

EVIDENCE FOR PHYSICAL QUENCHING OF SINGLET OXYGEN ($O_2(^1\Delta_g)$) BY DINITROPHENOLS

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Summary

The interaction of singlet molecular oxygen $O_2(^1\Delta_g)$ with 2,4-, 2,5- and 2,6-dinitrophenol was investigated. No reaction products were obtained even after several hours irradiation.

The inhibition of the self-sensitized photo-oxidation of rubrene by the dinitrophenols was studied. From the data, rate constants of the order of $10^6 M^{-1} s^{-1}$ were calculated for the physical quenching of $O_2(^1\Delta_g)$ by these compounds.

1. Introduction

The dye-sensitized photo-oxidation of phenols has been reviewed extensively in the literature [1] but, to the best of our knowledge, the behaviour of dinitrophenols (DNPs) under these conditions has not been reported as yet. The importance of examining these compounds lies in their pesticidal activity, especially the 2,4- and 2,6-dinitrophenols (2,4- and 2,6-DNP) [2].

It has been shown in several studies that the photo-oxidation of phenols can proceed through a mechanism which involves reaction with singlet oxygen ($O_2(^1\Delta_g)$), although a free-radical mechanism via 3O_2 can operate simultaneously [3 - 5].

With regard to the interaction of phenols with $O_2(^1\Delta_g)$, both oxidation and physical quenching has been reported [1].

In this paper we present evidence that DNPs can act as physical quenchers of $O_2(^1\Delta_g)$. However, no chemical change was observed, even after prolonged irradiation.

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2. Experimental details

$O_2(^1\Delta_g)$ was generated in benzene by irradiation of rubrene (R) at wavelengths greater than 500 nm (cut-off filter). Light from a mercury lamp (Osram, HBO 200/2) was passed through a water filter and focused onto a spectrophotometric cuvette of path length 1 cm which contained the aerated solution. The solutions were continuously stirred by a magnetic device.

The R concentration, which was initially about 10^{-5} M, was monitored by following its absorption at 520 nm, employing a Shimadzu UV-140-02 spectrophotometer. The absorption spectra were recorded with a Cary 17 instrument and the fluorescence intensities were measured with a modified [6] Aminco SPF 125. Fluorescence lifetimes were determined as previously described [7]. Thin-layer chromatography (TLC) of the photolysed solutions was performed using a solvent mixture of benzene, acetone and butanol (8:1:1.5 by volume) on silica-gel plates.

2,4-, 2,5- and 2,6-DNP were purchased from Fluka and used without further purification. They were dried and their purity was checked by TLC before use. R and 9,10-diphenylanthracene (DPA) (from Ega Chemie) and β -carotene (from Fluka) were used as received. 1,3-Dinitrobenzene (1,3-DNB) (from Aldrich) was purified by recrystallization. Benzene was purified by standard procedures.

All measurements were made at room temperature.

3. Results and discussion

For the evaluation of the rate constants of interaction of $O_2(^1\Delta_g)$ with the DNPs, the inhibition of the self-sensitized photo-oxidation of R by DNP was used. A modification of the treatment by Carlsson *et al.* [8] was employed, which considers the case in which the $O_2(^1\Delta_g)$ quencher also acts as a quencher of the excited singlet state of the sensitizer [1].

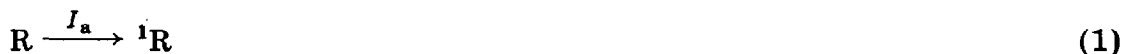
Initial rates of R consumption were measured in the absence (V^0) and the presence (V) of DNP. Since the irradiation conditions, the time, the fluence and the concentrations of R and O_2 were kept constant, the ratio of the initial rates can be taken as equal to the ratio of the quantum yields for R consumption.

We found that 2,4-, 2,5- and 2,6-DNP quench R fluorescence diffusionally ($k_q = (1.4 \pm 0.2) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). The agreement between dynamic and static fluorescence measurements was established by determining the lifetimes and fluorescence intensities (static) in the absence and the presence of DNP. The use of fluorescence intensities was preferred because of the better accuracy of the measurements.

The initial rates of R photo-oxidation (V^0/V) were compared with the ratios of the fluorescence intensities (I_f^0/I_f) under the same conditions. In each case the former was greater than the latter, indicating that there were

some other interactions in addition to the quenching of the sensitizer fluorescence.

A possible kinetic scheme for the photo-oxidation of R in the presence of DNP under a constant concentration of oxygen is the following:



where 1R and 3R represent the excited singlet state and the triplet state of R respectively, and R_{ox} is the oxidation product of R.

From steady state analysis, and assuming that $k_6[DNP] \ll k_5 + k_7[{}^3O_2]$, it follows that the ratio of the initial rates of R consumption is given by

$$\begin{aligned} \frac{V^\circ}{V} &= \left(1 + \frac{k_{10}[DNP]}{k_8 + k_9[R]}\right) \frac{k_2 + k_4 + k_3[DNP]}{k_2 + k_4} \\ &= \left(1 + \frac{k_{10}[DNP]}{k_8 + k_9[R]}\right) \frac{\tau^\circ}{\tau} \end{aligned} \quad (11)$$

where τ° and τ are the singlet state lifetimes of the sensitizer in the absence and in the presence of DNP respectively.

Since fluorescence quenching is a dynamic process, the ratio I_f°/I_f can be used instead of τ°/τ , I_f° and I_f being the fluorescence intensities of the sensitizer in the absence and in the presence of DNP respectively. Equation (11) can then be written as

$$\frac{V^\circ}{V} \frac{I_f}{I_f^\circ} = 1 + \frac{k_{10}[DNP]}{k_8 + k_9[R]} \quad (12)$$

A plot of $V^\circ I_f / V I_f^\circ$ vs. $[DNP]$ at constant $[R]$ should be linear. Such a plot is shown in Fig. 1, and from the slopes of the lines the relative values of k_{10} for the three DNPs can be obtained (Table 1).

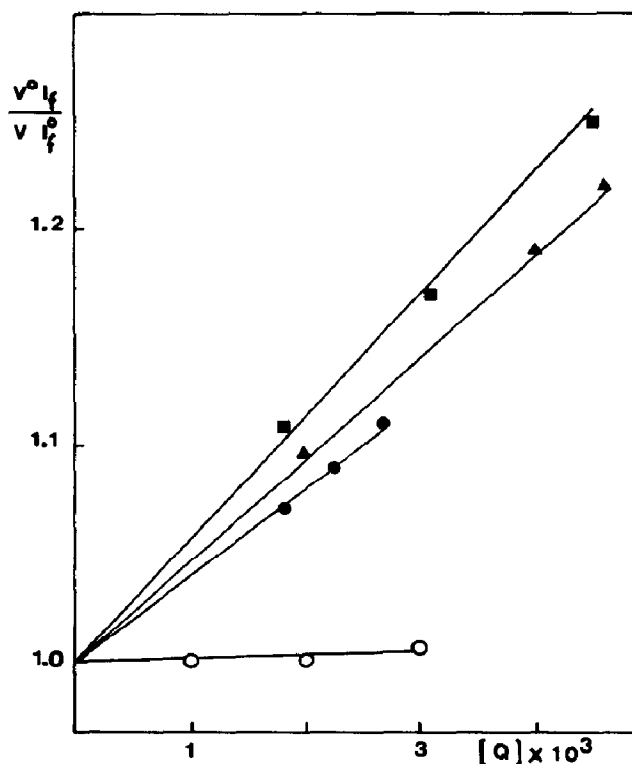


Fig. 1. Effect of DNP on R photo-oxidation (in air-saturated benzene solution at room temperature) plotted according to eqn. (11): ●, 2,4-DNP; ▲, 2,5-DNP; ■, 2,6-DNP; ○, 1,3-DNB.

TABLE 1

Rate constants for the quenching of $O_2(^1\Delta_g)$ by dinitrophenols in benzene at room temperature

Quencher	k_{rel}^a	$k_{10}^b (\times 10^6 M^{-1} s^{-1})$
2,4-DNP	1	1.4
2,5-DNP	1.14	1.6
2,6-DNP	1.43	2.0

^aRelative rate constant for $O_2(^1\Delta_g)$ quenching; estimated error, $\pm 5\%$.

^bUpper limit, see text.

In order to obtain the absolute values of k_{10} it is necessary to know k_8 and k_9 . Literature reports [9 - 11] for k_8 are in the range $(3.3 - 4.1) \times 10^4 s^{-1}$. We redetermined k_9 by irradiation of R alone at different initial concentrations. A value of $3.4 \times 10^7 M^{-1} s^{-1}$ was obtained in agreement with the results of other workers [8, 12]. Accordingly, for the concentrations of R employed in our experiments, $k_8 \gg k_9[R]$. Employing the lowest value [11] of k_8 ($(3.3 \pm 0.3) \times 10^4 s^{-1}$) an upper limit for k_{10} can be obtained (Table 1).

In order to check whether the observed inhibition of the peroxidation of R by DNP is due to reaction of the latter with $O_2(^1\Delta_g)$ or with 3R (reaction (6)), runs using β -carotene or DPA as auxiliary quenchers (Q_A) were carried out. β -Carotene is one of the most effective physical quenchers of $O_2(^1\Delta_g)$, and the process is diffusion controlled. Values between 1.3×10^{10} and $2 \times 10^{10} M^{-1} s^{-1}$ have been reported for the reaction



in benzene [13, 14].

DPA reacts chemically with $O_2(^1\Delta_g)$, with a rate constant $k_{13} = 1 \times 10^6 M^{-1} s^{-1}$ in benzene at room temperature [15].

The expression for the initial rate of R photo-oxidation in the presence of Q_A ($V_{Q_A}^\circ$) and Q_A plus DNP (V_{Q_A}) becomes

$$\frac{V_{Q_A}^\circ}{V_{Q_A}} = \frac{k_8 + k_9[R] + k_{10}[DNP] + k_{13}[Q_A]}{k_8 + k_9[R] + k_{13}[Q_A]} \frac{I_f^{\circ'}}{I_f'} \quad (14)$$

where $I_f^{\circ'}$ and I_f' are the fluorescence intensities in the presence of Q_A and Q_A plus DNP respectively.

For conditions in which $k_{13}[Q_A] \gg k_{10}[DNP]$, eqn. (14) may be simplified to

$$\frac{V_{Q_A}^\circ}{V_{Q_A}} = \frac{I_f^{\circ'}}{I_f'} \quad (15)$$

If eqn. (15) is fulfilled, it can be concluded that process (6) is unimportant. At the same time, if relation (15) is valid, it is confirmed that the only inhibitory process of R photo-oxidation by DNP is scavenging of $O_2(^1\Delta_g)$. It can be seen in Table 2 that the results agree with eqn. (15) within experimental error in each case.

We tried to distinguish between reactive and physical quenching by performing long-time photolysis, with replenishing of R, and looking for DNP consumption or the appearance of products. No changes were observed by UV-visible spectroscopy or TLC after photolysis for 5 h. From the initial rate of R consumption under similar conditions, assuming that a maximum change of 1% in DNP concentration could remain undetected after irradiation for 1 h, it can be estimated that less than 5% of the quenching events lead to chemical change. This chemical inertness of DNP towards $O_2(^1\Delta_g)$ is not a totally unexpected finding, since the two strong electron-withdrawing groups on the ring give these compounds electron-acceptor character rather than the electron-donor properties that are required for reaction with $O_2(^1\Delta_g)$ [16].

In contrast, phenols are known to be very reactive towards $O_2(^1\Delta_g)$ when the ring has alkyl-group substituents, leading to products from both quenching and oxidation. In most cases the elucidation of the relative importance of the two processes still remains open to question [1].

TABLE 2

Effect of competitive quenching on the photo-oxidation of rubrene in benzene at room temperature

Quencher	Quencher concentration ($\times 10^3$ M)	V_{QA}^0/V_{QA}	I_f^0/I_f'
2,4-DNP and β -carotene	2.0 0.011	1.30	1.31
2,5-DNP and β -carotene	3.05 0.011	1.66	1.63
2,6-DNP and DPA	1.0 20	1.18	1.17

Therefore, since the observed interaction of $O_2(^1\Delta_g)$ with DNP can be ascribed to physical quenching, the next question is which type of mechanism is operating.

First we tried to identify the group responsible for the interaction. For this purpose, 1,3-DNB was employed as a quencher. No effect beyond the fluorescence quenching of R was observed (Fig. 1). So it can be concluded that an OH group is necessary for the quenching of $O_2(^1\Delta_g)$.

Sterically hindered disubstituted phenols such as 2,6-di-*tert*-butylphenol (TBP) have a weak inhibitory effect in oxygenation reactions. Several workers [4, 17] have reported evidence for the participation of $O_2(^1\Delta_g)$ in hydrogen abstraction from the phenolic group but the total rate constant for the quenching process (chemical and physical quenching) remained of the order of $10^5 \text{ M}^{-1} \text{ s}^{-1}$ in benzene. A small inhibitory effect on the photo-consumption of R for the same compound was reported by Ouannes and Wilson [18], when high concentrations of TBP (about 0.3 M) were employed.

α -Tocopherol constitutes one of the natural phenols more extensively studied in relation to $O_2(^1\Delta_g)$ [19 - 21]. It was shown that it scavenges $O_2(^1\Delta_g)$ by a combination of physical and reactive quenching, but the most important contribution was found to be the former [19].

In this context the apparent absence of photo-oxidation in the case of DNP constitutes an expected result. Few speculations can be made about the mechanism for the physical quenching observed.

Fahrenholtz *et al.* [19] reported that for two substituted phenols the rate of reaction increases as the ionization potential of the substrate decreases. In our case, even considering the low value for the quenching rate constant, the operation of a mechanism related to a charge transfer component seems to be very unlikely, because the dinitrophenolic nucleus is a poor electron donor.

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