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Accounts

Structure and Reactivity of Amphoteric Oxygen Species

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The structure and chemical properties of 1,3-dipolar peroxidic species (X^+–O–O^-) such as ozone (X = O), nitroso oxides or nitrenium peroxides (X = RN), carbonyl oxides or carbenium peroxides (X = R_2C), and persulfoxides or sulfonium peroxides (X = R_2S) have been attracting much attention from synthetic, biological, and theoretical standpoints. These active oxygen species can be classified into two types depending on whether the X^+ is an *enium* (carbenium, nitrenium, silylenium etc.) ion or an *onium* (ammonium, oxonium, phosphonium, sulfonium etc.) ion, and their reactivities are quite different depending on the nature of X. The individual features as well as the overviews of structure and reactivities of these X–O–O species are reviewed. Ozone and nitroso oxides have an electrophilic character while carbonyl oxides usually act as a nucleophilic oxygen transfer agent, their reactivities being controlled by substituents. It is important to see whether or not XOO species can isomerize to the cyclic isomers. Although cyclic O_3 is thermodynamically unstable, dioxiranes, the cyclic form of carbonyl oxides, have been isolated and fully characterized. It has been suggested that nitroso oxides isomerize to the cyclic form yielding the corresponding nitro compounds unimolecularly. In the case of persulfoxides (X = R_2S), the dipolar structure (X^+–O–O^-) is important, their characteristic reaction being nucleophilic *O*-transfer to sulfoxides, while $3\lambda^5$-dioxaphosphirane (X = R_3P) can exist only in the cyclic form, showing electrophilic reactivity. Effects of X's on structure and reactivity of these oxides were systematically examined by the density functional BLYP/6-31G* calculations. The inductive effect through σ-framework has been found to dominate the thermodynamic stabilities of carbonyl oxides, while the π-donating property of substituents governs the activation energy for the cyclization to dioxiranes.

In recent years, much effort has been devoted to the exploration of the active sites of oxygenases and the chemical modeling of enzyme-catalyzed oxidations by molecular oxygen;[1] transition metal-dioxygen complexes play an important role in some industrial oxidation processes.[2] The structure-reactivity relationship of such complexes is quite complicated because molecular oxygen is coordinated to the metal as a ligating group in various forms and the metal center can take various spin states and oxidation numbers. On the other hand, active oxygen species such as $O_2^{-\bullet}$, $HO^\bullet$, $HOO^\bullet$, $^1O_2$, H_2O_2, HOO^-, etc. have been extensively studied due to biological and atmospheric importance, and at present their structure and reactivities are well characterized.[3] A series of similar peroxidic X–O–O species where X includes main group elements, e.g., ozone (X = O), carbonyl oxides (X = R_2C), peroxy nitrite (X = NO^-), etc., are known, and their importance has received attention from various standpoints.[4] They may exist in either open (**1**) or cyclic (**2**) form and their reactivities are significantly dependent on the nature of X's. The electronic structure of these species is even simpler than that of metal-oxygen complexes, and the systematic evaluation of their structure and reactivity may lead to better apprehension of activated dioxygen species.

The present article intends to explain the structure and reactivity of *amphoteric* peroxy species or 1,3-dipolar peroxides, represented as X^+–O–O^-, with even-numbers of electrons (Chart 1). These species can be classified into two types, depending on whether the X^+ is an *enium* ion with an empty *p*-orbital or an *onium* ion. In the former case (*enium-peroxide* type), the π-conjugation between X^+ and peroxide is important and its electronic structures are represented either as zwitterions (X^+–O–O^-, X=O^+–O^-, etc.) or as a singlet 1,3-diradicals ($X^\bullet$–O–$O^\bullet$), and in the cyclic form, X becomes neutral with its normal valence. In the latter case (*onium-peroxide* type), no π-bond exists since all valence orbitals are filled, and the corresponding cyclic isomer is a hypervalent molecule with a bipyramidal geometry in which one of the electronegative oxygen atoms will be preferably located at the apical position (Chart 2).

Possible candidates for X^+–O–O^- and their cyclic isomers in the periodic table are shown in Table 1; peroxy candidates are classified into (a) fully characterized species (in shadow frames), (b) postulated intermediates in reactions (in solid frames), (c) hypothetical ones suggested only by theoretical calculations (in dashed frames), and (d) structures which are estimated not to exist as a local minimum on the potential

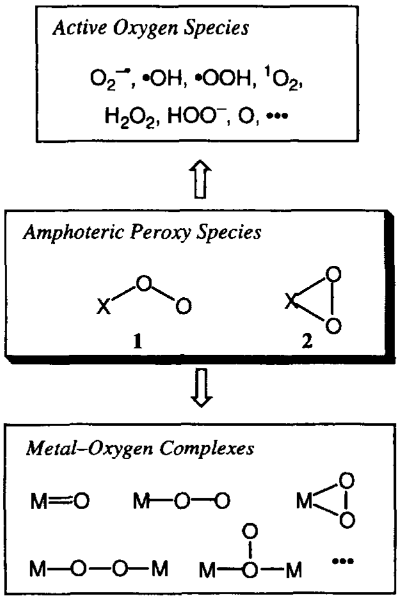


Chart 1.

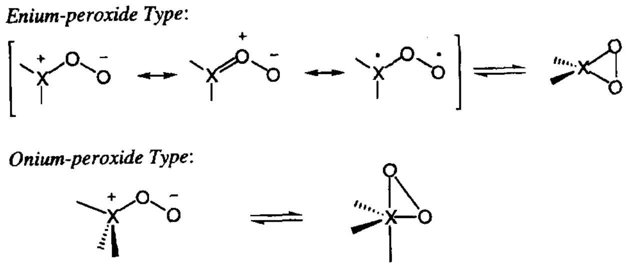


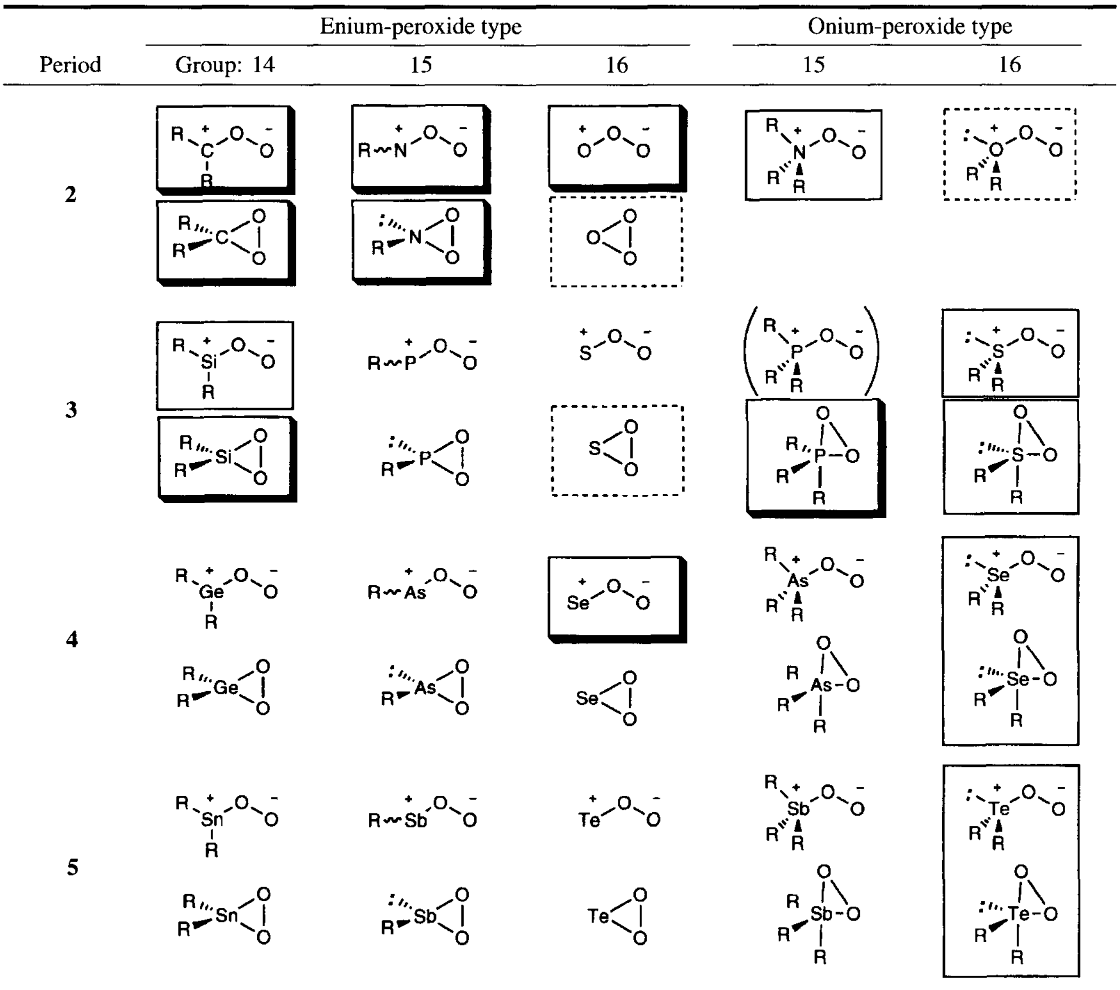
Chart 2.

energy surface (in parentheses).

Since the chemistry of X–O–O species is quite widespread, the present review focuses on a few important subjects, (a) philicity, (b) stability, and (c) fate, which are based on experimental results and explained by theoretical calculations.

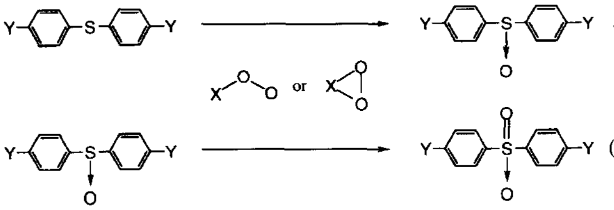
(a) Philicity, Either Nucleophilic or Electrophilic, on Oxygen-Atom Transfer Ability: A mechanistic probe for the philicity of oxidants commonly employed is the relative reactivity of sulfides vs. sulfoxides (Eqs. 1 and 2), based

Table 1. Possible Candidates for X^+–O–O^- Species and Their Cyclic Forms[a)]



a) Species are classified into (a) fully characterized species (in shadow frames), (b) postulated intermediates in reactions (in solid frames), (c) hypothetical ones suggested only by theoretical calculations (in dashed frames), and (d) structures which are estimated not to exist as a local minimum on the potential energy surface (in parentheses).

on the assumption that electrophilic oxidants preferentially oxidize sulfides while nucleophilic ones oxidize sulfoxides.



(1)

(2)

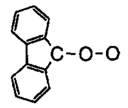
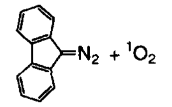
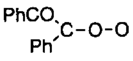
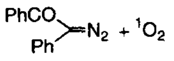
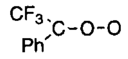
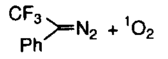
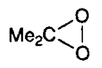
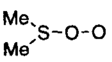
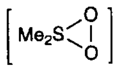
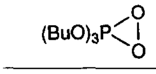
The Hammett correlations for the oxidation of aryl sulfides and sulfoxides are informative, the substituent effect on sulfoxide oxidation being of greater significance because sulfoxides are a biphilic substrate oxidized both nucleophilically and electrophilically. Here, care should be taken for a possible intermediacy of hypervalent λ^4-sulfane species in the sulfoxide oxidations.[5] Substituent effects for related oxidants are summarized in Table 2.

(b) Relative Stability and Interconvertibility Between Open and Cyclic Forms: Much structural information is available from the spectroscopic observations, and/or from theoretical calculations. As summarized in Table 1, some materials are characterized in low-temperature matrices by IR spectroscopy, in which the $^{18}O_2$ labelling experiment is useful in order to assign the O–O stretch band. Sometimes, scrambled oxygen gas, ^{16}—$^{18}O_2$, is employed to see whether two oxygen atoms are equivalent or not, e.g., to distinguish the O–O stretches of X–^{16}O–^{18}O and X–^{18}O–^{16}O.[6]

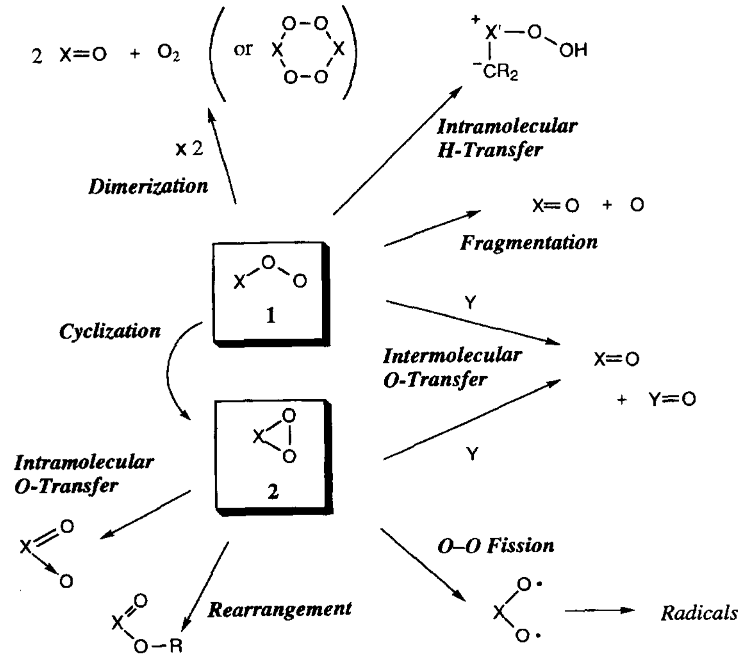
Except for ozone, open forms of XOO species are short-lived reactive intermediates because of their zwitterionic nature, while cyclic forms without formal charges may be stable, as in the case of isolable dioxiranes (X = R_2C),[7] but suffer from strains of the three-membered ring. Therefore, the relative stability between open and cyclic forms depends on many factors, e.g., electronegativity of X, X–O bond energy, etc.

(c) Fate of Peroxidic Species in the Absence of Trapping Agents: Typical deactivation pathways of these species are shown in Scheme 1, which can be classified into two styles leading to either mono- or di-oxygenated products. One oxygen loss via unimolecular or bimolecular processes leads to the formation of X = O species. On the other hand, the second oxygen atom may be incorporated in rearranged products or transferred intramolecularly affording XO_2 species if X has a lone pair. In such cases, mechanistically most important is whether the two oxygen atoms in the products are originated from the same oxygen molecule or not. The $^{16}O_2$–$^{18}O_2$ tracer experiments are useful to distinguish between intra-

Table 2. Substituent Effect on Oxygen Atom Transfers to Sulfides and Sulfoxides by Peroxy Species

Suggested intermediate	Method of generation	Reaction	ρ vs. σ	$\frac{Ph_2S}{Ph_2SO}$	Ref.
O–O–O		$Ar_2SO \to Ar_2SO_2$	−1.17	13	12
ArN–O–O	Ar–N:+$^3O_2$				
Ar = C_6H_5		$Ar_2S \to Ar_2SO$	−0.93 (0.24)[a]	5.7	12
		$Ar_2SO\{\to Ar_2SO_2$	−0.64		12
		$\to Ar_2S$	−0.34		12
Ar = 4-$MeOC_6H_4$		$Ar_2S \to Ar_2SO$	(0.25)[a]		52
Ar = 4-$O_2NC_6H_4$		$Ar_2S \to Ar_2SO$	(0.25)[a]		52
		$Ar_2SO \to Ar_2SO_2$	+0.26	0.06	25
 $PhCO(Ph)C{-}O{-}O$	 $PhCO(Ph)C{=}N_2 + {}^1O_2$	$Ar_2S \to Ar_2SO$	−0.32 (0.94)[a]		81
 $CF_3(Ph)C{-}O{-}O$	 $CF_3(Ph)C{=}N_2 + {}^1O_2$	$Ar_2S \to Ar_2SO$	−0.84 (0.54)[a]	0.61	27
		$Ar_2SO\{\to Ar_2S$	−0.74		27
		$\to Ar_2SO_2$	−0.64		27
	$Me_2CO + SO_5^{2-}$	$ArSMe \to ArSOMe$	−0.77		28
		$ArSOMe \to ArSO_2Me$	−0.76		28
 $Me_2S{-}O{-}O$	$Me_2S + {}^1O_2$	$Ar_2SO \to Ar_2SO_2$	+0.25		67
		$Ar_2S \to Ar_2SO$	(0.24)[a]		67
	$(BuO)_3P + {}^1O_2$	$Ar_2SO \to Ar_2SO_2$	−0.63	4	85

a) Relative reactivity of $(4\text{-}ClC_6H_4)_2S$ vs. Ph_2S.



Scheme 1.

and intermolecular processes; i.e., the formation of $^{16}O^{18}O$ products from a mixture of $^{16}O_2$ and $^{18}O_2$ undoubtedly implies the involvement of bimolecular processes.

1. Enium-Peroxide Type

The enium-peroxides are adducts between O_2 and electron deficient species with a sextet of valence electrons, e.g., carbenes or nitrenes. These are 1,3-dipolar species and are classified, according to Huisgen's descriptions,[8] as *1,3-dipoles without a double bond but with internal octet stabilization.* The 3-center 4-electron π-system in enium-peroxide type peroxides is isoelectronic with $C{=}C{-}C^-$, in which the central electronegative oxygen atom lowers the π-LUMO energy but changes the π-HOMO energy very little. Accordingly, the active oxygen species of this type have relatively high-lying HOMO and low-lying LUMO, and hence these peroxides may be nucleophilic, electrophilic, or both, as in the other 1,3-dipoles, displaying U-shape Hammett correlations in their reactivities toward dipolarophiles.

Another feature in these 1,3-dipoles concerns their diradical characters.[9] Since the electronic structure of these species can be represented as a singlet 1,3-biradical ($X^\bullet{-}O{-}O^\bullet$) rather than a zwitterion ($X^+{-}O{-}O^-$ or $X{=}O^+{-}O^-$), the radical-like reactivities such as hydrogen abstraction from C–H bonds have often been proposed for these species.[10] On the other hand, the spin-paired diradical structure of 1,3-dipoles is not directly related to radical reactivity,[11] and in a theoretical description at HF-level calculations the diradical nature vanishes when solvent effects are included.[12]

1.1. Ozone (X = O) and Other Chalcogenide-Analogues. The electrophilic nature of ozone (**1**, X = O) has been well established in ozonation chemistry as well as in their oxygen transfer reactivities.[13] Ozone oxidizes diphenyl sulfide 13 times faster than diphenyl sulfoxide, and substituted diphenyl sulfoxides are oxidized electrophilically as indicated by the negative ρ-value of -1.17 (vs. σ).[14]

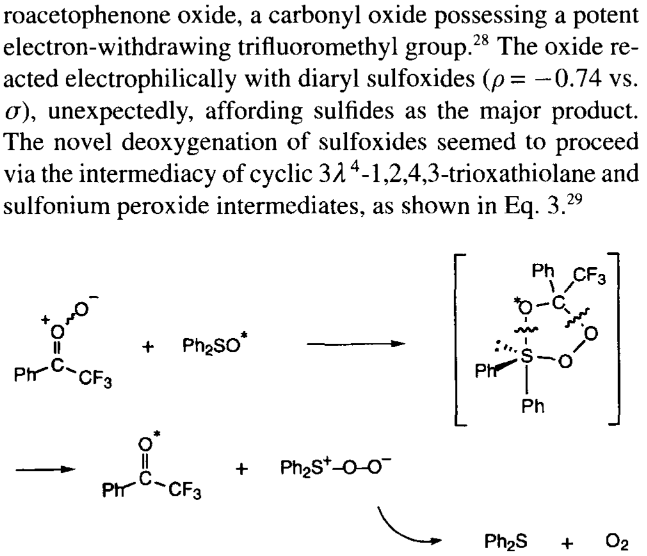
Ozone is stable at ambient temperature and essentially has no radical reactivity. Toward hydrocarbons (R–H), ozone inserts into C–H bonds via a concerted manner,[15] but the resulted hydrotrioxides (R–O–O–O–H) easily decompose and the fragments bring about radical reactions.[16] Upon photolysis, ozone does not cyclize but decomposes into O_2 and atomic oxygen in singlet or triplet spin multiplicities depending on the irradiation wavelength.[17] There has been no experimental evidence on the presence of cyclic ozone isomer (**2**, X = O), and recent ab initio calculations give estimates that the cyclic O_3 is a local minimum but 28—29 kcal mol^{-1} higher in energy than the open form.[18]

Little has been known about chalcogenide-equivalents of ozone. Typically, by the photochemical reaction of S_2 with O_2 in low temperature matrices, a lot of S_xO_y species were characterized spectroscopically, but not the sulfur analogue of ozone (S–O–O).[19] The cyclic form of SO_2 is estimated to be highly unstable, the exothermicity on the ring opening to sulfur dioxide being as high as ca. 90 kcal mol^{-1}.[20] The selenium analogue (Se–O–O) was identified recently;[21] it showed the O–O stretch band at 1061 cm^{-1} and was assigned by theoretical calculations as a singlet 1,3-dipole similar to ozone.

1.2. Carbonyl Oxides and Dioxiranes (X = R$_2$C). Carbonyl oxides are known as important intermediates formed in ozonolyses of olefins and can be generated cleanly by the reaction of carbenes and $^3O_2$[22] or by the $^1O_2$ oxidation of diazo compounds.[23] Their structure and reactivities have been of interest from various standpoints.[24] Dioxiranes, cyclic isomers of carbonyl oxides, can be prepared from ketones and monoperoxysulfate[7] and have been utilized as powerful and versatile oxygen transfer reagents.[25] Recently, we reviewed novel aspects of carbonyl oxide chemistry.[26] Pertinent points are summarized briefly in the following:

(a) In contrast to the electrophilic nature of ozone, carbonyl oxides generally possess nucleophilic reactivities.[27] Typically, the relative reactivity of fluorenone oxide toward Ph_2S vs. Ph_2SO was as low as 0.06 and the substituent effects for diaryl sulfoxides led to Hammett ρ-value of +0.26 (vs. σ),[27] which is consistent with the highly polarized zwitterionic structure of carbonyl oxides, R_2C^+–O–O^-, similar to peroxide anion (R–O–O^-).

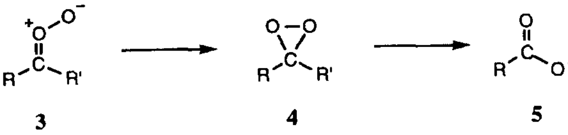
The reactivities of carbonyl oxides, however, can be controlled or even reversed by choosing substituents. Thus, quite unique chemistry has been revealed for α,α,α-trifluoroacetophenone oxide, a carbonyl oxide possessing a potent electron-withdrawing trifluoromethyl group.[28] The oxide reacted electrophilically with diaryl sulfoxides ($\rho = -0.74$ vs. σ), unexpectedly, affording sulfides as the major product. The novel deoxygenation of sulfoxides seemed to proceed via the intermediacy of cyclic $3\lambda^4$-1,2,4,3-trioxathiolane and sulfonium peroxide intermediates, as shown in Eq. 3.[29]



(3)

The reactions of 3,3-dimethyldioxirane (**4**, R = R′ = Me) with methyl *para*-substituted phenyl sulfides and sulfoxides showed the linear correlations with ρ-values of −0.77 and −0.76 (vs. σ), respectively,[30] showing their electrophilic *O*-transfer ability owing to the electron-deficient nature of the strained O–O bond.

(b) Calculations predict that the cyclization of carbonyl oxide (**3**, R = R′ = H) to dioxirane **4** is exothermic but is separated by a relatively high activation energy of 18—24 kcal mol^{-1}.[31] Upon the irradiation, carbonyl oxides generated in low temperature matrices either rearrange to dioxiranes or split off an oxygen atom, and the photochemical sequence of Eq. 4 was established as a two photon reaction:



(4)

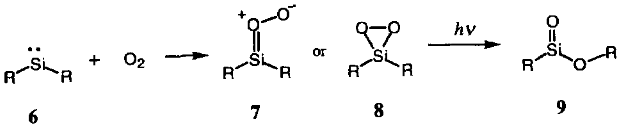
Ground-state reactions in solutions are not necessarily equal to the processes under the matrix-isolated conditions or to those in gas phase originating from intermediates in electronically or vibrationally excited states. In early studies on dark reactions, similar schemes were proposed for the rearranged products **5** occasionally obtained as side-products from carbonyl oxides. Later, the thermal unimolecular rearrangement such as Eq. 4 was ruled out for typical carbonyl oxides examined by the $^{16}O_2$–$^{18}O_2$ tracer experiments.[32]

On the other hand, an exceptional case of dioxirane formation during olefin ozonolyses was reported by Kopecky et al.[33] for carbonyl oxide **3** with R = Ph and R′ = OMe. It is shown that the oxide carrying strong π-donating methoxy substituent actually undergoes thermal isomerization to dioxirane in solutions. We also found on the photooxidation of $Ph(CF_3)C{=}N_2$ that the carbonyl oxide with R = Ph and R′ = CF_3 was converted to a secondary intermediate which could epoxidize olefins. Since the epoxidation was stereospecific and electrophilic (negative ρ-value of −1.66 (vs. σ) toward substituted styrenes), the dioxirane **4** with R = Ph and R′ = CF_3 was proposed for the oxidant formed by the isomerization of the corresponding carbonyl oxide.[29]

(c) The time-resolved absorption spectroscopy has revealed that the decay kinetics of carbonyl oxides in solutions are second order in the oxides.[34] Thus, the major deactivation pathway of carbonyl oxides is a bimolecular reaction between two oxide molecules affording two carbonyl compounds and one oxygen molecule. Based on an earlier $^{16}O_2$–$^{18}O_2$ labelling study which found no scrambling in evolved oxygen gas, an electrocyclic-type mechanism through a six- or five-membered transition state was suggested. On the other hand, the thermal decomposition of dioxiranes generates alkyl radicals[35] via the O–O fission followed by the decarboxylation.[36]

The most definitive results on the above three subjects were provided by Sander and co-workers,[37] who successfully observed dimesitylketone *O*-oxide (**3**, R = R′ = 2,4,6-$(CH_3)C_6H_2$) by NMR spectroscopy in freon or THF solutions. This finding unambiguously indicates that carbonyl oxides are thermally stable if stabilized kinetically with bulky substituents, and that they have no radical reactivity such as hydrogen abstraction from hydrocarbons. The thermolysis of the carbonyl oxide leads to the formation of the corresponding ketone and the hydroxylation of *o*-CH_3 group. The corresponding dioxirane was yielded quantitatively by the irradiation but not by the thermal reaction of the carbonyl oxide. Dimesityldioxirane (**4**, R = R′ = 2,4,6-$(CH_3)C_6H_2$) was also stable and even isolable as a solid.[38] Thus, the photochemical process of Eq. 4 is operative both in solutions and in low temperature matrices.

1.3. Silanone Oxides (X = R_2Si). In contrast to the reaction of carbenes, only a little has been known about the reaction of silylenes with O_2. Although laser photolysis experiments indicate that silylenes **6** rapidly react with oxygen,[39] no definitive characterization of the intermediates or product studies have been done in the solution phase reactions. The matrix isolation of silylene–O_2 adduct has been reported by Ando et al.[40] and by Sander et al.[41] In the former, the adduct of dimesitylsilylene and O_2 showed a strong IR absorption at 1084 cm^{-1}, which was assigned as dimesitylsilanone *O*-oxide (**7**, R = mesityl) on the basis of isotropic labelling experiments. In contrast, Sander reported that the IR band of an O_2 adduct of dimethylsilylene was observed at 1021 cm^{-1}, which did not split on the ^{16}—$^{18}O_2$ experiment. This compound was photolabile and upon irradiation rearranged to methoxylmethyl silanone (**9**, R = Me). These findings led to the assignment of this adduct as dimethyldioxasilirane **8**.



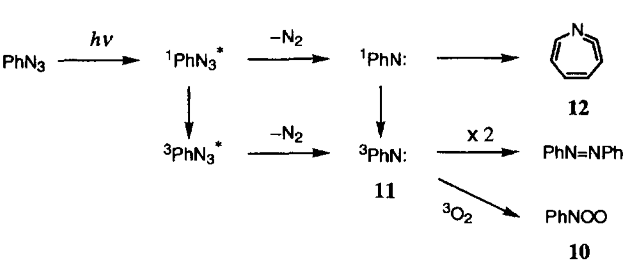
(5)

According to the MP2/6-31G* calculations,[41] the silanone *O*-oxide **7** (R = H) does exist in singlet state, but the corresponding dioxasilirane **8** is much more stable by 63.8 kcal mol^{-1}. Because of the larger exothermicity than that for carbonyl oxide (29 kcal mol^{-1}), the activation energy of cyclization to dioxasilirane of only 6.5 kcal mol^{-1} is much lower than that of carbonyl oxide (22.8 kcal mol^{-1}) at the same level of theory.[31]

Although the chemistry of carbenes and silylenes may be extended to the higher homologues, germylenes (R_2Ge:) and stannylenes (R_2Sn:),[42] O_2 adducts of these species are not known as yet since they are generally unreactive toward molecular oxygen.

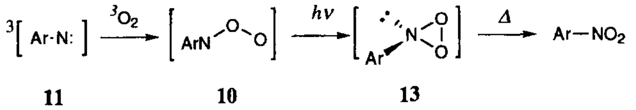
1.4. Nitroso Oxides (X = RN). The chemistry of nitroso oxides (RNOO) is important not only for the analogies of ozone and carbonyl oxides but also in relation to the NO_x chemistry and properties of peroxynitrite, $O{=}NOO^-$ ($R = O^-$), which is known as a biological toxin oxidizing lipid membranes which possibly contributes to cell death and tissue injury.[43] From the periodic table, one may expect an intermediate situation, i.e., between ozone and carbonyl oxides, for nitroso oxides. Theoretical calculations[44] predicted that the cyclic HNO_2 is less stable than HNOO and that the activation energy for the cyclization of HNOO was quite high, 45 kcal mol^{-1}. Then, it may be assumed that nitroso oxides do not isomerize to the corresponding cyclic form, as do ozone and carbonyl oxides. However, the experimental results were not so simple, as summarized below.

Nitrosobenzene *O*-oxide (**10**) is possibly formed from triplet phenylnitrene (**11**) and oxygen besides the complex reactions of aromatic azides.[45] When phenyl azide is photolyzed in solutions, the singlet nitrene rapidly undergoes the ring expansion to form a dehydroazepine (**12**) which reacts with the azide, leading to formation of polymeric tarry materials.[46] In low temperature matrices, triplet arylnitrenes were observed by ESR or IR spectroscopy; **12** was reversibly formed by the photochemical conversion of nitrenes.[47] To observe nitroso oxides directly in solutions, attempts were made by laser flash technique for 4-nitrophenyl-[48] and 2,4,6-tribromophenylnitrenes,[49] which do not cyclize to dehydroazepines; the nitrenes dimerized rapidly and did not appreciably react with $^3O_2$ within the time scale of the spectroscopy, i.e., the rates were less than 1×10^6 M^{-1} s^{-1}.



(6)

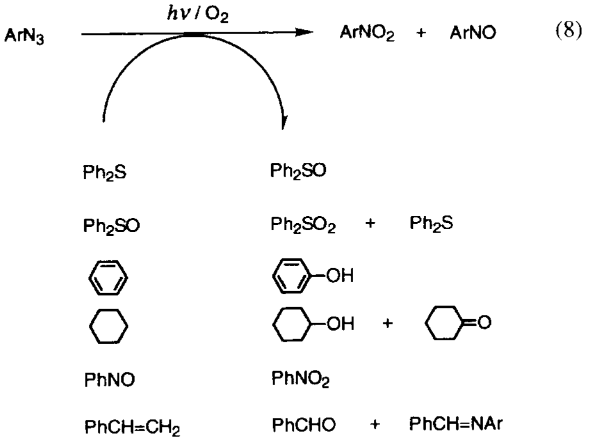
In low-temperature matrices, an earlier ESR study on the reaction of mononitrene of *p*-diazidobenzene and oxygen was reported,[50] which revealed the formation of unknown triplet species ($D = 0.11$ cm^{-1}). This was tentatively assigned as a triplet biradical form of nitrosoarene oxides ($^3ArN^{\bullet}{-}O{-}O^{\bullet}$). Recently, the low-temperature reactions with $^3O_2$ were reexamined by Bendig et al. for nitrenes from stilbene-type aryl azides,[51] showing the formation of intermediates with broad absorption bands around 500 nm. These species, assigned as nitroso oxides, were ESR-silent; i.e., not biradical but singlet species. Upon photolysis, the oxides were converted to other intermediates, which were assigned as three-membered peroxides, dioxaziridines **13**, from the similarity to photochemical transformation of carbonyl oxides to dioxiranes. These species were shown to undergo thermal reaction leading to nitro compounds (Eq. 7). The transformation proceeded at 77 K with the rate constant of 3×10^{-3} s^{-1}, implying that the barrier does not exceed a few kcal mol^{-1}. They calculated with DFT methods for the ring-opening of 3-phenyldioxaziridine to nitrobenzene a much higher activation energy of 18.8 kcal mol^{-1}. More direct information such as IR spectra is desired about the structures of the intermediates involved.



(7)

In solutions, it has been known that photolyses of aryl azides under oxygen atmosphere afford the corresponding nitrobenzenes in low yields.[52] The involvement of nitroso oxide intermediates **10** has been assumed, albeit with no direct evidence. From the $^{16}O_2$–$^{18}O_2$ tracer study, we found that nitrobenzenes were formed unimolecularly from one oxygen molecule, suggesting the thermal rearrangement of **10** via its cyclic form **13** (see Eq. 7).[53]

Oxygen transfers occur to various substrates added during the photooxidation of azides, as shown in Eq. 8.[14] Typically, sulfides were oxidized to sulfoxides, and the oxygenation and deoxygenation of sulfoxides proceeded concurrently, as in the previous case of $Ph(CF_3)COO$ (Eq. 3). The substituent effects on diphenyl sulfides and sulfoxides resulted in the negative ρ-values, indicating an electrophilic nature of the intermediate involved. The hydroxylation of aromatic ring was more efficient for benzenes with electron-donating groups in the order of anisole > toluene > benzene > chlorobenzene. For the cases of toluene and anisole, the side chain oxidation proceeded competitively, and even saturated hydrocarbons were oxidized, although in quite low yields. The loss of stereochemistry in the C–H oxidations proved that electrophilic radical species was involved. Trapping of the intermediates by added nitrosobenzenes, an well-known spin-trapping reagent, was most efficient, approaching 80% *O*-transfer. Reaction with styrenes gave C–C cleavage products, not affording epoxides. These *O*-transfer reactivities have shown that the active oxygen species in the photooxidation of azides behave as an electrophilic peroxyl radical. The relative reactivity order (styrene, PhN=O $\gg$ Ph_2S > Ph_2SO > PhH) was obtained from competitive trapping experiments.



13

The effect of substituents (*p*-MeO and *p*-NO_2) on azides was examined,[54] revealing that selectivities on the hydroxylation of benzenes and those on the reactions with sulfoxides were significantly affected by the substituents. Nitroso oxide with *p*-MeO group seemed to have a longer lifetime, since % *O*-transfer were > 50% for trapping with PhN=O, Ar_2S, and Ar_2SO. Since *p*-nitrophenylnitrene does not cyclize to dehydroazepine, the intervention of the seven-membered isomer seems to be ruled out in the co-oxidation reactions. The trapping of additives with peroxidic intermediates with *p*-NO_2 substituent was significantly less efficient, reflecting its much shorter lifetime.

Although it was assumed that nitroso oxides have intermediate reactivity values between ozone and carbonyl oxides, the radical-like reactivity shown in the photooxidation of azides is apparently not in line with others. Such oxidation reactions may be attributed not solely to nitroso oxides, but it is apparent from trapping experiments that a single intermediate is formed with over 50% selectivity. Thus, experimental results do not agree with theoretical calculations which predict that they do not have radical-like reactivities and the thermal unimolecular rearrangement affording nitrocompounds is unfavorable. Aryl-substituents may alter the electronic structure of nitroso oxides, as in other nitrogen-centered intermediates, e.g., arylnitrenes (Ar–N:)[55] and nitrenium ions ($Ar\text{–}NH^+$)[56] with significant double-bond character in the C–N bonds. Further experimental and theoretical examinations will elucidate the properties of intermediates in the nitrene–O_2 reactions.

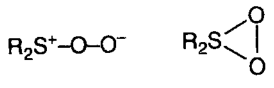
2. Onium-Peroxide Type

The structure of the onium-peroxide type 1,3-dipoles can be regarded as a charge-transfer (CT) complex of X and singlet oxygen. As noted in recent reviews,[57] bimolecular quenching of singlet oxygen by organic molecules containing π-bonds or heteroatoms can be explained in terms of exciplex formation, either reversibly or irreversibly, followed by competing reactions involving energy transfer, electron transfer, and chemical reactions. Physical quenching by charge transfer interactions was first demonstrated for amines, the efficiency of which increases with decreasing the ionization potential of the amines.[58] The present review treats only active oxygen species with *O*-transfer ability as the cases for quenchings by several kinds of sulfur- or phosphine-containing compounds. Photo-oxidation of selenides[59] and tellurides[60] with $^1O_2$ has also been found to afford the corresponding mono-oxides or their hydrates, but the mechanism has not been investigated in detail.

Another important electronic structure often proposed is a contact radical ion pair of $X^{+\bullet}$ and $O_2^{-\bullet}$, which may exist as a local minimum, especially on the triplet potential energy surface. In fact, a recent theoretical study has indicated that the oxygen adduct of water ($H_2O\text{–}O\text{–}O$) can exist as a triplet complex of $H_2O^{+\bullet}$ and $O_2{}^{-\bullet}$, which is suggested as a participant in the photonucleation of water droplets.[61] Here, it should be kept in mind that the radical cations of substrates and superoxide ion are occasionally generated on the $^1O_2$ reactions in polar solvents,[62] resulting in different types of reactions.[63]

2.1. Persulfoxides and Thiadixiranes ($X = R_2S$). Reactions of singlet oxygen with sulfides affording sulfoxides and sulfones,[64] have been extensively studied for over the past three decades. Many intermediates such as sulfonium peroxides or persulfoxides **14** and $3\lambda^4$-dioxathiiranes or thiadioxiranes **15** have been proposed,[65] but the overall oxygenation mechanism is not yet clarified (Chart 3).

A spectroscopic study on the O_2 adducts of various sulfides was reported by Akasaka, Yabe, and Ando,[66] in which the formation of adducts by irradiating the CT band of sulfide–$^3O_2$ complex in low-temperature oxygen matrix was evidenced by IR absorption bands at 997—1034 cm^{-1}. On the basis of ^{16}—$^{18}O_2$ isotropic labelling experiments showing that two oxygen atoms were not equivalent, the adducts were assigned as persulfoxides (**14**), which seemed to be supported by ab initio MP2/6-31G* calculations for H_2SOO predicting the S–O stretch band at 1023 cm^{-1}. The structural assignment, however, should be reevaluated, because the apical and equatorial oxygens in hypervalent thiadioxiranes (**15**) are also not equivalent. Subsequent theoretical

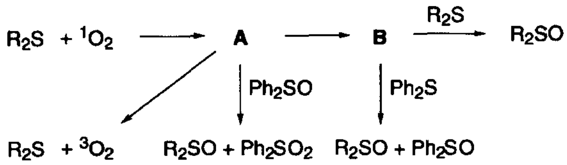


14 **15**

Chart 3.

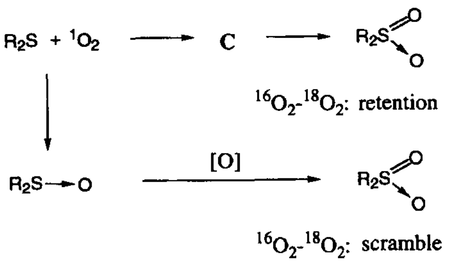
studies by Jensen on Me_2SOO and cyclic Me_2SO_2 implied that the observed isotopic shifts were only compatible with those calculated for thiadioxirane at 807 cm^{-1}. However, the structural assignment seems not to be definitive as yet, since the deviation of the calculated frequencies from the experimental ones is too large.

In solutions, the quenching of singlet oxygen by organic sulfides affords the formation of sulfoxides and sulfones.[67] After the pioneering work by Foote et al. by competitive trapping experiments,[68] it has been believed that the reaction in aprotic solvents involves at least two intermediates, as shown in Eq. 9; that is, the primary peroxidic intermediate **A** is converted into a secondary intermediate **B**. The former does not react with sulfides but is trapped by sulfoxides, while **B** is electrophilic and can oxidize sulfides. The intermediacy of zwitterionic persulfoxides (**14**) as **A** is widely accepted because of the nucleophilic oxygen-atom transfer ability.[69] Cyclic thiadioxirane (**15**) was proposed for the second species **B**, which may oxidize sulfides electrophilically.[70]



(9)

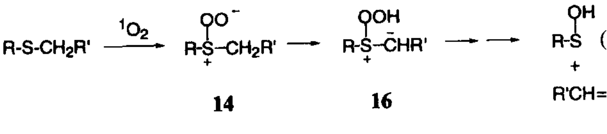
We found from the $^{18}O_2$–$^{18}O_2$ -tracer experiments that the photooxidation of sulfides yielded a mixture of sulfones with retention or scrambling of the two oxygen atoms (Eq. 10), the latter (scrambling) being afforded by the secondary reaction of sulfoxides.[71] At the initial stage of the photoreaction, the former (retention) was predominant, indicating that the sulfones were formed directly from sulfides and single molecules of O_2. The yields of retention sulfones were not affected by the initial concentration of sulfides or by the addition of diphenyl sulfide or sulfoxide. These facts suggest the presence of another intermediate **C** different from **B** in Eq. 9. This **C** is most likely **15**, which will undergo unimolecular rearrangement to afford sulfones. Above all, arguments were focussed on the participation of cyclic thiadioxiranes (**15**) in the formation of either sulfoxides or sulfones.



(10)

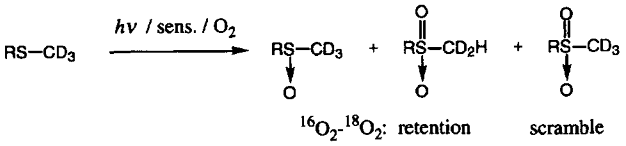
The first theoretical study on the sulfide–O_2 adducts was reported by Jensen and Foote.[72] They demonstrated an energy minimum for the open form, persulfoxide (**14**), but not for **15** on H_2S+O_2 potential energy surfaces. Later, the cyclic structure could be found as a local minimum by us,[71] Jensen,[73] and Foote et al.,[74] indicating that such calculations on **15** were quite sensitive to the level of theory. According to the MP2/6-31G* calculations for Me_2S+O_2 system,[73] **14** and **15** were almost isoenergetic, at least in the gas phase. However, the calculated barrier for conversion of **14** to **15** was quite high (> 20 kcal mol^{-1}), and no transition state was found for the direct formation of **15** by concerted reactions of Me_2S and $^1O_2$. Thus, the formation of **15** in the $^1O_2$ oxidation of sulfides was not reproduced at this level of theory.

Another important reaction of sulfides bearing active α-C–H bonds is C–S cleavage leading to fragmentation products (Eq. 11).[75] Suggested in these reactions is the third peroxidic intermediate, *S*-hydroperoxysulfonium ylide (**16**), which will be formed by the intramolecular abstraction of α-proton and may act as active species for epoxidations of olefins.[76]



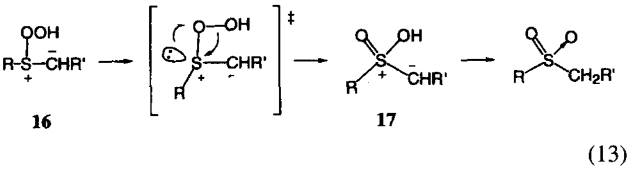
(11)

We have recently found from deuterium labelling experiments that the sulfone formation accompanies, unexpectedly, an exchange of one α-hydrogen atom.[77] That is, H–D exchange in the methyl group was observed during the formation of sulfones in the reaction of singlet oxygen with dimethyl-d_6 sulfide or thioanisole-α,α,α-d_3 in aprotic solvents (Eq. 12).



(12)

The hydrogen incorporated in the sulfones was shown to come from adventitious water, since the oxidation of $C_6H_5SCH_3$ in the presence of D_2O led to the formation of mono-deuteriated sulfone. The $^{16}O_2$–$^{18}O_2$ tracer study demonstrated no oxygen scrambling in the dedeuteriated sulfones. All the results indicate that the sulfones are formed intramolecularly via an intermediate possessing one activated proton exchangeable with trace water, a suggested structure for which is *S*-hydroperoxysulfonium ylide (**16**).



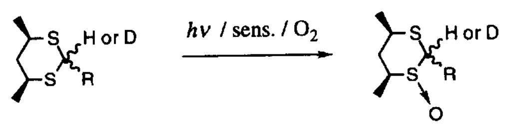
(13)

Kinetic isotope effects (k_H/k_D = 2—4) observed for methyl protons in the sulfone formation suggest that the rate-determining step is the intramolecular proton abstraction in the persulfoxides (**14**) generating *S*-hydroperoxysulfonium ylides. The conversion of ylides **16** to sulfones involves an 1,2-shift of OH group from O to S atom (Eq. 13) affording a *S*-ylide of sulfinic acid (**17**), i.e., a tautomer of sulfone. Such a pathway was qualitatively reproduced by semi-empirical PM3-calculations[77] and, more recently, confirmed by high-level ab initio calculations by McKee[78] and by Jensen et al.[79] The transformation from persulfoxides (**14**, R = CH_3) to

S-hydroperoxysulfonium ylides (**16**, $R = CH_3$, $R' = H$) has a very small activation energy of < 6 kcal mol^{-1}, and the following 1,2-shift of OH is also a viable reaction with a relatively low barrier of 8—12 kcal mol^{-1}.

Thiadioxiranes (**15**) are now shown not to be involved as intermediate **C** in Eq. 10, at least for simple sulfides. According to a series of studies by Clennan et al.,[80] the participation of thiadioxirane as the sulfoxide-forming intermediates (**B**) seems to be valid for the case of sulfides with heteroatom-substituents, which at apical position will stabilize a sulfurane structure such as **15**. However, the oxidation via **B** becomes predominant pathway at low temperature,[69,81] indicating that the activation energy for the conversion of **14** to **B** should be much lower than those of other competing processes. According to theoretical predications,[73] the activation energy for the conversion of **14** to **15** will not be so low, and hence the proposed intermediacy of **15** as **B** is not consistent with the calculation.

Recently, Jensen has proposed hydroperoxysulfonium ylides (**16**) not only as the intermediates **C** for sulfone formation but as **B** for sulfoxide formation.[79] This interpretation respecting **16** as the common intermediate seemed inconsistent with experiments since i) the H/D exchange and kinetic isotope effect (k_H/k_D) of α-hydrogen were observed only for sulfone formation, not for sulfoxide, and ii) the addition of sulfides or protic solvents affected sulfoxide formation but not sulfone formation. The absence of H/D exchange was explained by strong hydrogen bonding between H on HOO and ylide carbon of **16**. If one looked at the MP2/6-311+G(2df) optimized geometry of **16** with C$\cdots$H distance of 3.15 Å, such a strong interaction seemed not to be expected. More recently, Clennan et al. reported moderate kinetic isotope effects ($k_H/k_D = 1.3$—1.6) for sulfoxide formation from substituted 1,3-dithianes (Eq. 14).[82] Since the sulfoxide formation is not the exclusive pathway in this case, the generality of the kinetic isotope effect is not clear.



(14)

At least, we should consider another pathway to sulfoxides other than via ylides **16**, since the $^1O_2$ oxidation of some sulfides without α-hydrogens such as di-*t*-butyl sulfide is actually proceeding. The sulfoxide formation in aprotic solvents was found to be significantly affected by trace amounts of adventitious water, suggesting an adduct of water with persulfoxide **1** as a possible structure for **B**. In protic solvents, the reactivity of the intermediate is different from those in aprotic solvents, for which a hydroperoxy-λ^4-sulfane (**18**)[68] or a hydrogen-bonded persulfoxide (**19**)[69] are proposed (Chart 4). In protic solvents, it has been considered that the oxidations of sulfides ($\rho = -0.61$ vs. σ)[83] and of sulfoxides ($\rho = -0.05$ vs. σ)[69] occur electrophilically from one common oxidant. However, the relative reactivity of Ph_2S vs. Ph_2SO of 0.2 suggests the involvement of nucleophilic oxidants,[68,69] and quite complex solvent effects have been observed for alcohols,[84] indicating that persulfoxide interacts with protic solvents at various modes.

18 **19**

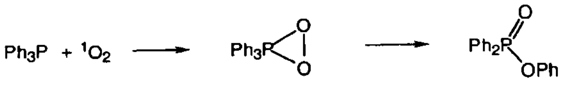
Chart 4.

Thus, the $^1O_2$ reaction of sulfides is much more complex than earlier estimations and, in spite of numerous studies, not fully characterized as yet. A further detailed study on the effect of protic solvents may clarify the structure of the intermediates involved.

2.2. Phosphadioxane ($X = R_3P$). The singlet oxygen oxygenation of phosphines and phosphites was reported to give phosphine oxides and phosphates in good yields[85] and the quenching rates by phosphites have been determined directly.[86] The intermediates in the singlet oxygen reaction of phosphites have been studied by trapping and tracer experiments.[87] Trapping study with diphenyl sulfides and sulfoxides on the $^1O_2$ oxidation of $(BuO)_3P$ revealed that the added substrate and the reactant phosphite are competing for the same intermediate. The relative reactivity of $(BuO)_3P/Ph_2S/Ph_2SO = 300:4:1$ and the negative ρ-value of -0.63 (vs. σ) for diphenyl sulfoxides were obtained. Such electrophilic *O*-transfer activity is not consistent with 1,3-dipolar phosphonium peroxides (R_3P^+–O–O$^-$), but indicative of cyclic λ^5-dioxaphosphiranes (**20**).

$$R_3P + {}^1O_2 \longrightarrow [\textit{active oxygen species}] \xrightarrow{R_3P} 2R_3P{=}O \qquad (15)$$

Similar results were obtained for the $^1O_2$ oxidation of Ph_3P, where a small amount (ca. 1%) of rearranged phenyl diphenylphosphinate was formed in addition to triphenylphosphine oxide (Eq. 16). Intermediacy of λ^5-dioxaphosphiranes was supported by the ^{16}O–^{18}O tracer study which indicated that the rearranged product was formed unimolecularly from $^1O_2$ and the phosphine. Such a rearrangement was also proposed by Jenkins et al.[88] on a reaction of triphenylphosphine with diethyl azodicarboxylate followed by the addition of hydrogen peroxide (Eq. 17), in which the major product was the phosphinate and only a small amount of $Ph_3P{=}O$ was formed. The product distribution different from those in the $^1O_2$ oxidation of Ph_3P is reasonable since the λ^5-dioxaphosphiranes (**20**) is generated in a Ph_3P-free condition without any trapping agents for the peroxide formed. Thus, the rearrangement of λ^5-dioxaphosphiranes is acceptable as the predominant pathway in the absence of efficient trapping agents.



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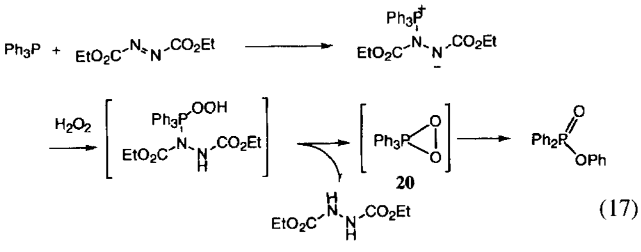
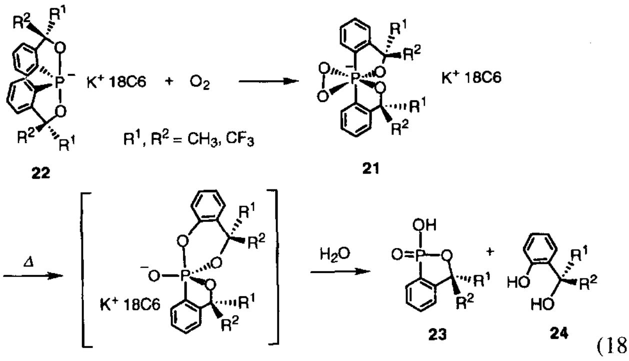
(16)



(17)

Theoretical calculations by us[87] and by Foote and coworkers[74] also supported the cyclic λ^5-dioxaphosphiranes as a sole energy minimum, since all attempts to locate acyclic peroxy species (R_3P^+–O–O^-) on the singlet potential energy surface led to only λ^5-dioxaphosphiranes. As for the reason why two minima are present in species of X = R_2S (**14** and **15**) but only one for X = R_3P (**20**), Foote et al. explained from either the presence or the absence of an additional lone pair on X.[74] That is, the stable persulfoxide has the terminal oxygen anti to the sulfur lone pair, and cyclization occurs when it rotated to anti to an S–R bond, but in the phosphonium peroxides (R_3P^+–O–O^-), the terminal oxygen is always in an apical position anti to one of the three P–R bonds which is ideally placed to attack phosphorus centers, affording the λ^5-dioxaphosphiranes intermediate with the trigonal bipyramidal configuration. Such an explanation, however, can not fully account for the predicted large activation energy (ca. 20 kcal mol^{-1}) on the cyclization of Me_2S^+–O–O^- which seems to be too high for the rotation barrier around the S–O bond. More important may be the difference in electronegativity between S (2.58) and P (2.19), since hypervalent species such as **15** (10-S-4) and **38** (10-P-5), in which the two apical ligands are joined to the center atom X by a three-center four-electron bond, are demanded by a significant net positive charge on X,[89] and hence their stabilities increase with the increasingly electropositive nature of X.

Very recently, novel λ^5-dioxaphosphiranes with 12-P-6 phosphate anion structure (**21**) were prepared by Nakamoto and Akiba.[90] The cyclic peroxides, formed by the reaction of 10-P-4 λ^5-phosphoranide anion (**22**) with molecular oxygen (Eq. 18), were surprisingly stable and isolable as single crystals. The structure was confirmed by X-ray crystallography, which showed that ligands were rotated upon the addition of O_2. Thermolysis (60 °C) of the λ^5-dioxaphosphirane led to the production of a phosphonate **23** and a phenol **24** (Eq. 18), showing that rearrangement of aryl group to oxygen took place as in the case of Ph_3PO_2 (Eq. 16).



(18)

The successful preparation of **21** is indicative of the intrinsic stability of such hypervalent cyclic λ^5-dioxaphosphirane; the strain of three-membered ring peroxides will be smaller in the hypervalent structure **21** than that in sp^3 center. Their kinetic stability seems to depend on whether the peroxide can oxidize the reactant **22** or not. In **21** with 12-P-6 phosphate anion structure, the electrophilicity of λ^5-dioxaphosphirane is significantly reduced by the net negative charge of the molecule. Such implications may be useful for the design of novel cyclic peroxides.

3. Theoretical Predictions with Density Functional Theory (DFT)

As described above, each X–O–O species show interesting properties depending on elements and substituents on X, but experimental examinations are limited by their short lifetimes and by the difficulty in generating them cleanly. The evaluation of the structure–reactivity relationship of various series may be achieved only by theoretical calculations for a wide variety of XOO species. Especially, the substituent effects on carbonyl oxides will provide a good starting point for this purpose. A systematic study providing qualitative insights into the structure of substituted carbonyl oxides was reported by Cremer et al. using MINDO/3-UHF methods.[91] However, the semiempirical calculations are not quantitatively reliable for such a highly correlated system and can not be extended to other elements for which parameters are unavailable. Thus, we have carried out theoretical examinations on structures of substituted carbonyl oxides and other enium-peroxide X–O–O intermediates from a common level of theory. Among various theories, the method of choice is the density functional BLYP/6-31G* calculations,[92] since the relatively large molecules employed in experiments can be handled and the observed IR spectra and dipole moments of ozone and substituted carbonyl oxides are best reproduced. The DFT calculations have been done for various substituted carbonyl oxides and other enium-peroxide type X–O–O species with X = RN (R = H, Ph), O, R_2Si (R = H, Me), H–P, S, H_2Ge, H–As, and Se, and the resulting interesting aspects are summarized in the following. Onium-peroxide type species are not discussed here, since similar DFT calculations are not appropriate for such type peroxides, e.g., as indicated for the DFT calculations on persulfoxides (**14**) which do not afford stable structures.[78]

3.1. Structural Properties and Biradical Character. Specific molecular properties of parent X=O and XOO species are summarized in Table 2. A common border seems to exist between X = second row elements and others; for instance, i) by adding O to X=O to form XOO, X–O bonds become longer by 5—6% for X = H_2C, H–N, and O, but by more than 10% for other elements in the third and fourth rows; ii) as shown by charge distributions, XOO is more polarized than X=O in the former but not for the latter; iii) upon going to a higher row, the negative charge on the central oxygen atom becomes closer to that on the terminal one, and in typical cases of X = H_2Si and H_2Ge, the order of magnitudes is reversed. Thus, XOO's with X at higher periods are regarded as weak O_2-complexes of sextet valence species, e.g., silylenes, germylenes, etc., rather than the O_2 adducts.

1,3-Dipoles such as ozone and carbonyl oxides have been suggested to have biradical character; the theoretical background for this is the lowering of energy by unrestraint of HF wavefunctions for α- and β-electrons, known as triplet instability or RHF-to-UHF instability.[93] The instability on DFT calculations seems to be a better indicator for open-shell biradicals than that on HF calculations since the electron correlations are involved in DFT. For most of 1,3-dipoles examined, the spin-restricted DFT wavefunctions are stable toward the relaxation of double occupancy constraint, indicating that all pairs of electrons are completely correlated. Such a closed-shell nature agrees with the observed properties of these species.

Exceptional cases showing the instability were found for *O*-oxides of silanones ($X = R_2Si$) and a germanone ($X = H_2Ge$), representing a substantial biradical character for these peroxides. The X-center in these species was, in contrast to the planar geometry of other closed-shell 1,3-dipoles, slightly pyramidized, indicating some contribution of sp^3 character on the sp^2 Si or Ge atom. This is because the overlap between 3p or 4p orbital on X and 2p orbital on adjacent oxygen is smaller than that in carbonyl oxides ($X = R_2C$). Thus, in contrast to a prediction of polar X^+–O–O^- structure owing to electronegativities (1.8) of Si and Ge lower than C (2.5), the biradical character $X^\bullet$–O–$O^\bullet$ becomes significant for the cases of higher-row elements.

Such an instability, however, does not appear for other elements in the third and fourth periods (X = H–P, S, H–As, and Se), since the X-center has a lone pair, pure p-orbitals being available on the sp^2 or sp-hybridizations. Thus, biradical character of the enium-peroxide species is dominated by the hybridization of X-center and the resulting overlap between p-orbitals.

3.2. Electron Distributions and Molecular Properties. In DFT calculations, orbital information is not available, and hence the estimation of reactivity is not so simple as in the Frontier orbital theory. However, it is found for the present XOO species that the BLYP/6-31G* calculated total atomic charge on terminal oxygen can be employed as an indicator of their reactivity. Typically, for XOO species ranging from ozone to RCO_3^- (this may be regarded as a variation of carbonyl oxide with a highly donating O^--substituent), experimentally determined Hammett's ρ-values (vs. σ) on reactivities toward substituted diphenyl sulfoxides are nicely correlated with the atomic charges on terminal oxygen, as shown in Fig. 1a. Thus, the philicity of XOO may be predictable from the atomic charges, which will switch at the charge of around −0.3.

Good linear relationships are also found for similar correlations, as shown in Figs. 1b and 1c, with O–O bond distances (R_{O-O}) at the BLYP/6-31G* optimized geometries and estimated O–O stretching frequencies (ν_{O-O}). The O–O stretching modes, which are easily assigned by isotope shifts on ^{18}O labelling, may be useful in diagnoses of their properties experimentally as well as theoretically. Interestingly, simplest peroxides, HOO^- and $HOO^\bullet$, also hold the correlations. From these calculations, structures and electron distributions of XOO species can be represented by two important canonical structures shown below (Chart 5):

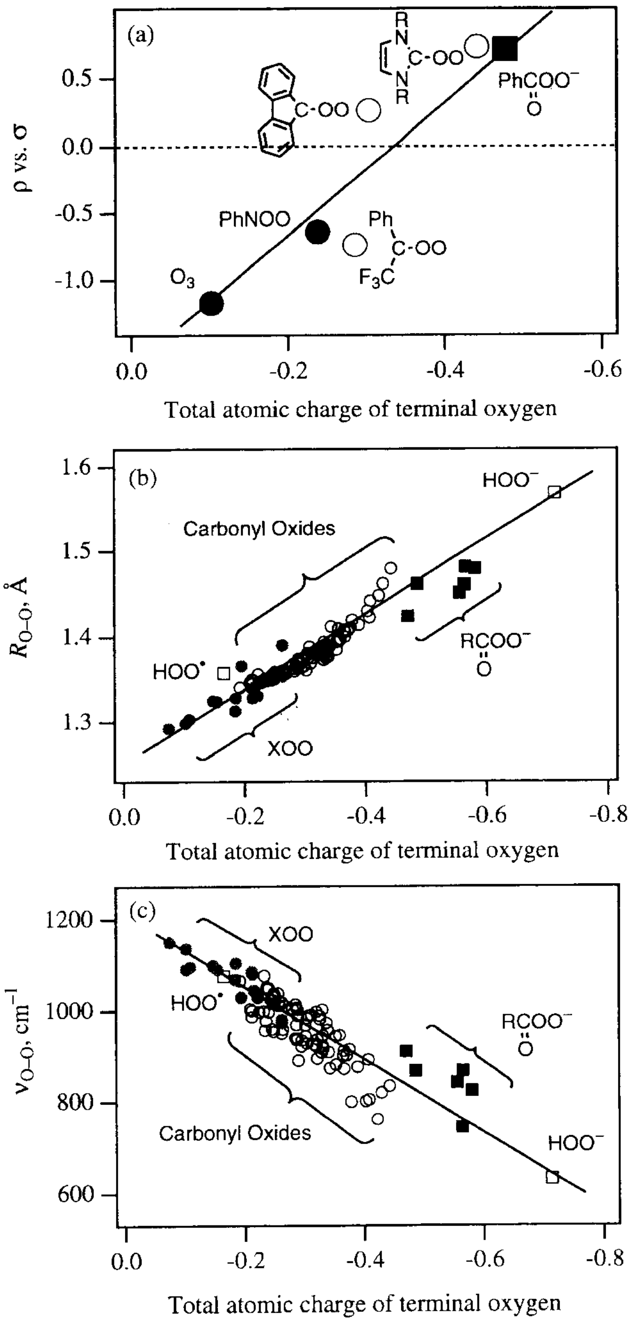


Fig. 1. Correlations between properties of XOO species and BLYP/6-31G* calculated total atomic charges on terminal oxygens; (a) experimentally determined ρ values (vs. σ) on reactivities toward substituted diphenyl sulfoxides, (b) calculated O–O bond lengths, and (c) O–O stretching frequencies.

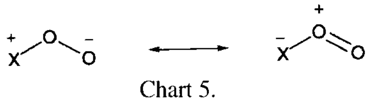


Chart 5.

When X stabilizes the positive charge, the O–O bond becomes longer and the double bond character is reduced, and vice versa. On the other hand, the X–O bond lengths and vibrational frequencies do not show simple correlations, because they are perturbed by substituents on X and other factors. The double bond character of X–O bonds will be discussed in Section 3.4.

3.3. Relative Oxygen Atom Affinity. The relative thermodynamical stabilities of substituted carbonyl oxides were evaluated, as compared with those of parent carbonyl compounds, from calculated enthalpy changes (ΔH_O) in oxygen transfer reactions of Eq. 19. The values may be

$$R^1R^2C{=}O + H_2C{=}O^+{-}O^- \xrightarrow{\text{O-Transfer}} R^1R^2C{=}O^+{-}O^- + H_2C{=}O - \Delta H_O \qquad (19)$$

regarded as the oxygen atom affinity values of carbonyl compounds relative to formaldehyde, which are directly related to the selectivities for carbonyl oxide formation on the decomposition of primary ozonides[94] and on the cycloreversion on five-membered heterocycles formed by $^1O_2$ and diazo compounds.[95]

The resulting ΔH_O values for various carbonyl compounds are shown in Fig. 2. The values in parentheses are not genuine, since the carbonyl oxide structures are perturbed by hydrogen bonding with hydrogens of *syn*-OH, NH$_2$, and COOH groups. The ΔH_O values are compared with the relative proton affinities (ΔH_H) evaluated from the reaction of Eq. 20.

$$R^1R^2C{=}O + H_2C{=}O^+{-}H \xrightarrow{\text{H}^+\text{-Transfer}} R^1R^2C{=}O^+{-}H + H_2C{=}O - \Delta H_H \qquad (20)$$

Figure 3 shows the correlation of relative oxygen atom affinities of carbonyl compounds with the corresponding proton affinities, which are classified by types of substituents. For simple aliphatic, alicyclic, and aromatic ketones and aldehydes (open circles in Fig. 3), proton affinities are widely varied in the range from −54 to +12 kcal mol^{-1}, but the alkyl and aryl substituents have only a minor effect on the oxygen affinities, typically, by ±5 kcal mol^{-1}. Moderate effects are shown for cyclopentanone (+5.9 kcal mol^{-1}) and $(CF_3)_2C{=}O$ (+5.0 kcal mol^{-1}), in which the σ-accepting effects destabilize the positively charged carbon of R_2COO. On the other hand, as shown in acyl- or cyano-substituted carbonyl compounds (squares in Fig. 3), the π-accepting

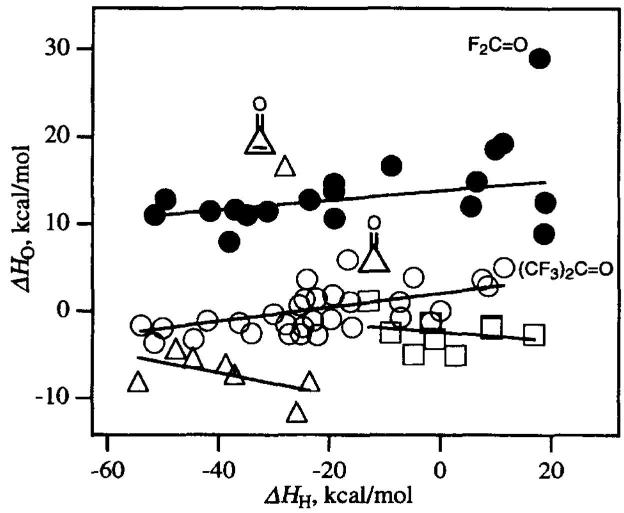
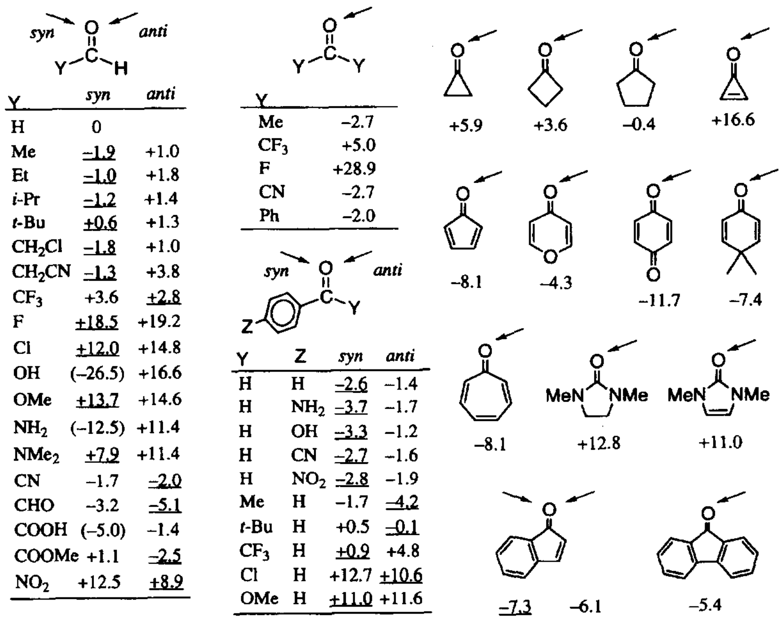


Fig. 3. Correlations of BLYP/6-31G* calculated relative oxygen atom affinities vs. proton affinities of carbonyl compounds shown in Fig. 2; open circles: aliphatic, alicyclic, and aromatic ketones, squares: ketones in cyclic π-conjugated systems, triangles: ketones conjugated with carbonyl or cyano group, and filled circles: ketones with heteroatom-centered substituents.



Y	syn	anti
H	0	
Me	−1.9	+1.0
Et	−1.0	+1.8
i-Pr	−1.2	+1.4
t-Bu	+0.6	+1.3
CH$_2$Cl	−1.8	+1.0
CH$_2$CN	−1.3	+3.8
CF$_3$	+3.6	+2.8
F	+18.5	+19.2
Cl	+12.0	+14.8
OH	(−26.5)	+16.6
OMe	+13.7	+14.6
NH$_2$	(−12.5)	+11.4
NMe$_2$	+7.9	+11.4
CN	−1.7	−2.0
CHO	−3.2	−5.1
COOH	(−5.0)	−1.4
COOMe	+1.1	−2.5
NO$_2$	+12.5	+8.9

Y	
Me	−2.7
CF$_3$	+5.0
F	+28.9
CN	−2.7
Ph	−2.0

Y	Z	syn	anti
H	H	−2.6	−1.4
H	NH$_2$	−3.7	−1.7
H	OH	−3.3	−1.2
H	CN	−2.7	−1.6
H	NO$_2$	−2.8	−1.9
Me	H	−1.7	−4.2
t-Bu	H	+0.5	−0.1
CF$_3$	H	+0.9	+4.8
Cl	H	+12.7	+10.6
OMe	H	+11.0	+11.6

Fig. 2. Relative oxygen atom affinities of carbonyl compounds (values in kcal mol^{-1}; arrows show the position of oxygen atom addition).

groups do not have such a destabilizing effect but slightly stabilize carbonyl oxides.

More characteristic results are shown for ketones involved in cyclic π-conjugated systems (triangles in Fig. 3), in which carbonyl oxide favors an *anti*-aromatic π-system rather than an aromatic one. This is apparent, for example, by comparing six-membered ring carbonyl oxides from 4-pyranone and *p*-quinone (**14** and **15**) (Chart 6), the former with 6-electron π-system (-4.3 kcal mol^{-1}) being much less favorable than the latter with *anti*-aromatic character (-11.7 kcal mol^{-1}).

The largest effects are shown for carbonyl compounds with heteroatom-centered substituents such as F, Cl, OR, NR_2, and NO_2 (filled circles in Fig. 3), indicating that the stability of carbonyl oxides is reduced by 10—20 kcal mol^{-1} owing to the σ-accepting ability of the electronegative atoms at the α-position. Interestingly, the highly π-donating NMe_2 group and π-accepting NO_2 group have similar magnitudes of destabilizing effects as nitrogen-centered substituents. Thus, in contrast to proton affinities, the addition of an oxygen atom to carbonyl groups is not greatly affected by π-donating or π-accepting ability of substituents. Upon the addition of O to carbonyl, an oxygen lone pair on the carbonyl is withdrawn by the oxygen atom, which is significantly retarded by the σ-accepting ability of heteroatom substituents. However, back donation from the oxygen atom results in an increase of π-electron density on the carbonyl. Thus, the donation from carbonyl to oxygen in σ-framework and the back-donation in the π-system play completely different roles (Chart 7).

The oxygen atom affinities of other XOO systems are also listed in Table 2. The ΔH_O values for O_3, SOO, and SeOO can not be directly compared with others since these are based on energies of O_2, SO, and SeO in triplet ground states; if singlet excited states are considered, the values become more negative by 20—30 kcal mol^{-1}. Thus, a general trend on the order of ΔH_O values in group elements is found as IV A > V A > VI A, indicating that oxide favors more electronegative elements. However, this may result not only from the stability of XOO but also the instability of X=O. The comparison among second-, third-, and fourth-rows is not straightforward, most complicated relationships being found for third-row elements. One reason will be the structural changes of XOO, as described before, from covalent dipolar species to weak O_2-complexes at higher periods.

25 **26**

Chart 6.

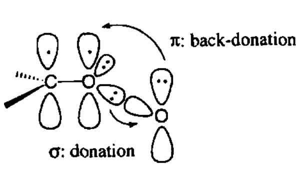


Chart 7.

3.4. Stereoisomers. *syn*- and *anti*-Isomers have been supposed to be involved for non-symmetrically substituted carbonyl oxides. In Fig. 2, more stable isomers are underlined, indicating that *syn*-forms are favorable for most oxides. By comparing the relative stabilities for *syn*- and *anti*-carbonyl oxides and protonated carbonyls ($R_2C{=}O^+{-}H$), the preference of *syn*-carbonyl oxides are due to three major reasons, as discussed in the following:

i) As for heteroatom-substituted carbonyls, the inductive effect by the electronegative atom reduces electron density of *anti*-lone pair on carbonyls, and hence both oxygen atom and H^+ favorably attach to the *syn*-side (Chart 8). The magnitude of this effect depends on the heteroatoms and can be as high as 3.5 kcal mol^{-1} when Y = NMe_2.

ii) Methyl group can stabilize *syn*-carbonyl oxides by 3 kcal mol^{-1} owing to the interaction between terminal oxygen and two C–H bonds at *gauche*-conformation as depicted in **27**.[96] The π-stabilization becomes stronger with increasing acidity of C–H bond, for instance, the maximum effect of 5 kcal mol^{-1} is indicated for the CH_2CN group. A similar interaction is operative but weak for C–C bonds of *t*-butyl group, resulting in the preference of *syn*-form only by 0.7 kcal mol^{-1}. Such a stabilization is not operative in H^+-adducts. The contrast becomes apparent in the favorable conformations for isopropyl derivatives, **28** and **29**, the former being sterically unfavorable but preferable for the interaction (Chart 9).

iii) In aryl-substituted carbonyl oxides, the hydrogen-bond type interaction between *o*-hydrogen and terminal oxygen stabilizes the *syn*-form by 1—2 kcal mol^{-1}. This effect depends on the charge density on terminal oxygen, and hence substituents on aryl also affect the stability through the π-conjugation. Typically, *p*-NH_2 and *p*-OH groups stabilize the *syn*-form but not the *anti*-form, the latter being most stabilized by π-accepting *p*-NO_2 group (Chart 10).

3.5. Cyclization. As described in Section 1.2, the cy-

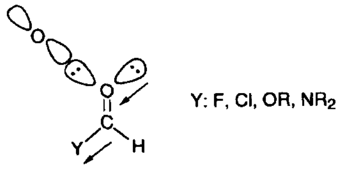
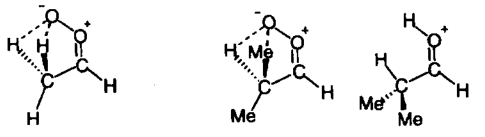


Chart 8.



27 **28** **29**

Chart 9.

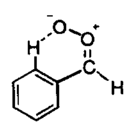
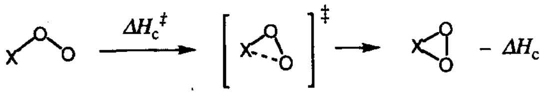


Chart 10.

clization of carbonyl oxide to dioxirane (Eq. 5) is highly exothermic but does not proceed in solutions because of the relatively high activation energy of ca. 20 kcal mol^{-1}. Here, exceptional cases of facile cyclization are demonstrated experimentally for Ph(X)COO with X = MeO[33] and CF_3.[29] Much lower activation energies to dioxiranes of ca. 10 kcal mol^{-1} were estimated by calculations for the conversions of mono-[97] and difluorocarbonyl oxides[98] and cyclopropenone *O*-oxide.[99] Such a dramatic effect of substituents is explained by their π-donor property to stabilize the transition state for the isomerization. Ab initio calculations have shown that the isomerization is initiated by the shift of electron from C atom to the neighboring O atom and is accelerated by substituents with π-donor properties. However, the substituent effects on the cyclization of carbonyl oxides are not fully clarified.

We have examined by the BLYP/6-31G* calculations the reaction enthalpies (ΔH_c) and activation energies ($\Delta H_c^{\ddagger}$) for the cyclization reactions of Eq. 21. The results for parent XOO species with various elements are summarized in the last two columns on Table 2.



(21)

The order of ΔH_c's in group elements of 14 < 15 < 16 indicates that open forms with more electronegative elements are preferred rather than cyclic forms. The plots of $\Delta H_c^{\ddagger}$'s vs. ΔH_c's as shown in Fig. 4a indicate that the cyclization can proceed with lower activation energies on going from second- to higher-row elements. This trend may be interpretable from the structure of XOO ; that is, XOO's with second-row elements are 1,3-dipoles with substantial double bond character in X-O, while the rotation around the X–O bond becomes easier for those with higher-row elements because of loss of bonding character between X and O_2.

The DFT calculations estimated low activation energies of 12.5 and 10.5 kcal mol^{-1} for the cyclization of *syn*- and *anti*-Ph(MeO)COO, respectively, and for Ph(CF_3)COO only the *syn*-to-phenyl form has a low activation of 14.1 kcal mol^{-1}, both of which are in good agreement with experimental observations. Calculations were done for various substituted carbonyl oxides corresponding to listed compounds in Fig. 2; as shown in Fig. 4b, quite complex relationships between ΔH_c's and $\Delta H_c^{\ddagger}$'s for all oxides were obtained. The poor correlation on the cyclization enthalpies and activation energies reflect various kinds of substituent effects. For most of carbonyl oxides without heteroatom-substituents (open circles, squares, and triangles in Fig. 4b), $\Delta H_c^{\ddagger}$'s are 20±5 kcal mol^{-1} independent of ΔH_c's, indicating that the C–O double-bond characters are not so affected by alkyl, aryl, and other C-centered substituents. But, the plots for a series of heteroatom substituted carbonyl oxides (filled circles in Fig. 4b) show a rough downward correlation, indicating that the activation energy is *reduced down* with decreasing exothermicity, and the activation energies for *anti*-forms are smaller than those for *syn*-forms.

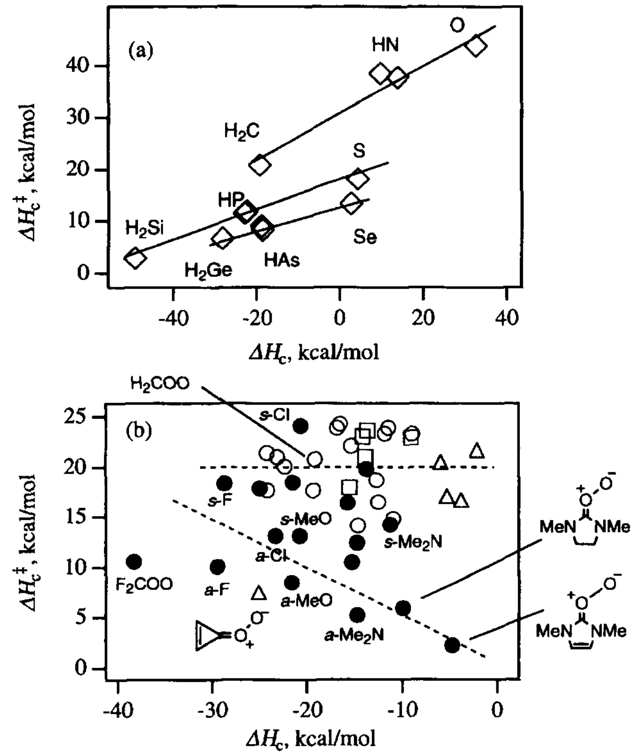


Fig. 4. Correlations of BLYP/6-31G* activation enthalpy ($\Delta H_c^{\ddagger}$) vs. reaction enthalpy (ΔH_c) for cyclization of XOO species; (a) XOO species with various elements as X, (b) substituted carbonyl oxides; for symbols, see the caption of Fig. 2; *s*- and *a*-F, Cl, MeO, and Me_2N denote *syn*- and *anti*-monosubstituted carbonyl oxides, respectively.

The theoretical results for cyclization of XOO's (Fig. 4a) follow a normal relationship between structure and reactivity, in which a less exothermic reaction proceeds with a larger activation energy (Fig. 5a). On the other hand, the predicted $\Delta H_c^{\ddagger}$'s and ΔH_c's for cyclization of heteroatom-substituted carbonyl oxides (filled circles in Fig. 4b) show an inverse correlation, representing an interesting example of violation of the reactivity–selectivity relationship. Introduction of heteroatom substituents as π-donors stabilizes carbonyl compounds and (to a lesser extent) carbonyl oxides but not dioxiranes, and therefore the exothermicity is decreased. In contrast, the activation energy for the isomerization does de-

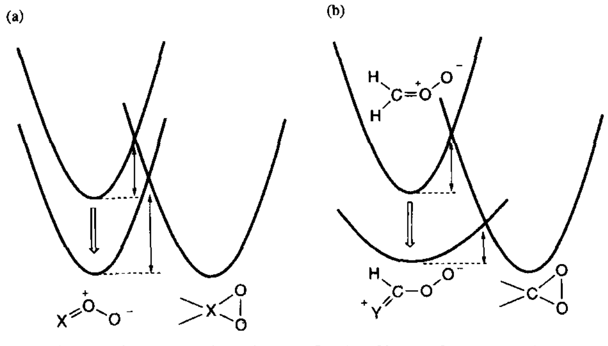


Fig. 5. Schematic drawings of (a) effect of X's on the cyclization of XOO's and (b) that of π-donating substituents on the cyclization of carbonyl oxides.

Table 3. BLYP/6-31G* Calculated Geometries and Properties for Parent X=O and X–O–O Species

X=O			X–O_1–O_2									
X=O	R_{X-O}	Atomic charge on O	X–O–O		R_{X-O}	R_{O-O}	Atomic charge		ν_{O-O}	ΔH_O[a)]	ΔH_c[b)]	$\Delta H_c^{\ddagger}$[b)]
	Å				Å	Å	O_1	O_2	cm^{-1}	kcal mol^{-1}	kcal mol^{-1}	kcal mol^{-1}
H_2C=O	1.218	−0.297	H_2COO		1.290	1.361	−0.023	−0.302	944	(0)	−19.1	20.8
HN=O	1.224	−0.197	HNOO	*syn*	1.298	1.331	0.072	−0.221	1033	−25.2	14.1	37.7
				anti	1.320	1.313	0.041	−0.184	1068	−21.0	9.9	38.4
O_2	1.240	0	O_3		1.298	1.298	0.203	−0.102	1089	−12.4	32.8	43.8
									1135			
H_2Si=O	1.550	−0.453	H_2SiOO		1.713	1.366	−0.203	−0.194	1029	3.5	−49.1	2.9
HP=O	1.520	−0.409	HPOO	*syn*	1.669	1.340	−0.148	−0.216	1044	−9.1	−22.3	11.8
				anti	1.683	1.340	−0.148	−0.212	1084	−8.6	−22.8	11.5
SO	1.545	−0.332	SOO		1.698	1.303	−0.073	−0.108	1094	−8.6	4.5	18.0
H_2Ge=O	1.679	−0.514	H_2GeOO		1.909	1.328	−0.185	−0.134	1103	−16.3	−28.1	6.7
HAs=O	1.670	−0.445	HAsOO	*syn*	1.837	1.324	−0.154	−0.196	1089	−20.6	−18.5	8.3
				anti	1.845	1.325	−0.147	−0.199	1098	−20.9	−18.7	9.0
SeO	1.693	−0.349	SeOO		1.875	1.292	−0.074	−0.101	1149	−16.1	2.8	13.3

a) Calculated enthalpy change for *O*-transfer of Eq. 19. b) Calculated enthaopy (ΔH_c) and activation energy ($\Delta H_c^{\ddagger}$) for the cyclization reaction of XOO (Eq. 21).

Table 4. Summary of Experimental Conclusions or Proposals on Structure and Reactivity of Amphoteric Oxygen Species

X in XOO	Structure Open or Cyclic	Philicity	Major deactivation pathway[a)] Thermal	 Photochemical
Enium-peroxide type				
O	Open	Electrophilic	Stable	Fragmentation
R–N	Open	Electrophilic	Intramolecular *O*-Transfer	Cyclization
R_2C	Open	Nucleophilic	Dimerization	Cyclization
	Cyclic	Electrophilic	O–O Fission	Rearrangement
R_2Si	Cyclic			Rearrangement
Onium-peroxide type				
R_2S	Open	Nucleophilic	(Cyclization or Intramolecular *H*-Transfer)	
	(Cyclic ?)	Electrophilic	Intermolecular *O*-Transfer	
R_3P	Cyclic	Electrophilic	Intermolecular *O*-Transfer, Rearrangement	

a) Major reaction of active oxygen species in the absence of trapping reagents.

pend on the π-donating property of substituents, leading to loss of C–O double-bond character. Such a polarized structure is more preferable for *anti*-forms. This is illustrated in Fig. 5b.

4. Concluding Remarks

Structural features and reactivities concluded or proposed for X–O–O species are summarized in Table 3. Although a lot of ambiguities still remain about their structures and mechanisms, some general features could be summarized as follows:

(a) *Philicity*: Three-membered cyclic peroxy species (X = R_2C and R_3P) are electrophilic, reflecting the electron-deficient nature of strained O–O bond. Enium-peroxide type 1,3-dipoles with electronegative elements as X (O_3 and RNOO) exhibit electrophilic *O*-transfers, while carbonyl oxides are generally nucleophilic. Such reactivities are highly sensitive to the nature of X and can be altered by substituents, indicating the flexible electron distribution in the π-bond of enium-peroxide 1,3-dipoles.

(b) *Cyclization*: The relative stability of the open form of enium-peroxide type X–O–O vs. its cyclic form increases on going to more electronegative X. From a thermochemical point of view, the relative stability is dominated by strain in the three-membered ring and by the energy of 3-center 4-electron π-bond in the 1,3-dipolar structure. Activation energies for the interconversion between them do not follow the exothermicity of the process but the double-bond character in X–O bonds, which are lowered by introduction of π-donating substituents or with higher-row elements as X.

For onium-peroxide species, the stability of open forms depends on the covalent vs. charge-transfer character in the X–O bonds, and for the cases of cyclic forms the stability of hypervalent structure is of significant importance. Although these two factors influence in a similar direction and more electropositive elements stabilize both forms, the results for X = R_2S and X = R_3P seem to indicate the greater importance of the hypervalent structure.

(c) *Fates*: For enium-peroxide type X–O–O, the photochemical cyclization followed by rearrangement is a general pathway, at least, for X = R_2C, RN, and R_2Si. While thermal reactions are different for each species, unimolecular cyclizations become facile on going to higher-row elements as X. Onium-peroxide species tend to isomerize to electrophilic oxidants, which undergo intermolecular *O*-transfers (Table 4).

The above conclusions, derived from a limited number of species, may be altered when the chemistry of other species in Table 1 is uncovered. Emphasized here is that, since the chemistry of X–O–O species is different depending on X's, the comparison between various elements will lead to the structure–reactivity relationships in these interesting class of peroxides extending from X = main group elements to X = transition metals.

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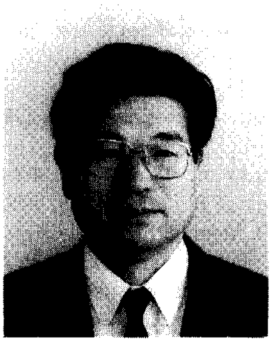

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