

## OXYGEN QUENCHING OF SINGLET AND TRIPLET STATES

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The rate constants of quenching of singlet and triplet states by oxygen have been measured for nine aromatic hydrocarbons in solution. Singlet quenching is diffusion controlled and similar in all cases but triplet quenching is slower and the quenching rate constant is closely related to the reciprocal of the triplet energy. This observation is interpreted in terms of the dominant role of Franck-Condon factors in the quenching mechanism.

Excited states of molecules are generally efficiently quenched by oxygen and the mechanisms by which this occurs, particularly in studies of the aromatic hydrocarbons, have received considerable discussion [1-5]. Porter and Wright [1] considered the general case of quenching by paramagnetic molecules and ions, proposed a mechanism involving the formation of a complex via which overall spin could be conserved and derived a general expression for the spin statistical factors. Kawaoka et al. [2] stressed the importance of the Franck-Condon factors and of energy transfer when this is possible.

Since singlet quenching usually occurs at a diffusion controlled rate, it is not by itself very useful in distinguishing between these factors. On the other hand, there are few data on the rate constants of quenching of triplet states by oxygen which are precise enough to be diagnostic. There are experimental difficulties in the study of triplet lifetimes in the presence of small quantities of dissolved oxygen, since chemical reaction often occurs, but the advent of nanosecond time resolution in flash photolysis studies makes it possible to study triplet quenching in solutions in equilibrium with air or oxygen at atmospheric pressure. We present here the results of such studies of singlet and triplet quenching of nine aromatic hydrocarbons by oxygen in cyclohexane solution and relate the quenching rate constants to the energies of the excited states.

Triplet lifetimes were measured with our ruby laser flash photolysis apparatus utilising the second harmonic at 347 nm as excitation source [6]. As the decay lifetime of the unquenched triplet was always at least one hundred times that in air saturated solutions, the rate

constant of triplet quenching by oxygen,  $k_{O_2}^T$ , is related to the triplet lifetime in oxygen,  $\tau_{O_2}^T$ , as follows:

$$\tau_{O_2}^T = \frac{1}{k_{O_2}^T} \frac{1}{[O_2]}.$$

Singlet lifetimes could also be measured using the flash apparatus but were obtained more accurately by means of a fluorescence lifetime apparatus which makes use of an oxygen spark and a sampling oscilloscope and were calculated by means of the standard convolution integral technique. This apparatus was capable of measuring lifetimes longer than 1.5 nsec within a precision of 0.2 nsec. The lifetimes were related to the quenching rate constant through the expression

$$\frac{1}{\tau_{O_2}^S} = \frac{1}{\tau^S} + k_{O_2}^S [O_2],$$

where  $\tau_{O_2}^S$  is the lifetime of the singlet fluorescence measured in air saturated solution,  $\tau^S$  is the lifetime in the absence of oxygen and  $k_{O_2}^S$  is the oxygen quenching rate constant of the singlet state.

The results of these studies are summarized in table 1 along with calculated rate constants and relevant energy level data. For the calculation of second order quenching constants the concentration of oxygen in air saturated cyclohexane at 25 °C was taken [4] as  $2 \times 10^{-3}$  M. The rates of singlet quenching were found to be diffusion controlled, in accord with the earlier work of other groups [4,7] but  $k_{O_2}^S$  exceeds  $k_{O_2}^T$  by more than an order of magnitude in some cases, the minimum being a factor of 9. We have observed

Table 1  
 Oxygen quenching of aromatic singlets and triplets

Compound	$\tau^T$ triplet in $O_2$ (nsec)	$k_{O_2}^T \times 10^{-9}$ ( $M^{-1} \text{ sec}^{-1}$ )	$\Delta E_T (T_1-S_0)$ ( $\text{cm}^{-1}$ )	$\eta$	$\frac{\Delta E-4000}{\eta}$ ( $\text{cm}^{-1}$ )	$\tau^S$ (nsec)	$\tau_{O_2}^S$ (nsec)	$k_{O_2}^S \times 10^{-10}$ ( $M^{-1} \text{ sec}^{-1}$ )
(1) 3,4-benzpyrene	190	2.63	14800	0.375	28.8	57.5	13.0	2.9
(2) 3,4-benzphenanthrene	490	1.02	20600	0.40	41.5	70		
(3) 1,2,5,6-dibenzanthracene	390	1.28	18300	0.38	36.7	37.5	12.0	2.9
(4) pyrene	310	1.61	16300	0.385	33.2	450	20	2.5
(5) 1,2-benzanthracene	260	1.93	16500	0.40	31.3	49.4	12.5	3.0
(6) 1,2,3,4-dibenzanthracene	340	1.47	17800	0.39	35.4	53.5	14.3	2.6
(7) anthracene	170	2.94	14700	0.42	25.5	4.9	3.8	3.1
(8) 3,4,9,10-dibenzpyrene	170	2.94	14100	0.40	26.2	143	16.5	2.7
(9) chrysene	480	1.04	19800	0.40	39.5	44.7	12.5	2.9

an empirical linear relationship between  $\tau_{O_2}^T$  and the  $(T_1-S_0)$  energy separation for the aromatic hydrocarbon in each system considered. This relationship is illustrated in fig. 1.

In the case of excited singlet aromatics, it is generally argued [8,9] that the principal mode of quenching is

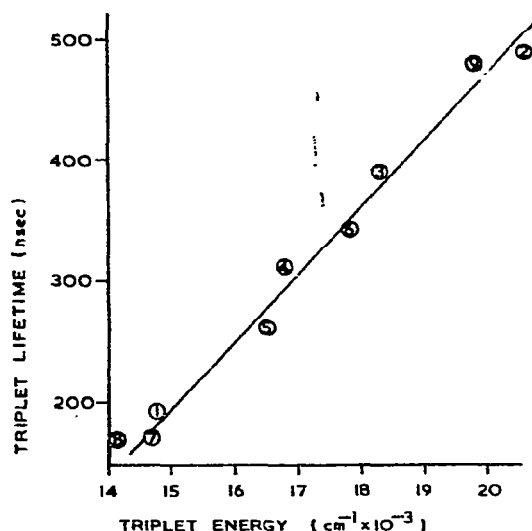
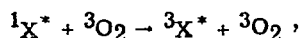
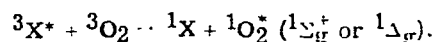


Fig. 1. Demonstration of the linear dependence of oxygen-quenched triplet lifetime of aromatic hydrocarbons in aerated cyclohexane on the triplet energy. (The numbers refer to the compounds listed in table 1.)

with production of singlet oxygen possible but not necessary. In support of this, Parmenter and Rau [4] have reported that, even in species having  $\Delta E(S_1-T_1)$  less than that required for production of ( $^1\Delta_g$ ) and ( $^1\Sigma_g^+$ ) oxygen (7883 and 12815  $\text{cm}^{-1}$  respectively), quenching proceeds at the diffusion controlled rate. Our results for chrysene and 1,2,5,6-dibenzanthracene are in agreement with their findings. Stevens and Algar [9] have noted that the induced intersystem crossing may involve upper triplet states of the aromatic which determine the intersystem crossing of the intermediate complex.

For quenching of aromatic triplets, Kawaoka et al. [2] have argued that the most probable route is



This view has found support from a variety of experimental evidence in which ( $^1\Delta_g$ )  $O_2$  has been produced from interaction with excited hydrocarbons in the gas phase [10]. Recent work by Algar and Stevens [5] on the inhibition of peroxidation has shown ( $^1\Delta_g$ )  $O_2$  to be produced in the triplet quenching of several hydrocarbons. Rates on the order of  $\approx 10^9 M^{-1} \text{ sec}^{-1}$  for  $k_{O_2}^T$  in 9,10-dimethyl anthracene and 9,10 dimethyl-1,2-benzanthracene are inferred from their results, falling in the region of the present measurements while Porter and Windsor [11] found  $k_{O_2}^T$  for anthracene to be  $4 \times 10^9 M^{-1} \text{ sec}^{-1}$ . It is noted by Algar and Stevens [5] and by Birks [3] that the ratio of values  $k_{O_2}^T/k_{O_2}^S$ , falls close to that predicted by the spin statistical factor for triplet-triplet annihilation,  $1/9$ , which is in agreement with our results for anthracene. How-

ever, some of the measured ratios here exceed this value considerably and the dependence upon  $\Delta E(T_1-S_0)$  indicates that the determining variable in the kinetics is the Franck-Condon factor,  $F$ , for the intermediate complex.

Kawaoka et al. [2] have drawn attention to the relatively small contribution to  $F$  from the diatomic  $O_2$ , leaving the major portion of the excess vibrational energy after intersystem crossing to be dissipated by the polyatomic aromatic species. Hence a relationship between  $F$  for the aromatic and the rate of quenching is of interest.

Kawaoka et al. [2] have derived from previous work [12-14] the following expression for  $F$

$$F \approx 0.15 \times 10^{-(\Delta E - 4000/5000)},$$

where  $\Delta E$  is the quantity of electronic energy converted to vibrational energy. If  $F \propto 1/\tau$ , as has been deduced on the basis of vibrational wavefunctions of initial and final states of the hydrocarbon transition, then

$$\log \tau \propto \Delta E - 4000$$

should be valid. A plot of  $\log \tau_{O_2}^T$  versus  $\Delta E(T_1-S_0)$  shows a small but probably significant departure from linearity.

Siebrand [12] has shown that for radiationless transitions in aromatic hydrocarbons, the role of  $F$  is expressed in the relationship

$$\log \tau \propto (\Delta E - 4000)/\eta,$$

the numerator on the right reflecting the vibrational energy of the CH modes while the denominator is  $\eta = N_H/(N_H + N_C)$ ,  $N_C$  and  $N_H$  being the numbers of carbon and hydrogen atoms, respectively. With the aromatic species being the principal contributor to the value of  $F$  for the intermediate complex  $(X \dots O_2)^*$ , the same relationship suggests itself in these studies. Over the

limited range of our work a plot of this relationship is linear within experimental error.

The singlet data are in agreement with the view that the mechanism of  $S_1$  quenching does not necessarily involve energy exchange with the  $^3O_2$  state, as well as showing that  $k_{O_2}^S/k_{O_2}^T$  may exceed the spin statistically based value of 9. More importantly, the correlations of  $\tau_{O_2}^T$  with  $F$  indicate the dominant role of Franck-Condon factors in determining the rate of triplet quenching by  $O_2$  as well as the mechanism by which this occurs.

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