**Oxygenation of Benzyldimethylamine by Singlet Oxygen. Products and Mechanism**

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*SUPPLEMENTARY INFORMATION*

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**Experimental Section.**

**Materials.** Benzyldimethylamine **1** (Aldrich), was passed through alumina before use. 1,4-dimethylnaphtalene endoperoxide (**2**)[1] and *N*-benzyl-*N*-methylformamide (**4**)[2] were prepared according to literature procedures. (benzyl-*d₂*)-dimethylamine (**1-d₂**) was prepared by $LiAlD_4$ (Aldrich, 99 % D) reduction of *N,N*-dimethylbenzamide in tetrahydrofuran and characterized by its 70 eV EI mass spectrum: *m/z* (rel intensity) 138 (6), 137 (M$^{+\bullet}$, 65), 136 (10), 135 (27), 94 (10), 93 (59), 67 (7), 66 (8) 60 (100).[3] Benzoquinone (Aldrich) was purified by sublimation. TPP (Aldrich), formaldehyde (Aldrich),2,4,6-tri-*t*-butylphenol (Aldrich), 1,3-diphenylisobenzofuran (Aldrich) and Acetonitrile (Carlo Erba, HPLC plus grade) were used as received

**Oxygenation by thermally generated singlet oxygen.** 1 mL of **2** (0.1 M) and **1** (from$10^{-2}$ to $5\times10^{-2}$ M) in MeCN were heated at 40°C (water bath) in the dark for 4 h. An internal standard (4-methyl-benzophenone) was added, and the mixture was analyzed by GC and GC-MS. Oxidations were also carried out in the presence of benzoquinone (2.5 mM) or 2,4,6-tri-*t*-butylphenol (5 mM). Products analysis (comparison with authentic specimens) was carried out on a Varian CP-3800 gas chromatograph and on a HP 5890 gas chromatograph equipped with a 5972 mass selective detector.

**Oxygenation by photochemically generated singlet oxygen.** Photooxygenation reactions were carried out in a Helios Italquartz reactor equipped with 10 4500-6000 Å lamps (14 watts each). 4 mL of a solution containing **1** ($10^{-2}$ M) and TPP ($10^{-4}$ M, added as 0.2 mL solution in chloroform) in acetonitrile was irradiated at 25° C in a thermostated jacketed tube for 30 min under a slight oxygen bubbling. An internal standard (4-methylbenzophenone) was added and the mixture was analyzed by GC and GC-MS. Experiments in the presence of DABCO (From $5 \times 10^{-4}$ to $1.5 \times 10^{-3}$ M) were also carried out. Products analysis (comparison with authentic specimens) was carried out on a Varian CP-3800 gas chromatograph and on a HP 5890 gas chromatograph equipped with a 5972 mass selective detector.

The amount of $H_2O_2$ was quantitatively determined by titration with iodide ion; the solution was treated, after dilution, with an excess of KI and few drops of AcOH. The amount of $I_3^-$ formed was determined from UV spectra ($\varepsilon = 2.50\times10^4$ M$^{-1}$cm$^{-1}$ at $\lambda_{max} = 361$ nm).[4] Blank experiments, performed in the absence of **1**, showed no formation of $H_2O_2$.

**Temperature effect on TPP-sensitized photooxygenation of benzyldimethylamine.** Photooxygenation reactions were carried out in a Helios Italquartz reactor equipped with an immersion medium pressure Hg lamp (125 watts) and thermostated at 25 or -48°C. 50 mL of a solution containing **1** ($10^{-2}$ M) and TPP ($10^{-4}$ M, added as 2.5 mL solution in chloroform) in acetonitrile was irradiated for 10 min under oxygen bubbling. An internal standard (4-methylbenzophenone) was added and the mixture was analyzed by GC and GC-MS.

**Determination of the intramolecular deuterium kinetic isotope effect.** $1$-$d_2$ ($10^{-2}$ M) was oxygenated by thermally and photochemically generated singlet oxygen as previously described. Product analysis was carried out by GC and GC-MS analysis. The intramolecular deuterium kinetic isotope effect was determined by dividing the **3/4** molar ratio (obtained in the oxidation of **1**) by the **3-d₁/4-d₂** molar ratio.

**Determination of the intermolecular deuterium kinetic isotope effect.** An equimolar mixture of **1** ($5 \times 10^{-3}$ M) and **1-d₂** ($5 \times 10^{-3}$ M) was oxygenated by thermally and photochemically generated singlet oxygen as previously described. The overall **3** + **3-d₁** and **4** + **4-d₂** amounts were determined by GC analysis while the **3/3-d₁** and **4/4-d₂** molar ratios were measured by GC-MS analysis (Single Ion Monitoring mode) by the ratio of the molecular peaks $m/z$ = 106-107 and 149-151 respectively, corrected for the $^{13}$C contribution.

**Determination of quenching rate constants ($k_q$) of $^1O_2$ by 1 and 1-d$_2$.** $^1O_2$ was produced by energy transfer to $O_2$ from the triplet state of phenalenone, generated by excitation at 355 nm from a Nd:YAG laser (pulse width ca. 7 ns and energy < 3 mJ per pulse). The phosphorescence emission of $^1O_2$ was detected by a germanium diode detector.[5] Rate constants for the quenching of $^1O_2$ ($k_q$) were determined from the decrease of $^1O_2$ emission lifetime in $O_2$-saturated MeCN, in the presence of various amounts of **1** or **1-d$_2$** (0.15-2.0 × 10$^{-3}$ M). All measurements were carried out at 22 ± 2 °C. The $k_q$ values are 9.7×10$^7$ and 9.9×10$^7$ M$^{-1}$s$^{-1}$ for **1** and **1-d$_2$**, respectively. As example, in Figure S1 the dependence of $k_q$ on **1** concentration is shown.
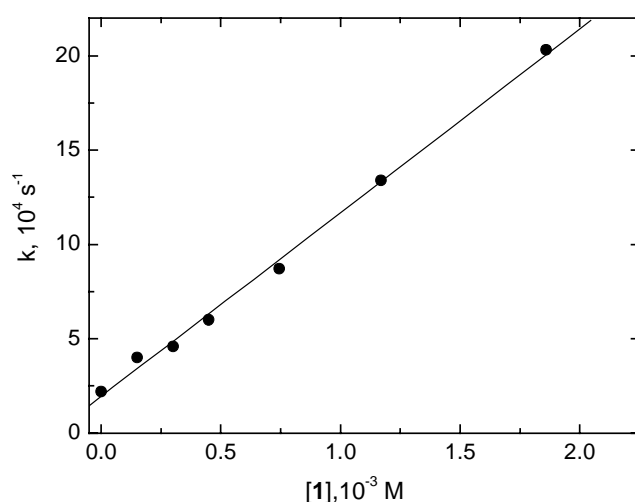


**Figure S1.** Dependence of $k_q$ on **1** concentration.

In order to determine the effect of temperature on the quenching rate constants, pulsed laser photolysis experiments were carried out, by following a procedure previously described.[6] Experiments were performed with a Nd:YAG laser,[7,8] by using 2-acetonaphtone as sensitizer, and the bleaching of diphenylisobenzofuran (DPBF) as the means of monitoring $^1O_2$ decay. Two $O_2$-saturated solutions containing same amount of 2-acetonaphtone (5.4 × 10$^{-2}$ M) and DPBF (3.0 × 10$^{-5}$ M), only one containing **1** (7.0 × 10$^{-4}$) M, were irradiated by laser pulse at 20° and -15 °C. A cryostat was used to control temperature. The $k_q$ values were obtained from the difference between the first-order constants for DPBF bleaching ($k$), determined in the presence and in the absence of **1** by eq. S1.

$$k = k' + k_r[\text{DPBF}] + k_q[\textbf{1}] \qquad (\text{S1})$$

where $k'$ and $k_r$ are the rate constants for the $^1O_2$ decay in the medium and for reaction of this species with DPBF, respectively. In our experimental condition $k$ values result $4.34 \times 10^4$ and $4.17 \times 10^4$ s$^{-1}$ in the absence of **1**, $1.36 \times 10^5$ and $1.43 \times 10^5$ s$^{-1}$ in the presence of **1**, at 20° and −15° C, respectively. By eq. 1, a value of $1.3 \times 10^8$ and $1.4 \times 10^8$ M$^{-1}$s$^{-1}$ were calculated for $k_q$ at 20° and -15° C, respectively.

**Table S1.** Effect of DABCO on the TPP-sensitized photooxygenation of **1** in oxygen saturated MeCN.

| [DABCO] (mM) | Products (μmol)[a] | |
| --- | --- | --- |
| | **3** | **4** |
| 0 | 4.8 (0.2) | 3.2 (0.1) |
| 0.5 | 4.1 (0.2) | 2.6 (0.1) |
| 1 | 3.7 (0.1) | 2.3 (0.1) |
| 1.5 | 3.2 (0.1) | 2.3 (0.1) |

[a] Determined by GC analysis. The error (standard deviation) in the last significant digit, is given in parentheses.

A progressive decrease in the products yields was observed by increasing the concentration of DABCO. Since DABCO competes with **1** for $^1O_2$, the relation reported in eq. S2 must hold, where $k_{dabco}$ and $k_1$ are the rate constants for the reaction of DABCO and **1** with $^1O_2$.

$$[\text{products}]°/[\text{products}] = 1 + k_{dabco}[\text{DABCO}] / k_1[\mathbf{1}] \qquad (S2)$$

The ratio between the product yields (**3** + **4**) in the absence and in the presence of DABCO is linearly correlated to the DABCO concentration (Figure S2). Knowing that $k_1 = 9.7 \times 10^7\,M^{-1}s^{-1}$ and [**1**] = 0.01 M, from the slope of the plot (304) it is possible to calculate $k_{dabco}$ ($3.0 \times 10^8\,M^{-1}\,s^{-1}$), which is in agreement with literature values.[9]
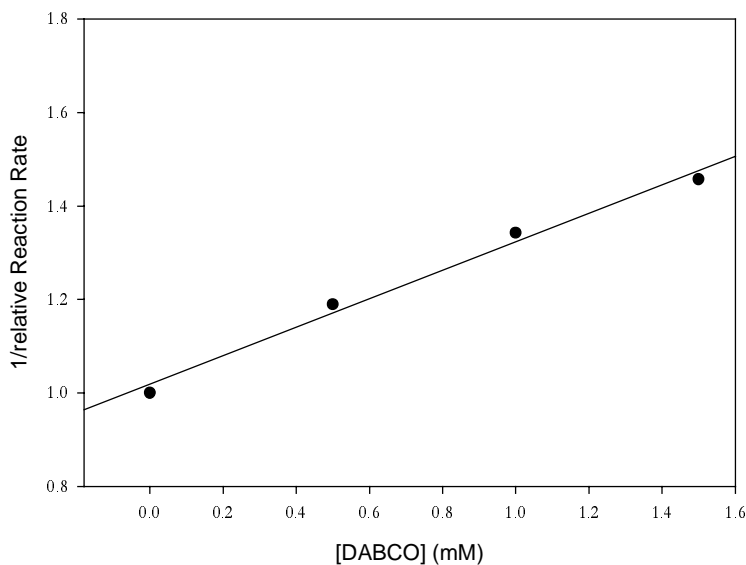


**Figure S2.** Reciprocal of the relative rate of **5** + **6** formation vs DABCO concentration ($r^2 = 0.988$) in the TPP-sensitized photooxygenation of **1** in oxygen saturated MeCN.

**References.**

(1)    Turro, N. J.; Chow, M. F. *J. Am. Chem. Soc.* **1981**, *103*, 7218.

(2)    Freudenreich, C.; Samama, J. –P.; Biellmann, J. –F. *J. Am. Chem. Soc.* **1984,** *106*, 3344.

(3)    Shaffer, S. A.; Sadilek, M.; Turecek, F. *J. Org. Chem.* **1996,** *61*, 5234.

(4)    Fukuzumi, S.; Kuroda, S.; Tanaka, T. *J. Am. Chem. Soc.* **1985,** *107*, 3020.

(5)    Elisei, F.; Aloisi, G. G.; Lattarini, C.; Latterini, L.; Dall'Acqua, F.; Guiotto, A. *Photochem. Photobiol*. **1996**, *64*, 67.

(6)    Gorman, A. A.; Gould, I. R.; Hamblett, I.; Standen, M. C. *J. Am. Chem. Soc* **1984**, *106*, 6956.

(7)    Romani, A.; Elisei, F.; Masetti, F.; Favaro, G. *J. Chem. Soc. Faraday Trans.* **1992**, *88*, 2147.

(8)    Görner, H.; Elisei, F.; Aloisi, G. G. *J. Chem. Soc. Faraday Trans.* **1992**, *88*, 29.

(9)    Wilkinson, F.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1995**, *24*, 663.