

## QUENCHING OF ACETONE TRIPLETS BY 1,3-DIENES IN FLUID SOLUTION

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### Summary

Rate constants for the quenching of acetone triplets by 1,3-dienes were determined by time-correlated single-photon counting phosphorescence measurements. Five acyclic 1,3-dienes of varying substitution patterns quench with comparable rate constants ( $k_q \approx (3 - 5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). It is found that *cis,cis*-1,3-cyclooctadiene, a molecule the conjugation of which is reduced because of structural constraints that cause twisting, quenches with a significantly lower rate constant ( $k_q \approx 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). That all of the 1,3-dienes quench at less than the diffusional rate is established by the observation that *trans*-1,2-dicyanoethylene demonstrates a quenching rate constant of approximately  $7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

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### 1. Introduction

The quenching of ketone triplets by 1,3-dienes held a special place in the development of molecular organic photochemistry as a quantitative discipline during the 1960s [1]. Initial investigations established that 1,3-dienes were excellent quenchers of ketone triplets [2], that the Stern-Volmer quenching efficiency was not significantly dependent on the 1,3-diene structure [3], that reactions between the ketone triplet and the 1,3-diene were minimal [4] and that, in non-viscous solvents, quenching generally behaved like a diffusion-controlled energy transfer process [5]. However, in spite of the intense interest in and use of 1,3-dienes as (presumed) diffusion quenchers of ketone triplets, relatively few data which refer to the absolute values of the appropriate quenching constants have actually been reported [6], especially for alkyl ketone triplets. We initiated, therefore, an investigation of the absolute rate constants for the quenching of acetone triplets at ambient temperature by a series of 1,3-dienes with the goals of determining the magnitude of structural effects of the 1,3-diene and of establishing whether the quenching constants are, in fact, comparable with that for diffu-

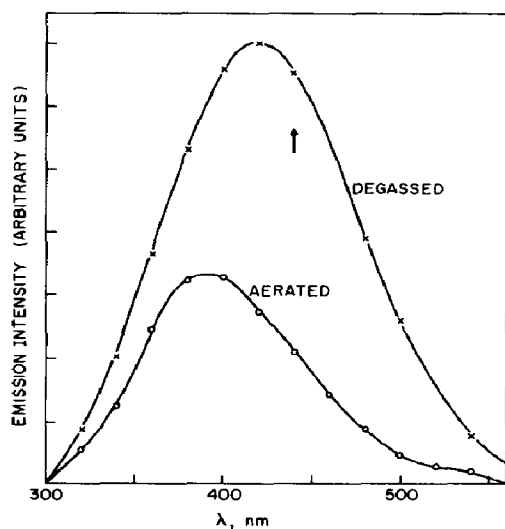


Fig. 1. Emission spectra of acetone in acetonitrile (concentration, 0.034 M;  $\lambda_{\text{ex}}$ , 290 nm). Phosphorescence lifetimes were observed at 440 nm ( $\uparrow$ ).

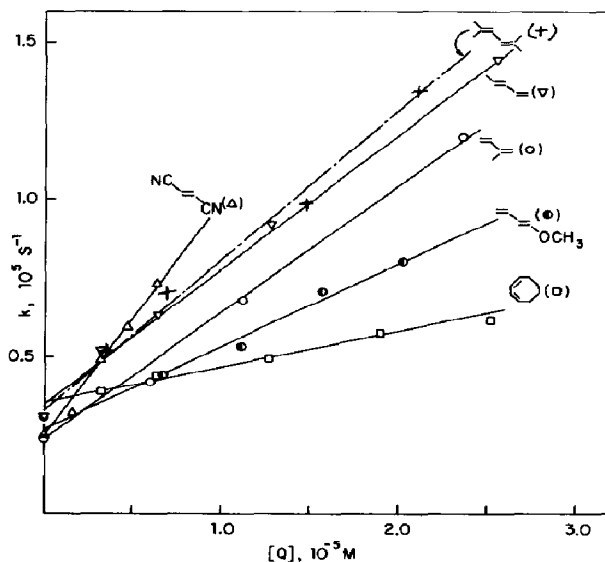


Fig. 2. The phosphorescence decay rate of acetone in acetonitrile as a function of the quencher concentration.

sion. Acetonitrile was selected as a solvent since it is commonly employed for photochemical studies.

## 2. Experimental

Acetone and acetonitrile (Aldrich, spectrophotometric grade) were used as supplied. 2-Methyl-1,3-butadiene and 1,3-pentadiene were used as obtained (Aldrich). 1-Methoxy-1,3-butadiene, 2,5-dimethyl-2,4-hexadiene, *cis,cis*-1,3-cyclooctadiene and *trans*-1,2-dicyanoethylene were available from previous studies and were employed without further purification.

The concentration of acetone was 0.034 M in acetonitrile. Solutions were degassed by several freeze-thaw cycles. The total emission spectra of an aerated acetonitrile solution of acetone and a degassed solution are shown in Fig. 1. The increase in the emission intensity and the shift of the emission maximum is associated with the enhancement of acetone phosphorescence in degassed acetonitrile solution. Because of the substantial overlap of acetone fluorescence (the acetone emission which appears in aerated solution) and phosphorescence, quenching of the steady state intensity of emission is subject to considerable error. However, the large difference in fluorescence (approximately 2 ns) and phosphorescence (approximately 40 000 ns) lifetimes in degassed solution allows for easy time resolution of singlet and triplet emissions.

The phosphorescence lifetimes of acetone in the presence and in the absence of quenchers were determined by correlated single-photon counting. The total emission from a deuterium lamp (Photochemical Research Associates) was used as an excitation light source. The pulse width of the lamp was approximately 80 ns with the application of a suitable capacitor in the lamp circuit. The repetition rate of the pulses was about 6 kHz. The phosphorescence intensities at 440 nm were measured at ambient temperature.

### 3. Results

The simplest mechanistic scheme required to interpret the data is



where A and Q symbolize acetone and quencher respectively, and the superscripts 0, 1 and 3 refer to ground state, excited singlet state and excited triplet state acetone respectively. According to the mechanism of eqns. (1) - (4), the measured phosphorescence lifetime is given by

$$\tau_p^{-1} (\text{measured}) = k_p + k_D + k_q [\text{Q}] \quad (5)$$

From eqn. (5) a plot of  $\tau_p^{-1}$  versus [Q] is predicted to yield a straight line of slope equal to  $k_q$  and an intercept equal to  $k_p + k_D$ . The results of measurements of acetone phosphorescence lifetimes  $\tau_p$  are shown in Fig. 2 in which  $\tau_p^{-1}$  is plotted as a function of quencher concentration. In each case studied eqn. (5) is obeyed to within  $\pm 10\%$  for the worst case (2,5-dimethyl-2,4-hexadiene). The intercepts vary from  $25 \times 10^3$  to  $35 \times 10^3 \text{ s}^{-1}$ , corresponding to lifetimes of  $(40 - 30) \times 10^{-6} \text{ s}$ . The values of  $k_q$  are summarized in Table 1.

Stern-Volmer plots of phosphorescence intensity at 440 nm versus [Q] were also determined for comparison purposes and to determine whether significant static quenching was occurring. In each case the Stern-Volmer constant  $k_q \tau_p$  was, on average, within a factor of 50% of the value determined by time-correlated single-photon counting.

### 4. Discussion

The values of  $k_q$  for the acyclic 1,3-dienes studied show relatively minor variation with respect to variation of the quencher structure, *i.e.*  $k_q =$

TABLE 1  
Quenching of acetone phosphorescence<sup>a</sup>

Quencher	$k_q (\times 10^9 \text{ M}^{-1} \text{ s}^{-1})$
$(\text{CH}_3)_2\text{C}=\text{CH}-\text{CH}=\text{C}(\text{CH}_3)$ , 2,5-dimethyl-2,4-hexadiene	$4.6 \pm 0.5$
$\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$ , 1,3-pentadiene	$4.4 \pm 0.3$
$\text{CH}_2=\text{CH}-\text{C}(\text{CH}_3)=\text{CH}_2$ , 2-methyl-1,3-butadiene	$3.9 \pm 0.3$
$\text{CH}_3\text{OCH}=\text{CH}-\text{CH}=\text{CH}_2$ , 1-methoxy-1,3-butadiene	$2.7 \pm 0.4$
$\text{CH}=\text{CH}-\text{CH}=\text{CH}-(\text{CH}_2)_4$ , <i>cis,cis</i> -1,3-cyclooctadiene	$1.1 \pm 0.3$
$\text{CHCN}=\text{CHCN}$ , <i>trans</i> -1,2-dicyanoethylene	$7.4 \pm 0.3$

<sup>a</sup>In acetonitrile solution at ambient temperature. The concentration of acetone is fixed at 0.034 M.

$(3 - 5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . For example, both 2,5-dimethyl-2,4-hexadiene, which has substantial steric hindrance at the terminal carbon atoms, and 2-methyl-1,3-butadiene, which has minimal steric hindrance at the terminal carbon atoms, display experimentally indistinguishable values of  $k_q$ , *i.e.*  $4.6 \times 10^9$  and  $3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  respectively.

The electron-releasing methoxy group of 1-methoxy-1,3-butadiene ( $k_q = 2.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) reduces the rate of quenching slightly relative to the methyl group of 1,3-pentadiene ( $k_q = 4.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ).

In contrast, *cis,cis*-1,3-cyclooctadiene (COD) is a significantly poorer quencher ( $k_q = 1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) than any of the acyclic 1,3-dienes. This result is in good agreement with previous reports [7] in which COD has been found to be a relatively poor alkanone triplet quencher. The twisted shape of ground state COD probably causes the energy gap between  $S_0$  and  $T_1$  to be larger than that for acyclic 1,3-dienes. Since the mechanism of 1,3-diene quenching presumably occurs by triplet-triplet energy transfer, the higher "triplet energy" of COD causes a reduction in  $k_q$  relative to that for the acyclic 1,3-dienes.

Finally, we address the issue of whether or not the value of  $k_q$  for any of the 1,3-dienes studied is equal to that for diffusion-limited quenching in acetonitrile. For "small" molecules (*e.g.* for molecules of molecular weight less than 100) the diffusion-limited rate constant  $k_{\text{DIF}}$  is expected to be of the order of  $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  [8]. We find that, as previously suggested [9], the value of  $k_q$  for *trans*-1,2-dicyanoethylene as a quencher of acetone triplets is close to that expected for the diffusion-limited quenching in acetonitrile (approximately  $7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). Thus the values of  $k_q$  for all of the 1,3-dienes investigated are apparently less than  $k_{\text{DIF}}$ .

## 5. Conclusions

The values of  $k_q$  for the quenching of acetone triplets by various acyclic 1,3-dienes in acetonitrile are similar in their approach to, but remain somewhat less than, the value for diffusion-limited quenching. The substantially lower value of  $k_q$  for *cis,cis*-1,3-cyclooctadiene is attributed to the high triplet energy which results from ground state distortion of this 1,3-diene system and which reduces the rate constant for triplet-triplet energy transfer.

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