Effect of singlet oxygen sensitizers and quenchers on the photo-oxidation of some unsaturated polymers

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The photo-oxidation of *cis*-polyisoprene was studied in the absence and in the presence of both singlet oxygen sensitizers (benzophenone, anthracene, rubrene) and quenchers (benzidine, diphenylamine, β-carotene). The amount of hydroperoxide which was formed at constant flow rate of oxygen during the u.v. irradiation of *cis*-polyisoprene increased by increasing the concentration of sensitizer as well as the number of quanta absorbed. The efficiency of the sensitizers used for the formation of hydroperoxide increased in the order: benzophenone < anthracene < rubrene. This effect was attributed to the fact that anthracene and rubrene can sensitize the photo-oxidation reaction by both physical and chemical generation of singlet oxygen while the generation of singlet oxygen is a purely physical process in case of benzophenone. In presence of quencher compounds β-carotene was more efficient than diphenylamine and the latter was more efficient than benzidine. The effect of a singlet oxygen oxidation on the different organic polymers was in the sequence: *cis*-polyisoprene > polybutadiene > styrene-polybutadiene > polychloroprene.

INTRODUCTION

The photo-oxidation of organic polymers may be achieved[1,2] either by triplet oxygen ($^{3-}\Sigma_g$) or singlet oxygen ($^{1+}\Sigma_g$, $^1\Delta_g$). The two forms of singlet oxygen had an excess energy of a fraction of a chemical bond: 37.5 and 22.5 Kcal mol^{-1} respectively. The photo-oxidation of commercial polyethylene which contains carbonyl groups as sensitizers was studied by exposing its surface to a stream of singlet oxygen yielding the formation of hydroperoxide[3]. The mechanism of energy transfer from an excited sensitizer molecule to oxygen is based on the formation of intermediate contact complexes of charge transfer type between the two species[4-7]. Singlet oxygen can be quenched by using several types of compounds which are able to de-activate (quench) it physically or chemically.

Here we report results on the photo-oxidation of some polymers in the absence and in the presence of different sensitizers as well as different singlet oxygen quenchers in fluid benzene media.

EXPERIMENTAL

Commercial samples of *cis*-polyisoprene, polybutadiene, styrene–polybutadiene (25% styrene–75% polybutadiene) and polychloroprene were purified by dissolving three times in spectroscopic benzene and precipitating with methanol. No traces of antioxidant or other additives could be detected by i.r. or u.v. spectroscopy. Benzene solution of the polymer (2% by weight) was prepared and stored in the dark. Chemically pure benzophenone, anthracene and rubrene were used as sensitizers, whereas β-carotene, benzidine and diphenylamine were used as singlet oxygen quenchers. The solvent was chemically pure benzene. Test solutions were prepared by mixing polymer, sensitizer and quencher solutions of the appropriate concentrations. The mixed solutions were irradiated by u.v. light (Hg-lamp, type HA-FI-300, 400 W., Holland) during passing a constant flow rate of oxygen gas (0.2 c.c. s^{-1}). Each irradiated sample tube was removed at intervals. The concentration of hydroperoxide formed was determined by the iodine–thiosulphate titrimetric method[8]. The number of quanta absorbed by the sample at a time was determined by using potassium ferrioxalate actinometer[9]. A calibration curve representing the variation of the number of quanta with irradiation time was constructed.

RESULTS

Photo-oxidation of cis*-polyisoprene*

(i) *In presence of benzophenone.* The photo-oxidation of *cis*-polyisoprene was carried out in absence and in presence of benzophenone as sensitizer in the concentration range of (2–8) × 10^{-3} mol l^{-1}. It was found that the amount of hydroperoxide increases with increase in the number of quanta as well as the concentration of benzophenone (*Figure 1*). The reaction was also carried out in presence of benzophenone in a similar concentration range in addition to constant concentration of the following singlet oxygen quenchers: benzidine (4 × 10^{-5} mol l^{-1}), diphenylamine (4 × 10^{-5} mol l^{-1}) and β-carotene (4 × 10^{-6} mol l^{-1}) (e.g. *Figure 2*). It is shown that the amount of hydroperoxide formed in presence of quencher compound is lower than that formed in absence of benzophenone. From *Figure 2* it can be observed that β-carotene is a more efficient quencher than diphenylamine and diphenylamine is more efficient than benzidine.

(ii) *In presence of anthracene.* Various concentrations of anthracene in the range of (1–6) × 10^{-4} mol l^{-1} were used

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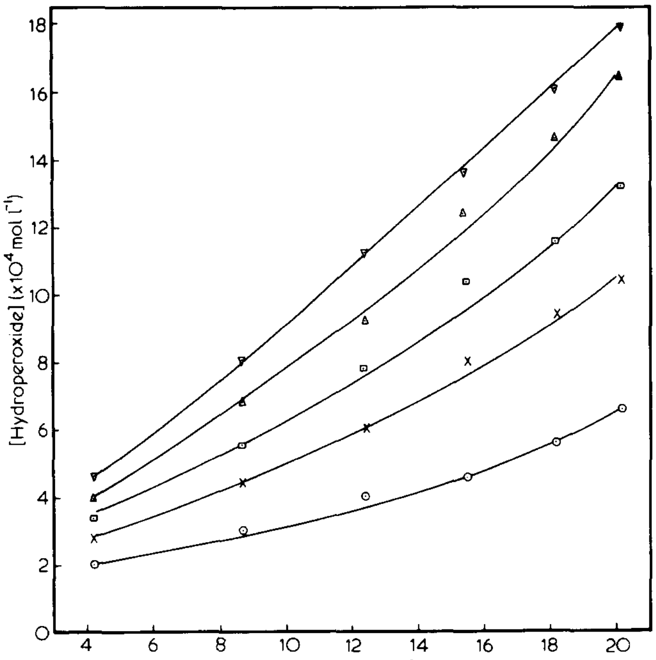


Figure 1 Illustration of the variation of hydroperoxide concentration with the number of quanta at various benzophenone concentrations: ○, without benzophenone; x, 2×10^{-3} mol l^{-1}; □, 4×10^{-3} mol l^{-1}; △, 6×10^{-3} mol l^{-1} and ▽, 8×10^{-3} mol l^{-1}

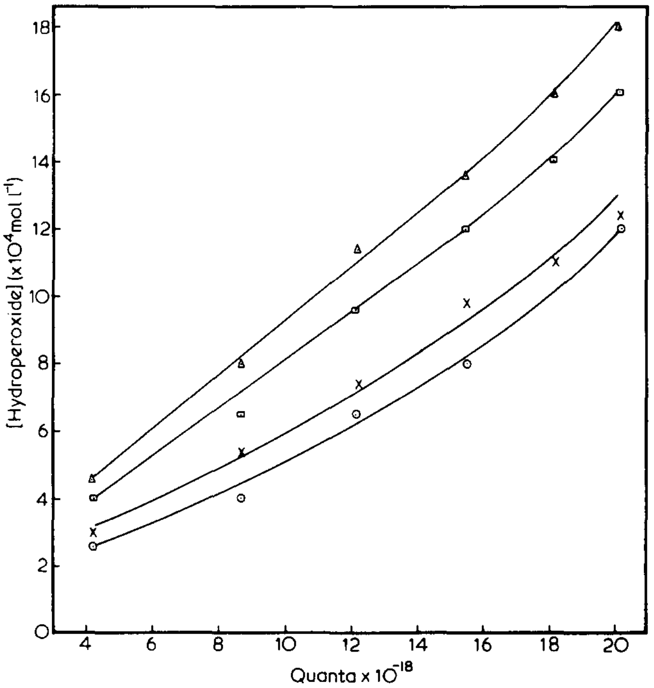


Figure 2 Representation of the relationship between hydroperoxide concentration and number of quanta in presence of 8×10^{-3} mol l^{-1} benzophenone with different singlet oxygen quenchers: △, without quencher; □, 4×10^{-5} mol l^{-1} benzidine; x, 4×10^{-5} mol l^{-1} diphenylamine and ○, 4×10^{-6} mol l^{-1} β-carotene

in the photo-oxidation reaction of polyisoprene in absence and in presence of constant concentration of each of: benzidine (8×10^{-4} mol l^{-1}), diphenylamine (8×10^{-4} mol l^{-1}) and β-carotene (8×10^{-6} mol l^{-1}). It was found that the amount of hydroperoxide increased with increase in the number of quanta absorbed as well as the concentration of anthracene. The amount of hydroperoxide formed in the process of photo-oxidation was plotted *versus* the concentration of anthracene in absence and in presence of the singlet oxygen quenchers concerned at constant number of quanta (e.g. *Figure 3*). It is clear that the amount of hydroperoxide increases with increase in anthracene concentration at a constant number of quanta. The addition of a constant concentration of any of the quencher compounds caused the concentration of hydroperoxide to decrease. It was also clear that β-carotene had the greatest effect as a singlet oxygen quencher in comparison with diphenylamine and benzidine although the concentration of the former was a hundred times smaller than that of the two latter quenchers.

(iii) *In presence of rubrene.* The photo-oxidation of *cis*-polyisoprene in presence of rubrene as sensitizer was carried out in the concentration range $(4\text{–}10) \times 10^{-6}$ mol l^{-1}. The relationship between the concentration of hydroperoxide and the number of quanta absorbed had the same features as previously shown for photo-oxidation in presence of benzophenone and anthracene. The order of efficiency of the three sensitizers under investigation was in the following sequence (*Figure 4*): rubrene > anthracene > benzophenone. This sequence was found experimentally without carrying out control experiments regarding the light stability of the sensitizers themselves, with and without the presence of the singlet oxygen quenchers. The decreased efficiency of anthracene and benzophenone could be due to their poor light stabilities. It was also found that β-carotene was a more efficient quencher than amino compounds like diphenylamine and benzidine.

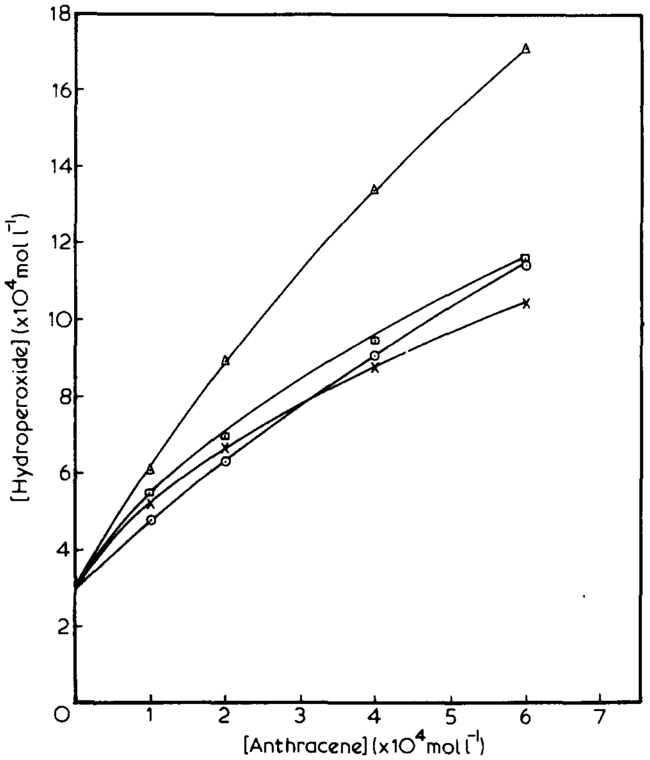


Figure 3 Variation of hydroperoxide concentration with the concentration of anthracene for *cis*-polyisoprene at number of quanta equal to 4.2×10^{18} in presence of different singlet oxygen quenchers: △, in absence of quencher; □, 8×10^{-6} mol l^{-1} β-carotene; x, 8×10^{-4} mol l^{-1} diphenylamine and ○, 8×10^{-4} mol l^{-1} benzidine

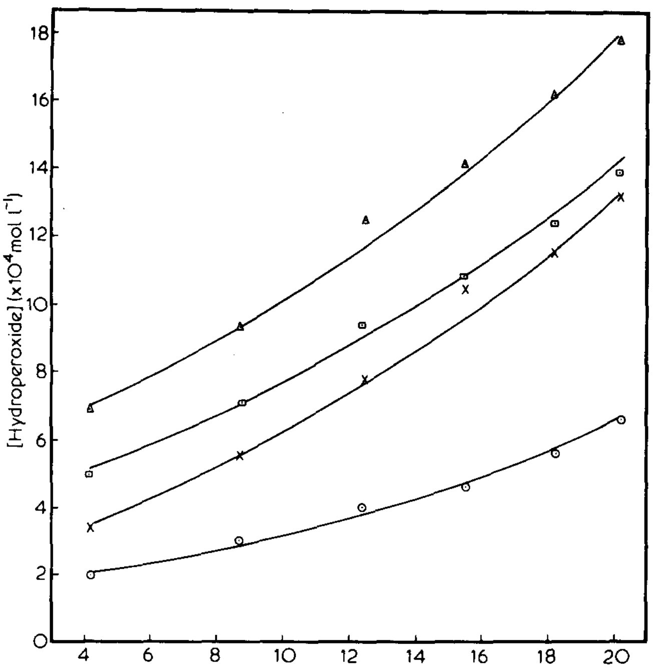


Figure 4 Variation of hydroperoxide concentration with the number of quanta in presence of different singlet oxygen sensitizers: ○, without any sensitizer; x, 4 x 10^{-3} mol l^{-1} benzophenone; □, 1 x 10^{-4} mol l^{-1} anthracene and △, 1 x 10^{-5} mol l^{-1} rubrene

Photo-oxidation of polybutadiene, styrene–polybutadiene and polychloroprene

The photo-oxidation processes of polybutadiene, styrene–polybutadiene and polychloroprene (neoprene) were carried out in absence and in presence of the three sensitizers under investigation. The concentration of benzophenone was (0.008–10) × 10^{-3} mol l^{-1}, (0.6–2) × 10^{-3} mol l^{-1} and (0.5–50) × 10^{-3} mol l^{-1} with respect to the sequence of the above mentioned polymers. In case of anthracene its concentration was (0.006–10) × 10^{-5} mol l^{-1}, (0.8–4) × 10^{-4} mol l^{-1} and (0.06–12) × 10^{-3} mol l^{-1} respectively. The concentration of rubrene was (0.6–10) × 10^{-5} mol l^{-1}, (0.6–2) × 10^{-5} mol l^{-1} and (0.6– × 10^{-5} mol l^{-1} respectively. As an example for the effect of the singlet oxygen quencher the most effective one (β-carotene) was chosen and its concentration was kept constant in case of each of the above mentioned polymers (8 × 10^{-6} mol l^{-1}, 4 × 10^{-6} mol l^{-1} and 1 × 10^{-6} mol l^{-1} respectively). *Figure 5* represents plots of the comparative relation between the hydroperoxide concentration and 2% by weight of each polymer at constant concentration of each of the three concerned sensitizers and at constant number of quanta (20.2 × 10^{18}). It is observed that polyisoprene is more sensitive than the other polymers towards the photo-oxidation reaction.

DISCUSSION

Unsaturated organic polymers like *cis*-polyisoprene, polybutadiene, styrene–polybutadiene and polychloroprene have the ability to be oxidized photochemically in the absence and in the presence of both sensitizer and quencher compounds. The photo-oxidation reaction was studied by determining the amount of hydroperoxide formed as a function of the number of quanta absorbed.

Cis- polyisoprene can be photo-oxidized in absence of sensitizers, but its ability to form hydroperoxide increases in presence of a carbonyl aromatic sensitizer like benzophenone. Benzophenone can absorb u.v. light to be transferred to excited singlet state which undergoes intersystem crossing to the state in which the energy can be transferred to triplet oxygen[10] forming singlet oxygen which attacks the double bond of polymer chain forming hydroperoxide groups. The amount of hydroperoxide formed in this way in the presence of polycyclic aromatic hydrocarbons like anthracene is greater than that of benzophenone (*Figure 4*). This is because a photochemical reaction also occurs between anthracene and oxygen with the formation of anthracene endoperoxide[11,12] which decomposes to give an excess of singlet oxygen[13]. The excess of singlet oxygen attacks the polymer chain forming a high concentration of hydroperoxide.

It is of interest to observe that the amount of hydroperoxide formed in presence of rubrene as sensitizer is larger than that formed in case of benzophenone and anthracene. This can be attributed to the ease of photo-oxidation of rubrene to form peroxide as well as to the ease of its decomposition to yield singlet oxygen. Therefore anthracene and rubrene can sensitize the photo-oxidation reaction by both physical and chemical generation of singlet oxygen while the generation of the singlet oxygen is a purely physical process with benzophenone.

It is clear that the amount of hydroperoxide formed in the presence of singlet oxygen quencher compounds like benzidine, diphenylamine and β-carotene is small. This effect is attributed to the reduction in the concentration of the generated singlet oxygen species. The quencher molecule can react with singlet oxygen in two ways, either physical or chemical quenching as follows:

$$^1O_2 + Q \rightarrow {}^3O_2 + Q^* \quad \text{physical quenching}$$

$$^1O_2 + Q \rightarrow QO_2 \quad \text{chemical quenching}$$

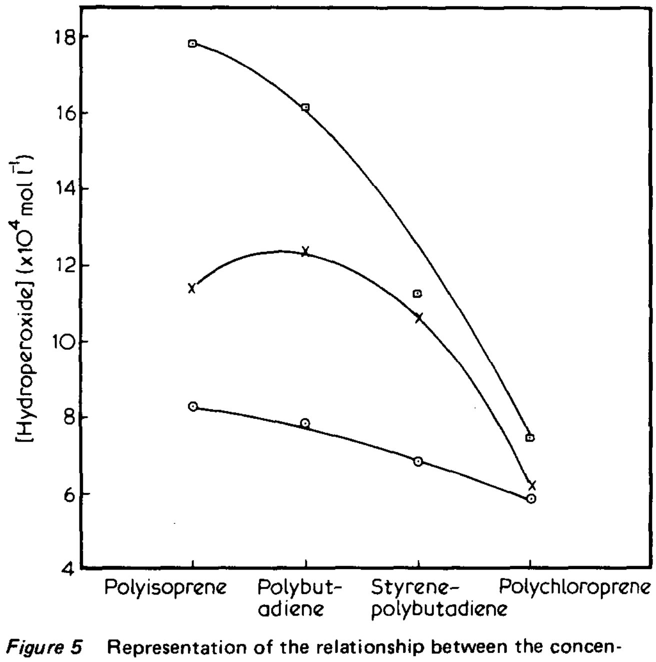


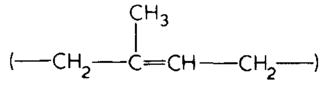
Figure 5 Representation of the relationship between the concentration of hydroperoxide and 2% by weight of each concerned polymer at constant number of quanta (20.2 x 10^{18}) in presence of different singlet oxygen sensitizers: ○, 6 x 10^{-4} mol l^{-1} benzophenone; x, 6 x 10^{-5} mol l^{-1} anthracene and □, 1 x 10^{-5} mol l^{-1} rubrene

β-carotene is by far the most extensive compound which was recognized to be a quencher of singlet oxygen. The quenching process is due to the presence of highly conjugated double bonds[14]. However, aromatic amines like benzidine and diphenylamine are less efficient quenchers of singlet oxygen than *β*-carotene. This was supported by the fact that the quenching process is influenced by charge transfer between amino groups as donors and singlet oxygen as acceptors[15-18]

The higher the energy in the triplet state of a sensitizer molecule, the greater is the amount of singlet oxygen formed in the energy transfer reaction. The singlet oxygen quenchers examined here may be more efficient triplet quenchers of anthracene and benzophenone compared with rubrene. The lowest triplet levels for benzidine and diphenylamine are almost certainly higher than that of *β*-carotene.

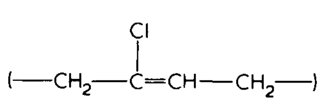
The effect of singlet oxygen oxidation on the different organic polymers under investigation decreased in the following sequence: *cis*-polyisoprene > polybutadiene > styrene–polybutadiene > polychloroprene. This sequence can be explained in terms of the relationship between the ease of oxidation of these polymers and their structures. The mechanism of singlet oxygen oxidation of these polymers was beyond the scope of the aim of the present work.

The reason that *cis*- polyisoprene



$$(\!-\!CH_2\!-\!\overset{CH_3}{\overset{|}{C}}\!=\!CH\!-\!CH_2\!-\!)$$

is more reactive than the other three polymers towards singlet oxygen is due to the known reaction of the singlet oxygen with allylic hydrogens. This is because of the greater reactivity of the double bonds towards singlet oxygen. The initial attack of singlet oxygen forms either peroxide or dioxetane intermediates which decompose to give the final products[19,20]. The presence of the methyl groups in *cis*-polyisoprene renders its oxidation by singlet oxygen more facile. On the contrary the presence of the chlorine groups in polychloroprene



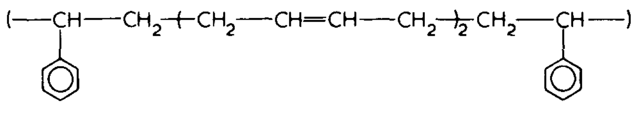
$$(\!-\!CH_2\!-\!\overset{Cl}{\overset{|}{C}}\!=\!CH\!-\!CH_2\!-\!)$$

renders its oxidation with singlet oxygen less facile. This is because the chlorine groups decrease the reactivity of the double bonds towards singlet oxygen.

The other two polymers: polybutadiene

$(\!-\!CH_2\!-\!CH\!=\!CH\!-\!CH_2\!-\!)$

and styrene–polybutadiene



come between *cis*-polyisoprene and polychloroprene in view of the ease of oxidation with singlet oxygen. Although their ability to be oxidized with singlet oxygen is comparable, yet the oxidation of styrene–polybutadiene is slower than that of polybutadiene. This is due to the inductive effect of the phenyl groups in the styrene–polybutadiene.

Studies of this type are numerous and are always regarded with great caution when trying to extrapolate the results to commercial polymers.

REFERENCES

1 Childe, W. H. J. and Mecke, R. *Z. Physik* 1931, **68**, 344

2 Herzberg, G. *Nature* London, 1934, **133**, 759

3 Kaplan, M. L. and Kelleher, P. G. *J. Polym. Sci. B* 1971, **9**, 565

4 Kearns, D. R. *Chem. Rev.* 1971, **71**, 395

5 Khan, A. U. and Kasha, M. *Adv. Chem.* 1968, Ser. **77**, 143

6 Tsubomura, H. and Mulliken, R. S. *J. Am. Chem. Soc.* 1960, **82**, 5966

7 Pouyet, B. and Chapelon, R. *C.R. Acad. Sci. Ser. C* 1971, **272**, 1753

8 Cass, W. E. *J. Am. Chem. Soc.* 1947, **69**, 500

9 Ranby, B. and Rabek, J. F. 'Photodegradation, photo-oxidation and photostabilization of polymers', Wiley, London, 1975

10 Trozzolo, A. M. *Adv. Chem. Ser.* 1968, No. **77**, 167

11 Birks, J. B. 'Photophysics of aromatic molecules', Wiley–Interscience, New York, 1970

12 Wan, J. K. S., McCormick, R. N., Baum, E. J. and Pitts, J. N. Jr. *J. Am. Chem. Soc.* 1965, **87**, 4409

13 Kearns, D. R. and Khan, A. U. *Photochem. Photobiol.* 1969, **10**, 193

14 Foote, C. S., Chang, Y. C. and Denney, R. W. *J. Am. Chem. Soc.* 1970, **92**, 5216

15 Ogryzlo, E. A. and Tang, C. W. *J. Am. Chem. Soc.* 1970, **92**, 5034

16 Smith, W. F. *J. Am. Chem. Soc.* 1972, **94**, 186

17 Matheson, I. B. C. and Lee, J. *J. Am. Chem. Soc.* 1972, **94**, 3310

18 Young, R. H., Martin, R. L., Feriozi, D., Brewer, D. and Kayser, R. *Photochem. Photobiol.* 1973, **17**, 233

19 Fenical, W., Kearns, D. R. and Radlick, P. *J. Am. Chem. Soc.* 1969, **91**, 3396

20 Kearns, D. R. *J. Am. Chem. Soc.* 1969, **91**, 655