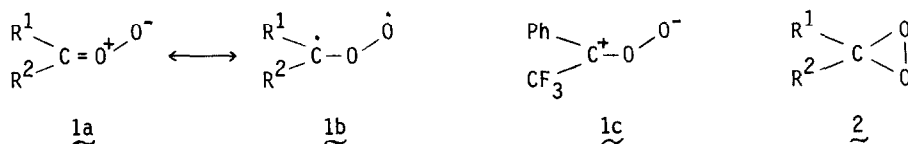


TURNING THE REACTIVITY OF CARBONYL OXIDES FROM NUCLEOPHILIC TO ELECTROPHILIC. A NOVEL DEOXYGENATION OF SULFOXIDES BY ELECTROPHILIC  $\alpha, \alpha, \alpha$ -TRIFLUOROACETOPHENONE  $\underline{Q}$ -OXIDE.

Katsuya Ishiguro, Yukimichi Hirano, and Yasuhiko Sawaki\*  
Department of Applied Chemistry, Faculty of Engineering  
Nagoya University, Chikusa-ku, Nagoya 464, JAPAN

**Summary:** The well-known nucleophilic reactivity of carbonyl oxides could be turned into electrophilic by a potent electron-attracting group. Thus  $\alpha, \alpha, \alpha$ -trifluoroacetophenone  $\underline{Q}$ -oxide oxidizes both sulfides and sulfoxides electrophilically, and the most characteristic reaction is the deoxygenation of sulfoxides.

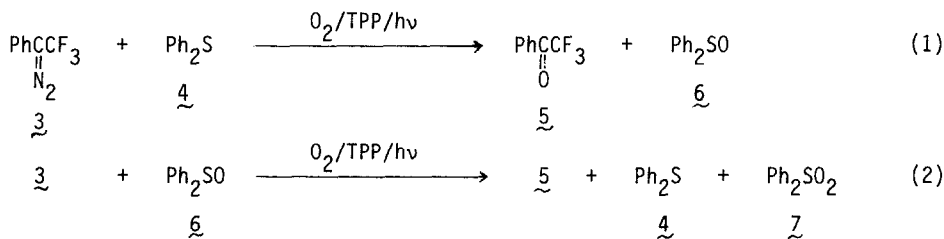
Carbonyl oxides (1), formed by the ozonolysis of olefins<sup>1)</sup> and the photo-oxidation of diazo compounds,<sup>2)</sup> have been attracted much attention as a model for oxygenases or oxenoid intermediates in relation to oxygen activation.<sup>3)</sup>



It has been shown that the characteristic reaction of carbonyl oxides is nucleophilic oxygen transfers,<sup>4-6)</sup> reflecting the importance of structure 1a rather than 1b or 2 which is in contrast to those of electrophilic oxenoids such as ozone<sup>7)</sup> and PhNOO.<sup>8)</sup> Recently, Adam and co-workers have reported on the reactivity of ten carbonyl oxides (1,  $R^1, R^2 = \text{aryl, alkyl, and acyl}$ ) by trapping experiments using thianthrene 5-oxide; all of them react as a nucleophilic oxygen transfer agent, sulfoxides being oxidized much faster than sulfides.<sup>9)</sup> Here, we wish to report that a turn-over in reactivity of carbonyl oxides from nucleophilic to electrophilic can be achieved by a potent electron-withdrawing substituent, trifluoromethyl, and that the electrophilic carbonyl oxide exhibits a novel deoxygenation of sulfoxides.

$\alpha, \alpha, \alpha$ -Trifluoroacetophenone  $\underline{Q}$ -oxide (1c,  $R^1 = C_6H_5, R^2 = CF_3$ ) was generated by the reaction of phenyltrifluoromethyldiazomethane (3) and singlet oxygen, and its reactivity was determined by trapping experiments with sulfides and sulfoxides. Irradiation ( $>400 \text{ nm}$ ) on oxygen-saturated solution of 3 (5.5 mM), 0.1 mM meso-tetraphenylporphine (TPP), and 0.1 M Ph<sub>2</sub>S (4) in dichloromethane-acetonitrile (3 : 1) at 18°C afforded over 90% yield of  $\alpha, \alpha, \alpha$ -

trifluoroacetophenone (5) together with 16.0% yield of Ph<sub>2</sub>SO (6) as an oxygen transferred product (eq 1).<sup>10)</sup> Surprisingly, by addition of sulfoxide 6, the major product was not sulfone 7 but a deoxygenated sulfide 4 (eq 2), the yields being 4.2 and 28.7%, respectively.<sup>11)</sup> Control experiments suggested that diazo compound 3 and singlet oxygen is necessary for this novel deoxygenation.<sup>12)</sup>



Substituent effects were studied to clarify the nature of the oxygenation and deoxygenation by carbonyl oxide 1c and summarized in Table I. The substituent effect on diphenyl sulfides resulted in the negative  $\rho$  value of -0.80, revealing an electrophilic oxygen transfer from 1c to sulfides as observed for other carbonyl oxides<sup>13)</sup> or nitroso oxides.<sup>8)</sup> To our surprise,  $\rho$  values for substituted sulfoxides were also shown to be negative both for sulfide and sulfone formations, -0.69 and -0.42, respectively. Thus, the carbonyl oxide 1c is shown to exhibit an electrophilic character, both in the oxygenation of sulfides and the deoxygenation of sulfoxides, due to the potent electron-withdrawing power of CF<sub>3</sub>. This feature is in sharp contrast to the case of other carbonyl oxides with nucleophilic O-transfer to sulfoxides. Competitive experiments showed that the deoxygenation of sulfoxide is faster than the oxygenation of sulfide; e.g., the deoxygenation of (p-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SO is three times faster than the oxygenation of Ph<sub>2</sub>S.

A possible scheme for the novel deoxygenation of sulfoxide involves, as outlined in Scheme I, a formation of persulfoxide intermediate 10. It is known that persulfoxides, generated from sulfides and singlet oxygen,<sup>14)</sup> easily lose O<sub>2</sub> at room temperature but are significantly stable at -78°C<sup>15)</sup> and oxidize sulfoxides efficiently.<sup>16)</sup> The intermediacy of persulfoxide in the present reaction of carbonyl oxide 1c and diphenylsulfoxide 6 seems not to be unreasonable because the product ratio of 0.15 for Ph<sub>2</sub>SO<sub>2</sub>/Ph<sub>2</sub>S at 18°C increased up to 0.50 at -78°C.

An alternative electrophilic species might be a dioxirane intermediate (2) which is shown to be formed from ketone and carboxate and to transfer oxygen atom to olefins and sulfoxides.<sup>17)</sup> Such a tendency is quite different from that of present reactions of 1c, thus denying the involvement of dioxirane type intermediate.

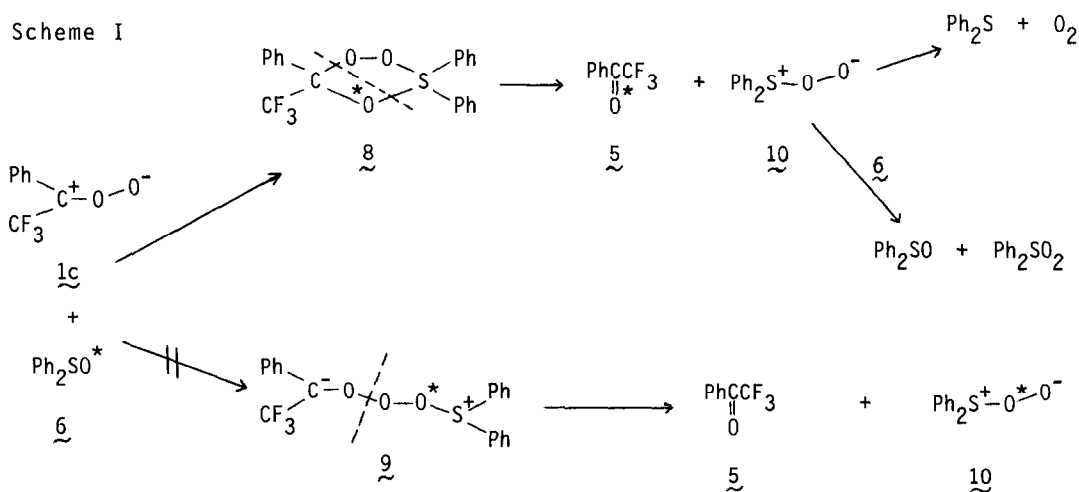
In order to clarify the mechanism in Scheme I an oxygen tracer study was carried out. Whether a cyclic (8) or acyclic intermediate (9) is involved

Table I. Relative Reactivities of Substituted Diphenyl Sulfides and Sulfoxides in the Photo-oxidation of Phenyltrifluoromethyldiazomethane (3).

Ar-	Relative Reactivity <sup>a</sup>		
	additive : Ar <sub>2</sub> S	Ar <sub>2</sub> SO	
	product : Ar <sub>2</sub> SO	Ar <sub>2</sub> S	Ar <sub>2</sub> SO <sub>2</sub>
p-MeOC <sub>6</sub> H <sub>4</sub> <sup>-</sup>	3.03	3.65	1.13
p-MeC <sub>6</sub> H <sub>4</sub> <sup>-</sup>	2.61	1.68	0.44
C <sub>6</sub> H <sub>5</sub> <sup>-</sup>	(1.00)	(1.00)	0.20
p-ClC <sub>6</sub> H <sub>4</sub> <sup>-</sup>	0.54	0.65	0.26
ρ <sup>b</sup>	-0.80	-0.69	-0.42

<sup>a</sup> Relative reactivities toward carbonyl oxide 1c by competitive reactions. Initial concentration; 7.0 mM 3, 0.1 mM TPP, 0.1 M each of sulfides or sulfoxides in MeCN-CH<sub>2</sub>Cl<sub>2</sub> (3 : 1); the solution was irradiated at >400 nm under oxygen at 20 °C for 30 min and products were determined by GLC. <sup>b</sup> the Hammett ρ-values vs. σ.

Scheme I



in the reaction of 1c with 6 could be answered by a tracer experiment using <sup>18</sup>O-labelled sulfoxide 6 (8.5% <sup>18</sup>O); if persulfoxide 10 is formed via cyclic trioxide (8), labelled oxygen from sulfoxide 6 should be transferred to ketone oxygen in 5. The observed <sup>18</sup>O content in 5 was 2.8±0.2%, showing that the oxygen in 6 is actually taken into 5 during the deoxygenation. This suggests the formation of persulfoxide 10 via the addition of electrophilic carbon of 1c to the nucleophilic oxygen atom of sulfoxide 6, i.e., via cyclic sulfurane

8.18)

Thus, the carbonyl oxide 1c is, in contrast to the case of reported oxides, shown to have a potent electrophilic character, which means that the reactivities of carbonyl oxides can be controlled by the nature of substituents. This might be applicable to the other case of X-O-O systems (X = RN, R<sub>2</sub>S, metal etc.).

## References and Notes

- (1) Bailey, P. S. "Ozonation in Organic Chemistry," Academic Press. New York, 1978, Vol. 1, Chap. 6.
- (2) (a) Highley, D. P.; Murray, R. W. J. Am. Chem. Soc. 1974, 96, 3330. (b) Kumar, S.; Murray, R. W. Ibid. 1984, 106, 1040.
- (3) Hamilton, G. A. in "Molecular Mechanism of Oxygen Activation," Hayaishi, O. Ed., Academic Press, New York, 1974, pp. 405.
- (4) Sawaki, Y.; Kato, H.; Ogata, Y. J. Am. Chem. Soc. 1981, 103, 3832.
- (5) Prayor, W. A.; Govindam, C. K. J. Am. Chem. Soc. 1981, 103, 7681.
- (6) Adam, W.; Hass, W.; Sieker, G. J. Am. Chem. Soc. 1984, 106, 5020.
- (7) Bailey, P. S. "Ozonation in Organic Chemistry," Academic press, New York, 1978, Vol. 1; 1982, Vol. 2.
- (8) Sawaki, Y.; Ishikawa, S.; Iwamura, H. J. Am. Chem. Soc. 1987, 109, 584.
- (9) Adam, W.; Dürr, H.; Haas, W.; Lohray, B. Angew. Chem. Int. Ed. Engl. 1986, 25, 101.
- (10) The yields of 6 were 5.4, 11.9 and 16.0% for the reaction with 0.016, 0.05 and 0.10 M 4, respectively. A plot of 1/[yield of 6] vs. 1/[4] is linear and the intercept shows ~30% O-transfer from the carbonyl oxide.
- (11) Similar deoxygenation of diphenylsulfoxides proceeds also for the case of nitroso oxides; Ishikawa, S.; Sawaki, Y. unpublished results.
- (12) Deoxygenation of sulfoxides by electrophilic carbenes is well known. However, Ph $\dot{C}$ CF<sub>3</sub> generated by the direct photolysis of 3 in oxygen-saturated benzene or acetonitrile does not yields a detectable amount of 5 but a complex mixture by reaction with solvent. This shows that the carbene is not generated under the photosensitized conditions.
- (13) Ando, W.; Kabe, Y.; Miyazaki, H. Photochem. Photobiol. 1980, 31, 191.
- (14) Foote, C. S.; Peters, J. W. J. Am. Chem. Soc. 1971, 93, 3795.
- (15) Gu, C. G.; Foote, C. S. J. Am. Chem. Soc. 1982, 104, 6060.
- (16) Sawaki, Y.; Ogata, Y. J. Am. Chem. Soc. 1981, 103, 5947.
- (17) Murray, R. W.; Jeyaraman, R. J. Org. Chem. 1985, 50, 2847.
- (18) A similar but acyclic sulfurane has been described to decompose to 10; J. D. Martin and J. C. Martin, J. Am. Chem. Soc. 1977, 99, 3511.

(Received in Japan 14 July 1987)