

Nonradiative Deactivation of Singlet Oxygen ($^1\text{O}_2$) by Cubane and Its Derivatives

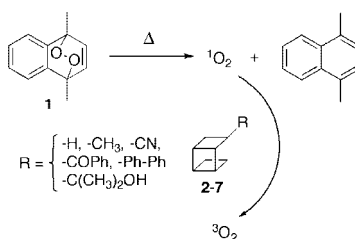
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ABSTRACT



The bimolecular quenching rate constants of singlet oxygen ($^1\text{O}_2$) by cubane and cubane derivatives were determined and found to be in the order of 10^3 – $10^4 \text{ M}^{-1} \text{ s}^{-1}$. These values represent larger values than expected for aliphatic alkanes as a model for C–H vibrational deactivation. This result is explained by the occurrence of two different deactivation mechanisms: energy transfer to cubane C–H vibrational modes and the formation of a charge-transfer complex between $^1\text{O}_2$ and cubane ($^1\text{O}_2^{\cdot-} \cdots \text{cubane}^{\cdot+}$).

After its initial synthesis in 1964, it was clear that pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane, also termed cubane, might find numerous uses because of its novel geometric structure.¹ To date, cubane and its derivatives have shown potential for application as high energy fuels and explosives,² as new novel materials, synthetic intermediates, and polymers;³ and as high refractive index fluids for immersion lithography due to high electron densities.⁴ Here, the cubane skeleton is used as an example of a highly strained hydrocarbon backbone with which to examine the nonra-

diative deactivation of an excited-state species. We report the quenching rate constants of singlet oxygen by cubane and several of its derivatives (Scheme 1).

Molecular oxygen in its ground state ($^3\Sigma$, $^3\text{O}_2$) can be electronically excited to produce singlet oxygen ($^1\Delta$, $^1\text{O}_2$). This excited-state decays inefficiently to the ground-state since the transition is spin-, symmetry-, and parity-forbidden. Despite this inefficiency, energy exchange by coupling with oscillators of neighboring molecules (especially C–H and O–H vibrations) has proven to be an important mechanism for the nonradiative relaxation of $^1\text{O}_2$.⁵ The study of the quenching of $^1\text{O}_2$ in different solvents has shown that different functional groups quench singlet oxygen with

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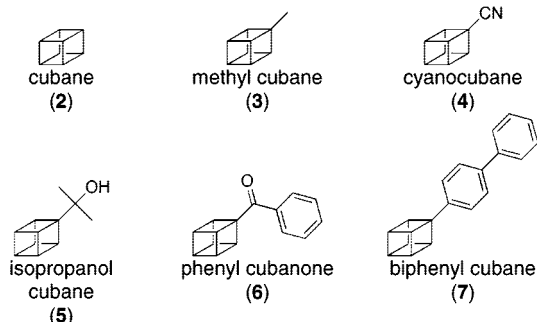
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different efficiencies.⁶ Furthermore, different arrangements of the hydrocarbon skeleton have been found to cause considerable differences in the $^1\text{O}_2$ -quencher interaction.⁷ Cubanes possess an unusual carbon skeleton that presents an interesting case study of the deactivation of $^1\text{O}_2$.

Scheme 1. Cubane Derivatives Used in Steady-State Analysis



The absolute quenching rate constant for $^1\text{O}_2$ quenched by cubane (2) was determined by a time-resolved phosphorescence quenching method.⁸ $^1\text{O}_2$ was generated by photosensitization with 5,10,15,20-tetraphenyl-21*H*,23*H*-porphyrin (TPP) and pulsed laser excitation (Nd:YAG laser at 532 nm, pulse width 10 ns). Decay traces of the $^1\text{O}_2$ phosphorescence at 1272 nm were recorded at different cubane concentrations (Figure 1, inset). The bimolecular quenching rate constant ($k_q = (6.8 \pm 0.4) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$) was extracted from the slope of the plot of the pseudo-first-order decay rate constant of the $^1\text{O}_2$ phosphorescence versus the cubane concentration (Figure 1). For these experiments, CCl_4 was selected as the solvent because of its low volatility and the relatively long lifetime of $^1\text{O}_2$,⁹ which makes it a convenient solvent for the determination of low quenching rate constant values that are expected in this case.

The $^1\text{O}_2$ rate constants for a series of cubane derivatives (3–7) were determined relative to the quenching constant of the unsubstituted cubane (2) using a steady-state chemiluminescence quenching method.^{5c,10} The thermal decomposition of 1,4-dimethylnaphthalene-1,4-endoperoxide (1) produces $^1\text{O}_2$ cleanly and in good yield. The quenching of the chemiluminescence emission (phosphorescence) of $^1\text{O}_2$ at 1272 nm produced by thermolysis of 1 was utilized to determine Stern–Volmer quenching constants.¹¹

The quenching of the phosphorescence of $^1\text{O}_2$ was studied in the presence of the cubanes listed in Scheme 1 at different

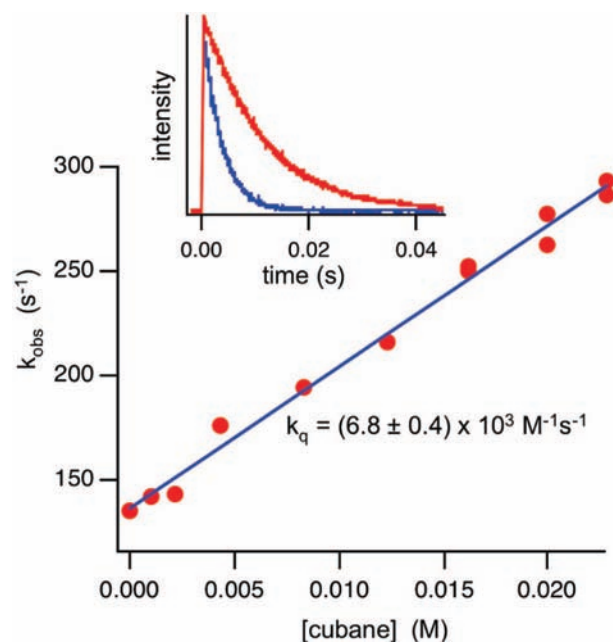


Figure 1. Pseudo-first-order $^1\text{O}_2$ phosphorescence decay rate constant (k_{obs}) vs the cubane concentration for the determination of the absolute $^1\text{O}_2$ quenching rate constant by cubane (2) in CCl_4 . The decay traces at 1272 nm were generated by laser excitation (532 nm) of the sensitizer TPP (2 μM). Inset: phosphorescence decay traces in the absence (red) and presence (blue) of cubane (0.023 M).

concentrations in CCl_4 . The Stern–Volmer plots for the quenching of $^1\text{O}_2$ by a variety of cubane derivatives are shown in Figure 2. The data for all of the cubanes studied present good linear behaviors. In order to convert the Stern–Volmer constants to bimolecular quenching constants, k_q , the Stern–Volmer constants were divided by the $^1\text{O}_2$ lifetime in CCl_4 under our experimental conditions. A $^1\text{O}_2$ lifetime of 31 ms was obtained using cubane (2) and the previously determined absolute quenching rate constant (Figure 1).

Table 1 shows that the experimentally determined k_q values for the cubane derivatives fall in a very narrow range between 6.3×10^3 and $1.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. The k_q constants follow the expected magnitude order based on the number of heteroatom-hydrogen bonds (C–H and O–H) present in the molecule: cyanocubane (4) contains the fewest heteroatom–hydrogen bonds and is found to have the smallest rate constant, while biphenyl cubane (7) contains the most and exhibits the largest rate constant.

A more appropriate description than that based on the number of heteroatom–hydrogen bonds should also consider the contribution of different types of heteroatom–hydrogen bonds to the energy exchange. In pioneering research by Hurst and Schuster^{6a} and Rodgers,^{6b} it was proposed that individual rate constants for different functional groups can be added to predict the bimolecular rate constant. Using this group contribution method, k_q constants were calculated for all of the cubanes in Table 1 (k_q'). Although the calculated

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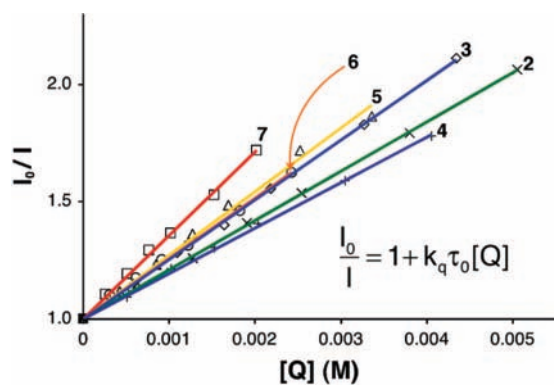


Figure 2. Stern–Volmer plots for the quenching of $^1\text{O}_2$ chemiluminescence by cubane derivatives **2–7** in CCl_4 . $^1\text{O}_2$ was generated by thermal decomposition of 1,4-dimethyl-1,4-endoperoxide (2 mM) at 22 °C.

Table 1. Experimental and Calculated Bimolecular Quenching Rate Constants for $^1\text{O}_2$ in the Presence of Cubane Derivatives **2–7**

quencher	k_q , exp ($10^3 \text{ M}^{-1} \text{ s}^{-1}$)	no. of X–H bonds	k_q' ($10^3 \text{ M}^{-1} \text{ s}^{-1}$) ^a	k_q'' ($10^3 \text{ M}^{-1} \text{ s}^{-1}$) ^b
7	11.0	16	4.90	9.8
5	8.6	14	4.02	8.9
6	8.3	12	3.10	8.0
3	8.1	10	1.18	6.1
2	6.8	8	0.72	5.6
4	6.3	7	0.70	5.6

^a Calculated using Rodgers' group contribution method for energy exchange. ^b Calculated assuming that the bimolecular quenching rate constant is a contribution of the formation of a charge-transfer complex between singlet oxygen ($k_{q,ct}$, assumed to be $4.9 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ as explained in the text) and the cubane and energy exchange (k_q') as expressed in the following equation: $k_q'' = k_{q,ct} + k_q'$.

values correctly predict the relative order of the rate constants, their magnitudes are underestimated by up to a factor of 10 compared to the experimental values.

To verify our technique, and to confirm the validity of the reported values, we determined the k_q constants for $^1\text{O}_2$ with several alkanes and alcohols in CCl_4 using the steady-state chemiluminescence quenching method with cubane (**2**) as a standard. These values are presented in Table 2 and show good agreement with values determined by Rodgers.^{6b}

One factor that can contribute to the mismatch between the calculated and experimental rate constants is that different geometries of the hydrocarbon skeleton are known to quench singlet oxygen with different efficiencies. Cubane is known to have a unique carbon skeleton that is highly strained and which possesses some double-bond character. This distinctive geometry may contribute differently to the k_q constant than a normal alkane C–H bond. Dividing the experimentally determined rate constant of cubane (**2**) by 8 (the number of C–H bonds in cubane), we determined that each cubane C–H bond should contribute approximately $850 \text{ M}^{-1} \text{ s}^{-1}$ to

Table 2. Bimolecular Quenching Rate Constant for the Quenching of $^1\text{O}_2$ by Some Reference Compounds

quencher	k_q , $\text{M}^{-1} \text{ s}^{-1}$ (this work) ^a	k_q , $\text{M}^{-1} \text{ s}^{-1}$ (literature values) ^b
hexadecane	9.5×10^3	1.20×10^4
1-decanol	8.3×10^3	1.06×10^4
1-nonanol	7.4×10^3	9.45×10^3

^a CCl_4 as solvent. ^b Quencher as solvent.

the overall quenching constant. This value is one order of magnitude higher than that calculated by Rodgers for a normal alkane C–H bond ($90 \text{ M}^{-1} \text{ s}^{-1}$). Although vibrational frequencies of strained alkane C–H bonds such as cubane are slightly higher in energy (2977 cm^{-1})¹² than in unstrained alkane C–H bonds such as hexane (2855 cm^{-1}),¹³ strain alone probably cannot account for such large differences in quenching rate constants. The higher frequency of saturated C–H bonds in strained hydrocarbons is expected to enhance k_q , but we believe that the effect of strain alone cannot account for the observed quenching constants of the cubanes.

Another factor that can be responsible for the quenching of $^1\text{O}_2$ is the formation of a charge-transfer complex. Charge-transfer quenching of $^1\text{O}_2$ by amines, aromatic hydrocarbons, metal complexes, and metallofullerenes has been reported in the literature with k_q constants that range from 10^3 to $10^9 \text{ M}^{-1} \text{ s}^{-1}$.¹⁴ Darmanyan, et al. have shown that if the ionization potential (IP) of the quencher is low enough ($< 8.5 \text{ eV}$) charge-transfer quenching can occur.^{14a} For example, the bimolecular quenching rate constant for charge-transfer ($k_{q,ct}$) for toluene (IP = 8.82 eV, $E_{1/2}^{\text{ox}} = 1.98 \text{ V}$)¹⁵ is estimated to be $9 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ while the measured value of $k_{q,ct}$ for *p*-bromoanisole (IP = 8.49 eV, $E_{1/2}^{\text{ox}} = 1.70 \text{ V}$)¹⁵ is $4.9 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$.^{14a} Thus, $k_{q,ct}$ should increase as IP and redox potential ($E_{1/2}^{\text{ox}}$) decrease. The IP and $E_{1/2}^{\text{ox}}$ of cubane are similar to those of *p*-bromoanisole, 8.46 eV and 1.73 V,¹⁵ respectively,¹⁶ which suggests that a large contribution to the rate constants in Table 1 comes from the formation of a charge-transfer complex between $^1\text{O}_2$ and cubane ($^1\text{O}_2 \cdots \text{cubane}^+$). Since the quencher molecules used by Rodgers^{6b} to extrapolate the contribution values for C–H bonds were, in general, alkanes and alcohols with large IP values, the formation of charge-transfer complexes was not accounted for in that model.

To obtain a better estimate of the bimolecular quenching constants for the quenching of $^1\text{O}_2$ by cubanes, we took into account the contribution from the charge transfer complex

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formation. Assuming that the IP and $E_{1/2}^{\text{ox}}$ values of the cubane derivatives (**3–7**) are not significantly affected by the substituents and that the substituents themselves do not contribute significantly to differences in the IP and $E_{1/2}^{\text{ox}}$, an estimated $k_{\text{q,ct}}$ of $4.9 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ was employed due to the similarities between the IP and $E_{1/2}^{\text{ox}}$ values of cubane and *p*-bromoanisole. Using this value together with Rodgers' values^{6b} for other common functional and hydrocarbon groups, k_{q} constants were calculated that are more in agreement with the experimentally obtained ones (Table 1, k_{q}''). While this is a crude estimation since the exact IP's and $E_{1/2}^{\text{ox}}$'s are not known for the cubane derivatives, the remarkably good match between the experimental and calculated values is consistent with the contribution of these two different deactivation mechanisms to the total bimolecular quenching rate constant. This calculation could be modified to a higher degree of precision if the exact IP and $E_{1/2}^{\text{ox}}$ were known for each derivative in order to determine a more accurate contribution of $k_{\text{q,ct}}$ to the overall quenching.

In conclusion, the quenching of $^1\text{O}_2$ by different cubane derivatives has been studied. The determined k_{q} constants are in the order of $10^3\text{--}10^4 \text{ M}^{-1} \text{ s}^{-1}$. A classical model of

nonradiative $^1\text{O}_2$ deactivation by energy transfer to C–H vibration modes cannot account for the value of the rate constants determined. The formation of a charge-transfer complex between the cubane and $^1\text{O}_2$ is supported by the ionization and redox potentials of cubane, and this model yields k_{q} constants in good agreement with the experimental values. Thus, the k_{q} values can be reasonably explained by a combination of two distinct mechanisms: energy transfer to C–H vibrational modes and charge-transfer quenching.

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Supporting Information Available: Time-resolved phosphorescence-quenching method and steady-state chemiluminescence quenching method to determine rate constants, synthetic procedures, and characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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