

Rate Constants for the Reaction of Singlet Oxygen with Conjugated Dienes^{†1}

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Abstract: Rate constants are reported for the reaction of 18 conjugated dienes and 13 cyclic monoolefins with singlet oxygen (¹O₂) in chloroform solution. A single mechanism for conjugated diene reaction with ¹O₂ cannot account for all the experimental observations. The preferred mechanism is a 1,4-cycloaddition of ¹O₂ to form an endoperoxide, a reaction which is relatively insensitive to the ionization potential of the olefin. When the cis form of the diene is inaccessible and/or the ionization potential of the olefin is lowered by terminal alkyl substitution, the reaction pathway is diverted to one which resembles the reaction of monoolefins with ¹O₂. Representative rate constants are: 1,3-cyclohexadiene, 7.1 × 10⁶ L/(M s); 2,5-dimethyl-2,4-butadiene, 5.3 × 10⁶ L/(M s); cholesta-3,5-diene, 7.4 × 10⁵ L/(M s); isoprene, 3.7 × 10⁴ L/(M s); and 1-methylcycloheptene, 2.4 × 10⁶ L/(M s).

Singlet oxygen (¹O₂) adds to cyclic conjugated dienes to form 1,4-endoperoxides.³⁻⁵ Acyclic conjugated dienes, however, yield allylic hydroperoxides, 1,2-dioxetane derived products, 1,4-endoperoxides, or mixtures of these products depending on the structure of the diene and the reaction conditions (Scheme I).⁶⁻⁹

Several measurements of β values or rate constants for the addition of ¹O₂ to one or several conjugated dienes have been reported,^{4,9-13} but no detailed study of these compounds has been carried out. By a technique previously described,¹⁴ the rate constants for the interaction of a series of 18 conjugated dienes with ¹O₂ have been measured. The mechanism of these reactions is discussed and it will be shown that a single mechanism for conjugated diene reaction cannot account for all the experimental observations. In addition, rate constants are reported for the addition of ¹O₂ to a series of cyclic monoolefins.

Experimental Section

Ergosterol acetate (4) was prepared from ergosterol.¹⁵ Abietic acid (7) was purified by the procedure of Harris and Sanderson.¹⁶ Cholesta-3,5-diene (9) was obtained from Steraloids, Inc. All other materials were commercial samples obtained from Aldrich Chemical Co., Tridom/Fluka, or Chemical Sample Co.

Three-milliliter samples of rubrene in chloroform, with and without added olefin and all containing the same initial concentration of rubrene (0.8 mM/L, optical density at 546.1, ~4), were pipetted into 1-cm square Pyrex UV absorption cells. The samples were irradiated simultaneously on a "merry-go-round"¹⁷ modified so that the turntable contained six 1-cm² holes. The 546.1-nm line of a Hanovia 679A36 450 W medium-pressure mercury-vapor lamp was isolated by a combination of Corning C.S. 1-60, 3-68, and 4-72 filters. Six samples, two without olefin and two each of two different olefin concentrations, were irradiated at the same time. The samples were open to the air to allow oxygen to diffuse in to replace that consumed during irradiation. Initial and final rubrene concentrations were determined spectrophotometrically with a Cary 219 spectrophotometer at 440 nm.

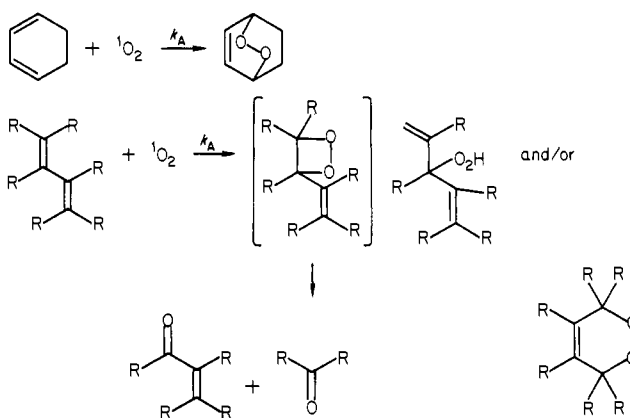
Reaction rate constants were calculated from the following:

$$k_A = \frac{k_R([R]_i^0 - [R]_f^0) + k_d \ln([R]_i^0/[R]_f^0)}{[D] \ln([R]_i/[R]_f)}$$

where k_R is the rate constant for reaction of ¹O₂ with rubrene, k_d the rate constant for ¹O₂ decay in chloroform, [R] the initial rubrene concentration, [R]_f⁰ and [R]_f⁰ the final rubrene concentration in the solutions with and without olefin, respectively, and [D] the concentration of olefin. Literature values for k_R (5.3 × 10⁷ L M⁻¹ s⁻¹)¹⁴ and k_d (1.7 × 10⁴ s⁻¹)^{13,18} were used.

At least two determinations were made for each compound and additional measurements were made if there was not good agreement between the values thus obtained. Errors are estimated from the range of

Scheme I



measured values. Systematic errors, such as those present in the values used for k_R and k_d , are not included in this estimate. A detailed de-

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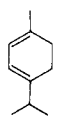
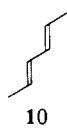


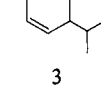

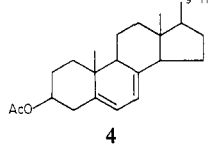





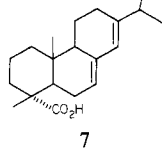



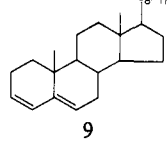

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[†] Dedicated to George S. Hammond on the occasion of his 60th birthday.

Table I. Rate Constants for Reaction of $^1\text{O}_2$ with Conjugated Dienes

diene	$k_A (\times 10^6 \text{ L}/(\text{M s}))^a$	diene	$k_A (\times 10^6 \text{ L}/(\text{M s}))^a$
	100 ^b		0.26
	100 ^b		0.16
	32 ^b		0.10
	27		0.078
	7.1 ^b		0.072
	5.3		0.065
	3.8		0.037
	1.1		0.024
	0.74		0.009

^a In chloroform; values $\pm 10\%$. ^b From data in methanol given in ref 10 and 13 the following are calculated: α -terpinene (1), $4.6 \times 10^7 \text{ L}/(\text{M s})$; cyclopentadiene (2), $3.2 \times 10^7 \text{ L}/(\text{M s})$; α -phellandrene (3), $1.4 \times 10^7 \text{ L}/(\text{M s})$; 1,3-cyclohexadiene (5), $3.2 \times 10^6 \text{ L}/(\text{M s})$. For 2 in toluene 3.9×10^7 has been reported (ref 14).

scription of the method has been previously published.¹⁴

As previously discussed, significant errors may arise if the added olefin quenches the rubrene singlet and/or triplet state.^{14,21} Fluorescence lifetimes for rubrene solutions containing olefins at the concentrations










(18) Recent measurements of the lifetime of $^1\text{O}_2$ in chloroform¹⁹ suggest that the value of 60 μs reported by Merkel and Kearns¹³ may be too short. The net result would be to make all of our rate constants too large since all of our measurements ultimately depend on the value.¹⁴ However, the generally good agreement between rate constants determined by this method and those determined by other methods for the same or similar compounds suggest that the value is approximately correct for the conditions under which we are working, i.e., commercially available chloroform (contains 1% ethanol) open to the air. In any case, the rate constants which we have reported^{14,20-22} are an internally consistent set of values since they have all been determined by the same procedure.

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Table II. Comparison with Fluorescence Quenching

diene	adiabatic IP (eV) ^a	$k_r^b (\times 10^9 \text{ L}/(\text{M s}))$	$k_{\text{cap}}^c (\times 10^8 \text{ L}/(\text{M s}))$	$k_A^d (\times 10^6 \text{ L}/(\text{M s}))$
	7.46	4.0	5.3	5.3
	7.88	2.5	3.0	7.1
	8.03	0.62	0.91	0.24
	8.06	0.51	0.98	0.10
	8.20	0.29		100
	8.42	0.11	0.14	0.023
	8.45	0.092		0.009
	8.54	0.015	0.074	0.078
	8.68	0.014	0.061	0.037

^a Reference 30. ^b Naphthalene fluorescence quenched by dienes (ref 26). ^c Camphorquinone fluorescence quenched by dienes (ref 29). ^d This work.

used in these experiments, measured with a phase shift taumeter, showed no fluorescence quenching. Significant diene quenching of rubrene triplet is unlikely since the rubrene triplet is estimated to be $\sim 29 \text{ kcal/mol}$ ²³ while diene triplets are about 58-60 kcal/mol.²⁴

Results and Discussions

Conjugated Dienes. Rate constants for reaction of a series of 18 conjugated dienes with $^1\text{O}_2$ are given in Table I. A variation of four orders of magnitude is observed. As previously discussed,^{14,22} these numbers are the sum of the rate constants for all processes by which the added diene removes $^1\text{O}_2$ from the system. They are assumed to be rate constants for diene oxidation, although the possibility that they contain a quenching component cannot be eliminated.

Cyclopentadiene and the cyclohexadienes, which form only endoperoxides from reaction with $^1\text{O}_2$, are the most reactive group. These values are in good agreement with rate constants for these compounds which can be calculated from the β values reported by Koch.¹⁰ 1,3-Cycloheptadiene and 1,3-cyclooctadiene, which also give endoperoxides^{12,25} with $^1\text{O}_2$ but whose conjugated double bonds are twisted out of co-planarity, are considerably less reactive than cyclohexadiene.

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(23) Estimated from the tetracene triplet energy (29.3 kcal/mol).²⁴

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Acyclic dienes and dienes whose double bonds are locked in a trans configuration are less reactive than cyclopentadiene and 1,3-cyclohexadienes, dienes whose double bonds are locked in a cis configuration. The ionization potentials and rate constants for quenching of naphthalene fluorescence and biacetyl fluorescence are given in Table II along with the rate constants for reaction with $^1\text{O}_2$. In general, alkyl substitution at the ends of the conjugated system decreases the ionization potential of the diene and increases the rate constant.

For mechanistic considerations it will be convenient to divide the dienes into four classes: (1) cyclopentadiene and 1,3-cyclohexadienes, dienes which have the conjugated system held in a cis configuration; (2) acyclic dienes without terminal substitution; (3) acyclic dienes with terminal substitution; and (4) dienes whose double bonds are locked in a trans configuration. An examination of the literature shows that cyclopentadiene, 1,3-cyclohexadienes, and acyclic dienes without terminal substitution produce 1,4-endoperoxides on reaction with $^1\text{O}_2$. Dienes whose double bonds are locked in a trans configuration produce allylic hydroperoxides and acyclic dienes with terminal substitution yield endoperoxides, allylic hydroperoxides, and/or cleavage products from decomposition of an intermediate 1,2-dioxetane on $^1\text{O}_2$ reaction.³⁻⁹

Two mechanisms have been proposed for the reaction of cyclopentadiene and 1,3-cyclohexadienes with $^1\text{O}_2$: (1) a concerted cycloaddition process similar to the Diels-Alder reaction,^{3b,e,31} and (2) formation of an intermediate perepoxide which rearranges to the endoperoxide.³² In the second process the rate-limiting step is proposed to be formation of a perepoxide, the same as in the reaction with monoolefins.

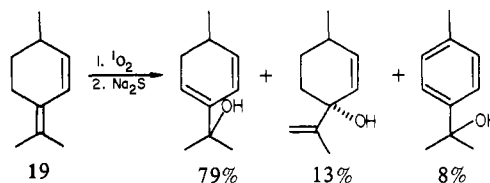
For addition of $^1\text{O}_2$ to cyclopentadiene Gorman, Lovering, and Rodgers¹¹ found an activation energy of 0.0 ± 0.4 kcal/mol and an entropy of activation of -25.8 cal/(mol deg). They concluded that the reaction is either (1) a single-step, entropy-controlled reaction or (2) production in a rate-determining, entropy-controlled step of an intermediate which rapidly rearranges to product. They further pointed out that a process with little if any activation energy should not be sensitive to the relative electron-donating abilities of the various substrates.

This is observed for cyclopentadiene and 1,3-cyclohexadiene. The rate constant for cyclopentadiene is more than twice as large as that for 1,3-cyclohexadiene despite an ionization potential that is 0.32 eV larger (Table II), and the rate constants for both dienes are greater than those of acyclic dienes with similar ionization potentials. Comparison with the fluorescence quenching data shows that these compounds are relatively much more reactive with $^1\text{O}_2$ than they are quenchers of aromatic hydrocarbon and diketone fluorescence, processes which are thought to depend on electron transfer.²⁶⁻²⁹

The rate constant for reaction of a monoolefin with $^1\text{O}_2$, a reaction for which an intermediate perepoxide has been proposed,^{33,34} is sensitive to the ionization potential of the substrate.^{3b,20,36} Since the rate constants for reaction of cyclopentadiene and 1,3-cyclohexadienes with $^1\text{O}_2$ are relatively insensitive to the ionization potential of the substrate and are much larger than what would be predicted on the basis of ionization potential alone, these compounds cannot react by the same mechanism as monoolefins. Since the mechanism for monoolefin reaction, presumably the perepoxide mechanism, has been eliminated, the most reasonable alternative mechanism for the reaction of $^1\text{O}_2$ with cyclopentadiene and 1,3-cyclohexadienes is a 1,4-cycloaddition reaction similar to the Diels-Alder reaction. This mechanism is consistent with the available experimental evidence¹¹ and is allowed from orbital symmetry considerations.^{3c}

Dienes which are locked in the trans configuration, such as

abietic acid (7) and cholesta-3,5-diene (9), must react by a different mechanism than cyclopentadiene and cyclohexadiene since no cis configuration is accessible to them. The rate constants for reaction of these compounds with $^1\text{O}_2$ are about the same or slightly larger than those for acyclic dienes with similar substitution patterns. These dienes react as if they were monoolefins to produce allylic hydroperoxides. The mechanism for the reaction must be the same as that for monoolefins. *p*-Mentha-2,4(8)-diene (19), for example, undergoes attack at the more highly substituted double bond, just as would be predicted if the double bonds were considered independently.³⁷

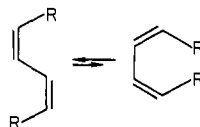


Acyclic dienes which lack terminal substitution, such as isoprene and β -myrcene, produce endoperoxide on reaction with $^1\text{O}_2$.^{3a,6} These products can arise from either or both of two mechanisms: (1) reaction of the *s*-cis conformation with $^1\text{O}_2$ in a 1,4-cycloaddition reaction^{3b} or (2) reaction of the *s*-trans conformation with $^1\text{O}_2$ to form an intermediate which rearranges to the endoperoxide.

Both theory³⁸ and experiment³⁹ indicate that the *s*-trans conformer is the predominant isomer. Molecular mechanics calculations show that the *s*-trans isomers of isoprene (16) and 2,3-dimethyl butadiene (13) are favored by 2.26 and 0.78 kcal/mol and that the double bonds of the *s*-cis isomers are twisted out of coplanarity by 37.4° and 43°, respectively.³⁸ If $^1\text{O}_2$ is only reacting with the *s*-cis isomer, and since the rate constant for the 1,4-cycloaddition reaction is not greatly affected by the ionization potential of the substrate, the measured rate constants should be about 1% of the rate constants measured for *cis* dienes, as observed.

If the *s*-trans isomer of these dienes were reacting via an intermediate which rearranges to the endoperoxide, the rate constants should be less than that measured for the piperlyenes (17 and 18) because isoprene and 2,3-dimethylbutadiene have higher ionization potentials than the piperlyenes (Table II). Although the piperlyenes are more efficient quenchers of naphthalene fluorescence and of biacetyl fluorescence than 2,3-dimethylbutadiene and isoprene, as predicted by their ionization potentials, isoprene and 2,3-dimethylbutadiene are more reactive with $^1\text{O}_2$ than the piperlyenes. The rate constant for reaction of *cis*-2,3-trans-4-hexadiene (12) with $^1\text{O}_2$ is only a factor of 1.3 larger than that for 2,3-dimethylbutadiene (13) despite a large ionization potential difference of 0.48 eV. In the quenching of naphthalene fluorescence and biacetyl fluorescence by dienes this ionization potential difference causes the rate constant to increase by factors of 34 and 13, respectively. Since the rate constant for the reaction of dienes which lack terminal substitution with $^1\text{O}_2$ is affected by factors other than ionization potential, this reaction does not proceed by the same mechanism as monoolefins. 1,4-Cycloaddition of $^1\text{O}_2$ to the *s*-cis isomer is the most reasonable alternative.

Terminally substituted acyclic dienes are the most complex cases since endoperoxide, allylic hydroperoxides, and products which come from cleavage of a 1,2-dioxetane have been observed from reaction of these compounds with $^1\text{O}_2$.^{3a,6,8,9} Terminal substitution of the diene should lower its ionization potential thus increasing the rate constant for reaction involving intermediate formation. Although terminal substitution in the *trans* position should have little effect, substitution in the *cis* position causes the double bonds of the *s*-cis conformer to be bent out of coplanarity.³⁸ For the



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













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Table III. Rate Constants for Reaction of Cyclic Monoolefins with $^1\text{O}_2$

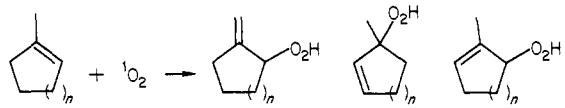
olefin	k_A ($\times 10^6$ L/(M s))	k_{rel}
	2.3 ^a	1.0
	2.7	1.2
	1.5	0.65
	0.36	0.16
	0.51	0.22
	0.40	0.17
	0.20	0.09
	2.4	1.0
	0.53	0.23
	8.7	3.8
	0.86	0.37
	4.8	2.1
	4.9	2.1
	0.61	0.27

^a Reference 20.

1,4-cycloaddition mechanism, the following order of reactivity would be predicted: *trans*-2,*trans*-4-hexadiene (10) \sim *trans*-piperylene (17) $>$ *cis*-2,*trans*-4-hexadiene (12) \sim *cis*-piperylene (18) $>$ 2,5-dimethylhexadiene (6). The order is not observed; correlation with the ionization potential is found. This, plus formation of allylic hydroperoxides and 1,2-dioxetane cleavage products from reaction of some of these compounds with $^1\text{O}_2$, indicates that these compounds are oxidized by a process like that of the monoolefin reaction.





We conclude that the reaction of $^1\text{O}_2$ with conjugated dienes takes place by two mechanisms. The preferred mechanism is a 1,4-cycloaddition of $^1\text{O}_2$ to a *cis* diene to form an endoperoxide, a reaction which is relatively insensitive to the ionization potential of the olefin. When the *cis* form of the diene is inaccessible and/or the ionization potential of the olefin is lowered by terminal alkyl substitution, the reaction pathway is diverted to one which resembles the reaction of monoolefins with $^1\text{O}_2$. This reaction,

Table IV. Products from Reaction of 1-Methyl Cycloolefins with $^1\text{O}_2$ ^a



$n + 4$	k_{rel}^b	k_{rel}^a	A	B	C
5	7.5	6.2	4	53	43
6	1	1	44	36	20
7	6.7	9.4	4	48	48
8	1.5	1.5	27	31	42

^a In 1:1 methanol-*tert*-butyl alcohol (ref 40). ^b This work.Table V. Relative Rates for Reaction of Ethylidene Cycloalkane with $^1\text{O}_2$

olefin	k_{rel}	olefin	k_{rel}
	10		5.6
	1		5.7

currently thought to entail formation of an intermediate peroxide, produces allylic hydroperoxides, endoperoxides, and 1,2-dioxetanes.

Cyclic Monoolefin. The rate constants for reaction of 13 cyclic monoolefins are given in table III along with rates constants relative to that of 2-methylbutene as a reference compound. Olefins with ring sizes varying from five to eight members and with either endocyclic or exocyclic double bonds have been investigated.

The relative rate constants for $^1\text{O}_2$ addition to a series of 1-methyl cycloolefins are given in Table IV along with the relative rates and product mixtures reported by Foote.⁴⁰ Similar relative rate and product data have recently been reported by Jefford and Rimbault.³⁵ The rate constant for 1-methylcyclohexene is anomalously low and the product mixture is quite different from that observed for 1-methylcyclopentene. 1-Methylcyclooctene is intermediate between both these compounds in both rate and product mixture.

It has recently been demonstrated that normal attack by $^1\text{O}_2$ on a trisubstituted olefin yields products derived from almost exclusive attack on the disubstituted side.^{34,41,42} However, in the case of 1-methylcyclohexene 44% of the product results from attack on the monosubstituted side of the olefin.⁴⁰ This suggests that the "normal" mode of attack is inhibited allowing the slower attack from the "abnormal" side to become competitive. This phenomenon has been recently discussed by Jefford and Rimbault.³⁵

The relative rate constants for reaction of $^1\text{O}_2$ with a series of ethylidene cycloalkanes are given in Table V. Jefford and Rimbault³⁶ have reported a similar, but much more pronounced, effect for the methylene cycloalkane series. Once again the six-membered ring analogue shows an anomalously low rate constant. Although the products from reaction of these olefins with $^1\text{O}_2$ have not been investigated, the ethylidene cyclohexane should impart an anomalous product mixture.

Acknowledgment. Able technical assistance was provided by Earl T. Jones, Jr.

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