Systematic Survey of Cyclic Silicon-Oxygen Compounds

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Abstract: Compounds with 0, 1, 2, or 3 oxygen atoms bridging 2 silicon atoms are investigated by ab initio calculations. Two such series of compounds, with and without a formal central Si–Si bond, are considered. The triplet states of the former set are also examined. For some of these compounds, the present calculations represent the first time they have been examined at a sufficiently rigorous level of theory. For the compounds that are formally bonded, this level is two configuration SCF (TCSCF) for singlets and ROHF for triplet states, using split valence polarized basis sets. The main result is that no central Si–Si bond exists when there are 2 or 3 bridging oxygens; instead, these are biradical species.

Introduction

Silicon–oxygen compounds such as silica (SiO_2) and various silicates, consisting of various fused tetrahedral structures, are important components of minerals and zeolites. Siloxanes (silicones) are linear or cyclic Si–O polymers and find applications such as lubricants. Accordingly, there has been much recent experimental[1-9] and theoretical[10-20] interest in cyclic silicon–oxygen compounds. Although each is mentioned at least once in the literature, we are unaware of any unified treatment of the two families of compounds shown in Chart I. The integer of the labeling scheme shows the number of bridging oxygen atoms, while the **B** compounds possess, at least formally, a silicon–silicon bond. The present paper considers the ground singlet state of the **A** sequence and the singlet and triplet states of the **B** sequence, at a consistent and adequate level of electronic structure theory.

Much speculation has centered on the nature of Si-Si bonding in these compounds. In particular, there has been speculation concerning the possibility of some degree of Si-Si bonding in **2A**[12,13] and **3A**,[15] as here the cross ring Si-Si distances are shorter than in the prototypal **0B**. However, earlier workers[10,11] preferred to invoke the strength of Si–O bonds, and O–O repulsions, rather than Si-Si bonding to explain the short distance in **2A**. Recent work in our group has shown that cross-ring Si-Si bonding in **2A** is fleetingly small at best.[14]

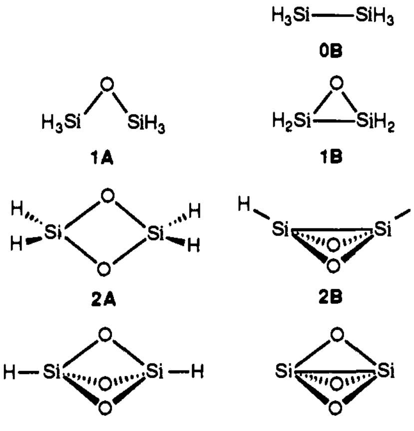
The major portion of this paper concerns itself with bonding (or the lack thereof) in the **B** series. The putatively bonded singlet states are compared to their $\sigma \rightarrow \sigma^*$ triplet states. Because of the large biradical character possessed by the singlets **2B** and **3B**, the calculations reported below are the first to describe these singlet molecules qualitatively correctly. We will use the term "biradical" in this paper only to describe singlet states with largely unpaired electrons, as of course all triplet states are biradicals. The triplet states of **1B**–**3B** are presently uncharacterized in the literature.

Method

Ab initio electonic structure calculations, all with the 6-31G* basis,[21] are used to characterize these compounds. The **A** compounds are treated with closed shell SCF (RHF) calculations. Two configuration SCF (TCSCF) calculations are used to treat the singlet **B** compounds, while their triplet states are treated with restricted open shell SCF (ROHF). It is entirely possible that the lowest triplet state for **0B** and **1B** is not the $\sigma \rightarrow \sigma^*$ state but rather some Rydberg state. Nonetheless, the valence state is the only triplet considered for these two compounds, as our main intent is comparison of the lowest singlet state to the triplet state that is lowest for the biradicaloids **2B** and **3B**.

TCSCF is the minimal treatment needed for a proper description of the singlet biradicaloids **2B** and **3B**, so this level of calculation is performed for the entire sequence **0B** to **3B**. TCSCF is also the simplest wave function permitting a *qualitative* comparison of singlet and triplet energy levels.[22] This may be seen by realizing that both the TCSCF singlet and ROHF triplet are actually examples of MCSCF calculations with 2 electrons in two active orbitals. Specifically, the wave functions

Chart I



$$\mathrm{ROHF} = \{(\phi)^1(\phi^*)^1\}\alpha\alpha$$

$$\mathrm{TCSCF} = \{C_1(\phi)^2 + C_2(\phi^*)^2\}(\alpha\beta - \beta\alpha)/\sqrt{2}$$

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(1) **1A**: innumerable references, including an electron diffraction structure with R(SiO) = 1.634 Å: Almenningen, A.; Bastienson, O.; Ewing, V.; Hedberg, K.; Traetteberg, M. *Acta Chem. Scand.* **1963**, *17*, 2455–2460.

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(3) **2A**: Yokelson, H. B.; Millevolte, A. J.; Adams, B. R.; West, R. *J. Am. Chem. Soc.* **1987**, *109*, 4116–4118.

(4) **2A**: Tamás, J.; Gomory, A.; Besenyei, I.; Nefedov, O. M.; Khabashesku, V. N.; Kerzina, Z. A.; Kagramanov, N. D.; Maltsev, A. K. *J. Organomet. Chem.* **1988**, *349*, 37–41.

(5) **2A**: Shepard, B. D.; Powell, D. R.; West, R. *Organometallics* **1989**, *8*, 2664–2669.

(6) **0B**: innumerable references, including a rotational Raman structure with R(SiSi) = 2.327 Å: Shotten, K. C.; Lee, A. G.; Jones, W. J. *J. Raman Spectrosc.* **1973**, *1*, 243–253.

(7) **1B**: An X-ray structure for a bulkily substituted compound has R(SiO) = 1.733 Å and R(SiSi) = 2.227 Å: Yokelson, H. B.; Millevolte, A. J.; Gillette, G. R.; West, R. *J. Am. Chem. Soc.* **1987**, *109*, 6865–6866.

(8) **1B**: Watanabe, H.; Tabei, E.; Goto, M.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 522–523.

(9) **1B**: Masamune, S.; Eriyama, Y.; Kawase, T. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 584–585.

(10) **2A**: Kudo, T.; Nagase, S. *J. Am. Chem. Soc.* **1985**, *107*, 2589–2595.

(11) **2A**: Brenstein, R.; Scheiner, S. *Int. J. Quantum Chem.* **1986**, *29*, 1191–1208.

(12) **1B**, **2A**: Grev, R.; Schaefer, H. F. *J. Am. Chem. Soc.* **1987**, *109*, 6577–6585.

(13) **2A**: Somogyi, A.; Tamás, J. *J. Phys. Chem.* **1990**, *94*, 5554–5556.

(14) **2A**: Gordon, M. S.; Packwood, T. J.; Carroll, M. T.; Boatz, J. A. *J. Phys. Chem.* **1991**, *95*, 4332–4337. The technique used in this work is the Atoms in Molecules method of R. F. Bader.

(15) **3A**, **3B**: Nagase, S.; Kudo, T.; Kurakake, T. *J. Chem. Soc., Chem. Commun.* **1988**, 1063–1064.

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Table I. Major Distances (Å)

	singlet RHF			singlet TCSCF		triplet ROHF	
compd	*R*(SiSi)	*R*(SiO)	compd	*R*(SiSi)	*R*(SiO)	*R*(SiSi)	*R*(SiO)
			0B	2.393		∞	
1A	3.186	1.638	**1B**	2.244	1.689	3.131	1.646
2A	2.401	1.676	**2B**	2.414	1.682	2.413	1.682
			2B′	2.418	1.679	2.412	1.683
3A	2.066	1.703	**3B**	2.084	1.711	2.078	1.711

are the most general triplet and singlet functions possible with two orbitals. The latter has been written in natural form to eliminate the singly occupied singlet coupled determinant. If closed shell SCF is appropriate for the singlet, C_1 will be close to 1 and C_2 close to 0, corresponding to bonding, whereas a complete biradical will have $C_1 = -C_2 = 1/\sqrt{2}$.

We can assess the importance of the antibonding orbital's contribution by means of the natural orbital occupation numbers. Of course, for the triplet state both orbitals are singly occupied. For the TCSCF singlet, the occupation numbers are $N(\phi) = 2C_1^2$ and $N(\phi^*) = 2C_2^2$. These two occupation numbers sum to exactly 2. They provide a direct quantitative measure of how close the wave function is to complete biradical character, $N(\phi) = N(\phi^*) = 1$.

For internal consistency all distances quoted below are from the present theoretical calculations, even in those cases where experimental values are available. Where experimental values are known, these are quoted in the references. There are no serious discrepancies between the computed and measured bond lengths. All distances in this paper are in angstrom units.

All structures were located with use of analytic gradients and were characterized as minima by analytic calculation of the matrix of energy second derivatives (hessian). All calculations were performed with use of the electronic structure code GAMESS,[23] to which the capability to calculate TCSCF analytic hessians[24] has recently been added.

Results and Discussion

We consider first the **A** sequence of compounds, in which the silicon atoms are not bonded. Triplet states are not considered in this series, as there are no Si-Si bonds. We are mainly concerned here with the closed shell SCF Si-Si separation, as well as the Si-O bond distances, which are shown in Table I.

Disiloxane **1A** clearly contains nonbonded silicon atoms, and its Si-O distance is quite close to the RHF bond length of 1.653 in the prototype Si-O compound, silanol.[25] As already noted, the Si-Si distance in cyclodisiloxane (**2A**) (which is near that for disilane (**0B**)) is suggestive of a possible bonding interaction, although a careful analysis of the wave function[14] shows that there is no such bond present. A similar conclusion had been reached earlier for the hydroxide tetrasubstituted analogue of **2A**.[26] The triply bridged compound **3A** is known only theoretically,[15,16] where a structure essentially identical with that presented here was obtained.[15] Note that the Si-Si distance is now notably shorter than that in **0B**! Nonetheless, there is no direct Si-Si bonding interaction in this compound. Calculations of localized orbitals[27] reveals two Si-H bonds, six Si-O bonds, and six O lone pairs, but no orbital with appreciable magnitude in the Si-Si region. Since the six Si-O bonds lie directly between these atoms, there is no indication of any three center or "banana bonding" between the silicons.

The steadily decreasing Si-Si distance in the sequence **1A**-**3A** thus appears to be due to purely geometric factors, rather than any electronic effects. Note that the Si-O distance increases slightly from 1.638 Å in **1A** to 1.703 Å in **3A**. Clearly the energy trade-off between crowding the silicon atoms together versus stretching the very strong Si-O bonds is resolved by preserving as short an Si-O bond as possible, at the expense of Si-Si crowding. A similar conclusion based on the constancy of the ratio of ring bond lengths to cross ring distances in homologous series was recently reached by Masamune and co-workers.[28]

The **A** series of compounds may be extended to the hypothetical **4A**, Si_2O_4. Geometry optimization within D_{4h} symmetry gives a structure with three imaginary frequencies: a degenerate e_g pair at 1327i and an a_{1u} mode at 405i cm^{-1}. **4A** is therefore not a molecule, hardly surprising as the Si atoms are no longer even approximately tetrahedral. Still, it is interesting to note that the geometry constraints noted for the **A** series persist. The SiO distance again lengthens to 1.788 Å, while the cross distance SiSi is 2.080 Å, about the same as in **3A**.

We now consider the sequence **0B**-**3B**, where in the singlet molecules the silicon atoms are formally capable of bonding. The Si-Si bond distance 2.244 Å of the oxadisilacyclopropane (**1B**) is somewhat shorter than the value of 2.393 Å in the unstrained disilane (**0B**). Note that these TCSCF distances are essentially similar to RHF results obtained for the same compounds, namely 2.200 Å for **1B** and 2.361 Å for **0B**. If *curved* bond paths rather than straight-line distances are used, the RHF bond distance in **1B** is 2.332,[18] which is essentially the same as that in **0B**. The TCSCF occupation numbers for the Si-Si σ^* orbital are corresponding small, 0.017 Å for **0B** and 0.047 Å for **1B**. The singlet states of the first two members of the sequence are thus well described by closed shell RHF wave functions. After geometry relaxation, the $\sigma \rightarrow \sigma^*$ ROHF triplet state of **1B** lies above TCSCF singlet **1B**, by about 18 kcal/mol. Of course, triplet **1B** has a greatly elongated Si-Si distance, and it is also distorted by a disrotatory ring opening into C_s symmetry. The triplet state of disilane **0B** dissociates to two silyl radicals.

The literature contains only one mention of singlet **2B**, again a theoretical calculation by Nagase and Kudo.[20] They performed RHF calculations with a basis essentially identical with that used here. Our RHF calculations give essentially the same result as theirs: a bicyclo compound with an Si-Si bond distance of 2.306 Å and a dihedral angle ω(OSiSiO) = 140°. As Nagase and Kudo point out, this RHF structure is not a minimum energy structure. Instead, it has a b_1 mode with an imaginary frequency of 734i cm^{-1}. The failure to obtain a positive definite hessian is an indication that the closed shell Lewis dot structure implied by the bicyclo drawing of **2B** may not be correct. Another clue that RHF may not be providing a good treatment of this molecule is that the lowest unoccupied MO (LUMO) of the RHF function has a negative energy! This b_1 symmetry Si-Si σ^* orbital has an energy[29] of −0.063 hartree, in contrast to a value of +0.087 hartree for the LUMO in **1B**.

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(16) **3A**: Streitweiser, A. *J. Am. Chem. Soc., Chem. Commun.* **1989**, 1261-1262.

(17) **1A, 1B**: Cremer, D.; Gauss, J.; Cremer, E. *J. Mol. Struct.* (*THEOCHEM*) **1988**, *169*, 531-561.

(18) **1B**: Boatz, J. A.; Gordon, M. S. *J. Phys. Chem.* **1989**, *93*, 3025-3029.

(19) **2B**: Nagase, S.; Kudo, T. *Organometallics* **1987**, *6*, 2456-2458.

(20) **3B**: Nagase, S.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1988**, 54-56.

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(23) (a) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE Bull.* **1990**, *10*, 52-54. (b) Contact NU070347 @ VM1.NODAK.EDU concerning this program.

(24) Duran, M.; Yamaguchi, Y.; Schaefer, H. F. *J. Phys. Chem.* **1988**, *92*, 3070-3075.

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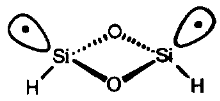
(26) O'Keeffe, M.; Gibbs, G. V. *J. Phys. Chem.* **1985**, *89*, 4574-4577.

(27) Foster, J. M.; Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 300-302.

(28) Kabe, Y.; Kawase, T.; Okada, J.; Yamashita, O.; Goto, M.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 794-796.

(29) Of course, the orbital energy for unoccupied orbitals is very dependent on the basis set. The values are quoted here only because the LUMOs of both **2B** and **3B** have negative energies and because they were all obtained with use of the equivalent atomic basis.

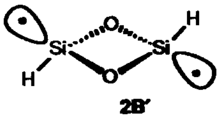
The TCSCF wave function for **2B** obtained at its bicyclo RHF geometry shows already a large biradical character. At this geometry, the electron occupation numbers are $N(\sigma) = 1.419$ and $N(\sigma^*) = 0.581$, and the corresponding TCSCF hessian is positive definite. The TCSCF energy at the RHF structure is 50 kcal/mol lower than the RHF energy! Full geometry optimization of **2B** with the TCSCF function leads to a further energy lowering of 11 kcal/mol, with a nearly planar ring and complete biradical character: $R(\text{Si–Si}) = 2.414$ Å, $\omega(\text{OSiSiO}) = 179.0°$, $N(\sigma) = 1.004$, and $N(\sigma^*) = 0.996$. This structure is essentially identical with that for triplet **2B**, $R(\text{Si–Si}) = 2.413$ Å, $\omega(\text{OSiSiO}) = 179.5°$. Thus the C_{2v} forms of both singlet and triplet **2B** are better represented as



2B

and can be thought of as arising from a doubly dehydrogenated **2A**. The two states are essentially degenerate, with the ROHF triplet lying just 0.7 kcal/mol below the TCSCF singlet, in accordance with Hund's rule. Its biradical nature makes singlet **2B** an implausible synthetic target except as a reactive intermediate, and indeed it is presently unknown in the laboratory.

It is clearly possible to imagine dehydrogenating **2A** from opposite faces, to produce the C_{2h} form **2B′**. The triplet state of



2B′

2B′ lies 1.3 kcal/mol above that of triplet **2B**. In contrast, the singlet state of **2B′** lies 6 kcal/mol below that of **2B** and possesses somewhat less biradical character than **2B**, as evidence by the occupation numbers $N(\sigma) = 1.440$ and $N(\sigma^*) = 0.560$ as well as the 0.25 eV stabilization of singlet **2B′** compared to its triplet state.

Singelt **3B** is also known only from theoretical calculations, again from the Nagase group.[15,19] Our RHF calculations on this tricyclo compound are essentially identical with Nagase's: a short Si–Si distance of 2.096 Å, with the RHF structure being an energy minimum. However, the RHF function again has a negative Si–Si σ^* orbital energy of –0.097, even larger than that for **2B**. TCSCF calculations on singlet **3B** do not change the geometry very much, as its three bridging oxygens do not give **3B** the ability to open to a full biradical. In fact, the TCSCF structure has a slightly shorter Si–Si distance of 2.084 Å, as the Si–O bonds decrease from 1.720 Å in the RHF calculation to 1.711 Å in the TCSCF. The occupation numbers show significant mixing of the LUMO into the wave function, $N(\sigma) = 1.637$ and $N(\sigma^*) = 0.363$. The large TCSCF mixing lowers the singlet energy by 36 kcal/mol! In consequence, **3B** is predicted to have a singlet ground state, with the TCSCF singlet lying 20 kcal/mol below triplet **3B**.

Superficially, it appears that there is more bonding in **3B** than in **2B′** or in **2B**, based on both the occupation numbers and the singlet–triplet splittings. However, a plot of the TCSCF orbitals is shown in Figure 1. Here the orbitals that are described in this paper as σ and σ^*, for want of a better term, are seen to be better described as nonbonding for all three molecules, as there is little electron density between the silicons in any of them. In contrast, RHF and TCSCF calculations on pentastanna[1.1.1]propellane (valence isoelectronic to **3B**) do in fact find a bonding orbital between the bridgehead tin atoms.[30] It should be noted in this regard that while this bonding interaction is small, a substituted pentastanna[1.1.1]propellane has recently been synthesized.[31] The orbitals shown in Figure 1, exposed as they are on the outer faces of the molecules, suggest experimental isolation of any of these is unlikely. On the other hand, the orbitals of **3B** afford the possibility of experimental isolation of a staffane-type[32] polymer, $-(\text{Si}_2\text{O}_3)_n-$.

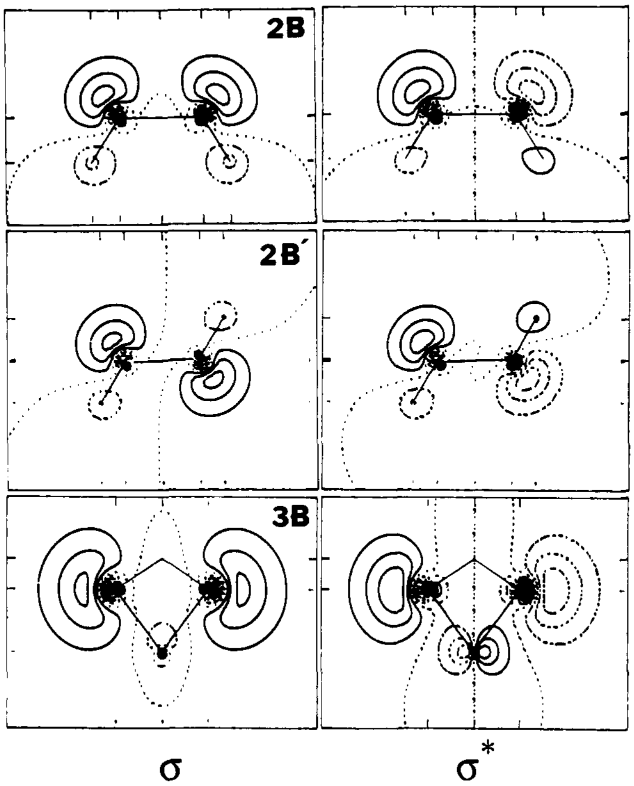


Figure 1. Contour plots of the pair orbitals in the TCSCF singlet wave functions.

Table II. Total and Orbital Energies (ϵ, hartree), and Electron Occupanices (N)

Singlet-State RHF Calculations

compd	energy	$\epsilon(\sigma)$	$\epsilon(\sigma^*)$	R(SiSi)	R(SiO)
0B	–581.304 946	–0.402	+0.134	2.362	
1B	–655.020 052	–0.345	+0.087	2.200	1.693
2B	–728.672 034	–0.279	–0.064	2.306	1.699
3B	–802.402 061	–0.379	–0.097	2.096	1.719

Singlet-State TCSCF Calculations

compd	energy	$N(\sigma)$	$N(\sigma^*)$
0B	–581.314 164	1.983	0.017
1B	–655.035 224	1.953	0.047
2B	–728.768 150	1.004	0.996
2B′	–728.777 899	1.440	0.560
3B	–802.459 245	1.637	0.363

Triplet-State ROHF Calculations

compd	energy	$\epsilon(\sigma)$	$\epsilon(\sigma^*)$
0B	–581.209 506	–0.136	–0.136
1B	–655.006 687	–0.119	–0.133
2B	–728.769 263	–0.143	–0.143
2B′	–728.767 181	–0.171	–0.116
3B	–802.426 942	–0.279	–0.181

Full details of the **0B**–**3B** wave functions described above are contained in Table II. The RHF singlet structures are presented in this table, for completeness, although as noted above these are completely incorrect for **2B**.

Conclusions

Bridging oxygen atoms are very effective at constraining bridgehead Si–Si distances. The nonbonded silicon atoms are compressed successively closer together in the sequence **1A**, **2A**,

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J. Am. Chem. Soc. **1991,** *113,* 6001-6011

and **3A**, to a value much shorter than a typical Si–Si bond, as the compounds strive to maintain their strong Si–O bonds. The strain engendered by two bridging oxygens overwhelms the possibility of Si–Si bonding in the biradicals **2B** and **2B′**. If there are three bridges as in **3B** the silicons are held at a bonding distance, but inspection of the orbitals shows **3B** is also a biradical. Thus experimental isolation of **2B**, **2B′**, or **3B** seems unlikely.

It is important to use the appropriate level of electronic structure theory to describe these compounds. RHF calculations on **2B** are completely misleading, while the use of RHF calculations for singlet **3B** does not correctly predict the multiplicity of the ground state. The availability of analytically computed TCSCF energy second derivatives, necessary to verify the existence of minima on a potential energy surface, is a key component of these calculations.

Acknowledgment. This work was supported by grants from the National Science Foundation (CHE89-11911) and the Air Force Office of Scientific Research (90-0052). All calculations were performed on a Stardent 1520 loaned to NDSU by Stardent Corp.

Nature of the Transition Structure for Oxygen Atom Transfer from a Hydroperoxide. Theoretical Comparison between Water Oxide and Ammonia Oxide

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Received November 26, 1990

Abstract: A theoretical study of the mechanism of oxygen atom transfer from hydrogen peroxide and an alkyl hydrogen peroxide is described. Ab initio molecular orbital calculations were carried out with the 6-31G* basis set (and larger basis sets for selected reactions). All key equilibrium geometries and transition states were optimized at the MP2 level; barriers were calculated at the MP4SDTQ level with use of the MP2 optimized geometry. The barrier for HOOH → H_2OO is ca. 54 kcal/mol. The reverse reaction, H_2OO → HOOH, shows no barrier at the MP4 level when the HF optimized geometries are used, but it does have a barrier of 3.9 or 3.7 kcal/mol when the geometry is optimized at the MP2 or MP4 level, respectively. By contrast, a comparatively high barrier (27 kcal/mol) is found for $H_3NO \rightarrow H_2NOH$, which is relatively insensitive to correlation effects on the geometry. The oxidation of ammonia by hydrogen peroxide is shown to be a 2-step process dominated by a 1,2-hydrogen shift (54-kcal/mol barrier) followed by a facile S_N2-like displacement (2-kcal/mol barrier) to afford $H_3NO + H_2O$. The active bonds in the transition state are generally shorter when optimized at the MP2, CASSCF, CISD, and QCISD levels than at the HF level. All four levels agree that the barrier for oxygen transfer from water oxide is very low. The $NH_3 + H_2O_2$ reaction has been compared to the two identity reactions, $H_2O + H_2O_2$ and $NH_3 + H_3NO$, and an orbital interaction picture has been developed to explain the differences. The high barrier for the 1,2-hydrogen shift (e.g. HOOH → H_2OO) that must precede all of the oxygen transfers can be dramatically lowered by adding one or two molecules of solvent water. The solvent water forms a cyclic transition state and allows the hydrogen shift to occur by a 1,4 mechanism involving a proton relay. Likewise, one and two molecules of water are shown to decrease the barrier for $NH_3 + H_2O_2$ by ca. 20 kcal/mol per solvent water relative to isolated reactants or ca. 10 kcal/mol per water relative to solvated reactants. The same behavior is found for CH_3OOH. These data suggest that the accepted mechanism for oxygen atom transfer from the hydroperoxide functional group involving a direct displacement in concert with a 1,2-hydrogen shift must be modified to include the energetics of the 1,2-hydrogen shift. An ionic pathway for oxidation of NH_3 with H_2O_2 catalyzed by one water where the hydrogen is transferred after the rate-limiting oxygen transfer has a barrier 4.3 kcal/mol higher than the above concerted process.

Introduction

Few chemical transformations are as important and diverse as those involving oxygen atom transfer. The transfer of an oxygen atom involving cleavage of an oxygen–oxygen σ bond is one of the most significant biological transformations known,[1] and this type of oxidative insertion also enjoys a unique status in synthetic organic chemistry.[2] A detailed mechanistic picture of how such transformations occur remains the goal of both experimental and theoretical chemists. One of the problems that has impeded an understanding of the mechanism of oxygen atom transfer has been the long-standing perception historically that such oxidizing reagents are electrophilic in nature and hence the transferring oxygen has often been written as having a partial positive charge. The reacting partners, such as alkenes, amines and sulfides, in such oxidation reactions typically exhibit nucleophilic properties. Consistent with this philosophy, when the nucleophilicity of a substrate such as a carbon–carbon double bond is enhanced by increasing alkyl substitution, the rate of oxygen atom transfer is increased. Conventional wisdom dictates that reagents of opposite charge have the highest attraction for each other. The idea of a highly reactive oxygen transfer reagent having a negatively charged "electrophilic" oxygen disturbs one's sensibilities, despite the fact that oxygen is the second most electronegative element.

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