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PHOTOINDUCED REACTIONS—LIX

REACTIVITY OF SINGLET OXYGEN TOWARD METHOXYBENZENES[1]

I. SAITO, M. IMUTA and T. MATSUURA

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

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Abstract—The dye-sensitized photooxygenation of a series of methoxybenzenes (Ia–Ie) in methanol has been investigated. Highly substituted methoxybenzenes (Ig, Ii–Il) were susceptible to photooxygenation, while less substituted methoxybenzenes (Ia–Ig, Ih) were found to be unreactive under similar conditions. The participation of singlet oxygen in the reaction was elucidated by photooxygenation using sensitizers having different triplet energies and by quenching experiments. Relative reaction rates of methoxybenzenes with singlet oxygen were shown to correlate with their half-wave oxidation potentials ($E_{1/2}$) and with their charge-transfer maxima ($\bar{\nu}_{c.t.}$) with tetracyanoethylene.

CYCLOADDITION to diene systems and allylic hydroperoxide formation are well established reactions of singlet oxygen.[2,3] It is known that, in the dye-densitized photooxygenation of olefins involving singlet oxygen, electron-donating substituents increased the reaction rate.[2,4–6] Kearns has shown that in some substituted olefins, there is a good correlation between ionization potential and reactivity toward singlet oxygen.[7] We previously reported the 1,4-cycloaddition of singlet oxygen to electron-rich monocyclic aromatic systems such as t-butylated methoxybenzenes,[8] whereas the addition to polynuclear aromatic compounds is well known.[9] The results prompted us to invesitgate the dye-sensitized photooxygenation of electron-rich monocyclic benzene derivatives, methoxybenzenes. The present paper shows that the reactivity of methoxybenzenes toward singlet oxygen is related to their π-ionization potentials.

A series of methoxybenzenes (Ia–Il) was photooxygenated by visible light in MeOH containing rose bengal (RB) as sensitizer. Ig and Ii–Il consumed smoothly an equimolar amount of oxygen, while Ia–If and Ih were found to be unreactive.* Relative rates of photooxygenation of methoxybenzenes were determined by competitive reactions.[4] When methylene blue (MB), which has a lower triplet energy (E_T = 34 kcal/mole) than that of rose bengal (E_T = 39·4 kcal/mole), was used as a sensitizer, the results were virtually identical. Relative rates of photooxygenation were compared with the value of the half-wave oxidation potentials ($E_{\frac{1}{2}}$) in MeCN and also with the frequencies of the charge-transfer band ($\bar{\nu}_{c.t.}$) with tetracyanoethylene (TCNE) in CH_2Cl_2 obtained by Zweig *et al.*[10,11] (Table 1). The results indicate that methoxybenzenes having less than +1·24 V *vs.* s.c.e. are susceptible to photooxygenation.

A semilog plot of the relative rate of photooxygenation of methoxybenzenes (Ig, Ii–Il) *vs.* $E_{\frac{1}{2}}$ and $\bar{\nu}$c,t, is shown in Fig 1. For methoxybenzenes Ig and Ii–Il there is good correlation between the relative rate and $E_{\frac{1}{2}}$, while with the exception of 1,2,4-trimethoxybenzene (Ig) the frequency of c.t. maxima ($\bar{\nu}_{c.t.}$) is also linearly related to the relative rate. Although the reason for the deviation of Ig from the plots based on

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* Details of the reaction products will be described in a subsequent paper.

Table 1. Relative rate of photooxygenation of methoxybenzenes

Compound		Relative rate RB	Relative rate MB	$E_{1/2}$ (oxid), V, *vs.* s.c.e.[a] in MeCN	$\nu_{c.t.}$[b] cm^{-1} $\times 10^3$
Anisole	Ia	0	0	+1·76	19·7
1,2-Dimethoxybenzene	Ib	0	0	1·45	16·9
1,3-Dimethoxybenzene	Ic	0	0	—	18·2
1,4-Dimethoxybenzene	Id	0	0	1·34	16·1
1,2,3-Trimethoxybenzene	Ie	0	0	1·42	19·4
1,3,5-Trimethoxybenzene	If	0[c]	0	1·49	18·2
1,2,4-Trimethoxybenzene	Ig	0·086	–	1·12	14·6
1,2,3,4-Tetramethoxybenzene	Ih	0	0	1·25	17·9
1,2,3,5-Tetramethoxybenzene	Ii	0·150	0·146	1·09	16·5
1,2,4,5-Tetramethoxybenzene	Ij	1·0	1·0	0·81	12·5
Pentamethoxybenzene	Ik	0·185	0·202	1·07	16·4
Hexamethoxybenzene	Il	0·030	0·032	1·24	19·5

[a] Ref. 10. [b] With tetracyanoethylene in CH_2Cl_2.[11] [c] The compound was photooxygenated at an extremely slow rate.

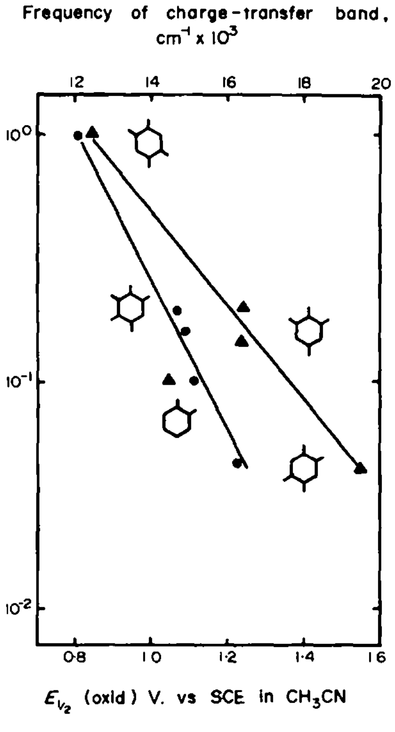

Fig 1. Semilog plot of the relative rate of photooxygenation of methoxybenzenes (Ig, Ii ~ Il) *vs.* half-wave oxidation potentials (●) and frequency of charge-transfer maxima with TCNE (▲)

the *c.t.* band is not yet understood, lack of molecular symmetry and less steric hindrance than methoxybenzenes Ii ~ Il may contribute to the deviation.

As described above, the relative rates of photooxygenation of the methoxybenzenes using sensitizers (rose bengal and methylene blue) with different triplet energies were virtually the same. The result strongly supports that singlet oxygen might be the reactive species in the photooxygenation. Such a criteria has been argued for the participation of singlet oxygen in photosensitized oxygenation.[12] The result also suggests that, if singlet oxygen is involved, it should be the ${}^1\Delta g$ state, since the ${}^1\Sigma g$ state has a higher excitation energy (37 kcal/mole) than the triplet energy (34 kcal/mole) of methylene blue.[2]

In order to ascertain further the participation of singlet oxygen in these reactions, we carried out quenching experiments on the photooxygenation of Ii, Ij and Il using β-carotene[13] or Et$_3$N[14] as quencher (Table 2). Although the quenching efficiencies depend upon the rate of conversions, β-carotene and Et$_3$N, which are well known as singlet oxygen quenchers, quench the photooxygenation of the methoxybenzenes. The result also supports that the reactive species in the above reaction is singlet oxygen. Although the mechanism involving a cation radical of methoxybenzene, produced from an excited methoxybenzene or by electron transfer with a triplet sensitizer, can not be completely eliminated, the finding that sensitizers having relative low triplet energy such as rose bengal and methylene blue are effective in the photooxygenation suggests that a singlet oxygen mechanism is more reasonable than other such mechanisms.*

TABLE 2. EFFECT OF QUENCHERS ON THE PHOTOOXYGENATION OF METHOXYBENZENES

	Substrate	Initial conc. (× 10^{2}M)		Conversion (%)
		Substrate	Quencher	
A	β-Carotene			
	Ii	6·3	—	37·8
		6·3	0·63	29·4
		6·3	6·3	6·6
	Ij	6·3	—	28·5
		6·3	0·063	25·0
		6·3	0·63	18·5
		6·3	6·3	1·1
	Il	4·7	—	20·6
		4·7	0·047	17·0
		4·7	0·47	15·7
		4·7	4·7	6·5
B	Triethylamine			
	Ii	6·3	—	37·8
		6·3	0·63	10
	Ij	6·3	—	48·6
		6·3	0·063	29·0
		6·3	0·63	23·3

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* Oxidation with singlet oxygen generated from hydrogen peroxide and hypochlorite could not be applied to the methoxybenzenes, which were easily oxidized with hydrogen peroxide alone in methanol to give the corresponding benzoquinones.

The above results indicate that those methoxybenzenes which have lower π-ionization potentials are more reactive to singlet oxygen. Kearns has applied first-order orbital symmetry theory to the concerted cycloaddition of singlet oxygen.[7] He predicted that, in the concerted addition of singlet oxygen ($^1\Delta g$) to olefins or dienes, molecules having a lower ionization potential should be more endothermically correlated to product formation and, therefore, more reactive.[7] Our results indicate that the reactivity of methoxybenzenes toward singlet oxygen ($^1\Delta g$) is linearly related to their π-ionization potentials. This conclusion is also compatible with the electrophilic character of singlet oxygen.

EXPERIMENTAL

Anisole (Ia) and the three dimethoxybenzenes (Ib, Ic, Id) were commercially available. Pyrogallol trimethyl ether (Ie) was obtained by methylation of pyrogallol.[15] Phloroglucinol trimethyl ether (If) was obtained by a similar procedure.[16] 1,2,3,4-Tetramethoxybenzene (Ih) was prepared according to the method of Benington *et al.*[17] 1,2,3,5-Tetramethoxybenzene (Ii) was prepared by the method of Backer.[18] 1,2,4,5-Tetramethoxybenzene (Ij) was obtained by reduction and subsequent methylation of 2,5-dimethoxybenzoquinone.[17] Pentamethoxybenzene (Ik) was prepared from Ii by the method of Backer.[17] Hexamethoxybenzene (Il) was prepared from 2,6-dimethoxybenzoquinone by the method of Robinson *et al.*[19]

Relative rates of photooxygenation. Relative rates of methoxybenzenes were determined by competitive reactions by the procedure of Foote *et al.*[4] A methanolic solution (10 ml) which contain two methoxybenzenes and a sensitizer (2 mg) was irradiated with a tungsten-bromine lamp through a window glass under bubbling oxygen. Concentration of each methoxybenzene was 0·05 M in all experiments, which were carried out at 20°. Relative rates were determined by measuring the disappearance of the substrates by GLC (Silicon DC 550, 200°, 1·5 Kg/cm^2) analysis. Three rate determinations were carried out for each experiment. Error limits were ca. ±10%.

Quenching experiments. Solutions containing various molarities (0–0·63 M) of a quencher (Table 2), a methoxybenzene (0·63 M) and rose bengal (5 mg) were made up to 4 ml with MeOH in the calibrated Pyrex tubes. After the solutions were saturated with oxygen by bubbling for 30 min, the tubes were sealed and irradiated in a Rayonet merry-go-round apparatus at approximately 20° for 50 min. Biphenyl (16 mg) was then added to the solution as internal standard, and the disappearance of the substrate was measured by GLC (Silicon DC 550, 200°, 1·5 Kg/cm^2).

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