

REACTIVITY OF SINGLET OXYGEN TOWARD STRAINED SUBSTRATES AND A NOVEL NON-PHOTOCHEMICAL  
METHOD FOR DETERMINATION OF QUENCHING CONSTANTS OF SINGLET OXYGEN.

Nicholas J. Turro,\* Ming-Fea Chow, Sheldon Kanfer and Marcia Jacobs

Department of Chemistry, Columbia University

New York, New York 10027

**ABSTRACT:** Rate constants for quenching of  $^1O_2$  by a number of strained molecules have been determined by the competitive rubrene photooxidation method; the rate constant for quenching by Q may be evaluated by adaption of a kinetic analysis already in the literature for the rubrene photooxidation method.

**INTRODUCTION.** Although rate constants for deactivation of singlet molecular oxygen ( $^1O_2$ ) by a large number of quenchers in fluid solution have been reported<sup>1</sup> only a few values pertain to the quenching of "strained substrates." Because of their inherent reactivity, complications can occur when strained substrates are employed as quenchers. It is, however, of interest to determine whether the "strain" which enhances chemical reactivity can also induce an enhanced reactivity toward quenching of  $^1O_2$ . It is known, for example, that "strained" olefins are more reactive toward autooxidation than "unstrained" olefins.<sup>2</sup> A first goal of this study was to measure the constants for deactivation of  $^1O_2$  by strained substrates.

For nearly all reported quenching data  $^1O_2$  is indirectly produced via direct photoexcitation of a sensitizer. Such quantitative methods possess the following inherent difficulties: (1) interactions between excited sensitizer and quencher may occur; (2) the quencher itself may absorb light and then react; (3) oxygen induced intersystem crossing of the excited singlet sensitizer may occur. A second goal of this study was to devise a non-photochemical method for measuring quenching constants for  $^1O_2$ . The method developed is based on the well-established procedure involving inhibition, by quenchers, of the self-sensitized photoperoxidation of rubrene.<sup>3</sup> In our novel method thermolysis of 1,4-dimethylnaphthalene-1,4-endoperoxide is utilized to generate  $^1O_2$ .

**RESULTS. Quenching of  $^1O_2$  by Strained Molecules.** The inhibition of self-sensitized photooxidation of rubrene<sup>3</sup> was employed to measure the rate constants for quenching of  $^1O_2$  by various strained substrates (Table 1). Tetramethylethylene (1) was employed as a standard to calibrate the method against literature data. Our value of  $k_q^{O_2}$  ( $5.6 \pm 0.3 \times 10^7 M^{-1} sec^{-1}$ ) is in complete agreement with the literature value ( $5.8 \pm 0.9 \times 10^7 M^{-1} sec^{-1}$ ).<sup>3</sup>

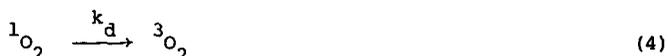
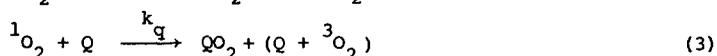
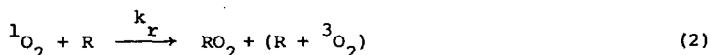
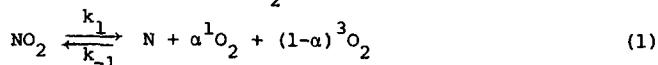
Three strained seven membered cyclic acetylenes (2-4) were employed as quenchers.<sup>4,5</sup> Each was found to be less reactive than 1. Thus, either strain in cyclic acetylenes does not inherently enhance reactivity toward quenching  $^1O_2$  or the tetramethyl substituents flanking the triple bond introduced steric hindrance that reduces the inherent reactivity. However, since the reactivity of the cycloalkene analogue (9) of 2 is of a degree comparable to 2, and is much higher than that of cyclooctene, we conclude that attack on sulfur is a major quenching

pathway.<sup>4</sup> It should be noted that cyclooctyne (5) is only slightly more reactive than an unstrained cyclic alkene (10).<sup>4</sup>

Although quadricyclane is several times a better quencher of  $^1\text{O}_2$  than is norbornadiene, both are relatively poor quenchers with reactivities comparable to those of unstrained cyclic alkenes (e.g., 10). On the other hand, electron rich alkynes (11 and 12) display the largest rate constants of any of the compounds studied. Presumably, these enhanced rate constants are due to a polar effect rather than to inherent strain.

A final point of interest is the observation that the quenching constant for bis-adamantylidene (BA) is considerably smaller than that for tetramethylethylene (1). It has been reported<sup>6</sup> that BA is an unusual example of an alkene which reacts with  $^1\text{O}_2$  to form a dioxetane in good yield. The rate constant for quenching of  $^1\text{O}_2$  by BA is quite low relative to the value for (1). Thus, it appears that the reason for formation of dioxetane is not a faster rate of attack of  $^1\text{O}_2$  on BA, but an inhibited rate of allylic hydrogen abstraction.

A Novel Non-Photochemical Method for Determining Quenching Constants of  $^1\text{O}_2$ . We have developed a novel method for measuring quenching constants for  $^1\text{O}_2$ . This method employs thermolysis of 1,4-dimethylnaphthalene-1,4-endoperoxide<sup>7</sup> ( $\text{NO}_2$ ) as a method for generating  $^1\text{O}_2$ . The latter is then quenched by rubrene (R) and a competitive quencher, Q. From such quenching experiments and knowledge of the literature value of the quenching constant of  $^1\text{O}_2$  by rubrene<sup>8</sup>, the rate constant for total (physical plus chemical) quenching of  $^1\text{O}_2$  by Q may be evaluated.<sup>9</sup>



From eq. 1-4 it can be seen that step (1) is analogous to the energy transfer step in the photosensitized generation of  $^1\text{O}_2$ . In such an analogy the quantity  $\alpha$  corresponds to the quantum yield for formation of  $^1\text{O}_2$ . The complication of reversibility of step (1) may be overcome by employing conditions such that  $(k_r[\text{R}] + k_q[\text{Q}] + k_d) \gg k_{-1}[\text{N}]$ . Whenever an excess amount of Q is used, the concentration of Q can be treated as a constant, [Q]. The magnitude of  $k_q$  can then be evaluated from eq. 5

$$k_q = \frac{k_d \ln\left(\frac{[\text{R}]_0^{\text{Q}}}{[\text{R}]_t^{\text{Q}}}\right) + k_r([\text{R}]_t^{\text{Q}} - [\text{R}]_t)}{[\text{Q}] \ln([\text{R}]_0^{\text{Q}}/[\text{R}]_t^{\text{Q}})} \quad (5)$$

where  $[\text{R}]_0$  is the initial concentration of rubrene,  $[\text{R}]_t$  and  $[\text{R}]_t^{\text{Q}}$  are the final concentrations of rubrene in the absence and presence of Q, respectively. The magnitude of  $k_d$  and  $k_r$  are  $1.7 \times 10^4 \text{ s}^{-1}$  and  $5.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , respectively.

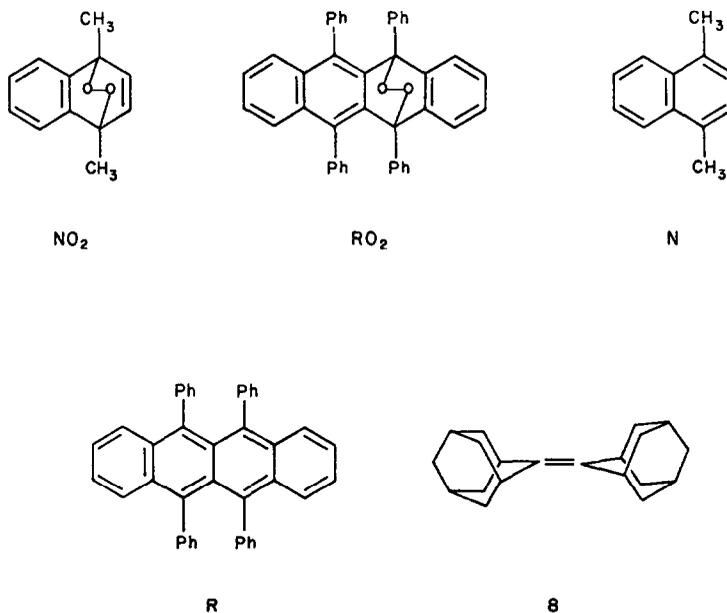
In order to test the validity of the assumptions of the method we developed, quenchers with well established values of  $k_q$  were employed. Correspondence of literature values of  $k_q$  with those obtained by our method (Table 2) would confirm the validity of the assumed kinetic scheme. The quenchers selected were tetramethylethylene, trimethylethylene, and 1-methylcyclohexane. From

the data in Table 2, it can be seen that there is excellent agreement between the literature values of  $k_q$ , the values derived from eq. 5, and the values derived from the photoexcitation method.

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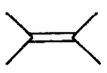
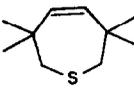
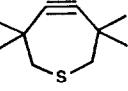
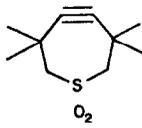
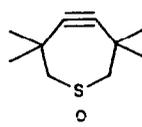
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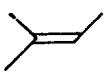
Scheme 1. Structures referred to in the text.

Table 1. Quenching Rate Constants of Various Quenchers.

Quencher	$k_q$ ( $M^{-1}S^{-1}$ )	Quencher	$k_q$ ( $M^{-1}S^{-1}$ )	Quencher	$k_q$ ( $M^{-1}S^{-1}$ )
<u>1</u>	 $(5.6 \pm 0.3) \times 10^7$	<u>5</u>	 $(1.5 \pm 0.4) \times 10^5$	<u>9</u>	 $(3.5 \pm 0.1) \times 10^6$
<u>2</u>	 $(3.5 \pm 0.5) \times 10^6$	<u>6</u>	 $(4.8 \pm 0.2) \times 10^4$	<u>10</u>	 $(4.8 \pm 0.9) \times 10^4$
<u>3</u>	 $(2.6 \pm 0.7) \times 10^5$	<u>7</u>	 $(1.7 \pm 0.3) \times 10^4$	<u>11</u>	$CH_3C \equiv CNET_2$ $(2.4 \pm 0.7) \times 10^8$
<u>4</u>	 $(7.2 \pm 1) \times 10^4$	<u>8</u>	BA $(9.0 \pm 0.2) \times 10^5$	<u>12</u>	$Et_2NC \equiv CNET_2$ $(2.8 \pm 0.8) \times 10^8$

(a) Singlet oxygen was generated by photosensitization in  $CHCl_3$  at room temperature. Values below  $10^5 M^{-1}S^{-1}$  may represent upper limits, since quenching excited rubrene and other complications become significant for such poor quenchers.

Table 2. Quenching Rate Constant by Thermal Generation of  $^1O_2$ .<sup>a</sup>

Compound	Method	Thermal <sup>b</sup> Generation ( $M^{-1}S^{-1}$ )	Photogeneration ( $M^{-1}S^{-1}$ ) <sup>c</sup>	
			This Work	Literature <sup>3</sup>
		$(5.6 \pm 0.3) \times 10^7$	$(5.4 \pm 0.2) \times 10^7$	$(5.8 \pm 0.9) \times 10^7$
		$(2.3 \pm 0.4) \times 10^6$	$(1.5 \pm 0.1) \times 10^6$	$(2.3 \pm 0.4) \times 10^6$
		$(3.3 \pm 0.5) \times 10^5$	$(3.4 \pm 0.2) \times 10^5$	$(3.6 \pm 0.6) \times 10^5$

(a) The measurements were performed in  $CHCl_3$  at room temperature.

(b) Singlet oxygen was generated by thermolysis of 1,4-dimethylnaphthalene-1,4-endoperoxide.

(c) Singlet Oxygen was generated by photosensitization via excited rubrene.

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