

## QUENCHING OF SINGLET OXYGEN BY NICKELOCENE

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## Summary

The rate constants  $k_q^\Delta$  for the quenching of singlet oxygen by nickelocene were determined in various solvents at 295 K by employing the competition technique based on 532 nm laser flash photolysis and 1,3-diphenylisobenzofuran bleaching kinetics. Contrary to the behavior of paramagnetic nickel(II) complexes in general, nickelocene is an efficient quencher of singlet oxygen ( $k_q^\Delta = (2.8 - 6.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). The quenching mechanism involves both energy transfer and reversible charge transfer interactions.

## 1. Introduction

Organonickel complexes have been studied in some detail as quenchers of singlet oxygen ( $^1\text{O}_2^*$ ,  $^1\Delta_g$ ) [1 - 9] because of their use as photostabilizers for polymeric materials. The bimolecular rate constants  $k_q^\Delta$  for the quenching of singlet oxygen by nickel complexes vary over four orders of magnitude ( $(2.1 \times 10^6) - (1.1 \times 10^{10})$  in chloroform solution [9]). Interestingly, diamagnetic complexes are far more efficient quenchers than those which are paramagnetic [9]. Correlations have been observed between  $k_q^\Delta$  and the rate constants for the quenching of pentacene triplet [7] and rubrene fluorescence [9]. The efficient quenching of singlet oxygen by diamagnetic complexes probably occurs by a non-destructive physical mechanism involving energy transfer from  $^1\text{O}_2^*$  to low-lying excited states of the complexes [7 - 9].

We have been interested in performing a kinetic study of the quenching of  $^1\text{O}_2^*$  by nickelocene for several reasons. First, in spite of the considerable interest in the interaction of  $^1\text{O}_2^*$  with metal complexes, including ferrocene [10], to the best of our knowledge nickelocene has not yet been studied. Second, this work represents an obvious continuation of our recent kinetic study of the quenching of organic triplets by nickelocene [11]. It has been observed that, like oxygen, nickelocene is an efficient universal quencher of organic triplets, including those with an energy  $E_T$  close to that of  $^1\text{O}_2^*$  (e.g. pentacene and  $\beta$ -carotene). Third and most important, nickelocene is a non-planar paramagnetic nickel(II) complex (triplet) possessing excited

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state and redox properties that favor energy and charge transfer interactions. Its behavior towards  $^1\text{O}_2^*$  has a number of implications regarding the energetic, steric and spin-statistical factors which affect the rates of quenching.

## 2. Experimental details

Nickelocene (Alfa) was recrystallized from *n*-hexane (under argon) and then sublimed under vacuum. 4,4'-Dimethoxythiobenzophenone (DMTBP; Aldrich) and 1,3-diphenylisobenzofuran (DPBF; Aldrich) were recrystallized from an 80vol.%cyclohexane–20vol.%dichloromethane mixture and ethanol respectively. The solvents were spectral grade.

The laser flash photolysis experiments were performed employing, for excitation, 532 nm laser pulses (second harmonic; 10 mJ or below; about 6 ns) from an Nd–YAG system (Quanta-Ray DCR-1). Rectangular quartz cells of path length 2 mm were used in a front-face geometry. Details of the kinetic spectrophotometer and data collection system are available elsewhere [12, 13]. For the measurement of the depletion of DPBF at 420 nm during laser flash photolysis, an Oriel 5429 interference filter was placed in the path of the analyzing light in front of the photolysis cell. All experiments were carried out in air-saturated solutions. In order to avoid the loss of nickelocene by oxidation, microliter quantities of the stock solution (1 - 2 mM nickelocene) under argon were added to the photolysis solution immediately before flash excitation. Exposure of the solutions to room light was kept to a minimum during their preparation and during the photolysis experiments.

## 3. Results

We employed DMTBP to photosensitize the production of  $^1\text{O}_2^*$ . The use of DMTBP has the following advantages. First, it is characterized by a broad absorption band system in the visible ( $\lambda_{\text{max}} = 580$  nm in benzene) arising from the lowest-lying  $n \rightarrow \pi^*$  singlet transition. Solutions of 0.4 - 0.6 mM DMTBP in various solvents have absorbances close to 0.02 in 2 mm cells at 532 nm. At these and lower concentrations a window becomes available at 300 - 320 nm through which it can be checked whether nickelocinium cations are formed (from the quenching of  $^1\text{O}_2^*$ ). Furthermore, the absorbances due to DMTBP remain negligible in the spectral region (420 - 430 nm) over which the bleaching of DPBF is monitored. Second, under 532 nm excitation, DMTBP has intersystem crossing yields and triplet-mediated  $^1\text{O}_2^*$  sensitization yields close to unity (in benzene [14]). Third, although thioketones are known [15] for photo-oxidation as a result of their reaction with  $^1\text{O}_2^*$ , laser flash excitation (532 nm) of DMTBP at a sub-millimolar concentration in an air-saturated solution does not lead to any significant bleaching in the region of its strong ground state absorption (340 - 380 nm).

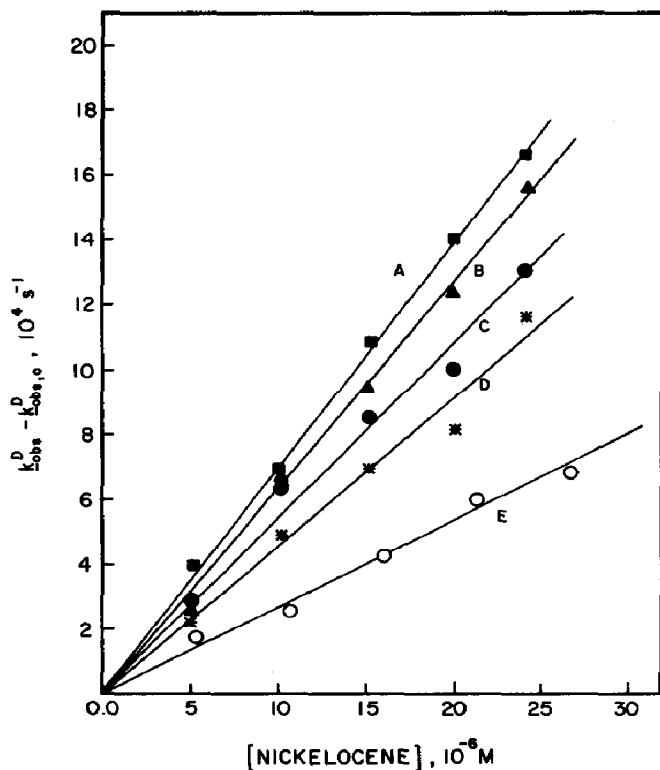


Fig. 1. Plots according to eqn. (8b): curve A, methanol; curve B, acetonitrile; curve C, benzene; curve D, cyclohexane; curve E, carbon tetrachloride.

TABLE 1

Bimolecular rate constants  $k_q^{\Delta}$  for the quenching of singlet oxygen by nickelocene in various solvents at 295 K

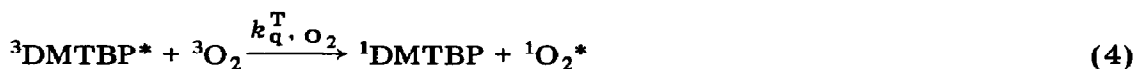
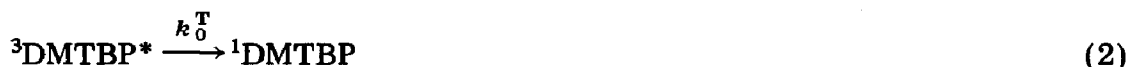
Solvent	$\epsilon^a$	$\eta^a$ (cP)	$k_q^{\Delta}$ <sup>b</sup> ( $\times 10^9$ M <sup>-1</sup> s <sup>-1</sup> )
Cyclohexane	2.023 <sup>c</sup>	0.980 <sup>c</sup>	4.5
Carbon tetrachloride	2.238 <sup>c</sup>	0.90	2.7
Benzene	2.275	0.61	5.4
Chloroform	4.806 <sup>c</sup>	0.542	4.4
<i>tert</i> -Butanol	12.47	3.316	2.8
2-Propanol	18.3	2.04	2.9
Acetone	20.7	0.316	4.8
Methanol	32.70	0.547	6.8
Acetonitrile	37.5 <sup>c</sup>	0.345	6.4

<sup>a</sup>Taken from refs. 20 and 21.

<sup>b</sup>Maximum error,  $\pm 20\%$  (from  $2\sigma$ ,  $\sigma$  being the standard deviation of the least-squares best fits based on eqn. (8b)).

<sup>c</sup>At 293 K; the other values are at 298 K.

DPBF was used to monitor  $^1\text{O}_2^*$ . Its reaction with  $^1\text{O}_2^*$ , which leads to an endoperoxide and results in the bleaching of the ground state absorption, is well established [7, 16, 17]. The various processes initiated by the laser flash excitation of DMTBP in the presence of DPBF and nickelocene in aerated solutions are represented by the reactions



where  $\text{NiCp}_2$  denotes nickelocene. The possible modes of quenching of  $^1\text{O}_2^*$  by nickelocene (reaction (7)) will be discussed below. The rate constants for the quenching of  $^3\text{DMTBP}^*$  by oxygen [14] and nickelocene [11] in benzene are  $3.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  respectively. Also, since the triplet energy of DPBF ( $E_T = 33.9 \text{ kcal mol}^{-1}$  [18]) is much lower than that of DMTBP ( $E_T = 41.1 \text{ kcal mol}^{-1}$  [19]), it is expected that  $^3\text{DMTBP}^*$  will be quenched by DPBF at a diffusion-controlled rate. However, since the concentrations of DPBF (0.04 - 0.05 mM) and nickelocene (0.0 - 0.03 mM) used in our experiments are much lower than those of oxygen (2 - 3 mM) under air saturation, the decay of  $^3\text{DMTBP}^*$  is dominated by the energy transfer quenching by oxygen (reaction (4)) in competition with self-quenching (reaction (3),  $k_{\text{SQ}} = 2.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in benzene [14]). On the condition that the consumption of DPBF and nickelocene (see below) by  $^1\text{O}_2^*$  is small compared with their concentrations, the pseudo-first-order rate constant for the depletion of DPBF is given by the equations

$$k_{\text{obs}}^D = k_0^\Delta + k_D^\Delta [\text{DPBF}] + k_q^\Delta [\text{NiCp}_2] \quad (8a)$$

$$k_{\text{obs}}^D = k_{\text{obs},0}^D + k_q^\Delta [\text{NiCp}_2] \quad (8b)$$

where  $k_{\text{obs},0}^{\text{D}}$  represents the rate constant for the bleaching of DPBF at  $[\text{NiCp}_2] = 0$ . From eqn. (8b), the linear plot of  $(k_{\text{obs}}^{\text{D}} - k_{\text{obs},0}^{\text{D}})$  against  $[\text{NiCp}_2]$  should have a slope equal to  $k_{\text{q}}^{\text{A}}$ .

Figure 1 shows some representative plots based on eqn. (8b). The data for  $k_{\text{q}}^{\text{A}}$  in various solvents are presented in Table 1. As expected, at a given  $[\text{DPBF}]$  the absorbance change  $\Delta\text{OD}^{\text{D}}$  due to DPBF loss after the completion of the bleaching process is found to decrease with increasing  $[\text{NiCp}_2]$ . On the condition that the quenching of  $^3\text{DMTBP}^*$  by nickelocene is negligible,  $\Delta\text{OD}^{\text{D}}$  is given by the equation

$$\frac{\Delta\text{OD}_0^{\text{D}}}{\Delta\text{OD}^{\text{D}}} = 1 + \frac{k_{\text{q}}^{\text{A}}}{k_{\text{obs},0}^{\text{D}}} [\text{NiCp}_2] \quad (9)$$

where  $\Delta\text{OD}_0^{\text{D}}$  corresponds to DPBF bleaching at  $[\text{NiCp}_2] = 0$ . Figure 2 shows a typical plot based on eqn. (9). The slope of this plot is  $3.5 \times 10^4 \text{ M}^{-1}$ . The value of  $k_{\text{obs},0}^{\text{A}}$  at the  $[\text{DPBF}]$  used is  $1.6 \times 10^5 \text{ s}^{-1}$ . From these data, we obtain  $5.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for  $k_{\text{q}}^{\text{A}}$  (in methanol), which is in reasonable agreement with the value ( $6.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) determined from the concentration dependence of the DPBF depletion kinetics.

In the absence of DPBF and at nickelocene concentrations sufficiently high to quench more than 50% of the  $^1\text{O}_2^*$ , we looked for transient absorbance changes (if there were any) at 300 - 320 nm over 50 - 100  $\mu\text{s}$ . In none of the solvents used was any significant absorbance change observed that could be attributed to nickelocene consumption or to the formation of nickelocinium cation as a result of the interaction of nickelocene with  $^1\text{O}_2^*$ . Note that the nickelocinium cation has an intense absorption band system with  $\lambda_{\text{max}} = 306 \text{ nm}$  ( $\epsilon_{\text{max}} = 2.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) [22].

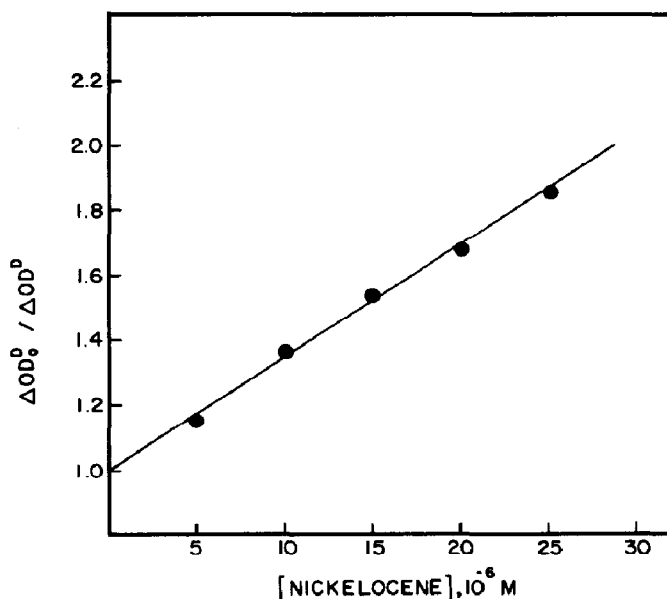


Fig. 2. Representative plot based on eqn. (9) (solvent, methanol).

#### 4. Discussion

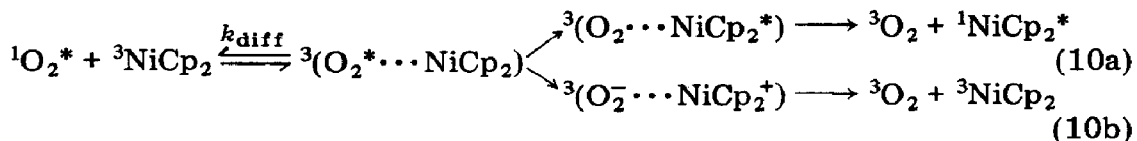
It is evident from the kinetic data in Table 1 that nickelocene proves to be an efficient quencher of  ${}^1\text{O}_2^*$  in each solvent examined. In this respect, it differs sharply from ferrocene ( $k_q^\Delta < 10^7 \text{ M}^{-1} \text{ s}^{-1}$  [2, 10]) and paramagnetic nickel complexes containing two unpaired electrons ( $k_q^\Delta \leq 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  in chloroform [8]). To be specific, as a quencher of  ${}^1\text{O}_2^*$  nickelocene compares well with the diamagnetic square-planar nickel(II) Schiff base complexes ( $k_q^\Delta = (3 - 4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in chloroform [8]). For the nine solvents studied, no well-defined correlation was observed between  $k_q^\Delta$  (for nickelocene) and the polarity or the viscosity of the solvent (Table 1).

It is conceivable that several types of interactions are implicated in the quenching of  ${}^1\text{O}_2^*$  by nickelocene. These include energy transfer, reversible charge transfer, spin exchange (paramagnetic interaction) and the heavy-atom effect. Of these, spin-exchange and heavy-atom interactions may be considered to be relatively unimportant, as was established by the studies with ferrocene and triplet paramagnetic nickel(II) complexes [2, 8, 10]. Also, a recent report [23] on the quenching of  ${}^1\text{O}_2^*$  by stable nitroxyl radicals (doublet) has shown that the most favorable electron exchange interaction in collision complexes leads to a maximum value of  $1.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  for  $k_q^\Delta$  (for di-*tert*-butyldiphenyl nitroxide in acetonitrile).

The lowest energy band system observed in the electronic absorption spectrum of nickelocene is located at  $33.6 \text{ kcal mol}^{-1}$  and is assigned to a spin-forbidden  ${}^3\text{A}_{2g} \rightarrow {}^1\text{A}_{1g}$  transition (metal-centred, d-d) [23]. On this basis, one would expect energy transfer from  ${}^1\text{O}_2^*$  ( $E_S = 22.5 \text{ kcal mol}^{-1}$ ) to nickelocene to be improbable. However, we have shown in a recent study [11] that nickelocene quenches several low energy triplets at diffusion-controlled rates; these triplets include systems such as pentacene and  $\beta$ -carotene which have  $E_T$  values of close to or lower than the  $E_S$  of  ${}^1\text{O}_2^*$ . Furthermore, it has been shown [11] that the charge transfer interactions of these low energy triplets with nickelocene are highly endothermic; this leaves energy transfer as the only feasible mechanism for the quenching and is taken to suggest that there is an even lower lying triplet  $\rightarrow$  singlet transition (below  $21 \text{ kcal mol}^{-1}$ ) in nickelocene (not observed in the absorption spectrum). This is supported by an earlier theoretical calculation by Warren [24] which indicated the presence of a singlet excited state in the vicinity of  $20 \text{ kcal mol}^{-1}$ .

The oxidation potential of nickelocene is  $-0.09 \text{ V}$  vs. the standard calomel electrode (SCE) in acetonitrile [25]. Combining this with the reduction potential of oxygen ( $-0.82 \text{ V(SCE)}$  in acetonitrile [26]) places the charge transfer level of  $(\text{O}_2^- \cdots \text{NiCp}_2^+)$  at an energy (about  $17 \text{ kcal mol}^{-1}$ ) lower than the  $E_S$  of  ${}^1\text{O}_2^*$  ( $22.5 \text{ kcal mol}^{-1}$ ). Thus, the charge transfer interaction between  ${}^1\text{O}_2^*$  and nickelocene is moderately exothermic.

In the light of the considerations above, the efficient quenching of  ${}^1\text{O}_2^*$  by nickelocene is explainable in terms of a combination of electron and energy transfer. These interactions can be represented as follows:



Evidently, for either of the pathways, there is no spin-statistical restriction on  $k_{\text{q}}^{\Delta}$ ; this means that  $k_{\text{q}}^{\Delta}$  can attain the maximum value of  $k_{\text{diff}}$  in a given solvent. The situation is analogous to the quenching of singlet excited states by oxygen (triplet ground state) where the quenching rate constants  $k_{\text{q},\text{O}_2}^{\text{S}}$  are almost universally equal to  $k_{\text{diff}}$  (for example, the  $k_{\text{q},\text{O}_2}^{\text{S}}$  for aromatic hydrocarbon singlets are  $(2.5 - 3.1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  in cyclohexane [27]). The most probable reason why the observed  $k_{\text{q}}^{\Delta}$  (for nickelocene) are considerably lower than the  $k_{\text{diff}}$  is that neither the exothermicity of the electron transfer nor that of the energy transfer is sufficiently high to render these processes irreversible (against back electron/energy transfer in the collision complex, and its back dissociation (see reactions (10a) and (10b))). The steric factor, *i.e.* the fact that the approach of  ${}^1\text{O}_2^*$  to nickelocene cannot be as close as that of  ${}^3\text{O}_2$  to a planar singlet or that of  ${}^1\text{O}_2^*$  to a planar nickel(II) complex, may also be important, because energy and electron transfer processes involve exchange interactions and require favorable orbital overlap between the partners.

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