Detection of Carbonyl Oxide from Singlet *p*-Nitrophenylchlorocarbene and Oxygen

Michael T. H. Liu,[a] **Roland Bonneau**[b] **and Charles W. Jefford**[c]

[a] *Department of Chemistry, University of Prince Edward Island, Charlottetown, PEI Canada C1A 4P3*
[b] *UA 348 du CNRS, Laboratorie de Chimie Physique A. Université de Bordeaux I, 33405 Talence, France*
[c] *Dept. de Chimie Organique, Université de Genève, 1211 Genève 4, Switzerland*

p-Nitrophenylchlorocarbene reacts with oxygen with a rate constant $2.24 \times 10^7\ \text{M}^{-1}\ \text{s}^{-1}$ in isooctane at 25 °C giving rise to an intermediate carbonyl oxide which absorbs at 400 nm.

The literature is replete with information[1] on the reaction of triplet carbene with oxygen. Matrix isolation spectroscopy[2] has been used to obtain evidence for the formation of carbonyl oxide and/or dioxirane by photo-oxidation of carbene from diazo compounds or diazirine precursors. The kinetics of these reactions and the detection of carbonyl oxides have also been studied by laser flash photolysis (LFP).[3] Thus far, the novel spin-forbidden oxygen addition to singlet phenylchlorocarbene to form carbonyl oxide has been detected only by low-temperature matrix spectroscopy.[2c] LFP studies of 3-chloro-3-phenyl-diazirine,[4] have shown that the reactions of $\text{Ph–}\ddot{\text{C}}\text{–Cl}$ with numerous substrates are insensitive to the presence of oxygen indicating that the rate constant for $\text{Ph–}\ddot{\text{C}}\text{–Cl}$ with oxygen must be $<10^4\ \text{M}^{-1}\ \text{s}^{-1}$. We were surprised to find that the singlet $p\text{-NO}_2\text{–C}_6\text{H}_4\text{–}\ddot{\text{C}}\text{–Cl}$ (PNCC)[5] reacts with oxygen at room temperature and the rate of reaction can be measured in the nanosecond domain.

Pulsed laser photodecomposition of 3-chloro-3-*p*-nitrophenyldiazirine in isooctane (N_2 purged) with the third harmonic of a mode-locked (200 ps) Nd–YAG laser produced a transient absorption ($\lambda = 320$ nm) assigned to PNCC.[5] In contrast to the lack of reactivity of $\text{Ph–}\ddot{\text{C}}\text{–Cl}$ with oxygen on the nanosecond time scale, the singlet PNCC can be readily scavenged by oxygen, as evidenced by the decrease in lifetime in the presence of increasing oxygen concentrations. The decay of PNCC follows clean pseudo-first-order kinetics in the presence of oxygen. A plot of the reciprocal lifetimes for PNCC decay *vs.* the oxygen concentrations (Fig. 1) yielded the quenching rate constant, $k_q = 2.24 \pm 0.05 \times 10^7\ \text{M}^{-1}\ \text{s}^{-1}$.

$$\underset{\text{PNCC}}{p\text{-NO}_2\text{C}_6\text{H}_4\text{–}\ddot{\text{C}}\text{–Cl}} + \text{O}_2 \xrightarrow{k_q} \underset{\mathbf{1}}{p\text{-NO}_2\text{C}_6\text{H}_4\dot{\text{C}}\text{(Cl)–O–}\dot{\text{O}}}$$

This value is two orders of magnitude smaller than for the reaction of triplet carbenes with oxygen,[3a,b] where $k_q = 10^9\ \text{M}^{-1}\ \text{s}^{-1}$.

LFP of the same diazirine in an isooctane solution saturated with oxygen produces a new broad transient absorption ($\tau > 50$ μs) in the 350–500 nm range ($\lambda_{max} = 400$ nm), Fig. 2. This spectrum is similar to carbonyl oxides which have been observed by LFP[3a,b] and by matrix spectroscopy.[2h,c] We assigned these signals to the formation of carbonyl oxide, **1**.

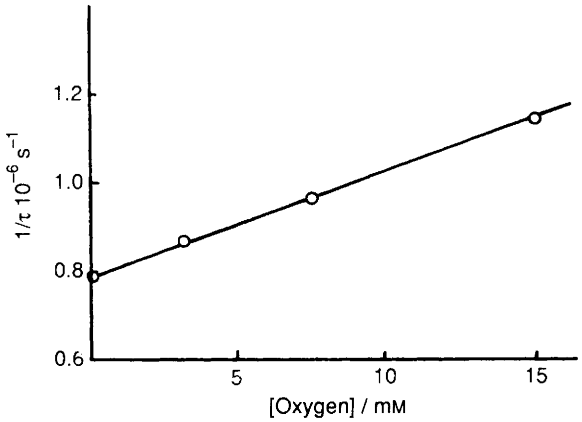

Fig. 1 Plot of reciprocal lifetime of PNCC *vs.* oxygen concentration at 25 °C

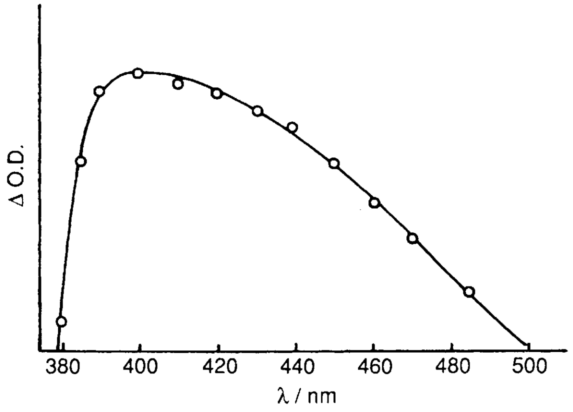

Fig. 2 Transient absorption spectrum obtained 1 μs after excitation of a 10^{-4} M solution of 3-chloro-3-*p*-nitrophenyldiazirine in isooctane (25 °C) containing 1.51×10^{-2} M oxygen

The quantum yield for the decomposition of diazirine is unity[6] and the quantum yield for the formation of **1** can be calculated to be 0.3, $\Phi\ (1) = k_q[O_2]/k_{decay} + k_q[O]_2$. The extinction coefficient ($\varepsilon = 3 \times 10^2\ M^{-1}\ cm^{-1}$) of **1** at 400 nm can be estimated by the relative actinometry technique[7] using benzophenone in benzene as a reference.

Continuous irradiation of diazirine **1** (0.1 M) with oxygen (0.015 M) in isooctane gave several main products: *p*-$NO_2C_6H_4CHO$ (25%), *p*-$NO_2C_6H_4COCl$ (35%), and *p*-$NO_2C_6H_4CHCl_2$ (40%). The isolated yields account for 65% of the starting diazirine. Azine was not detected.

The scavenging of singlet PNCC by oxygen would be allowed if it yielded initially a triplet **1** followed by spin-inversion to the singlet **1**. *Ab initio*[9] and MINDO/3 calculations[9] indicated that the ground states of simple carbonyl oxides are singlets. Decomposition of carbonyl oxide **1** to *p*-$NO_2C_6H_4COCl$, should be straightforward either by disproportionation or by oxygen atom transfer or loss.

The precise origin of *p*-$NO_2C_6H_4CHO$ is unknown but traces of moisture will be expected to give chlorohydrin with singlet PNCC. Subsequent loss of hydrogen chloride from chlorohydrin would give *p*-$NO_2C_6H_4CHO$. The HCl thus liberated could then further add to the singlet carbene to give *p*-$NO_2C_6H_4CHCl_2$. It is likely that the carbene will react with water at rates several orders of magnitude faster than with oxygen since methanol is known to be an extremely efficient singlet carbene scavenger.[6] It is possible, therefore, that even with reasonably carefully dried and handled solvents and equipment, the 25–40% yields of the benzaldehyde and benzal products are understandable. In any event, singlet Ph–$\ddot{C}$–Cl is known to react with aqueous t-butyl alcohol to form benzaldehyde and benzal chloride.[10] In a related study by one of us,[2c] phenylchlorodiazirine was photolysed in an argon matrix in the presence of oxygen, the carbonyl oxide formed was converted to dioxirane by the photolysis of the carbonyl oxide with visible light (λ >410 nm). The formation of dioxirane was also evidenced by its isomerization to phenyl chloroformate. However, chloroformate was not detected among the products of the present work; this suggests that the cyclization of carbonyl oxide to dioxirane can only be achieved at very low temperature.

Finally, we have carried out the photolysis of the diazirine in the presence of *Z*-4-methyl-2-pentene at 25 °C under oxygen or nitrogen. It is well known that singlet carbenes add in stereospecific fashion to alkenes, whereas triplets undergo stepwise addition, giving products in which the stereochemistry of the original alkene is lost. The results demonstrate clearly that all additions take place stereospecifically with no discernible effect by oxygen.

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