

## THE RATE CONSTANT FOR THE REACTION OF THE SINGLET STATE OF CORONENE WITH OXYGEN IN NON-POLAR SOLVENTS

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### Summary

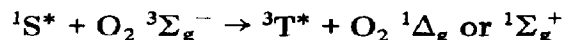
An early measurement of oxygen quenching of coronene fluorescence in cyclohexane by Parmenter and Rau indicated that the rate of the reaction was very much less than diffusion controlled. More recent determinations of the rate of this reaction show that it is diffusion controlled in polar solvents. In this paper the rates of the reaction measured in several non-polar solvents, namely cyclohexane, hexane and methylcyclohexane, are reported. In contrast with the results of Parmenter and Rau, the rates are also close to diffusion controlled in non-polar solvents.

When the rates of the reaction of the singlet state of coronene with oxygen in the different solvents are compared a small effect of solvent polarity is apparent. It is suggested that this may arise from a minor charge transfer interaction between the reactants.

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### 1. Introduction

In investigating the mechanism of the quenching of excited singlet states of aromatic hydrocarbons by oxygen, Parmenter and Rau [1] determined the rate constants of this reaction for a number of hydrocarbons which have different first excited singlet-triplet energy separations. Amongst the hydrocarbons examined was coronene which might be expected [1, 2] to exhibit a different rate of oxygen quenching from many other aromatic hydrocarbons because of its small singlet-triplet separation. This forbids the usual singlet rate reaction with oxygen, *i.e.*



On the basis of an assumed fluorescence lifetime of 54 ns, the reaction between the singlet state  ${}^1C^*$  of coronene and oxygen was calculated to have a rate constant of  $1.2 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$  in cyclohexane [1]. However, it is now known that the fluorescence lifetime of coronene in the absence of quencher is about 300 ns in toluene [3], dioxan [4] and polymethylmethacrylate [4].

Recalculation of the rate constant for the quenching reaction using a fluorescence lifetime of 300 ns and the fluorescence quenching data [1] gives a value of  $1.9 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$  which is about a factor of 10 lower than would be obtained if the reaction were diffusion controlled. This result is unusual because with few exceptions (*e.g.* fluoranthene and some of its derivatives [5]) the rates of reaction of the singlet states of aromatic hydrocarbons with oxygen are close to those expected for diffusion-controlled reactions. The quenching of coronene fluorescence by oxygen has recently been measured in polar and polarizable solvents, namely acetonitrile [5] and benzene [6], and the results indicate that the reaction is nearly diffusion controlled in these solvents. A similar result was obtained by Bowen [7] from the oxygen quenching of coronene fluorescence in chloroform. Differences between rate constants in polar (or polarizable) and non-polar solvents occur if charge transfer interactions are involved in the reaction. Evidence for the involvement of these interactions in the oxygen quenching of the fluorescence of aromatic hydrocarbons has been sought recently [5]. This prompted a re-examination of the quenching of coronene fluorescence by oxygen in some non-polar solvents.

## 2. Experimental details

The coronene was supplied by Aldrich and was checked chromatographically before use. The hexane and cyclohexane were BDH spectroscopic grade solvents. The methylcyclohexane was purified by passage through a silica column at low temperature. The rate constants for the reaction in cyclohexane and hexane were determined at 25 °C by measuring the rates of the fluorescence decay from  $3 \times 10^{-5} \text{ mol l}^{-1}$  solutions of coronene excited by 20 ns pulses of light at 351 nm from a frequency-tripled neodymium laser. The solutions were bubbled with either oxygen-free nitrogen or a 0.79% mixture of oxygen in nitrogen. The concentrations of oxygen present in cyclohexane and hexane were determined by measuring the rates of decay of the triplet state of anthracene and taking the rate constants for the reaction of the triplet state with oxygen as  $3.33 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$  in hexane [8] and  $2.94 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$  in cyclohexane [9].

The oxygen quenching of the steady state fluorescence intensity from coronene in methylcyclohexane was also measured and the rate constant for the quenching reaction in this solvent was derived from the Stern-Volmer equation.

The intrinsic lifetimes  $\tau_0$  of coronene fluorescence in benzene and acetonitrile were also determined in order to calculate the rate constants for the reaction of  $^1\text{C}^*$  with oxygen in these solvents from previously published fluorescence intensity quenching data [5, 6]. The concentration of oxygen in oxygen-saturated acetonitrile was determined by gas chromatography to be  $8.5 \times 10^{-3} \text{ mol l}^{-1}$ .

The rates reported here are the averages of five independent measurements and the reported uncertainties are the extreme deviations of the measurements from their average values.

### 3. Results and discussion

The rate constants for the quenching of coronene fluorescence by oxygen are given in Table 1.

TABLE 1  
Solvent dependence of the rate of oxygen quenching of coronene fluorescence

<i>Solvent</i>	$\tau_0$ <sup>a</sup> (ns)	$k[\text{O}_2]$ <sup>b</sup>	$k_q$ ( $\times 10^{-10} \text{ l mol}^{-1} \text{ s}^{-1}$ )	$^{25}k_{\text{diff}}$ <sup>c</sup> ( $\times 10^{-10} \text{ l mol}^{-1} \text{ s}^{-1}$ )
Cyclohexane	300	—	$0.9 \pm 0.1$	1.1
Hexane	300	—	$1.2 \pm 0.1$	3.3
Methylcyclohexane	300	58.8	1.6	1.4
Acetonitrile	290	58.5 [5]	2.4	2.9
Benzene	285	44 [6]	1.7	1.6

<sup>a</sup> $\tau_0$  is the intrinsic lifetime of coronene fluorescence.

<sup>b</sup> $k[\text{O}_2]$  is the Stern–Volmer constant derived from the ratio of fluorescence intensity without oxygen to that of a solution saturated with oxygen.

<sup>c</sup> $^{25}k_{\text{diff}} = 8RT/2000\eta$ . It is not necessarily the true diffusion-controlled rate constant for reactions involving oxygen at 25 °C but it gives a guide to the relative magnitudes of this rate constant.

The ratio of steady state coronene fluorescence in oxygen-saturated cyclohexane to that in oxygen-free cyclohexane determined by Parmenter and Rau [1] gives a rate constant which is too low. They claim to have used a cyclohexane solution containing  $1 \times 10^{-3} \text{ mol coronene l}^{-1}$  but coronene is not very soluble in this solvent and there may be undissolved material present in their solutions. This could explain the low value of the oxygen quenching constant they obtained. Another possible explanation is the presence of impurities such as 1,12-benzoperylene.

When the differences in the diffusion coefficients of oxygen in the solvents where rates of oxygen quenching of coronene fluorescence have been determined (see Table 1) are allowed for, there is only a small effect of solvent polarity on the rate constant. This indicates that there may be a small contribution from charge transfer interactions in the reaction between  $^1\text{C}^*$  and oxygen but not as great as that suggested by the data of Parmenter and Rau [1].

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