[26a]

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Table I. Occupancy Numbers of the Fractionally Occupied UHF Natural Orbitals for the Transition States: (3-21G, 3-21G*), $\langle S^2 \rangle$, UHF Total Energy,[a] and UNO-CAS Total Energy[b]

transition state	occupancy no. of fractionally occupied UHF-NO				$\langle S^2 \rangle$	total energy	
						UHF	UNO-CAS
C_4H_6	1.8777	1.7452	0.2548	0.1223	0.70	−153.975 19	−154.024 35
$C_2H_2O_2$	1.8130	1.5348	0.4652	0.1870	1.07	−225.178 06	−225.231 18
C_3H_4O	1.9058	1.6900	0.3100	0.0942	0.72	−189.591 57	−189.643 30
$C_2H_2S_2$	1.8977	1.2901	0.7099	0.1023	1.13	−867.724 06	−867.738 72
C_3H_4S	1.8824	1.6156	0.3844	0.1176	0.86	−510.855 44	−510.896 61

[a] The 3-21G(*) closed-shell SCF total energies for the transition states may be found in Tables VI or X for comparison. [b] The 3-21G(*) CASSCF total energies for the transition states may be found in Tables VI or X for comparison. The $C_2H_2S_2$ UHF showed a spatial symmetry breaking.

Table II. Fractional Occupancy Numbers of the CISD Natural Orbitals for the Transition States

transition state	basis set (symmetry)	occupancy no. (symmetry) of fractionally occupied CISD natural orbitals			
$C_2H_2O_2$	6-31G*	1.9462	1.8928	0.1174	0.0474
	3-21G	1.9476	1.8499	0.1555	0.0527
	(C_2)	(b)	(a)	(b)	(a)
C_3H_4O	6-31G*	1.9699	1.9516	0.0496	0.0331
	3-21G	1.9613	1.9228	0.0779	0.0440
	(C_1)	(a)	(a)	(a)	(a)
$C_2H_2S_2$	6-31G*	1.9493	1.8599	0.1561	0.0434
	3-21G*	1.9531	1.8542	0.1555	0.0454
	(C_2)	(b)	(a)	(b)	(a)
C_3H_4S	6-31G*	1.9568	1.9041	0.1004	0.0451
	3-21G*	1.9521	1.8941	0.1096	0.0509
	(C_1)	(a)	(a)	(a)	(a)

The nearly complete substitution structure of thiete has been determined.[27] Basis set effects on the geometry of thiete were carefully examined by DePaz and Yanez.[28] No vibrational spectrum of thiete has been reported. There are a number of ab initio predictions[29,30] of the structures of *trans*- and *cis*-thioacrolein and on the barrier to rotation between them. The vibrational spectrum of *cis*-thioacrolein has been computed.[30]

An important qualitative analysis of perturbed pericyclic reactions by Snyder should be noted.[31] A number of heterosubstituted butadienes (including acrolein and thioacrolein) and their ring closures were considered by semiempirical calculations and frontier orbital theory. Shifts in the nodes in the highest occupied π molecular orbitals of the heterosubstituted dienes as ring closure proceeds were emphasized in Snyder's model.[31]

The present work emphasizes a consistent survey at reasonably high levels of computation of the four heterosubstituted cyclobutene ring-opening reactions. Higher level theoretical predictions on the cyclobutene ring opening than previously available[3-6] also are given. Generally reliable split-valence and split-valence plus polarization basis sets were used in rigorous geometry optimizations at the SCF level. The natures of all stationary points located were verified by harmonic vibrational frequency analyses. The effects of MCSCF geometry optimizations were considered for three of the reactions. Account of the effects of electron correlation on barrier heights and reaction energies was taken through CISD, CASSCF,[32] and MP4[44] computations.

Computational Methods

Calculations were carried out with the GAMESS[35] and GAUSSIAN86[36] programs. 3-21G or 3-21G* for S and 6-31G* basis sets[37,38] were employed. SCF geometries of minima and saddle points were determined with energy gradient methods and the algorithms of Schlegel[39] and Baker[40] as implemented in GAUSSIAN86 and GAMESS. Harmonic vibrational frequencies were computed at the SCF level with use of the analytic second-derivative[41] methods in GAUSSIAN86. Any frequency calculations done with GAMESS involved the force method,[42] i.e., numeric second derivatives as finite differences of analytic gradients at suitably distorted geometries. Prior to any comparisons with experiment or as the best predictions of the location of unknown modes, the SCF harmonic vibrational frequencies were scaled[43] by 0.9. Fourth-order Moller–Plesset perturbation theory (MP4SDTQ)[44] calculations of the electron correlation energy were done with the 6-31G* basis at the 6-31G* SCF optimized geometries.

Configuration-interaction[45] (CISD) and multiconfiguration SCF[46] of the CASSCF[32] type computations were carried out with GAMESS. Although an MCSCF approach is not mandatory for the symmetry-allowed conrotatory ring opening of cyclobutene, Breulet and Schaefer[5] and Pulay[33b] have stressed the importance of an MCSCF description of the transition state. The fundamental choice in any CASSCF calculation is the selection of a suitable active space. Pulay has proposed an automatic procedure[33a] for defining the active space using the fractionally occupied (occupation numbers, σ, greater than 0.02 or less than 1.98) natural orbitals of the UHF wave function.[34] Considerable care is needed in finding the best UHF solutions for formally closed-shell species. With GAMESS and GAUSSIAN86, it proved necessary to use the guess equals mix or alter options to destroy any α–β orbital symmetries, to specify no symmetry, and to turn off the DIIS SCF convergence accelerator in order to calculate the low-energy UHF solutions for the transition states. Several hundred SCF cycles were required to obtain convergence. A much more efficient procedure for finding UHF solutions is now published.[33c]

In the present study for all the transition-state structures, Pulay's criterion[33a] for fractionally occupied UHF-NO ($0.02 < \sigma < 1.98$) neatly defined a 4-electron/4-orbital active space. The UHF-NO were used: (1) in a full CI in the space of the fractionally occupied UHF-NO, i.e., the UNO-CAS approach of Pulay[33b] and (2) as starting orbitals in CASSCF[32] calculations, which, of course, allow orbital relaxation. In

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Table III. Final Occupancy Numbers of the CASSCF Natural Orbitals (3-21G, 3-21G*) with the Fractionally Occupied UHF-NO Used To Define the Active Space and as Starting Orbitals for the CASSCF

transition state	symmetry	occupancy no. (symmetry) of CASSCF natural orbitals			
$C_2H_2O_2$	C_2	1.8927 (b)	1.7572 (a)	0.2431 (b)	0.1069 (a)
C_3H_4O	C_1	1.9216 (a)	1.8452 (a)	0.1557 (a)	0.0775 (a)
$C_2H_2S_2$	C_2	1.9008 (b)	1.7851 (a)	0.2152 (b)	0.0989 (a)
C_3H_4S	C_1	1.9117 (a)	1.8192 (a)	0.1830 (a)	0.0861 (a)

Table IV. Occupancy Numbers of the CISD Natural Orbitals for the Molecules

molecule		basis set (symmetry)	occupancy no. (symmetry) of the CI natural orbitals			
$C_2H_2O_2$	ring	6-31G*	1.9924	1.9458	0.0558	0.0096
		(C_2)	a	b	b	a
		3-21G	1.9662	1.9424	0.0585	0.0367
		(C_2)	a	b	a	b
	cis	6-31G*	1.9517	1.9401	0.0713	0.0386
		3-21G	1.9353	1.9077	0.1406	0.0544
		(C_2)	b	a	b	a
C_3H_4O	ring	6-31G*	1.9987	1.9509	0.0498	0.0019
		3-21G	1.9557	1.9396	0.0613	0.0050
		(C_s)	a′	a″	a″	a′
	cis	6-31G*	1.9585	1.9327	0.0735	0.0360
		3-21G	1.9464	1.9123	0.0941	0.0481
		(C_s)	a″	a″	a″	a″
$C_2H_2S_2$	ring	6-31G*	1.9797	1.9700	0.0328	0.0226
		3-21G*	1.9761	1.9665	0.0373	0.0257
		(C_2)	a	b	b	a
	gauche	6-31G*	1.9396	1.9072	0.1029	0.0516
		3-21G*	1.9355	1.8772	0.1328	0.0584
		(C_2)	b	a	b	a
C_3H_4S	ring	6-31G*	1.9880	1.9496	0.0527	0.0140
		3-21G*	1.9835	1.9412	0.0612	0.0186
		(C_s)	a′	a″	a″	a′
	cis	6-31G*	1.9493	1.9140	0.0941	0.0433
		3-21G*	1.9453	1.9020	0.1046	0.0485
		(C_s)	a″	a″	a″	a″

Table V. Final Occupancy Numbers of the CASSCF Natural Orbitals for the Molecules

molecule	basis set (symmetry)	occupancy no. (symmetry) of the CASSCF natural orbitals			
$C_2H_2O_2$	6-31G*	1.9365	1.9197	0.0803	0.0635
(ring)	3-21G	1.9017	1.9124	0.0876	0.0983
	(C_{2v})	a_1	b_2	a_2	b_1
$C_2H_2O_2$	6-31G*	1.9293	1.9093	0.1010	0.0604
(cis)	3-21G	1.9149	1.8805	0.1307	0.0738
	(C_{2v})	b_2	a_2	b_2	a_2
C_3H_4O	6-31G*	1.9735	1.9206	0.0794	0.0265
(ring)	3-21G	1.9644	1.9123	0.0877	0.0356
	(C_s)	a′	a″	a″	a′
$C_2H_2S_2$	3-21G*	1.9596	1.9170	0.0830	0.0404
(ring)	(C_{2v})	a_1	b_2	a_2	b_1
$C_2H_2S_2$	3-21G*	1.9087	1.8418	0.1683	0.0812
(gauche)	(C_2)	b	b	b	b
C_3H_4S	3-21G*	1.9671	1.9125	0.0875	0.0329
(ring)	(C_s)	a′	a″	a″	a′
C_3H_4S	3-21G*	1.9237	1.8655	0.1415	0.0693
(cis)	(C_s)	a″	a″	a″	a″

the C_1 symmetry characteristic of the oxetene–acrolein or thiete–thioacrolein transition states, the full CI or CASSCF with 4 electrons/4 orbitals involved 20 configurations.

Table I presents the UHF total energies, the value of $\langle S^2 \rangle$, and the occupancy numbers of the fractionally occupied UHF-NO. The closed-shell HF total energies are given in Table X. The UHF energies of the transition states are 0.011 (C_4H_6) to 0.031 ($C_2H_2S_2$) au below the closed-shell HF energies. The UNO-CAS, full CI in the space of these fractionally occupied UHF-NO, total energies are also presented in Table I and may be compared with the CASSCF energies in Table X. The UNO-CAS total energies are 0.0018 au for C_4H_6 to 0.0193 au for $C_2H_2S_2$ higher than the CASSCF results. The energy differences between UNO-CAS and CASSCF for C_4H_6, C_3H_4O, and C_3H_4S are in general agreement with Pulay's observation[33b] of ca. 1 mhartree/active orbital energy differences between UNO-CAS and CASSCF calculations. The energy differences between UNO-CAS and CASSCF methods for $C_2H_2O_2$ and $C_2H_2S_2$ are larger. The $C_2H_2S_2$ UHF result showed an energetically unfavorable spatial symmetry breaking.

The applicability of this UHF-NO selection scheme for the active space depends, of course, on the instability of the singlet HF wave function and the ability to find the UHF solution.[33c] For both the ring (e.g., dithiete) and open or cis molecules (e.g., glyoxal), it proved even more difficult to find the low-energy UHF wave functions. Thus, the fractional occupancies of the UHF-NO could no longer serve as an active-space selection criterion. A chemically intuitive choice of active space for the stable molecules could have been made through a study of the molecular orbitals. A more automated approach was sought. To this end, a singles and doubles CI was carried out with use of the four highest doubly occupied orbitals and four lowest virtual orbitals from the closed-shell SCF for a total of ~150 configurations in C_1 symmetry. The occupancy numbers of the CI natural orbitals were examined to define the active space for a subsequent CASSCF. For the transition states, the CISD-NO (Table II) and UHF-NO (Table I) both clearly defined a 4-electron/4-orbital space with the same fractional occupancy number selection criterion, $0.02 < \sigma < 1.98$. Judging on the basis of the occupation numbers (e.g., using the 3-21G basis and C_3H_4O: UHF-NO 1.9058, 1.6900, 0.3100, 0.0942; CISD-NO 1.9613, 1.9228, 0.0779, 0.0440; final CASSCF-NO (Table III) 1.9216, 1.8452, 0.1557, 0.0775), the extent of nondynamical electron correlation lies between an overestimation at the UHF-NO level and an underestimation at the CISD level. Table III presents the 3-21G or 3-21G* final CASSCF occupation numbers for the active orbitals of the transition states.

Table IV gives the fractionally occupied CISD-NO occupation numbers for the ring and open molecules and compares the results with the 6-31G* and 3-21G or 3-21G* basis sets. In all but the cases of dioxetene and oxetene with the 6-31G* basis, the same active-space selection criteria as used for the transition states applied to the CISD-NO of the stable molecules generate a 4-electron/4-orbital active space to be employed in the CASSCF. With the larger basis set for dioxetene and oxetene, one essentially doubly occupied orbital ($C_2H_2O_2$, $\sigma = 1.9924$; C_3H_4O, $\sigma = 1.9987$) and one essentially unoccupied orbital ($C_2H_2O_2$, $\sigma = 0.0096$; C_3H_4O, $\sigma = 0.0019$) were included somewhat arbitrarily in the active space to keep its dimensions at 4 electrons and 4 orbitals. The inclusion of such orbitals *cannot* be recommended in general.[32,33a] Table V reports the final occupancy numbers of the CASSCF natural orbitals for the reactant and product molecules.

Results and Discussion

Table VI presents our 6-31G* SCF, CISD, CASSCF, MP2, and MP4SDTQ energetic results and 6-31G* SCF and CASSCF key structural parameters for the "reference" cyclobutene to butadiene reaction. Comparisons are drawn with the previous studies by Bruelet and Schaefer[5] and Rondan and Houk[6] and with preliminary results reported by Bofill and Pulay (Table V of ref 33b).

Table VII presents the 6-31G* SCF level scaled vibrational frequencies for oxetene and thiete. Vibrational frequencies for dioxetene may be found in the Carnegie-Mellon Quantum Chemistry Archive, and the vibrational spectrum of dithiete has been thoroughly discussed elsewhere.[23,25] The 6-31G* SCF level scaled vibrational frequencies for *cis*-acrolein, *cis*-thioacrolein, and *gauche*-dithioglyoxal are given in Table VIII and improve on previous 3-21G* SCF vibrational frequency predictions for thioacrolein and dithioglyoxal.[25,30] The computed 6-31G* SCF level scaled vibrational frequencies in Table IX for the saddle points serve to verify that these are true transition states with one and only one imaginary frequency.

Table X contains the total energies and barrier heights relative to the minima for the heterosubstituted cyclobutenes and butadienes with the SCF, CISD, and CASSCF methods and the 3-21G or 3-21uG* and 6-31G* basis sets. The 6-31G* MP2, MP3, MP4SDQ, and MP4SDTQ total and relative energies are collected in Table XI. The geometries used in the CI, MCSCF, and MP calculations were the SCF-optimized ones with the same basis set.

Figures 1, 2, 4, and 5 present the SCF-optimized geometries with the 3-21G or 3-21G* and 6-31G* bases for the ring compound, the isomerization transition state, and the open cis or gauche isomer for the four heteroatom-perturbed reactions. Figure 3 compares the 3-21G SCF- and 3-21G MCSCF-optimized

Table VI

(a) 6-31G* SCF, CISD, CASSCF, MP2, and MP4SDTQ Energies for the Cyclobutene to Butadiene Isomerization Reaction[a] (Total Energies, au; Relative Energies, kcal·mol^{-1})

	SCF	CISD	CASSCF	MP2	MP4SDTQ	Breulet–Schaefer[c] DZd TCSCF	Rondau–Houk[d] 3-21G SCF	Rondau–Houk[d] 3-21G MP2	expt
cyclobutene	−154.899 62	−154.919 11	−154.945 49	−155.409 00	−155.466 66		−154.030 72	−154.384 92	
transition state	−154.824 83	−154.859 51	−154.887 19	−155.349 52	−155.408 20		−153.964 36	−154.337 2	
gauche-butadiene	−154.914 83	−154.951 58	−154.971 01	−155.416 82	−155.477 82				
reaction barrier[b]	46.9	37.4	36.6	37.3	36.7	39.4 (35.8)	41.6	32.8	32.9[e]
reaction energy[b]	−9.5	−20.4	−16.0	−4.9	−7.0	−5.0	−14.6		−9.1[f], −11.4[g]

(b) Key Geometrical Variables[h] for Cyclobutene, the Ring-Opening Transition State, and *gauche*-Butadiene at 6-31G* SCF and CASSCF Levels[i]

	geometrical variable	6-31G* SCF	6-31G* CASSCF	Breulet–Schaefer DZd TCSCF	Rondan–Houk 3-21G SCF	Bofill–Pulay 4-31G GVB	Bofill–Pulay 4-31G CASSCF
cyclobutene	$r(C_1C_2)$	1.322	1.342	1.362	1.326		
	$r(C_1C_4)$	1.515	1.515	1.533	1.539		
	$r(C_3C_4)$	1.563	1.600	1.578	1.593		
	$\alpha(C_4C_1C_2)$	94.6	94.9	94.0	95.0		
transition state	$r(C_1C_2)$	1.369	1.364	1.351	1.369	1.347	1.359
	$r(C_1C_4)$	1.413	1.443	1.462	1.421	1.452	1.451
	$r(C_3C_4)$	2.129	2.233	2.238	2.138	2.416	2.243
	$\alpha(C_4C_1C_2)$	104.3	106.6	108.1	104.3		
	$t(C_4C_1C_2C_3)$	22.0	18.8	16.4	14.5	17.0	17.7
gauche-butadiene	$r(C_1C_2)$	1.478	1.478	1.458			
	$r(C_1C_4)$	1.321	1.343	1.349			
	$\alpha(C_4C_1C_2$	125.3	125.5	127.6			
	$t(C_4C_1C_2C_3)$	38.5	32.6	0 (assumed)			

[a] The results from this work are at the 6-31G* SCF geometries except for the CASSCF for which structures were reoptimized at that level. [b] These calculated energy differences have not been corrected for changes in zero-point vibrational energies. Zero-point vibrational corrections will lower the barrier height by ~2.0 kcal·mol^{-1} (see refs 5 and 6). [c] Reference 5. The value in parentheses is a TSCF + CISD result. [d] Reference 6. [e] Cooper, W.; Walters, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 4220. Carr, R. W.; Walters, W. D. *J. Phys. Chem.* **1965**, *69*, 1073. [f] See Table VI in ref 5. [g] Wiberg, K. B.; Fenoglio, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3395. [h] Units: distances, Å; angles, deg. [i] More elaborate treatments of cis-butadiene are available in the literature. See, for example: Rice, J. E.; Liu, B.; Lee, T. J.; Rohlfing, C. M. *Chem. Phys. Lett.* **1989**, *161*, 277. Alberts, I. L.; Schaefer, H. F. *Chem. Phys. Lett.* **1989**, *161*, 375. Wiberg, K. B.; Rosenberg, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 1509.

Table VII. Scaled SCF Vibrational Frequencies by the 6-31G* SCF Method for the Ring Molecules (Calculated IR Intensities, km/mol)

	C_3H_4O				C_3H_4S		
	symmetry	0.9calcd	IR intens	expt	symmetry	0.9calcd	IR intens
1	a″	426	39.9	425 (s)	a″	362	5.1
2	a″	715	43.0	665 (s)	a′	602	6.2
3	a′	887	56.4	880 (s)	a′	685	3.3
4	a′	921	18.3	920 (s)	a″	688	65.4
5	a″	925	1.3		a′	819	15.7
6	a′	941	10.3		a″	901	1.0
7	a″	1009	19.9		a″	939	4.4
8	a′	1032	87.7	1025 (s)	a′	944	1.5
9	a″	1120	2.4		a″	1069	5.0
10	a′	1150	23.3		a′	1071	0.5
11	a′	1238	1.0		a′	1189	10.0
12	a′	1329	19.7	1285 (m)	a′	1275	9.7
13	a′	1489	2.6		a′	1453	2.8
14	a′	1618	33.1	1565 (m)	a′	1611	9.5
15	a′	2928	47.8	2970 (m)	a′	2939	31.0
16	a″	2981	38.6	3000 (s)	a″	2992	11.2
17	a′	3075	10.2	3020 (w)	a′	3055	5.7
18	a′	3152	1.9		a′	3095	11.6

structures in the case of the oxetene to acrolein reaction.

Our results at slightly higher levels of theory for the cyclobutene to butadiene reaction are discussed first. The four heteroatom-perturbed electrocyclic isomerizations are then discussed briefly in separate sections followed by an analysis of trends over the set of reactions.

Cyclobutene–Butadiene. Table VIa contains the energetic predictions of this work for the activation barrier and exoergicity of the cyclobutene to butadiene reaction. Comparisons are drawn with earlier computations[5,6,33b] and with experiment. The 6-31G* SCF barrier is 46.9 kcal·mol^{-1} substantially higher than the 6-31G* CISD, CASSCF, MP2, and MP4SDTQ results, which range from 36.6 to 37.4 kcal·mol^{-1}. These are classical barrier heights and will be reduced by ~2.0 kcal·mol^{-1} by zero-point vibrational energy corrections.[5,6] Thus, a best estimate of the 6-31G* CASSCF reaction barrier is 36.6−2.0 = 34.6 kcal·mol^{-1}, in good agreement with the experimental value of 32.9 kcal·mol^{-1}. The CASSCF involved 4 electrons/4 orbitals and is the same size as used for the heterosubstituted cyclobutene reactions in the following sections. The 6-31G* CASSCF and MP4SDTQ reaction energies of −16.0 and −7.0 kcal·mol^{-1} bracket the experimental values of −9.1 and −11.4 kcal·mol^{-1}.

Key geometrical parameters of cyclobutene, the transition state, and butadiene at the 6-31G* SCF and CASSCF levels of theory are given in Table VIb. Focusing on the 6-31G* CASSCF transition-state geometry, the structure is qualitiatively similar (i.e., C_2 symmetry, $C_3C_4 \approx 2.23$ Å) to earlier DZd TCSCF[5] and 4-31G CASSCF[33b] geometries. Thus, for this relatively well-characterized transition state, the methods used in this work are shown to be reliable.

Dioxetene–Glyoxal. Since Budzelaar et al.[9b] report computations on this reaction, this section will focus on our CISD, CASSCF, and MP4 results. A brief discussion of the 6-31G* SCF geometries will be given in comparing the transition state to that for the cyclobutene reaction.

The final 3-21G CASSCF natural orbital occupancies for the transition state are 1.8927, 1.7572, 0.2431, and 0.1069 (Table III) as compared to the values for dioxetene of 1.9124, 1.9017, 0.0876,

Table VIII. Scaled SCF Vibrational Frequencies by the 6-31G* SCF Method for the Open Molecules (IR Intensities, km/mol)

	$C_2H_2S_2$		C_3H_4O				C_3H_4S	
	symmetry	0.9calcd	symmetry	0.9calcd	IR intens	expt[20]	symmetry	0.9calcd
1	a	111	a″	156	11.8	230 ± 40	a″	90
2	a	208	a′	281	8.2	312	a′	247
3	b	520	a″	556	9.5		a′	549
4	b	751	a′	665	21.7	548	a″	560
5	a	779	a′	902	72.6	930	a′	840
6	a	938	a″	1008	9.9		a″	907
7	b	1052	a″	1032	52.5		a′	1000
8	a	1171	a″	1041	0.7		a″	1012
9	a	1327	a′	1049	7.1		a″	1030
10	b	1398	a′	1289	3.8		a′	1135
11	b	2976	a′	1408	1.5		a′	1307
12	a	2992	a′	1416	51.4	1486	a′	1391
13			a′	1661	68.6	1635	a′	1418
14			a′	1806	181.1	1733	a′	1648
15			a′	2856	140.1		a′	2986
16			a′	3012	11.2		a′	3014
17			a′	3030	11.9		a′	3030
18			a′	3097	4.3		a′	3101

Table IX. Scaled SCF Vibrational Frequencies at the 6-31G* Level for the Transition States

	$C_2H_2O_2$		C_3H_4O	$C_2H_2S_2$		C_3H_4S
	symmetry	0.9calcd	0.9calcd	symmetry	0.9calcd	0.9calcd
1	a	1799i	941i	a	1125i	754i
2	a	586	431	a	394	394
3	b	728	593	b	590	604
4	a	812	789	a	648	658
5	b	909	826	b	714	718
6	a	1026	989	b	877	836
7	b	1074	1007	a	901	936
8	a	1204	1056	a	1039	995
9	b	1289	1085	a	1194	1009
10	a	1435	1169	b	1289	1085
11	b	3099	1243	b	3047	1141
12	a	3128	1396	a	3066	1330
13			1469			1440
14			1532			1508
15			2962			2994
16			2998			3034
17			3067			3055
18			3106			3093

and 0.0983 or glyoxal of 1.9149, 1.8805, 0.1307, and 0.0738 (Table V). Taking the differences of these numbers from 2 or 0 as one measure of the importance of nondynamic electron correlation, the transition structure is, as expected, in greater need of a CASSCF treatment than the end points.

The energetics of the dioxetene to glyoxal reaction were discussed at the 3-21G and 6-31G* SCF and MP2 levels by Budzelaar et al.[9b] Substantial SCF level barriers of 25.9 or 28.4 kcal·mol^{-1} (3-21G, 6-31G*) are markedly reduced with the inclusion of electron correlation. The CASSCF barriers predicted here of 11.0 kcal·mol^{-1} (3-21G) or 10.2 kcal·mol^{-1} (6-31G*) are similar, both to our CISD results and to MP2 values. The MP2 6-31G* barrier is predicted to be 10.4 kcal·mol^{-1}, while at MP4SDTQ the value is 10.9 kcal·mol^{-1}. There is an important effect due to triple excitations as the 6-31G* MP4SDQ activation energy is 16.5 kcal·mol^{-1}. The importance of triples is not unexpected as these higher excitations must be correcting for the lack of a multireference starting wave function. All these results for the ring-opening barriers suggest that dioxetene may be isolable as an intermediate[7,8] even though the ring opening to glyoxal is predicted to be strongly exothermic.

The dioxetene molecule has the structure (Figure 1) anticipated for a localized cyclic peroxide species.[9b] In the transition-state structure the two HCO groups twist into a C_2 conformation as expected on orbital symmetry grounds.[1,2] The dioxetene to glyoxal transition state is clearly earlier, that is, closer to reactant than the cyclobutene to butadiene one.[5,6] Defining the dioxetene geometry as 0% and that of *cis*-glyoxal as 100%, the percentage advancement of the reaction may be quantified and compared to a similar analysis[6] of the cyclobutene–butadiene case. For the

Table X. Calculated Total Energies by the Closed-Shell SCF, CISD, and CASSCF Methods (Energies, au; Energy Differences, kcal/mol)

	closed-shell SCF[a]		CISD		CASSCF[b]	
molecule	3-21G(*)	6-31G*	3-21G(*)	6-31G*	3-21G(*)	6-31G*
$C_2H_2O_2$ (ring)	−225.171 65	−226.428 28	−225.215 38	−226.452 12	−225.255 65	−226.499 58
ΔE	25.9	28.4	12.0	10.2	11.0	10.2
$C_2H_2O_2$ (TS)	−225.130 34	−226.383 06	−225.196 28	−226.435 90	−225.238 19	−226.483 39
ΔE	105.7	125.6	107.9	123.0	89.6	106.9
$C_2H_2O_2$ (cis)	−225.298 76	−226.583 23	−225.368 18	−226.631 89	−225.380 94	−226.653 84
C_3H_4O (ring)	−189.634 03	−190.706 39	−189.656 39	−190.723 11	−189.690 21	−190.757 11
ΔE	32.2	35.1	20.6	27.5	26.8	32.2
C_3H_4O (TS)	−189.582 74	−190.650 39	−189.623 56	−190.679 29	−189.647 49	−190.705 81
ΔE	67.2	68.6	74.6	75.7	68.5	71.6
C_3H_4O (cis)	−189.689 89	−190.759 77	−189.742 43	−190.799 99	−189.756 61	−190.819 88
$C_2H_2S_2$ (ring)	−867.744 17	−871.863 83	−867.770 61	−871.884 88	−867.789 70	
ΔE	32.1	35.5	19.5	21.1	19.9	
$C_2H_2S_2$ (TS)	−867.693 08	−871.807 23	−867.739 52	−871.851 26	−867.758 01	
ΔE	33.5	35.1	35.6	33.2	30.5	
$C_2H_2S_2$ (gauche)	−867.746 52	−871.863 10	−867.796 29	−871.904 19	−867.806 60	
C_3H_4S (ring)	−510.890 33	−513.383 87	−510.922 69	−513.410 30	−510.937 73	
ΔE	31.9	34.4	21.0	23.9	24.5	
C_3H_4S (TS)	−510.839 51	−513.329 11	−510.889 19	−513.372 25	−510.898 75	
ΔE	43.1	42.3	43.4	42.8	41.3	
C_3H_4S (cis)	−510.908 24	−513.396 48	−510.958 31	−513.440 40	−510.954 55	

[a] 3-21G(*) UHF total energies for the transition states may be found in Table I for comparison. [b] 3-21G(*) UNO-CAS, full CI in the space of the fractionally occupied UHF-NO, total energies for the transition states may be found in Table I for comparison.

Table XI. Moller–Plesset Perturbation Theory Energies (Energies, au; Energy Differences, kcal/mol) (6-31G*)

molecule	MP2	MP3	MP4SDQ	MP4SDTQ
$C_2H_2O_2$ (ring)	−227.04377	−227.05007	−227.06166	−227.08643
ΔE	10.4	17.6	16.5	10.9
$C_2H_2O_2$ (TS)	−227.02673	−227.02203	−227.03541	−227.06901
ΔE	94.0	100.0	100.9	93.8
$C_2H_2O_2$ (cis)	−227.17652	−227.18142	−227.19616	−227.21850
C_3H_4O (ring)	−191.26213	−191.28076	−191.29036	−191.31211
ΔE	28.3	33.0	29.8	26.6
C_3H_4O (TS)	−191.21709	−191.22823	−191.24280	−191.26973
ΔE	55.9	60.4	58.8	55.1
C_3H_4O (cis)	−191.30626	−191.32450	−191.33655	−191.35756
$C_2H_2S_2$ (ring)	−872.35960	−872.38925	−872.39558	−872.41801
ΔE	23.1	26.2	26.1	21.9
$C_2H_2S_2$ (TS)	−872.32271	−872.34755	−872.35391	−872.38307
ΔE	24.3	25.6	28.0	25.0
$C_2H_2S_2$ (gauche)	−872.36152	−872.38834	−872.39852	−872.42995
C_3H_4S (ring)	−513.88701	−513.91742	−513.92421	−513.94504
ΔE	28.8	31.5	30.3	26.7
C_3H_4S (TS)	−513.84104	−513.86724	−513.87599	−513.90256
ΔE	33.4	35.6	35.9	33.2
C_3H_4S (cis)	−513.89421	−513.92402	−513.93321	−513.95544

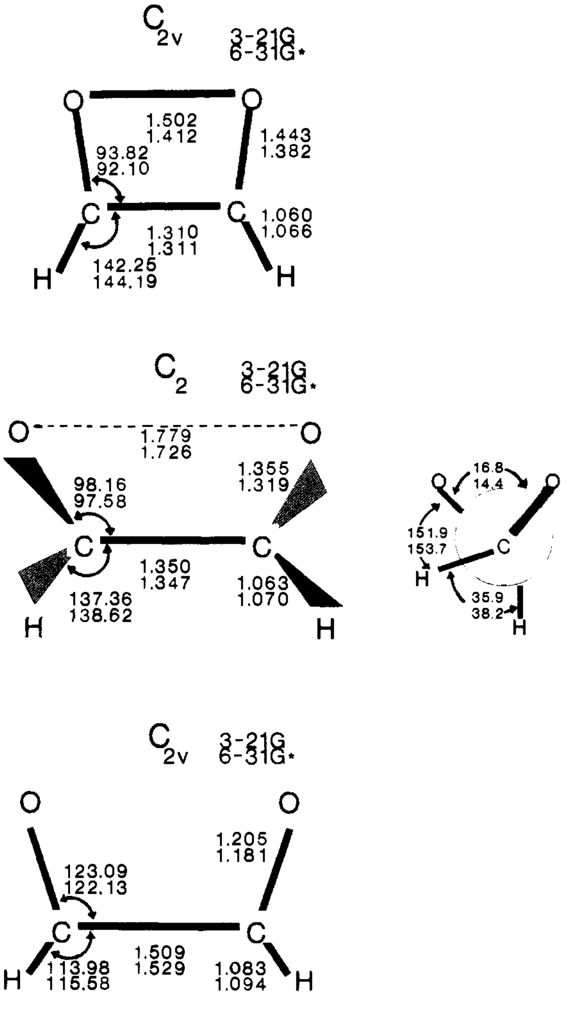

Figure 1. SCF-optimized geometries with the 3-21G and 6-31G* basis sets for dioxetene, the isomerization transition state, and *cis*-glyoxal. Structures for the stable molecules are from the Carnegie-Mellon Quantum Chemistry Archive.

transition structure the percent advancement of the bond lengths (6-31G*) ranges from 17% for r(CC) to 31% for r(CO). The CCO angle, important in the reaction coordinate, is 97.6° in the transition state, an 18% advancement from 92.1° in the ring isomer toward 123.1° in glyoxal. Rondan and Houk[6] found percent progress of 28–54% at the transition state in the 3-21G SCF study of the cyclobutene ring opening. The earlier transition state for dioxetene may be rationalized by Hammond's postulate,[47] as the cyclobutene to butadiene exothermicity is ~10 kcal·mol^{-1} while that for dioxetene to glyoxal is very much larger.

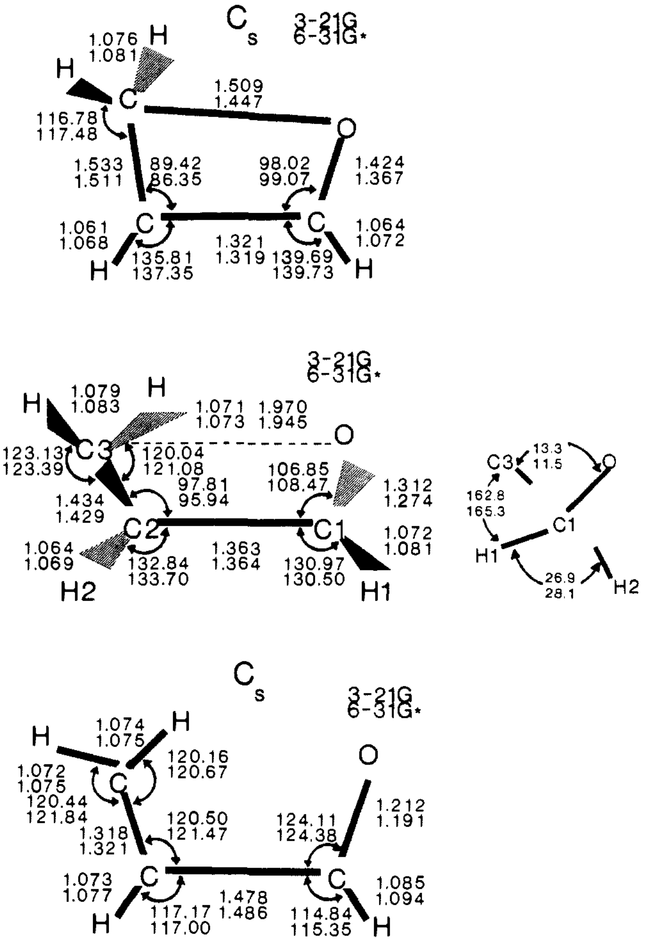

Figure 2. SCF-optimized geometries with the 3-21G and 6-31G* basis sets for oxetene, the isomerization transition state, and *cis*-acrolein.

With a relatively small energy barrier of 10–11 kcal·mol^{-1}, it is important to consider if the use of SCF level geometries for the CASSCF calculations had an important effect. 3-21G CASSCF geometries were optimized for dioxetene, the transition state, and glyoxal, and the nature of the stationary points was verified by vibrational analyses. Particularly with the 3-21G basis set, CASSCF is likely to overemphasize antibonding character and, thus, to overestimate most bond lengths relative to experiment. Here, however, the question is simpler: Do the MCSCF geometry optimizations have similar effects on the three stationary points?

For the reactant dioxetene, important structural features at the 3-21G SCF//CASSCF levels are r(CO) = 1.443//1.445 Å; r(CC) = 1.310//1.322 Å; and α(CCO) = 93.82//97.15°. In the product glyoxal, bond lengths at the 3-21G SCF//CASSCF levels are r(C=O) = 1.205//1.235 Å and r(CC) = 1.509//1.492 Å. The transition-state geometries may be compared at the 3-21G SCF//CASSCF levels by considering the important parameters r(CO) = 1.355//1.428; r(CC) = 1.350//1.318; and α(CCO) = 98.2//107.0°. Substantial changes in geometry occur when the CASSCF approach is used. Do these modify the energetic predictions?

The 3-21G CASSCF exothermicity with the SCF-optimized geometries is 78.6 kcal·mol^{-1}, while with the CASSCF-optimized structures the energy of dioxetene is −225.26489 au and that of *cis*-glyoxal is −225.38347 au and, thus, the exothermicity is 74.4 kcal·mol^{-1} or only 4 kcal·mol^{-1} less than the CASSCF at SCF geometries value. The use of a CASSCF-level structure is more important for the transition state. The saddle-point energy with CASSCF geometry optimization is −225.25657 au, only 5.2 kcal·mol^{-1} higher than dioxetene and a full 5.8 kcal·mol^{-1} less than

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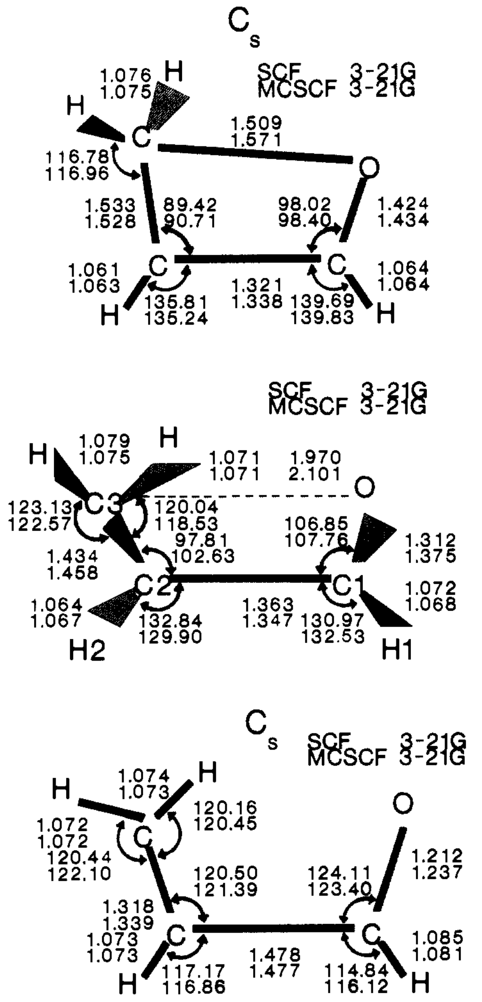

Figure 3. Comparison of 3-21G SCF and 3-21G MCSCF optimized geometries for oxetene, the isomerization transition state, and *cis*-acrolein.

the result from using CASSCF at SCF geometries. From the unscaled 3-21G CASSCF harmonic vibrational frequencies, the transition state has 1.1 kcal·mol^{-1} less zero-point vibrational energy than dioxetene, thus decreasing this reaction barrier to *only 4.1 kcal·mol^{-1}*. Clearly, a final decision on the stability of dioxetene will require a larger basis set CASSCF computation supplemented by CI to include dynamic electron correlation.

Oxetene–Acrolein. The electrocyclic ring opening of oxetene to acrolein is of particular interest as it has been studied experimentally in the gas-phase by Martino and Shevlin.[15] Thus, the theoretical energetics for this particular ring opening can be calibrated against experiment. In addition, the predicted vibrational frequencies for oxetene may be compared to the experimental infrared spectrum.[15]

The SCF-level barriers at SCF geometries to the oxetene ring opening are 32.2 kcal·mol^{-1} (3-21G) and 35.1 kcal·mol^{-1} (6-31G*). These activation energies decrease (although not as dramatically as in the dioxetene case) with the incorporation of electron correlation. The CASSCF predictions for the activation energies are 26.8 kcal·mol^{-1} (3-21G) and 32.2 kcal·mol^{-1} (6-31G*). The 6-31G* MP4SDTQ result is 26.6 kcal·mol^{-1}. Martino and Shevlin[15] have determined an activation enthalpy of 24.1 ± 1.5 kcal·mol^{-1} and an activation entropy of 0.0 ± 3.1 eu for the oxetene isomerization. For tetramethyloxetene in heptane solution,[14] a ΔH^{*} of 25.09 ± 0.68 kcal·mol^{-1} and a ΔS^{*} of −1.4 ± 2.1 eu were found experimentally. The predicted results are in good accord with experiment.

The oxetene to acrolein rearrangement is predicted to be significantly more exothermic than the cyclobutene to butadiene reaction. Computed exothermicities at the SCF level are 35.0 kcal·mol^{-1} (3-21G) or 33.5 kcal·mol^{-1} (6-31G*). The CASSCF reaction energy predictions are 41.7 kcal·mol^{-1} (3-21G) and 39.4 kcal·mol^{-1} (6-31G*). The 6-31G* MP exoergicities are in the range 27.4–29.0 kcal·mol^{-1}. No direct experimental number for this energy difference is available. A best estimate of the exothermicity would be ~35 kcal·mol^{-1}.

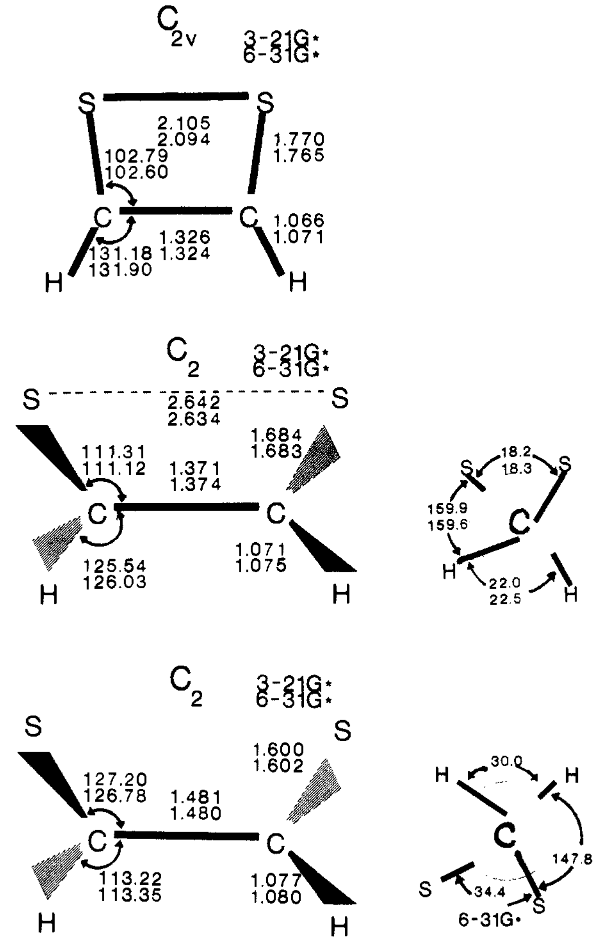

Figure 4. SCF-optimized geometries with the 3-21G* and 6-31G* basis sets for dithiete, the isomerization transition state, and *gauche*-dithioglyoxal. The structural results for dithiete and the 3-21G* results for *gauche*-dithioglyoxal are from ref 25.

The scaled 6-31G* SCF vibrational frequencies and IR intensities for oxetene are given in Table VII, along with the experimental assignments of Martino and Shevlin.[15] No predicted frequency differs by more than 45 cm^{-1} from experiment (ν_{12}) and all the observed frequencies can be matched against calculated ones with substantial intensities. Only two difficulties arise in the comparison. ν_7 and ν_8 are calculated to appear at 1009 and 1032 cm^{-1}, and both have reasonable intensities, 19.9 and 87.7 km·mol^{-1}. There is a strong band observed experimentally at 1025 cm^{-1},[15] which could be either ν_7 or ν_8. The intensity data would favor the latter. Intense bands were predicted for ν_{10} at 1150 cm^{-1} with intensity 23.3 km·mol^{-1} and ν_{12} at 1329 cm^{-1} with 19.7 km·mol^{-1}. The experimental band of medium strength at 1285 cm^{-1} must be assigned to one of these two. The calculated position and medium intensity would favor ν_{12}. The agreement between the calculated spectrum, in terms of both band positions and intensities, and the experimental assignment[15] is quite good.

The SCF-optimized geometries for oxetene, the transition state, and *cis*-acrolein are shown in Figure 2. Oxetene and the transition state are of particular interest. The structural results on *cis*-acrolein match those of other workers.[18,19] The vibrational frequencies of *cis*-acrolein (Table VIII) are in reasonable agreement with experiment.[20] Oxetene has been synthesized so the predicted geometry may assist in its structure determination by microwave spectroscopy. Oxetene's dipole moment, a key parameter for a microwave spectroscopic study, is calculated to be 1.61 D (6-31G* SCF). The 6-31G* SCF geometry is more reliable than the 3-21G

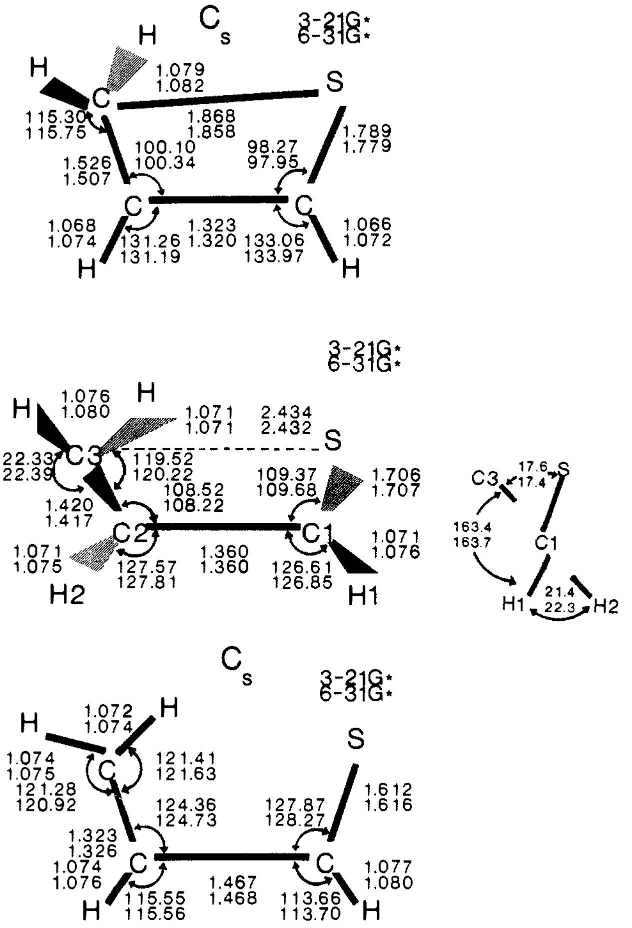

Figure 5. SCF-optimized geometries with the 3-21G* and 6-31G* basis sets for thiete, the isomerization transition state, and *cis*-thioacrolein. The 3-21G* geometry for *cis*-thioacrolein is from ref 30.

SCF one for this small, strained ring. This strain is evident in the CCC angle of 86.35° and CCO angle of 99.07°. The 6-31G* SCF computed equilibrium rotational constants of oxetene (in GHz) are A_e = 15.2928, B_e = 14.1511, and C_e = 7.7078.

The transition structure (6-31G* SCF) is analyzed in terms of the advancement of key parameters from oxetene (0%) to *cis*-acrolein (100%). As expected on orbital symmetry grounds, the transition-state structure is twisted out of plane with a $C_3C_2C_1O$ dihedral angle of 11.5° and a $H_1C_1C_2H_2$ dihedral of 28.1°. The CCC ring angle is 95.9°, which is 27% of the way from the oxetene toward *cis*-acrolein. The CCO angle is 99.1° in oxetene and has advanced by 39% to 108.5° in the transition state. The CO distance changes from 1.367 Å in oxetene to 1.274 Å at the saddle point (−53%). The C=C bond in oxetene of 1.319 Å changes by +27% to 1.364 Å in the transition state. These percentages are greater than for dioxetene since the oxetene reaction is significantly less exothermic.[47]

As a comparison may be drawn with the experimental barrier height[15] for oxetene ring opening, geometries were reoptimized at the 3-21G CASSCF level. The 3-21G CASSCF geometries are compared with the 3-21G SCF structures in Figure 3. A lengthening of most of the bonds is observed on going to the CASSCF level, as expected, since antibonding character is being built into the wave function. At the CASSCF-optimized geometries, the total energies of oxetene and the transition state are −189.69197 and −189.65237 au, respectively. Thus, a barrier of 24.8 kcal·mol^{-1} is predicted from 3-21G CASSCF at 3-21G CASSCF optimized structures. Recall that the 3-21G CASSCF calculations at SCF geometries yielded a barrier of 26.8 kcal·mol^{-1} or only 2 kcal·mol^{-1} different from the more consistent procedure. With unscaled 3-21G CASSCF harmonic vibrational frequencies, differences in the zero-point vibrational energies in oxetene and the transition state reduce the classical barrier height by 2.4 kcal·mol^{-1} to a final value of 22.4 kcal·mol^{-1}. This prediction is in agreement with the experimental activation enthalpy of 24.1 ± 1.5 kcal·mol^{-1}.

Dithiete–Dithioglyoxal. Earlier ab initio computations[23-25] on dithiete and dithioglyoxal favor the *trans*-dithioglyoxal form by ~5 kcal·mol^{-1}, although dithiete has been isolated experimentally. "*cis*-Dithioglyoxal" has been predicted by one of us[25] and confirmed by other calculations[23] not to be cis and planar but to adopt a gauche C_2 conformation. Only a qualitative analysis[26] aided by semiempirical calculations had been published previously on the reaction barrier between the nearly isoenergetic dithiete and dithioglyoxal isomers.

The barrier for dithiete to ring open to dithioglyoxal is calculated to be 32.1 kcal·mol^{-1} (3-21G* SCF) or 35.5 kcal·mol^{-1} (6-31G* SCF). The 3-21G* CASSCF calculation predicted a barrier of 19.9 kcal·mol^{-1}. The 6-31G* MP4SDTQ method predicts an activation energy of 21.9 kcal·mol^{-1}. Thus, there is a substantial barrier to the isomerization of dithiete to *gauche*-dithioglyoxal. The dithiete and C_2 *gauche*-dithioglyoxal are very close in energy (within 3 kcal·mol^{-1}) at the SCF or Moller–Plesset levels. This result is consistent with past work on the dithiete and *trans*-dithioglyoxal energy difference[23-25] when it is recognized that the *gauche*-dithioglyoxal is on the order of 4–5 kcal·mol^{-1} less stable than the trans conformer.

SCF-optimized geometries for dithiete[25] for the ring-opening transition state, and for C_2 dithioglyoxal (3-21G* values from ref 25) are given in Figure 4. Both basis sets yield very similar structural predictions for the $C_2H_2S_2$ species, with all bond distances agreeing within 0.01 Å and bond angles within 0.5°. The 6-31G* SCF structure is the most reliable geometry prediction for C_2 *gauche*-dithioglyoxal published to date.

The reaction is nearly thermoneutral, and a transition-state geometry nicely intermediate between dithiete and dithioglyoxal is found. The CCS ring angle of 111.1° in the transition state is 35% of the way from dithiete to dithioglyoxal. In the transition-state geometry, the CS distance of 1.683 Å is 0.082 Å less than in dithiete and 0.081 Å greater than in dithioglyoxal. As expected from orbital symmetry arguments, the HCS groups have twisted out of plane into a C_2 arrangement at the saddle point.

Thiete–Thioacrolein. Thiete's structure was determined by analysis[27] of its microwave spectrum. However, there has been no experimental study of its vibrational spectrum nor of its ring opening to thioacrolein. The 3-21G* and 6-31G* SCF methods predict barriers of 31.9 and 34.4 kcal·mol^{-1} to the ring opening of thiete. With CASSCF, these activation energies decrease to 24.5 kcal·mol^{-1}. The 6-31G* MP4SDTQ barrier height is 26.7 kcal·mol^{-1}. As the 6-31G* MP4 and 3-21G* CASSCF results for the activation energy are probably reliable, the activation barrier for thiete to thioacrolein is seen to be quite similar to that for oxetene to acrolein. However, the exothermicity for the thiete to thioacrolein reaction is less than for the oxygen-containing molecule. At the SCF level, the thiete ring opening is predicted to be exothermic by 7.9–12.4 kcal·mol^{-1}. With the CASSCF or Moller–Plesset perturbation theory methods, exothermicities of 4.1–6.8 kcal·mol^{-1} are predicted. It is easier to accommodate the less electronegative S in the four-membered ring in comparison to the O, thus stabilizing thiete relative to thioacrolein in comparison to oxetene versus acrolein.

The 6-31G* SCF optimized geometries for thiete can be compared with the results of the microwave study.[27] All 6-31G* bond lengths are within 0.01 Å of the experimental distances except for r(C=C). The calculated C=C length is 1.320 Å, while an experimental value of 1.350 Å was deduced.[27] All calculated bond angles for thiete are in agreement with expeirment to within 0.8°. The 6-31G*-optimized structure for *cis*-thioacrolein is quite similar to the 3-21G* geometry previously reported.[30]

The thiete to *cis*-thioacrolein transition state (6-31G* SCF) twists about the C2C1 bond (Figure 5), with the methylene group also rotating. The ring CCS angle of 109.7° in the transition state is 38% of the way from thiete toward *cis*-thioacrolein. The CCC ring angle progresses from 100.1° in thiete to 108.2° (+33%) in the transition state. The CS bond length in the transition state has decreased by 47% from 1.779 Å in thiete to 1.707 Å. The

CC single bond in thiete, which evolves into the CC double bond in thioacrolein, changes from 1.507 to 1.417 Å (−50%). In terms of transition-state structure and exothermicity, the thiete to thioacrolein reaction is reminiscent of the cyclobutene to butadiene case.

The scaled 6-31G* SCF vibrational frequencies for thiete in Table VII are of interest as the molecule has been made, but its vibrational spectrum is unexplored. The three most intense bands are predicted to occur at 688 cm^{-1} (65.4 km·mol^{-1}), 819 cm^{-1} (15.7 km·mol^{-1}), and 2939 cm^{-1} (31.0 km·mol^{-1}). The probable reliability[43] of the frequency predictions is ±30 cm^{-1}.

Trends in the Ring-Opening Reactions. All of the transition-state structures are qualitatively similar in that a twist into a C_2 or ("C_2 like" in the case of C_1 symmetry) structure occurs as would be anticipated on orbital symmetry grounds.[1,2] As discussed previously,[17] the absence of a C_2 axis in the oxetene or thiete reactions has no important effect on the course of the ring opening. The reaction proceeds much as in the cyclobutene to butadiene case, except that in the absence of CH$_2$ groups the distinction between conrotatory and disrotatory processes is removed.[31]

Heteroatom substitutions for the methylene groups in cyclobutene do have significant effects upon the height of the reaction barriers and in two cases upon the reaction energies. The cyclobutene to butadiene conversion is about 10 kcal·mol^{-1} exothermic.[5,6] Incorporation of one or two oxygens to give oxetene or dioxetene leads to much more strongly exothermic reactions. The strength of the CO double bond in the open isomer and the difficulty of incorporating strongly electronegative elements into the four-membered ring can explain this trend. With one or two sulfurs substituted for the CH$_2$ groups in cyclobutene, the reactions are calculated to be slightly exothermic. Sulfur can much more readily adapt to the four-membered ring environment than can oxygen. The differential energy effect between CS single and double bonds also is not as large as for these bond types involving oxygen.

With the exception of dioxetene, all the rings face barriers of ~20–25 kcal·mol^{-1} to opening. These barriers are 8–13 kcal·mol^{-1} less than the cyclobutene activation energy[5,6] predicted to be ~33 kcal·mol^{-1} by comparable theoretical methods. The qualitative analyses[30] of heterosubstituted butadienes suggested a barrier lowering of ~7–11 kcal·mol^{-1} with a single oxygen or sulfur substituted for a CH$_2$ group, and this prediction has been confirmed here. Such a reduced barrier will have a dramatic effect on the rates of isomerization of these rings.[14,31] Dioxetene is predicted to face a small barrier, and further high-level computations will be required to definitively establish its stability. The barrier for dithiete isomerization to dithioglyoxal is quite substantial at 20–22 kcal·mol^{-1}. The experimental isolation of the dithioglyoxals along with dithiete[23] should be possible.

Concluding Remarks

The ring openings of dioxetene, oxetene, dithiete, and thiete are of interest both individually and as orbital symmetry allowed electrocyclic isomerizations analogous to the cyclobutene to butadiene reaction. Spectroscopic and/or kinetic studies of these reactions should be assisted considerably by the theoretical predictions of this research.

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NMR Studies of Bond Order in Distorted Aromatic Systems

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Abstract: The $^4J_{\mathrm{H{-}C{=}C{-}Me}}$ coupling constant has been previously established[1,2] as a probe of bond order. This has now been used to examine the bond orders of compounds containing severely distorted benzene nuclei. In the case of 3,4-di-*tert*-butyltoluene, no electronic distortions in the aromatic ring can be detected by this method. A series of moderately to severely distorted paracyclophanes show no perturbation of electronic structure, with the possible exception of 8-methyl[6]paracyclophane, which exhibits a barely significant deviation from unstrained values. These conclusions are supported by the results of SCF–MO calculations.

Introduction

The orthobenzylic coupling constant involving a methyl group, $^4J_{\mathrm{H{-}C{=}C{-}Me}}$, henceforth referred to as J_{OB}, has been shown to correlate well with the square of the SCF bond order and the Pauling bond order.[2] This coupling constant has been used previously to probe the electronic structure of quinonoid, hydroaromatic, heterocyclic and other systems.[3] This work describes the use of this method to probe the bond orders in systems containing distorted benzene nuclei. The systems examined were

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