

# REACTIVITIES IN PHOTSENSITIZED OLEFIN OXIDATIONS

KARL R. KOPECKY AND HANS J. REICH

*University of Alberta, Edmonton, Alberta*

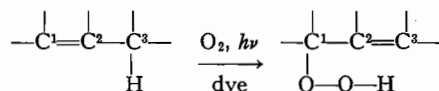
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## ABSTRACT

The rate of the methylene blue photosensitized oxidation of olefins increases in the order: 1-nonene < 4-methylcyclohexene < cyclohexene < 2,3-dimethyl-1-butene < 2-hexene < cyclopentene < 1-methylcyclohexene < 2,3-dimethylcyclohexene < 1-methylcyclopentene < 1,2-dimethylcyclohexene < 2,3-dimethyl-2-butene. The last compound is oxidized 5 500 times as fast as cyclohexene. Comparison of this reactivity sequence with those obtained in other reactions confirms that the reactive intermediate in the photosensitized oxidations is electrophilic. The relative rates ( $k_A/k_B$ ) of photo-oxidation of 1-methylcyclopentene (A) and of 1-methylcyclohexene (B) are 10 and do not vary significantly with five different sensitizers. Thus the same reactive intermediate, presumably singlet oxygen, is formed using each of the five sensitizers.

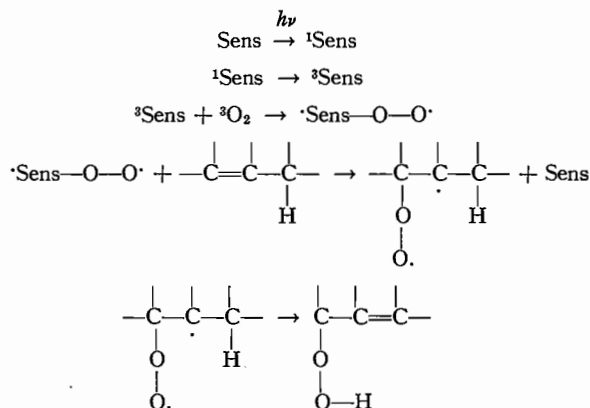
## INTRODUCTION

The dye-photosensitized oxidation of olefins to allylic hydroperoxides has been studied extensively by Schenck and his co-workers (1). A shift of the double bond was reported always to take place. The reaction is stereospecific in cyclic systems (2) and has recently been used to advantage in several synthetic studies (3-5).



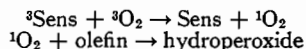
Two mechanisms for this transformation are currently popular.

Schenck, adapting a mechanism suggested by Schönberg (6) has proposed the following mechanism for the photosensitized oxidation of mono-olefins (1).



In this mechanism a sensitizer molecule (Sens) is excited by radiation (light absorbed only by the dye molecule is sufficient for reaction) to an excited singlet state which undergoes internal conversion to give the triplet (7). This reacts with oxygen to give a "diradical" adduct ( $\text{Sens---O---O}\cdot$ ). The adduct reacts with an olefinic double bond, regenerating the sensitizer and forming a "diradical" adduct of oxygen and olefin. Hydrogen transfer then yields the allylic hydroperoxide.

Kautsky (8), and, more recently, Sharp (9) and Foote (10, 11) have suggested that the metastable  $^1\Delta_g$  state of the oxygen molecule is the reactive intermediate involved in photosensitized oxidations.



Energy transfer from triplet sensitizer to triplet oxygen yields the ground state sensitizer and singlet oxygen, because of conservation of electron spin angular momentum during energy transfer (12, 13). Singlet oxygen then reacts with the olefin to produce the hydroperoxide.

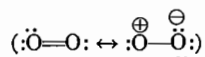
In support of the second mechanism Foote (10) has shown that products identical to those formed in dye photosensitized photo-oxidations are produced when sodium hypochlorite is added to solutions containing hydrogen peroxide and an oxidizable substrate. Singlet oxygen has been observed spectroscopically when sodium hypochlorite was added to hydrogen peroxide (14–17). In addition, singlet oxygen generated by electrodeless discharge oxidizes anthracenes to the corresponding endoperoxides (18).

The rate of disappearance of the reactive intermediate in the sensitized oxidation of  $\alpha$ -terpinene to ascaridole is independent of sensitizer used (19a). It has been suggested that a common intermediate is thus involved when different sensitizers are used (11). However, the activation energy for this reaction is only ca. 0.5 kcal/mole (19a), and the only conclusion one may safely make regarding any intermediates in these reactions is that they are all very reactive.

Schenck (19b) and Sharp (9) have measured the rate of sensitized oxidation of several olefins and found that increasing substitution of the double bond greatly increased reactivity. We report here similar reactivity studies but find that the response of the reactive intermediate to variation in olefin structure is much greater than that reported by Sharp but similar to that found by Schenck. We also compare the relative rates of photo-oxidation of olefins with the relative rates of their reactions with a number of free radicals and electrophiles. In addition, it is shown that the relative rates of photo-oxidation of two mono-olefins, a reaction which must proceed with activation energy (19a), does not vary with several sensitizers.

## RESULTS AND DISCUSSION

Schenck's adduct would be expected to show radical reactivity while singlet oxygen



(9) may be electrophilic. A number of studies have been made in which the relative reactivities of a number of olefins toward a variety of reagents have been measured. A comparison of the relative reactivities of olefins of different structural types toward photosensitized oxidation and towards the other reagents can thus be made.

We have measured the relative rates of the photo-oxidation, sensitized by methylene blue, of a number of olefins. These were measured by oxidizing olefins in pairs, thus allowing them to compete for the reactive intermediate, and measuring the amounts of olefin remaining at various intervals by g.l.c. analysis. The relative rates are summarized in Table I along with the relative rates of the reactions of a variety of olefins with peracetic acid (20), phthaloyl peroxide (21), bromine (22), methyl radical (23), trifluoromethyl radical (24), and trichloromethyl radical (25, 26). The photo-oxidation reaction is seen to be extremely sensitive to structure. Indeed, the reactive intermediate involved is the most discriminating reagent of those listed in Table I. There is a close similarity in the

TABLE I  
Relative reactivity of olefins towards various reagents

Olefin	Photo-oxidation	Peracetic acid <sup>a</sup>	Phthaloyl peroxide <sup>b</sup>	Bromine <sup>c</sup>	Methyl radical <sup>d</sup>	Trifluoromethyl radical <sup>e</sup>	Trichloromethyl radical <sup>f</sup>
Ethylene	0.1 <sup>g</sup>	0.032 <sup>h</sup>	0.021 <sup>a</sup>	1	1	1	
Alkylethylene	1.7 <sup>h</sup>	0.71 <sup>i</sup>		2.03 <sup>i</sup>	0.65 <sup>j</sup>	1.4	4.2 <sup>n</sup>
2-Methylpropene		0.71 <sup>j</sup>		5.5	1.1	3.8	
<i>cis</i> -2-Butene					0.1	1.3	
<i>trans</i> -2-Butene					0.2		
2-Hexene	9	0.76					
4-Methylcyclohexene	0.67						
Cyclohexene	1	1	1				1
Cyclopentene	16	1.51					3.3
1-Methylcyclohexene	45						
2-Methyl-2-butene		9.61	9.3	10.4			3.8
1-Methylcyclopentene	390	17.2	31.3				
1,2-Dimethylcyclohexene	29 00						
2,3-Dimethyl-2-butene	55 00	3 000 <sup>k</sup>	100	14		1.2 <sup>m</sup>	

<sup>a</sup>Reference 20.<sup>b</sup>Reference 21.<sup>c</sup>Reference 22.<sup>d</sup>Reference 23.<sup>e</sup>Reference 24.<sup>f</sup>References 25, 26.<sup>g</sup>1-Nonene.<sup>h</sup>2,3-Dimethyl-1-butene.<sup>i</sup>Propylene.<sup>j</sup>Isomer not indicated.<sup>k</sup>Estimated by Greene (27) from data collected by Swern (20).<sup>l</sup>1-Decene.<sup>m</sup>Calculated from data of ref. 28.<sup>n</sup>1-Octene.

variation of rate with structure between the photosensitized oxidation of olefins and their reaction with peracetic acid, bromine, and phthaloyl peroxide. No such similarity exists at all between the rate of the photosensitized oxidation of olefins and the rate of addition of any of the radical reagents listed in Table I to olefins. Even the electrophilic trifluoromethyl radical (24) does not respond to structural changes in the manner that the reactive intermediate in the photosensitized oxidation reaction does. This intermediate thus has strong electrophilic character and does not exhibit any radical properties. It is quite unlikely that the intermediate has the structural features of the diradical described by Schenck (29). The reactivity is best explained by the suggestion (9-11) that singlet oxygen is the reactive intermediate.

Product formation is best described by the suggestion of Sharp (9) that an intermediate perepoxyde is formed which rearranges with a concurrent proton shift to yield the allylic hydroperoxide (Chart I). However, our data do not provide evidence against a concerted cycloaddition as proposed by Nickon (30).

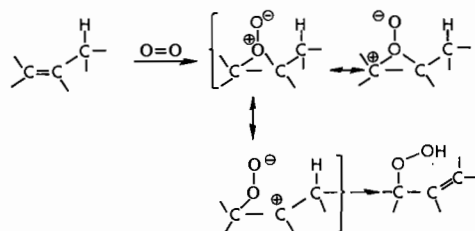


CHART I.

Sharp reports that the relative rates of tetraphenylporphine sensitized photo-oxidation of 1-hexene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene are 1, 94, and 100, respectively. We find a much greater difference in reactivity with comparably substituted olefins, as does Schenck (19b). The relative rates of photo-oxidation of 1-nonene, 1-methylcyclohexene, 1-methylcyclopentene, and 2,3-dimethyl-2-butene are, from Table I, 1, 450, 3 900, and 55 000, respectively. The reason for this discrepancy is not clear. It is probably not due to a difference in sensitizer. The relative rates of photo-oxidation of 1-methylcyclohexene and 1-methylcyclopentene with a variety of sensitizers are listed in Table II and do not vary with sensitizer. It may be that Sharp's relative rates were measured indirectly. If so, the relative errors may have accumulated to yield the data reported.<sup>1</sup>

TABLE II  
Effect of sensitizer on relative reactivities

Sensitizer	$k_A/k_B^*$
Methylene blue	$8.6 \pm 0.9$
Eosin Y	$10.8 \pm 1.4$
Rose bengal	$11.5 \pm 1.9$
Erythrosin B	$8.8 \pm 1.6$
Hematoporphyrin	$9.4 \pm 1.8$

\*A = 1-methylcyclopentene, B = 1-methylcyclohexene.

The oxidation reactions reported in this paper must have an activation energy significantly different from zero. The data of Table II therefore provide the first evidence that a common reactive intermediate is formed in oxidations involving different sensitizers.

<sup>1</sup>A referee has pointed out that reactivity depends upon concentration, and that the discrepancies may be due to this factor.

The activation energies of the rose bengal sensitized photo-oxidation of dicyclohexylidene and  $\beta$ -pinene are reported to be 1.3 and 4.5 kcal, respectively (19a). Dicyclohexylidene is thus about 700 times as reactive as  $\beta$ -pinene at 25°. This is in good agreement with the reactivity difference to be expected on the basis of the data in Table I.

## EXPERIMENTAL

### Preparation of Olefins

Cyclohexene (Eastman Kodak White Label), 2-hexene (Phillips 66 Pure Grade) and 4-methylcyclohexene (Eastman Kodak White Label) were distilled from lithium aluminium hydride. Pyrolysis of 1-nonylacetae yielded 1-nonene. The remaining olefins were obtained from the phosphoric acid catalyzed dehydration of the appropriate alcohols. The physical properties of those olefins obtained in the pure state were (boiling points in this study were obtained at 700 mm unless otherwise indicated and are uncorrected; the boiling points cited in the literature references are all for 760 mm unless otherwise indicated): cyclohexene b.p. 79–80°,  $n_D^{25}$  1.4441 (reported (31) b.p. 82.9°,  $n_D^{25}$  1.4438); cyclopentene b.p. 43°,  $n_D^{25}$  1.4199 (reported b.p. 44° (32),  $n_D^{25}$  1.4194 (33)); 1-methylcyclopentene b.p. 72–74°,  $n_D^{25}$  1.4293 (reported (34) b.p. 75.8°,  $n_D^{25}$  1.4330); 1-methylcyclohexene b.p. 106–107°,  $n_D^{25}$  1.4478 (reported (31) b.p. 110°,  $n_D^{25}$  1.4478); 4-methylcyclohexene b.p. 98–99°,  $n_D^{25}$  1.4392 (reported (31) b.p. 102.7°,  $n_D^{25}$  1.4389); 2-hexene b.p. 65–66°,  $n_D^{25}$  1.3941 (reported for *cis*-2-hexene (35) b.p. 68.8°,  $n_D^{25}$  1.3948; for *trans*-2-hexene (35) b.p. 67.8°,  $n_D^{25}$  1.3907); 2,3-dimethyl-2-butene b.p. 70–71°,  $n_D^{25}$  1.4098 (reported (35) b.p. 73°,  $n_D^{25}$  1.4094); 1-nonene b.p. 61–62° at 48 mm,  $n_D^{25}$  1.4136 (reported b.p. 33.5° at 11 mm (36),  $n_D^{25}$  1.4133 (37)). These olefins were shown to be more than 97% pure by g.l.c. analysis.

Dehydration of 1,2-dimethylcyclohexanol produced a mixture, shown by g.l.c. analysis to consist of 58% 1,2-dimethylcyclohexene, 37% 2,3-dimethylcyclohexene, and 5% of an unidentified compound. This mixture was used as such in the rate studies. The small amount of 2,3-dimethyl-1-butene, which was formed along with 2,3-dimethyl-2-butene upon dehydration of 2,3-dimethyl-2-butanol and which was used in the rate studies, was shown by g.l.c. analysis to contain 16% ether and 9% 2,3-dimethyl-2-butene as the only detectable impurities. The results obtained from these impure compounds fit well into the general pattern and are considered accurate enough for the present purpose.

### Determination of Relative Reactivities of Olefins

Pairs of olefins were chosen for the competition reactions on the basis of suitable reactivity. Approximately equimolar amounts of the two olefins (0.5 to 2.0 ml), 1.0 ml of an internal standard (benzene, toluene, or ethylbenzene) and 30 mg of methylene blue were dissolved in 200 ml of redistilled methanol. The resulting solution was poured into an immersion photochemical reactor (38) just filling the annular space. A slow stream of oxygen was passed through the solution which was kept at 15 °C while it was being irradiated. The light source was a 200 W Hanovia mercury vapor lamp, type S, No. 654A. A filter sleeve, Hanovia No. 516-27-116 was used to cut off all radiation below 3 600 Å. Samples were withdrawn from the solution initially and at intervals, after mixing, during the irradiation until one component had decreased to about 10% of its original concentration. The samples were analyzed by g.l.c. using the internal standard method of Keulemans (39). A Wilkins Aerograph 202 gas chromatographic instrument was used with a 5 ft column packed with Apiezon M on 60–80 Chromosorb W which gave good separation between methanol and all the olefins. From the relative amounts of olefins remaining, the relative rate constants were calculated by the method of Ingold and Shaw (40). The results are summarized in Table III. The relative rates given represent the average of several determinations and the average errors are indicated. Control experiments showed that no olefin was consumed in the absence of light or in the absence of dye when the lamp was on for the time required for 90% oxidation of the more reactive component except in the case where 1-nonene was a

TABLE III  
Relative rates of photosensitized oxidation of olefins

Expt. No.	Olefin A	Olefin B	$k_B/k_A$
1	1-Nonene	Cyclohexene	10*
2	4-Methylcyclohexene	Cyclohexene	1.5 ± 0.2
3	Cyclohexene	2-Hexene	8.5 ± 0.2
4	2-Hexene	Cyclopentene	1.8 ± 0.4
5	Cyclopentene	2,3-Dimethylcyclohexene	3.0 ± 0.1
6	1-Methylcyclohexene	2,3-Dimethylcyclohexene	1.07 ± 0.03
7	1-Methylcyclohexene	1-Methylcyclopentene	8.6 ± 0.9
8	1-Methylcyclopentene	1,2-Dimethylcyclohexene	7.5 ± 0.7
9	1,2-Dimethylcyclohexene	2,3-Dimethyl-2-butene	1.9 ± 0.2
10	Cyclohexene	2,3-Dimethyl-1-butene	1.7 ± 0.4

\*Estimated value. Oxidation of 1-nonene proceeded so slowly that evaporation losses became significant.

competitor. In another control experiment a solution containing 0.4 g of 2,3-dimethyl-3-hydro-peroxy-1-butene (41) and 1.0 g of 2,3-dimethyl-2-butene were photolyzed in the above apparatus. After 15 min 5% of the olefin had been consumed. Thirty mg methylene blue was added and the photolysis was continued. After 15 min 90% of the olefin had been consumed. The relative reactivities reported in Table II were determined in the manner described above using solutions made up from 2.0 ml ethylbenzene, 1.0 ml each of 1-methylcyclopentene and 1-methylcyclohexene, 30 mg of sensitizer, and 200 ml of distilled methanol.

#### ACKNOWLEDGMENT

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