JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 10, 787–796 (1997)

REVIEW COMMENTARY

NOVEL ASPECTS OF CARBONYL OXIDE CHEMISTRY

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The structural and chemical properties of 1,3-dipolar peroxidic species (X—O—O) such as ozone (X = O) and carbonyl oxides (X = R_2C) depend significantly on the nature of X. Although cyclic O_3 is thermodynamically unstable, dioxiranes, cyclic isomers of carbonyl oxides, are isolable and have been fully characterized. In contrast to the well known electrophilic nature of ozone, carbonyl oxides usually act as a nucleophilic oxygen transfer agent, but their reactivity could be altered by substituents. It is expected that the chemistry of R_2C—O_2 species will provide a good starting point for a better understanding of dioxygen complexes (X—O_2) with various Xs. Interesting aspects of carbonyl oxide chemistry are discussed, including methods of generation, cyclization to dioxiranes and the nature of their oxygen transfer activities. © 1997 John Wiley & Sons, Ltd.

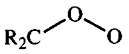
J. Phys. Org. Chem. **10**, 787–796, (1997)   No. of Figures: 7   No. of Tables: 0   No. of References: 93

Keywords: carbonyl oxide; ozone; structure and reactivity; oxygen atom transfer

Received 17 February 1997; revised 27 March 1997; accepted 30 April 1997

INTRODUCTION

Carbonyl oxides (**1**) are key intermediates in ozonolyses of alkenes,[1] and their structure and reactivities have been attracting attention from synthetic, biological and atmospheric standpoints. The fundamental features of carbonyl oxides are well understood, as summarized in three comprehensive reviews published during 1990–92.[2–4] A review by Sander[2] (1990) focused on aspects of spectroscopic characterization, especially based on matrix isolation techniques. Structural features and characteristic reactions of various carbonyl oxides were reviewed by Bunnelle[3] (1991) with particular emphasis on factors controlling their reactivity under various conditions from gas-phase, matrix and solution studies. McCullough and Nojima[4] (1992) summarized the formation and reactions of peroxidic species in the ozonation of various organic compounds.



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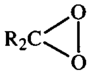

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As an alternative point of view, it is interesting to compare carbonyl oxides with a series of related active dioxygen species (X—O—O), ranging from the simplest case of ozone (X = O) to transition metal–oxygen complexes (X = metal) as involved in enzyme-catalyzed oxygenations[5] and in industrial oxidation processes.[6] The chemistry of active dioxygen species is broad and their structure–reactivity relationships are not always straightforward. For example, the metal center in transition metal–oxygen complexes can take various spin states and oxidation numbers, and they may exist in either open or three-membered cyclic forms. When X is a main group element, the former complication could be eliminated, and the nature of X—O—O species may be systematically understood.

The case of X = R_2C is unique because both the open form (**1**) and the cyclic dioxiranes (**2**) can be generated and characterized independently. Recent advances in the chemistry of carbonyl oxides and dioxiranes have demonstrated that their reactivities change significantly depending on the nature of X. The methodology to generate these species in solution is expanding, and the substituent effects on their reactivity may provide a good starting point for the evaluation of the structure–reactivity relationships of X—O—O species.

The major objective of the present review is to provide such an approach to understanding the characteristics of dioxygen species. Recent findings on the generation of carbonyl oxides and dioxiranes are briefly reviewed, followed by discussions on general and specific features of their reactivities as compared with those of ozone (X = O).

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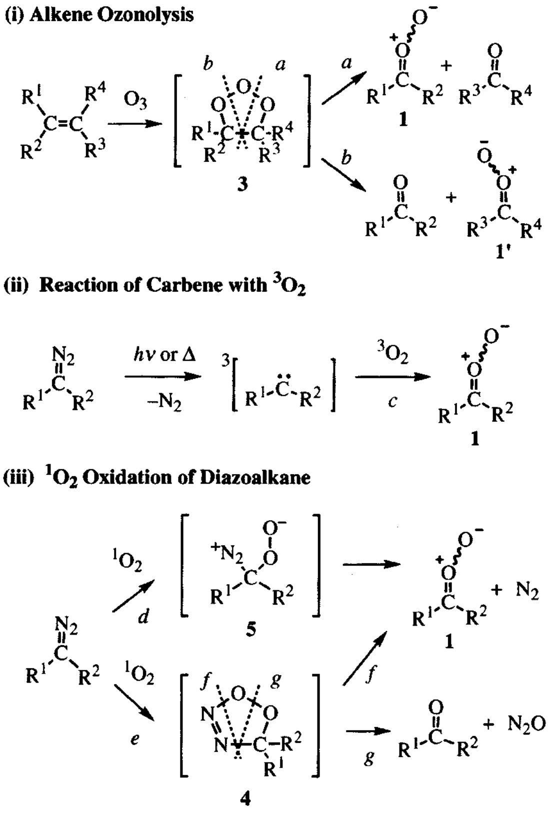


Scheme 1.

Particular emphasis is placed on the relative stability and interconvertibility between open and cyclic forms relating to their oxygen transfer ability.

METHODS OF GENERATION

Olefin ozonolyses

Carbonyl oxides are known to be formed [Scheme 1(i)] by the decomposition of primary ozonides (**3**). Extensive investigations of the mechanism of alkene ozonolysis has confirmed the essential features of the pathway originally proposed by Criegee.[7] For the cleavage of primary ozonoides, Fliszár *et al.*[8] and Griesbaum and co-workers[9] derived a useful rule that cleavages of primary ozonides tend to occur along the pathway to yield carbonyl oxides with electron-donating substituents such as methyl, whereas electron-withdrawing groups such as acyl and halogen are incorporated in the carbonyl products. This imposes a severe restriction on the generation of carbonyl oxides with electron-accepting substituents.

Recently, Wojciechowski *et al.*[10] found that the decomposition of primary ozonides from substituted vinyl ethers could give rise to the selective generation of the corresponding carbonyl oxides, because of the strong bias of the alkoxy group against incorporation in the carbonyl oxides. Sugiyama *et al.*[11] reported that the ozonolyses of alkenes incorporating both an electron-withdrawing and an alkoxy group, which have opposing directive effects on the regioselectivity, lead to the successful generation of *O*-oxides of keto esters and diketones. Because of minimal intereference from by-product esters, the electron-deficient carbonyl oxides were shown to undergo cycloadditions with added dipolarophiles, which was applied in syntheses of novel cyclic peroxides.[12] Such a methodology, although not appropriate for the spectroscopic characterization of short-lived intermediates, is potentially useful for generating various substituted carbonyl oxides in solutions.

Photooxidation of diazo compounds

The oxides can also be generated by the reaction of carbenes and $^3O_2$ [Scheme 1 (ii), path c][13] or by the oxidation of diazo compounds with singlet oxygen, $^1O_2$ [Scheme 1 (iii)],[14] which have been utilized in spectroscopic studies by laser flash photolysis[15] and low-temperature matrix techniques.[2,16] In solution, the third method may be the most advantageous since the intervention of highly reactive ozone or carbenes is avoided. The applicability of this method is limited when the quenching of $^1O_2$ by diazo compounds is reduced by introducing electron-withdrawing substituents. Another disadvantage is an involvement of direct ketone formation [Scheme 1 (iii), path g] via 1,2,3,4-dioxadiazole intermediates (**4**).[14,17]

We investigated the mechanism of the $^1O_2$ oxidation of diazo compounds from the selectivity of ketones vs carbonyl oxides, which could be determined from the ratios of evolved N_2O/N_2.[18] The selectivity of benzophenone oxide (i.e. $R^1=R^2=Ph$) from $^1O_2$ and diphenyldiazomethane did not depend on solvents, e.g. 62, 55 and 56% in acetonitrile, benzene and methanol, respectively. The observed small solvent effect is not consistent with the intervention of the highly polar zwitterionic intermediate **5**. If zwitterions such as **5** were involved in the formation of carbonyl oxides, protic solvents would stabilize **5** by hydrogen bonding at the terminal anionic oxygen resulting, contrary to observation, in the more selective elimination of N_2. Simlar results were obtained for the case of 1-phenyl-1-diazopropane (i.e. $R^1=Ph$, $R^2=Et$).

Recently, we found from a laser kinetic spectroscopic study that the rates of quenching of $^1O_2$ by diazo compounds were virtually unaffected by solvents. The decay of $^1O_2$ was almost correlated with the build-up of carbonyl oxides, indicating the short-lived nature of five-membered heterocycles **4**.[19] Theoretical calculations predicted that the cycloreversions of dioxadiazole **4** leading to ketone–N_2O (Scheme 1, path g) and carbonyl oxide–N_2 (path f) are very facile, the activation energies being as low as 3–8 kcal mol^{-1} (1 kcal = 4·184 kJ). Consequently, a concerted 1,3-dipolar cycloaddition of $^1O_2$ to a diazo compound (path

e) is predominant, and the resulting dioxadiazole **4** rapidly undergoes the competitive cycloreversion reactions.

Substituent effects on the selectivity for carbonyl oxides were examined in order to clarify how versatile the third photooxidation method is. On photooxidation of alkyl(phenyl)diazomethanes [$Ph(R)C{=}N_2$] in MeCn, the carbonyl oxide yields decreased with increasing bulkiness of alkyl groups in the order R = Me (78%), Et (72%), *i*-Pr (64%) and *t*-Bu (53%), which may be well explained by the steric effect in destablizing the oxides. A similar trend was reported in the cycloreversion of primary ozonides from dialkylethylenes.[20] The carbonyl oxide selectivity (70%) for phenyldiazomethane decreased to 64% on introducing an electron-withdrawing *p*-Cl group and increased to 85% with an electron-donating *p*-MeO group. The resulting negative Hammet ρ value of $-0{\cdot}83$ (vs σ) for the relative selectivity indicates that electron-donating substituents favor oxide formation; a similar selectivity was observed in the cleavage of primary ozonides from substituted stilbenes (i.e. $\rho = -1{\cdot}25$ vs σ).[21] These results revealed that the selectivity was affected mostly by the relative stability of the resulting carbonyl oxides. Carbonyl oxide formation was still one of the major pathways in the $^1O_2$ oxidation of diazoalkanes with electron-withdrawing groups, i.e. 7-diazo-8-acenaphthenone (55%)[22] and $Ph(CF_3)C{=}N_2$ (40%).[23]

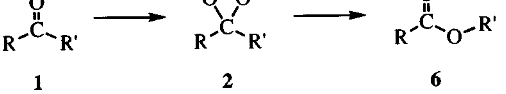
On the other hand, the quenching of $^1O_2$ by diazo compounds is significantly affected by substituents. As the lifetimes of $^1O_2$ in common organic solvents are of the order of 10^{-5} s,[24] the practical limit for determining $^1O_2$ quenching was *ca* $10^6\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ with conventional methods. Recently, we determined, with time-resolved phosphorescence measurements, the rate constants for the reaction of $^1O_2$ with $Ph(R)C{=}N_2$ (R = H, Me, *t*-Bu and Ph) of $(3–8)\times10^8\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ whereas that with $Ph(CF_3)C{=}N_2$ was decreased to *ca* $2\times10^6\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$,[25] the latter being nearly the lower limit.

The $^1O_2$–diazo method is not applicable to carbonyl oxides having heteroatomic substituents such as RO, since the corresponding diazo compounds are not available. For such cases, the carbene–$^3O_2$ reaction also does not work because carbenes in the singlet ground state are generally unreactive toward $^3O_2$. These limitations in conventional methods are still hindering the exploration of the broad chemistry of carbonyl oxides with extremely electron-donating or -accepting substituents. The development of novel methods such as electron-transfer oxygenation of diazo compound[26] and $^1O_2$ oxidation of singlet carbenes is in progress in this laboratory, which might provide a breakthrough in this area.

ISOMERIZATION TO DIOXIRANES

Dioxiranes (**2**) are well known to be produced by the peroxysulfate oxidation of ketones.[27] Recently, difluorodioxirane (**2**, R = F), the first isolable dioxirane as a pure substance in the gas phase at room temperature, was prepared from FCO_2F with CsF catalysis.[28] The potential of dioxiranes as very powerful and versatile oxygen transfer reagents has been summarized in several excellent reviews,[29] and a recent topic is diastereo- and enantioselective epoxidation using well designed dioxiranes.[30]

Theoretical calculations predicted that the parent dioxirane (**2**, R = H) is 24–29 kcal mol^{-1} more stable than the parent carbonyl oxide (**1**, R = H), and that both forms can exist as distinct species divided by the activation energy as high as 18–24 kcal mol^{-1}.[31] Such a preference for the cyclic form is in contrast to the case of ozone (X = O), for which the cyclic isomer was estimated to be 28–29 kcal mol^{-1} higher in energy[32] and no experimental evidence for the cyclization was given for the cyclization under thermal or photolytic conditions.[33] Thus, the relative stability of open X—O—O species versus its cyclic form seems to decrease on going to more electropositive X, since the large difference in electronegativities between X and terminal O results in a highly polarized structure (X^+—O—O^-) where the charges are rather localized and hence the delocalization energy of π-electrons is minimized.

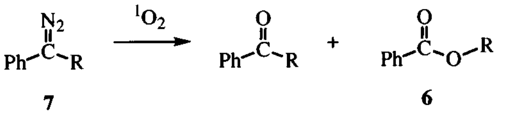


(1)

It has been suggested that dioxiranes isomerize to a rearranged product **6**, as a highly exothermic process. Such a sequence [equation (1)] has been shown to proceed photochemically in low-temperature matrices, where the two intermediates (**1** and **2**) have been characterized by IR and UV–visible absorption spectroscopoy.[2,15] Primary thermal products on the reaction of triplet carbenes with O_2 were carbonyl oxides, which upon irradiation either rearranged to dioxiranes or split off oxygen atoms. In the gas-phase ozonolysis of ethylene, the parent dioxirane (**2**, R = H) was identified by microwave spectroscopy,[34] and a reaction scheme similar to equation (1) was proposed in which a vibrationally excited carbonyl oxide, instead of its electronically excited state, was involved. The adaptability of such a sequence [equation (1)] in solutions, in relation to the matrix and gas-phase reactions, has been argued for a long time as described below.

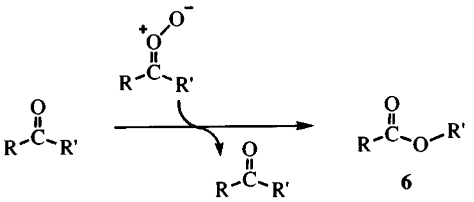
Formation of esters in solutions

In early studies, rearranged products (**6**) were frequently obtained as side-products during the $^1O_2$ oxidation of diazo or related compounds [equation (2)]. In most cases, a unimolecular pathway similar to equation (1) was proposed for the formation of **6**.[35]



(2)

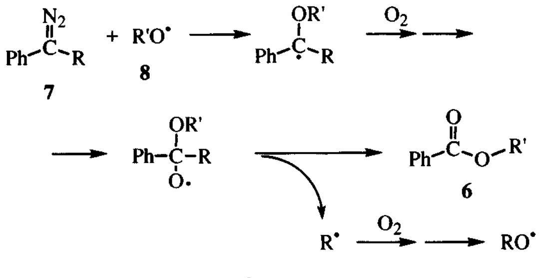
Later, we studied mechanistically the $^1O_2$ oxidation of various diazo compounds. $^{16}O_2$–$^{18}O_2$ tracer experiments revealed that the two oxygen atoms in **6** did not originate from the same oxygen molecule.[36] Thus, the unimolecular rearrangement according to equation (1) was clearly ruled out for all cases examined. From a detailed study[22] it was concluded that the rearranged products resulted from the Baeyer–Villiger oxidation of carbonyl compounds with carbonyl oxide intermediates [equation (3)].



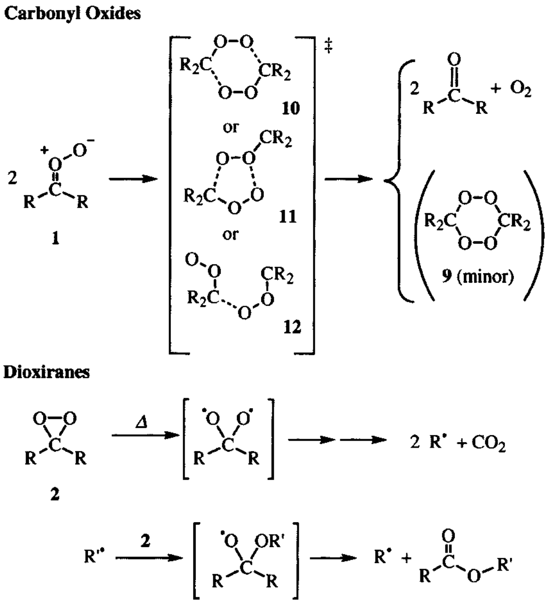
(3)

For more common cases of alkylphenyldiazomethanes (**7**), esters were obtained via a radical chain decomposition involving alkoxyl radicals (**8**) as a chain carrier (Scheme 2). The latter mechanism could be confirmed by an ^{18}O-tracer study and the complete scrambling of alkoxy and acyl groups in the alkyl benzoates formed. These findings clearly indicated that carbonyl oxides (**1**) do not rearrange to esters (**6**) in solution. However, the isomerization of **1** to dioxiranes (**2**) could not be eliminated since at that time the fate of **2** was not clear.

The isomerization of carbonyl oxides to dioxiranes cannot be the major deactivation pathway in solutions, at least for substituted benzophenone *O*-oxides, since their decay kinetics are second order in the oxides, as observed by time-resolved absorption spectroscopy.[37] The photooxidation of diazo compounds at room temperature led to the almost quantitative formation of the corresponding ketones and no evidence was given for the formation of diperoxides (**9**), although they were obtained at low temperatures.[38] Thus, the resulting ketones at room temperature are formed by the bimolecular reaction between two carbonyl oxides with loss of one oxygen molecule. An earlier $^{16}O_2$–$^{18}O_2$ labeling study indicated no evolution of scrambled oxygen gas ($^{16}O^{18}O$), eliminating the possible coupling of **1** at terminal oxygens. Other mechanisms were proposed such as those through six- (**10**)[37a] or five-membered electrocyclic transition state (**11**),[37b] and an acyclic S_N2-type one (**12**).[3] However, no conclusive, experimental or theoretical evidence has been provided.



Scheme 2

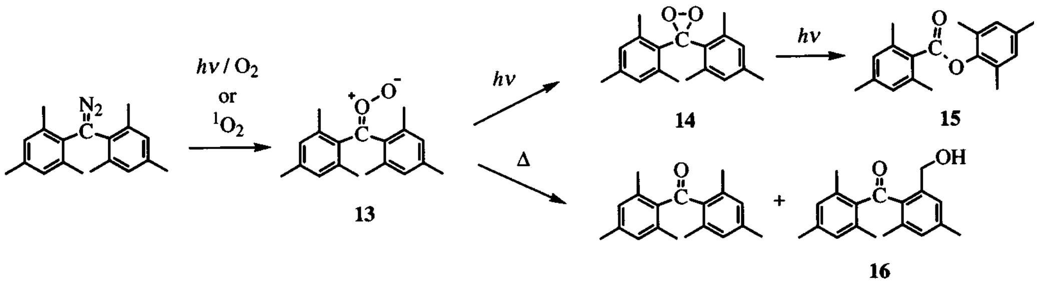


Scheme 3

On the other hand, it has been proposed that the thermal decomposition of dioxiranes does yield esters via an intermolecular pathway (Scheme 3). The initial step is O—O fission with an activation energy of 24·9 kcal/mol^{-1},[39] followed by C—C fission and decarboxylation, generating two alkyl radicals and CO_2. The alkyl radical attacks the oxygen atom of another molecule of **2**, yielding esters with scrambling of alkyl groups (see Scheme 3, Dioxiranes).[40] The unimolecular rearrangement of dioxiranes to esters may take place only when catalyzed by Lewis acids.[41] These findings shows that the interconvertibility from carbonyl oxides to dioxiranes is not directly related to the formation of rearranged products in solution.

Thermal and photochemical reactions of a stable carbonyl oxide

A good example in this area was provided recently by Sander *et al.*,[42] who successfully prepared the first stable carbonyl oxide, dimesityl ketone *O*-oxide (**13**), which was observable at low temperature by NMR spectroscopy in Freon or THF solution. Upon photolysis, **13** was converted into the corresponding dioxirane **14** (Scheme 4). Dimesityldioxirane (**14**), the first solid dioxirane,[43] was also photolabile and transformed to a rearranged ester (**15**), which is similar to those of common carbonyl oxides in low-temperature matrices. Thermolysis of **13** yielded the corresponding ketone and rearrangement product **16** but not dioxirane **14**. It may be concluded that the thermal isomerization of carbonyl oxides to dioxiranes does not



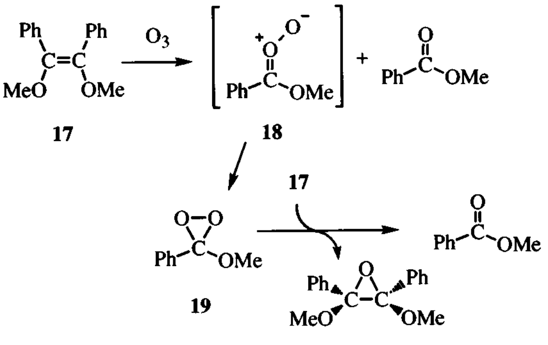
Scheme 4

proceed even when all the species have adequate kinetic stability.

Another important finding in this study was the significant stability of the oxide in common organic solvents such as THF. The lack of formation of oxidized products from THF indicates that the oxide does not abstract hydrogen from hydrocarbons. Although the oxidation of hydrocarbons was proposed when diazo compounds were photooxidized in the presence of hydrocarbons,[44] it is difficult to specify the actual hydrogen abstractor. This experimental evidence indicates that a theoretical description of such 1,3-dipoles as a biradical (X$^{\cdot}$—O—O$^{\cdot}$)[45] does not always imply a radical reactivity of such spin-paired species.[46] Care should be taken in the interpretation of radical reactions, since such reactions might be triggered by some secondary processes. Typically, ozone has been shown to insert into C—H bonds via a concerted pathway,[47] but the resulting hydrotrioxides (C—O—O—O—H) easily decompose to produce radicals at ambient temperature.[48] It has been shown that free radical reactions are induced during the oxidation of hydrocarbons by dimethyldioxirane.[49]

Effect of π-donating substituents

It is interesting that interconvertibility from carbonyl oxides to dioxiranes could be attained by introducing some specific substituents. Recently, the first example of dioxirane formation from the ozonolysis of an alkene (Scheme 5) was reported by Kopecky *et al.*[50]. The ozonolysis of (*Z*)-1,2-dimethoxy-1,2-diphenylethene (**17**) in CD_2Cl_2 at −20 °C resulted in the formation of dioxirane **19**, which was characterized by a typical ^{13}C NMR absorption at δ 109·1 ppm. The addition of excess **17** to a solution of **19** led to the stereospecific conversion of the alkene into the corresponding oxirane. Oxide **18**, carrying a strong π-donating methoxy group, in contrast to common carbonyl oxides, actually undergoes cyclization to dioxirane **19** in solution.



Scheme 5

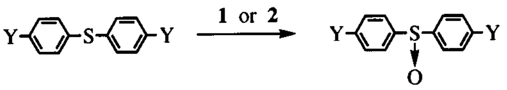
Such a dramatic effect of the methoxy substituent in **18** is explained by its π-donor property which stabilises the transition state for isomerization. *Ab initio* calculations have shown that the isomerization to dioxiranes, which is initiated by the shift of an electron from a C atom to the neighbouring O atom, is accelerated by substituents with π-donor properties.[51] Cremer *et al.*[52] estimated from theoretical calculations activation energies of 17·1 and 7·9 kcal mol^{-1} for the conversion of *syn*- and *anti*-monofluorocarbonyl oxides (HFC—O—O), respectively, to the corresponding dioxiranes, which were much lower than that for the parent carbonyl oxide (25·0 kcal mol^{-1}). The cyclization of F_2COO was suggested experimentally in the gas-phase reaction of CF_2 with $^3O_2$,[53] the isomerization barrier for which was predicted to be 11·2 kcal mol^{-1}.[54] A similar acceleration is reasonably expected for the π-donating methoxy substituent in **18**.

OXYGEN-TRANSFER ACTIVITY

General philicity of carbonyl oxides and dioxiranes

Carbonyl oxides are typical 1,3-dipolar molecules with a three-center, four-electron π-system[55] which is isoelectronic with that of the allyl anion. The molecular orbital picture shows that an electronegative atom at the center of 1,3-dipole lowers the π-LUMO energy but changes the π-HOMO energy very little. Accordingly, common 1,3-dipolar species have relatively high-lying HOMO and low-lying LUMO, the biphilic nature of which has been demonstrated from the U-shaped Hammett correlation in their cycloadditions.[56] In other words, the active oxygen species of this type may behave as a nucleophilic and/or an electrophilic oxidant, which is the most notable feature of the chemistry of carbonyl oxides and related peroxides.

The philicities of oxidants are determined from the Hammett-type correlation for the oxidation of substituted substrates such as aryl sulfides or sulfoxides [equations (4) and (5)]. The latter is more informative, because sulfoxides



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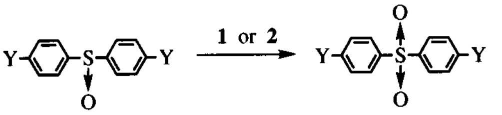
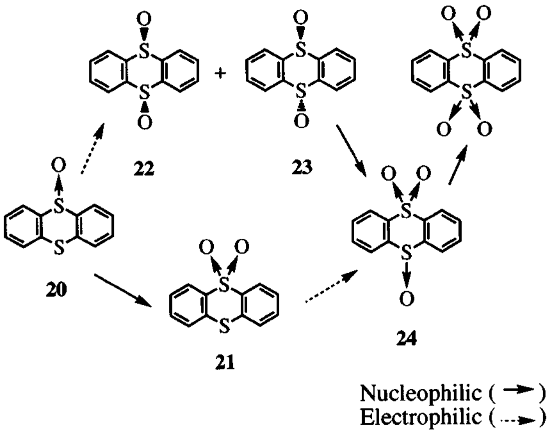


(5)

behave as a biphilic substrate acceptable for both nucleophilic and electrophilic oxidation. The oxidation of diphenyl sulfoxides with fluoronone *O*-oxide afforded a Hammett ρ-value of $+0\cdot26$ (vs σ).[57] In a similar way, carbonyl oxides were shown to possess nucleophilic reactivity towards sulfoxides, reflecting their highly polarized zwitterionic structure, R_2C^+—O—O^-, just like the peroxy anion (R—O—O^-).

The relative oxidation rates of sulfides and of sulfoxides are also useful as a mechanistic probe for the philicity of oxygen atom transfers, which is based on the assumption that electrophilic oxidants preferentially oxidize sulfides whereas nucleophilic oxidants oxidize sulfoxides. For fluorenone *O*-oxide, the relative reactivity toward Ph_2SO vs Ph_2S is as high as 17,[57] which again demonstrates the strong nucleophilic character of the oxide. Thianthrene 5-oxide (**20**) has often been employed as a philicity probe (Scheme 6). In an original study by Adam and co-workers employing a nucleophilicity protocol, $X_{\mathrm{Nu}}=\mathbf{221}/(\mathbf{21}+\mathbf{22})$, all carbonyl oxides examined showed the nucleophilic character ($X_{\mathrm{Nu}}>0\cdot8$),[58] in contrast to electrophilic ozone ($X_{\mathrm{Nu}}=0\cdot17$).[59] Dioxiranes were also shown to be moderately nucleophilic ($X_{\mathrm{Nu}}=0\cdot57$–$0\cdot67$).[58] However, in this study, the nucleophilicity was overestimated because one of the major products (*trans*-bissulfoxide, **23**) was missed in the analyses, and the oxidation reactions were re-examined recently with a new analytical protocol, $X_{\mathrm{SO}}=(\mathbf{21}+\mathbf{24})/[\mathbf{21}+\mathbf{22}+\mathbf{23}+(2\times\mathbf{24}]$.[60] Although dioxiranes were definitely shown to be electrophilic with $X_{\mathrm{SO}}<0\cdot13$, the results for carbonyl oxides varied in the range from $X_{\mathrm{SO}}=0\cdot86$ for 4,4′-dimethoxybenzophenone oxide to $X_{\mathrm{SO}}=0\cdot21$ for dibenzosuberenone oxide. The electrophilic nature ($X_{\mathrm{SO}}<0\cdot5$) of the latter carbonyl oxide was unexpected, because the π-system stabilizing cationic charge would result in increased nucleophilicity. They explained the unexpected result by assuming the photoisomerization of the oxide to yield the corresponding dioxirane. A more detailed study is necessary before conclusions can be drawn. It has also been pointed out that thianthrene 5-oxide (**20**) is not always an ideal probe because the reactivities of sulfide and sulfoxide groups in **20** are considerably modified by the electronic effect between them through the π-system or transannular interaction.[61] In this respect, earlier results obtained from intermolecularly competitive trapping experiments seem to be more reliable.



Scheme 6

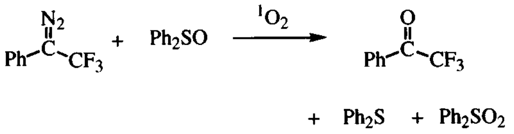
The nucleophilicity of carbonyl oxides is in contrast to the electrophilic nature of ozone, which has been well established in ozonation chemistry[62] and in their oxygen transfer reactions.[4,63] Typically, ozone oxidizes diphenyl sulfide 13 times faster than diphenyl sulfoxide, and even in the reaction with substituted diphenyl sulfoxides the oxidation proceeds electrophilically, as indicated by large negative ρ value of $-1\cdot17$ (vs σ).[17]

Dioxiranes have also been shown to have electrophilic properties. The reactions of dimethyldioxirane (**2**, R = Me) with a series of *para*-substituted phenyl methyl sulfides and sulfoxides showed a linear correlation with ρ-values of $-0\cdot77$ and $-0\cdot76$ (vs σ), respectively.[64] Similarly, linear free energy relationships were observed for the dioxirane epoxidation of substituted styrenes ($\rho=-0\cdot90$ vs σ),[65] oxidation of phenethyl alcohols ($\rho=-1\cdot57$ vs σ)[66] and C—H insertion into cumenes ($\rho=-2\cdot76$ vs σ).[67] Thus, it is apparent that dioxiranes act as potent electrophilic *O*-transfer reagents, reflecting the electron-deficient nature of the strained O—O bond in **2**. Toward substrates with low oxidation potentials, however, their electron-transfer activity results in complex radical reactions, as demonstrated in several cases.[68]

Effects of CF_3 substituent

The contrasting reactivities of electrophilic ozone and nucleophilic carbonyl oxides indicate that the reactivities of carbonyl oxides may be controlled or even reversed by choosing substituents. Among various substituted carbonyl oxides examined, a unique chemistry has been revealed for α,α,α-trifluoroacetophenone oxide (**25**).[69] The oxide, possessing a potent electron-withdrawing trifluoromethyl group, reacted electrophilically with diaryl sulfoxides

($\rho = -0{\cdot}74$ vs σ) affording, unexpectedly, sulfides as the major product [equation (6)].



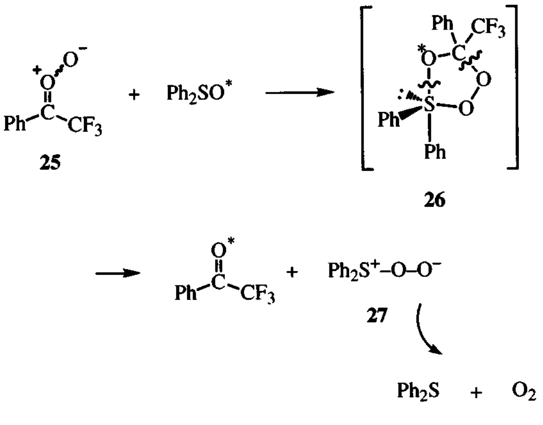
(6)

The proposed mechanism for the novel deoxygenation of sulfoxides is shown in Scheme 7. The intermediacy of persulfoxides (**27**) formed via cyclic peroxidic sulfuranes (**26**) was supported by an ^{18}O-tracer study employing $Ph_2S^{18}O$ and by C—S fission in a benzyl-substituted persulfoxide.[23]

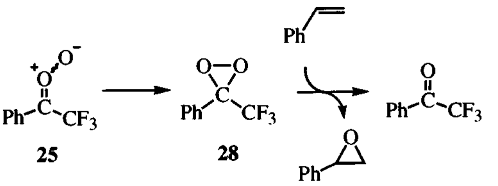
The unexpected deoxygenation is unique in comparison with the known chemistry of carbonyl oxides, suggesting that the reactivity of the oxides can be controlled by substituents. The remarkable effect of the CF_3 group was also demonstrated in the IR spectrum of the carbonyl oxide **25** showing O—O stretch bands at 943 and 1009 cm^{-1},[70] which were much larger than those of common carbonyl oxides (839 and 890 cm^{-1} for benzaldehyde *O*-oxide)[71] and were close to the harmonic frequencies of symmetric (1135 cm^{-1}) and asymmetric (1089 cm^{-1}) O—O stretches of ozone.[72]

Subsequent study revealed that alkenes were oxidized to epoxides during the photooxidation of $Ph(CF_3)C{=}N_2$.[23] Detailed competitive trapping experiments have indicated that the carbonyl oxide **25** is converted to a secondary oxidant which is reactive towards alkenes. The epoxidation proceeded almost stereospecifically and the substituent effect on styrenes resulted in the negative ρ-value of $-1{\cdot}66$ (vs σ), which is close to the value reported for dimethyldioxirane ($\rho = -1{\cdot}53$ vs σ).[73] Thus, the corresponding dioxirane (**28**) was proposed as the second intermediate, which might be formed by the isomerization of **25** to **28** [equation (7)].

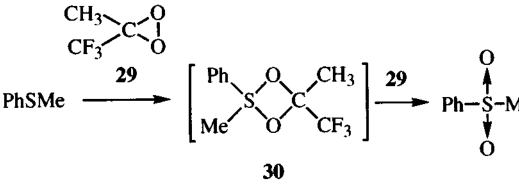
Recently, a notable effect of CF_3 substitution for dioxiranes was demonstrated.[74] Methyl(trifluoromethyl) dioxirane (**29**) reacts with sulfides to give sulfones, the direct sulfone formation being preferential even in the presence of competing sulfoxides. From solvent effects and tracer experiments using ^{18}O and ^{2}H labeling, the involvement of cyclic sulfurane **30** was proposed [equation (8)].



Scheme 7



(7)



(8)

The above examples illustrate a specific effect of a CF_3 group on the reactions of these peroxides with sulfur-containing compounds, which may be attributed to the ability of CF_3 to stabilize the negative charge on apical ligands of hypervalent sulfuranes such as **26** and **30**.[75]

SUMMARY AND OUTLOOK

The structures and chemical properties of 1,3-dipolar peroxidic species (X—O—O) are so different and depend on the nature of X, as exemplified for ozone (X=O) and carbonyl oxides ($X{=}R_2C$) by the reversed relative stability between open and cyclic forms and by the opposite philicity in their oxygen transfer activities. It has been shown that the reactivity of carbonyl oxides can be controlled by substituents. Typically, the isomerization to dioxiranes is facilitated by introducing π-donating groups, and a strong electron-withdrawing trifluoromethyl group turns the nucleophilic nature of common carbonyl oxides to an electrophilic nature. More extreme cases were not explored because of the limitation of conventional methods to generate carbonyl oxides with specific substituents.

The effects of various substituents on carbonyl oxides are not yet fully explained theoretically because of the difficulty in calculations on such highly correlated 1,3-biradicaloids. A systematic study on substituted carbonyl oxides was reported by Cremer *et al.*[76] using MINDO/3-UHF calculations, but the reliability of this method is not acceptable. Typically, the MINDO/3 parameters fails to afford reasonable structure for some specific functional groups such as CF_3. Recently, we have found that calculations on carbonyl oxides with modern density functional theory are capable of reproducing molecular properties such as vibrational frequencies.[77] Such calculations may illustrate the structural features of this difficult class of molecules.

The next step in elucidating the full structure–reactivity relationship of X—O—O species is the comparison among those with various elements for X. We are interested in the chemistry of nitroso oxides ($X=RN$) because the intermediate situation is expected.[63,78] The active species generated on photolyses of aryl azides under an oxygen atmosphere revealed a radical-like reactivity,[79] which is apparently not in line with those of ozone and carbonyl oxides. Further examinations are required to elucidate the structure of nitrene–O_2 adducts.

On going to third-row elements, only the silylene–O_2 adducts have been explored experimentally,[80] but the spectral assignment is still controversial. An interesting comparison between H_2Si—O—O and H_2O—O—O was made from theoretical calculations.[81] Notably, even though the lower electronegativity of Si (1·90) than that of C (2·55) would favor a zwitterionic structure, R_2Si^+—O—O^-, the silanone *O*-oxide has a significant biradical character. Accordingly, the thermal instability of H_2Si—O—O results in a larger exothermicity and much lower activation energy for cyclization than those for carbonyl oxides. This indicates that π-bond character is minimized by the smaller overlap between 3p (Si) and 2p (O) orbitals, contributing significantly to the thermal stability of X—O—O species. This may be a common feature when X is an element in higher than the third period.

Finally, another series of X^+—O—O^- species where the X^+s are *onium* ions are discussed briefly. Peroxides of this type, in which all the valence orbitals on X^+ are filled and no π-bond exists, have a structure regarded as a charge-transfer complex of X and singlet oxygen.[82] The quenching of $^1O_2$ by compounds containing sulfur,[83] phosphorus,[84] selenium[85] and tellurium[86] is shown to generate active oxygen species with *O*-transfer ability. Most extensively studied are the $^1O_2$ adducts to sulfides,[87] the structure of which is not yet fully understood, however. Theoretical calculations demonstrated energy minima both for the persulfoxides (R_2S^+—O—O^-) and the cyclic thiadioxiranes.[88–90] Widely accepted in the intermediacy of persulfoxides, which act as nucleophilic oxidants,[91] but the participation of thiadioxiranes is still only speculative. On the other hand, the intermediates in the $^1O_2$ oxidation of phosphines and phosphites have been characterized as cyclic phosphadioxiranes, which have an electrophilic O-transfer activity.[93] Theoretical calculations supported the phosphadioxirane as the sole intermediate.[90,93] Such a difference between $X=R_2S$ and $X=R_3P$ is interesting and has been discussed from the conformation of X—O—O species[90] and from the difference in electronegativities between S and P.[93] A conclusion may be drawn when the chemistry of other peroxides of this type is elucidated.

Thus, among a variety of X—O—O species and their cyclic forms with different elements, only a few as described have been explored so far. Further studies will clarify the structure–reactivity relationships in these interesting classes of molecules ranging from $X=$main group elements to $X=$transition metals.

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