Nucleophilic O-Transfer, Cyclizaton, and Decarboxylation of Carbonyl Oxide Intermediate in the Reaction of Stable Imidazolylidene and Singlet Oxygen

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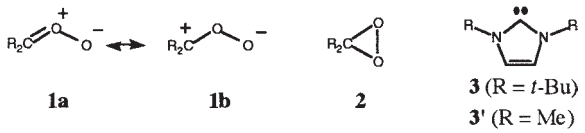
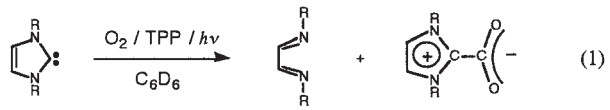
The $^1O_2$ oxidation of 1,3-dialkylimidazol-2-ylidene (alkyl= *tert*-butyl) resulted in the formation of a carbonyl oxide intermediate which was shown to react as a nucleophilic O-transer and to cyclize to an unstable dioxirane intermediate leading to, as final products, bis-imine RN=CH–CH=NR and carbene-CO_2 adduct.

Carbonyl oxides (**1**) are known as a key intermedieate in ozonolyses of olefins[1] and have attracted much attention in the fields of synthetic, biological, and atmospheric chemistry.[2] Cyclic isomers of carbonyl oxides, dioxiranes (**2**), can be prepared by the peroxysulfate oxidation of ketones[3] and are widely employed as versatile oxygen transfer agents.[4] The structural and chemical properties of these peroxidic species are so different depending on their substituents;[5] for example, quite unique property was revealed for a carbonyl oxide carrying a potent electron-withdrawing group.[6] The effect of strong π-donating alkoxy or amino group might be interested as an alternative extreme.



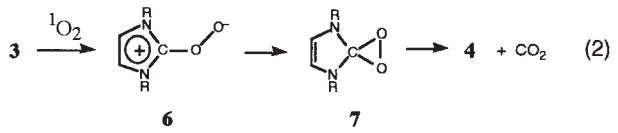
Well-known methods to generate carbonyl oxides are the reaction of triplet carbenes with oxygen $^3O_2$[7] and the oxidation of diazo compounds with singlet oxygen, $^1O_2$,[8] but, the two methods are not easy to apply for heteroatom substituted cases. Arduengo et al. have established the preparation of isolable singlet carbenes, imidazol-2-ylidenes (cf., **3**),[9] which might lead to the reaction of nucleophilic carbenes with $^1O_2$. Here, we wish to report the unique chemistry of the resulting carbene-O_2 adducts.

1,3-Di-tert-butylimidazol-2-ylidene (**3**), a diamino carbene, was prepared according to the literature.[9b] Irradiation (>400 nm) of an oxygen-saturated benzene solution of **3** (13.1 mM) and *meso*-tetraphenylporphyrine (TPP, 0.1 mM) resulted in rapid consumption of **3** and the fomation of bis-imine **4** (51%) and carbene-CO_2 adduct **5** (43%) as shown in eq 1. In the absence of



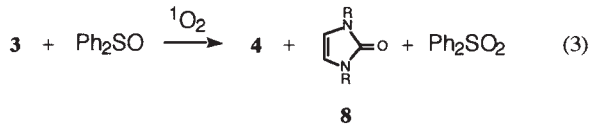
(1)

TPP or O_2, carbene **3** was not consumed under the irradiation conditions, suggesting that **3** was oxidized with $^1O_2$ but not with $^3O_2$. It is interesting to note here that the reaction of singlet carbene **3** with oxygen is controlled by the spin selection rule; i.e., no reaction with $^3O_2$. Carbene **3** was shown to quench the luminescence (1270 nm) of $^1O_2$ with the rate constant of $(9.6 \pm 1.2) \times 10^7\ M^{-1}\ s^{-1}$.[10] The CO_2-adduct **5**,[11] which could be prepared independently by introducing CO_2 into the solution of **3**, was not accumulated when the evolved gas was removed by continuous bubbling of O_2. Thus, it is evident that bis-imine **4** and CO_2 are produced by the reaction of **3** with $^1O_2$ and that **5** is formed by the secondary reaction of CO_2 with **3**; here conceivable is the intermediacy of carbonyl oxide **6** and dioxirane **7** as shown in eq 2.



(2)

Possible intermediacy of **6** and/or **7** was examined by trapping experiments with sulfides and sulfoxides. In the presence of 0.1 M diphenyl sulfoxide, well-known trapping agent for carbonyl oxides,[12] the formation of bis-imine **4** was suppressed, and imidazolone **8** and diphenyl sulfone were obtained (eq 3). Product ratio of **8** and sulfone was 1 : 1 only at the lower conversion because **8** was consumed by the further reaction with $^1O_2$. The sulfone yields increased with the increasing concentration of Ph_2SO, and the extrapolated yield at $[Ph_2SO]=\infty$ was as high as (96 ± 2)%.



(3)

The competitive oxidations with substituted diphenyl sulfoxides, $(p\text{-}XC_6H_4)_2SO$, led to the relative rates of 0.57 : 0.66 : 1.0 : 3.0 for X=MeO, Me, H, and Cl groups, respectively. The resulting Hammett's ρ-value of +0.73 (vs σ, r = 0.977) was larger than those for other carbonyl oxides (e.g., $\rho = +0.26$ for fluorenone *O*-oxide).[12] In contrast to reported cases of common carbonyl oxides,[13] Ph_2S and Me_2S were not oxidized during the photooxidation of **3**. Thus, the highly nucleophilic character of carbonyl oxide **6** was revealed reflecting its zwitterionic structure (cf. eq 2). No observation of O-transfer to sulfides indicates an electrophilic intermediates such as **7** is too short-lived to be trapped intermolecularly.

In order to clarify the mechanism of eq 2, density functional BLYP/6-31G* calculations were carried out for **3′–7′** species (R=Me), the results being summarized in Figure 1. The carbonyl oxides **6′** has a stationary point at almost planar geometry, in which negative charges (−0.284 and −0.400) on central and terminal oxygens of C–O–O are much larger, in good accordance with the observed high nucleophilicity of **6**, than those (−0.023 and −0.302) for the parent carbonyl oxide (**1**, R=H).[14]

The isomerization of common carbonyl oxides to dioxiranes

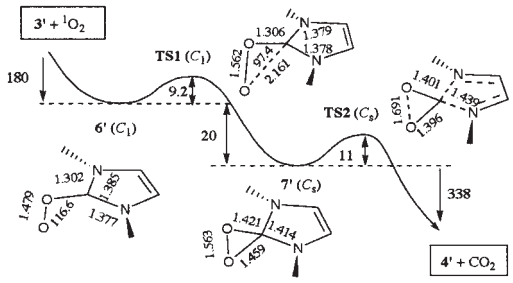


Figure 1. BLYP/6-31G* potential energy surface for the conversion of $\mathbf{3}' + {}^1O_2$ to $\mathbf{4}' + CO_2$. Geometries are shown in Å and degree, and relative energies are given in kJ/mol.

is known to occur photochemically[15] or via vibrationally excited states[16] but does not proceed thermally in solutions.[17] The BLYP/6-31G* calculations, as in recent high-level ab initio results,[18] predict that the cyclization of the parent carbonyl oxide (**1**, R=H) to dioxirane (**2**, R=H) is exothermic by 79.9 kJ/mol but should cross the high energy varrier of 87.0 kJ/mol.[14] For the present cyclization of **6**′ to **7**′, the DFT calculation indicated that the exothermicity and the activation energy were reduced down to 19.7 and 9.2 kJ/mol, respectively. Thus, by introducing a strong π-donating group, the thermochemical stability of carbonyl oxides increases since polarized zwitterionic structure (cf., **1b**) is stabilized; the transition state for the cyclization is likewise favorable since the double-bond character of C–O is minimized, making the C–O–O group be twisted more easily. Such an anomalous substituent effect seems to be characteristic for carbonyl oxides; similar examples have been suggested experimentally for the methoxy substituted case[19] and predicted theoretically for fluoro-,[20] and cyclopropene carbonyl oxides.[21] Present results by trapping experiments and calculations affords a clear-cut demonstration of the oxides.

Another interesting point is that the elimination of CO_2 from the spiro-dioxirane **7**′ is a concerted three-bond cheletropy with the activation energy of only 10.9 kJ/mol. For dialkyl dioxiranes a similar three-bond fission is reported yielding two alkyl radicals and CO_2, but in a stepwise manner with much higher activation energy of 100 kJ/mol.[22] In the present cheletropy from **7**′ to perpendicularly located **4**′ and CO_2, when constrained in C_{2v} symmetry,[23] the symmetry of occupied orbitals is completely conserved in the fragmentation.

In summary, the reaction of a stable singlet carbene **3** with $^1O_2$ is shown to yield carbonyl oxide intermediate with unique properties. The carbonyl oxide **6** has a highly nucleophilic reactivity toward sulfoxides and can easily isomerize to dioxirane **7**, which is expected, according to DFT calculations, to undergo the facile ring-opening with the concerted three-bond fission.

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11 a) ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.76 (s, 18H, 6 × CH_3), 7.36 (s, 2H, C*H*); ^{13}C (500 MHz, $CDCl_3$): δ 30.2 (*C*H$_3$), 60.9 (*C*Me$_3$), 119.7 (*C*H), 175.5 (N$_2$*C*CO$_2$), 207.8 (*C*CO$_2$). Similar adducts are known to be formed from nucleophilic carbenes and carbon disulfide. See Ref. 11b. b) M. Regitz, *Angew. Chem., Int. Ed. Engl.*, **35**, 725 (1996).
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23 Since nitrogens in **7**′ are slightly pyramidized, the spiro-dioxirane has two energy minima corresponding to syn (C_s) and anti (C_2) forms in out-of-plane methyls, the former being 1.42 kJ/mol more stable. The planer C_{2v} structure is a doubly transition state of two nitrogen inversions but is only 2.34 kJ/mol higher in energy than the most stable C_s structure.