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PHOTOSENSITIZED OXIDATION OF 1-PHENYLCYCLOBUTENE. THE ROLE OF REACTIVE OXYGEN SPECIES OTHER THAN SINGLET OXYGEN

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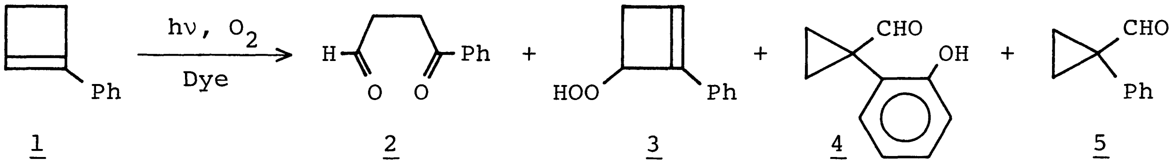
On dye-sensitized photooxidation of 1-phenylcyclobutene the formation of 3-benzoylpropanal and 2-phenyl-3-hydroperoxycyclobutene was ascribed to oxidation with singlet oxygen, whereas a reactive oxygen species other than singlet oxygen was responsible for the formation of 1-(2-hydroxyphenyl)cyclopropanecarbaldehyde. Some attempts to explore the latter oxygen species were made.

Dye-sensitized photooxidation is now accepted as proceeding through singlet oxygen mechanism;[1] the product distribution is controlled by sensitizers, solvents, and temperature.[2-4] However, much attention has not been focused on other oxygen species responsible for the product distribution than singlet oxygen. Recently it has been shown that superoxide anion as well as singlet oxygen is generated on irradiation of rose bengal under oxygen atmosphere.[5,6]

1-Phenylcyclobutene (1) has been reported to give, on dye-sensitized photooxidation, the ketoaldehyde (2), the hydroperoxide (3), and the cyclopropanecarbaldehydes (4) and (5) with varying distributions depending on the solvent/sensitizer combinations.[2] We now wish to report our findings on the photosensitized oxidation of 1 that the cyclopropanecarbaldehyde (4) does not arise from the singlet oxygen oxidation but from oxidation with some other oxygen species, and some attempts to characterize the species responsible for the formation of 4.



1 2 3 4 5

We reexamined solvent effects on the photooxidation of 1 using a given sensitizer in various solvents.[7] Table 1 summarizes the results. In all solvent/sensitizer combinations employed, the three compounds, 2, 3, and 4, were obtained, and were accompanied by polymeric material in most cases; the product distribution appears to depend on the combinations.[8] Although the proportion of the oxygenation products shown in Table 1 was not always high, inspection of the ratios among these products leads to important features. When methylene blue (MB) was used as sensitizer, the ratio of the yields, 2/3, seems not to depend on the polarity of the

Table 1. Product Yields in Photooxidation of 1-Phenylcyclobutene (1) with Methylene Blue (MB) or Zinc Tetraphenylporphin (ZnTPP) in Various Solvents[a]

Solvent	Sensitizer	Additive	Conversion (%)	Product yield (%)[b]			Ratio	
				2	3	4	2/3	(2+3)/4
C_6H_6	ZnTPP		48	19	8	6	2.4	4.5
	ZnTPP	DABCO[e]	75	4	4	92	1.0	0.09
CH_2Cl_2	MB		50	15	8	3	1.9	7.7
	ZnTPP		48	25	17	9	1.5	4.7
CH_3COCH_3	MB		91	7	11	46	0.64	0.39
	ZnTPP		81	15	19	8	0.79	4.3
CH_3CN	MB		60	12	9	38	1.3	0.55
	MB	$PhCOCO_2H$[f]	88	19	8	2	2.4	14
	ZnTPP		95	8	29	1	0.28	37
CH_3OH	MB		71	12	10	30	1.2	0.73
	MB	$PhCOCO_2H$[f]	56	44		8		5.5[h]
	RB[d]		58	10	9	32	1.1	0.59
CH_3OH-H_2O[c]	MB		70	18	6	27	3.0	0.89
	MB	Tiron[g]	50	28	6	24	4.7	1.4

a) [1] = 1 x 10^{-2} M. b) Yield based on 1 consumed. c) [H_2O] = 1.3-4.0 vol%. d) Rose Bengal. e) 1,4-Diazabicyclo[2.2.2]octane, 5 x 10^{-3} M. f) 1 x 10^{-2}M. g) 1,2-Dihydroxybenzene-3,5-disulfonic acid, 5 x 10^{-3} M. h) 2/4.

solvents; however, on sensitization with zinc tetraphenylporphin (ZnTPP) the ratio, 2/3, tends to be larger in less polar solvents. This could be explained by stabilization of a perepoxide intermediate in polar solvents as proposed by Jefford and Rimbault.[2] On the other hand, the ratio, (2+3)/4, is altered to a greater extent by the solvent/sensitizer combinations; especially when MB was used as sensitizer, the photooxidation in acetone and acetonitrile gave high ratios of 4, but in dichloromethane the ratio of 4 was much lower. In acetone and acetonitrile the use of MB as sensitizer gave 4 in much higher ratios than did the use of ZnTPP.

The fact that the ratio of 4 in the same solvent depends on the sensitizers employed could not be explained only by difference in the stabilization of intermediates in the reaction of the olefin with free singlet oxygen.

It would be a more reasonable explanation that another reactive oxygen species, for example, superoxide anion or an adduct of oxygen with sensitizer, is generated together with singlet oxygen and gives different products from those resulting from singlet oxygen, and that the ratio of the oxygen species generated changes among the solvent/sensitizer combinations.

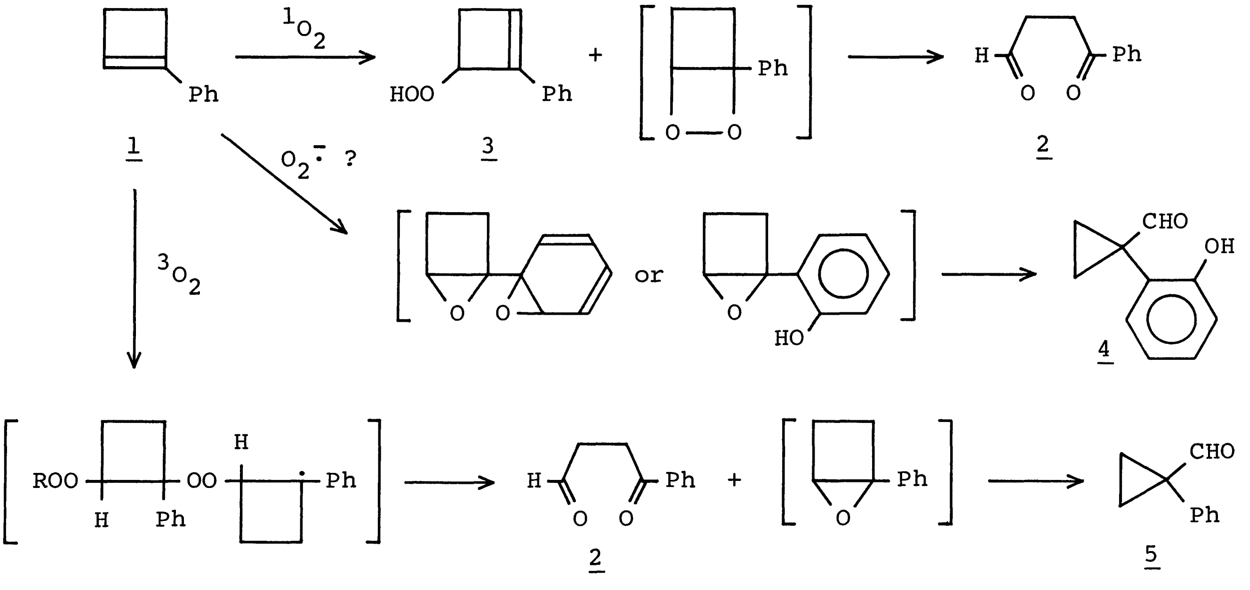
Addition of the singlet oxygen quencher, 1,4-diazabicyclo[2.2.2]octane (DABCO),[9,10] led to a pronounced decrease of 2 and 3 accompanying a prominent increase of 4. Thus, on ZnTPP-sensitized photooxidation of 1 in benzene, DABCO increased the yield of 4 up to 92% at the expense of 2, 3 (2+3, 8%), and polymeric material.[11] This result clearly shows that 2 and 3 result from singlet oxygen, while 4 does not arise from singlet oxygen but from another oxygen species.

Some attempts were made to elucidate the species responsible for the formation of 4. Involvement of ground-state oxygen is eliminated since autoxidation of 1 in the dark gave the ketoaldehyde, 2, and the cyclopropanecarbaldehyde, 5, but gave none of 4. The autoxidation of 1 was inhibited by hydroquinone, whereas the formation of 4 in the photooxidation was not affected by phenolic radical scavengers.[12]

It has been known that phenylglyoxylic acid is inert towards singlet oxygen[14] but undergoes efficient decarboxylation with superoxide anion to give benzoic acid.[15] 1-Phenylcyclobutene, 1, was subjected, together with phenylglyoxylic acid, to photooxidation using benzene/ZnTPP and methanol/MB combinations. As shown in Table 1, the ratio of the yields, 2/4, was highly increased in each case compared with the case in the absence of phenylglyoxylic acid, and phenylglyoxylic acid was competitively oxidized into benzoic acid.[16]

The formation of 4 was also retarded by 1,2-dihydroxybenzene-3,5-disulfonic acid (Tiron), which has been reported to be an efficient quencher of superoxide anion.[17,18] Thus, on photooxidation of 1 in methanol containing water (1.3-4.0 vol%) using MB as sensitizer the ratio of (2+3)/4 was ca. 0.9 (Table 1). The rate of disappearance of 1 in the presence of Tiron under the otherwise same conditions was reduced by a factor of 1.4 and the ratio of (2+3)/4 was increased to ca. 1.4. This shows that the rate of formation of 2 and 3 was not affected by Tiron but that of 4 was diminished to three-fifths of the rate in the absence of Tiron.

Scheme 1



These findings suggest that, on irradiation of dyes in solution under oxygen, not only singlet oxygen but also another oxygen species, which is at least similar in nature to superoxide anion, would be generated to a varying extent depending on solvent/sensitizer combinations, and that the latter oxygen species would play an important role in the product distribution of the photooxidation of 1. Plausible oxidation processes of 1 are depicted in Scheme 1.

Further investigation elucidating the oxygen species and oxidation mechanism is now in progress.

References and Notes

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7) Photooxidation of 1-phenylcyclobutene (1) was carried out in a usual manner by irradiating a solution of 1 (1 x 10^{-2} M) in a solvent under oxygen atmosphere with a 500-W xenon lamp through an appropriate cut-off filter for 5-30 min. The reaction mixture was, after treatment with triphenylphosphin, analyzed quantitatively by GLPC. The product distribution was not altered by the irradiation time. Because of high susceptibility of 1 to ground-state oxygen attack hydroquinone (2 x 10^{-4} M) was added to the solution to prevent autoxidation of 1.

8) A trace amount of 5 was obtained in some cases. The formation of 5 could be attributed to autoxidation of 1.

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11) DABCO quenched bleaching of the sensitizer. This might affect the conversion of the olefin.

12) A possibility that superoxide anions or hydroperoxyl radicals were generated from interaction of singlet oxygen with hydroquinone[13] can be ruled out because DABCO did not reduce the yield of 4 on photooxidation of 1 in the presence of hydroquinone.

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16) Under these reaction conditions, the hydroperoxide, 3, was not consumed in the presence of phenylglyoxylic acid.

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