PHOTOSENSITIZED OXYGENATION OF OLIGOISOPRENES

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Summary

The results of investigations of the rose-bengal-sensitized photo-oxygenation of the oligoisoprenes 2,6,10-trimethyl-2,6,10-dodecatriene (TMDT or M_3), 2,6,10,14-tetramethyl-2,6,10,14-hexadecatetraene, squalene and an oligomer containing 20 units are discussed. Regardless of the polymerization number, (i) the maximum number of oxygen molecules consumed during the photo-oxygenation is almost equal to the number of 1,4 units and (ii) the reactivity of the oligoisoprene towards $^1O_2$ oxygen is equal to the sum of the reactivity of all the units. The rate constants of the consecutive reactions

$$M_3 \xrightarrow[k_1]{^1O_2} M_2(MOOH) \xrightarrow[k_2]{^1O_2} M(MOOH)_2 \xrightarrow[k_3]{^1O_2} (MOOH)_3$$
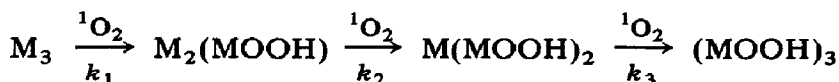
are estimated for TMDT and it is concluded that the reactivity of a unit is not appreciably modified by the presence of neighbouring hydroperoxidized units. The consequences of these results with respect to the photo-oxidation of polymers are discussed.

1. Introduction

We have recently reported detailed studies of the nature and kinetics of the photosensitized oxygenation of model compounds of *cis*- and *trans*-polyisoprene containing one [1] and two units [2, 3]. Golub [4] has studied the sensitized oxygenation of the corresponding polymers and some of the results for the two classes of compounds suggest that the fundamental behaviour of macromolecular olefins is similar to that of their small molecule counterparts. Thus the use of model compounds to investigate this type of reaction is a valuable technique for obtaining information that could not readily be obtained from experiments using the polymers themselves.

In this paper we attempt to provide additional insight into the mechanism of polyisoprene reactions with $^1O_2$ by reporting a study of the photosensitized oxygenation of oligoisoprenes containing three or more units.

2. Experimental details

2.1. Synthesis of oligoisoprenes

2.1.1. 2,6,10-trimethyl-2,6,10-dodecatriene

2,6,10-trimethyl-2,6,10-dodecatriene (TMDT) was obtained by reducing nerolidol with sodium in liquid ammonia:

$$\text{Na/NH}_3$$
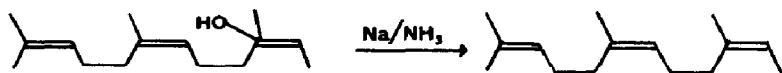
2.1.2. 2,6,10,14-tetramethyl-2,6,10,14-hexadecatetraene

2,6,10,14-tetramethyl-2,6,10,14-hexadecatetraene (TMHT) was synthesized from nerolidol using a procedure [5] based on Carroll and Wittig reactions:

$$\text{CH}_3\text{CO CH}_2\text{COO Et}$$
Carroll reaction

$$(\text{C}_6\text{H}_5)_3\text{ P} =$$ Wittig reaction
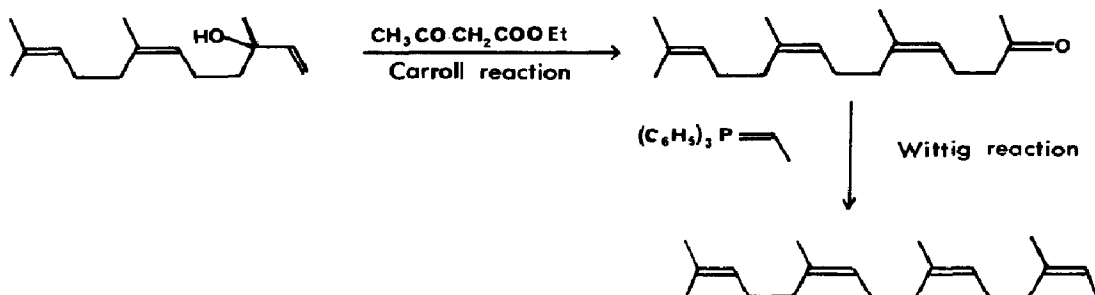
2.1.3. Oligomer PN 20

An oligomer containing 20 units (PN 20) was obtained by anionic polymerization initiated by *tert*-butyllithium as previously described [6]. Nuclear magnetic resonance (NMR) examination showed that 60% of the units were in the 1,4 addition mode.

2.2. Irradiation

The reactions were performed at -20 °C in the presence of rose bengal (3 g l^{-1}) in methanolic solutions, except for PN 20 which was dissolved in butanol for reasons of solubility. The solutions were irradiated in an immersion photoreactor using a Philips model HPK lamp (125 W) equipped with a device to monitor the oxygen consumption. We have checked that under these conditions (i) processes occurring during irradiation in an inert atmosphere are very slow with respect to photo-oxygenation and therefore can be neglected, (ii) no photolysis of the hydroperoxides takes place and (iii) interactions between excited states of the sensitizer and the substrates or hydroperoxides are negligible. It can be concluded as before that oxygenation takes place by $^1\text{O}_2$ attack only (type II photo-oxygenation [7]).

2.3. Measurements

The β values, *i.e.* the ratios of the decay rate of $^1O_2$ to its rate of reaction, were obtained by comparing the maximum oxygen consumption rate of the substrate with that of a very active acceptor under the same conditions. The absolute rate constant k_1 of the first addition of $^1O_2$ was obtained by assuming a value of 9×10^{-6} s for the lifetime of $^1O_2$ in methanol.

As before [1 - 3] the kinetic study of TMDT was performed by using vapour phase chromatography (VPC) to monitor its disappearance (in conditions where [TMDT] is much less than β) and the appearance of oxygenated products as a function of time; this allowed us to obtain the pseudomonomolecular rate constants $k_1[^1O_2]$, $k_2[^1O_2]$ and $k_3[^1O_2]$ (see scheme in Section 3.1). Since k_1 is known we can calculate the yield of $^1O_2$ under our experimental conditions and the overall absolute rate constants k_2 and k_3 of the second and third additions.

2.4. Characterization of the products

The hydroperoxides were identified by VPC, mass spectrometry (MS) and a combined VPC—MS system after reduction to alcohols and trimethylsilylation as described previously [1]. It has been shown that trimethylsilylethers give weak parent peaks and intense peaks at $m/e = M - 15$ corresponding to the loss of a $-CH_3$ group.

3. Results

3.1. 2,6,10-trimethyl-2,6,10-dodecatriene

TMDT can be considered as a model for a polyisoprene with polymerization number 3 with a 1,4 *cis* or *trans* addition mode. The number of oxygen molecules consumed during photo-oxygenation is slightly greater than 3 per TMDT molecule. The chromatogram of the silylethers (column SE 30) corresponding to an incomplete photo-oxygenation shows three groups of broad peaks.
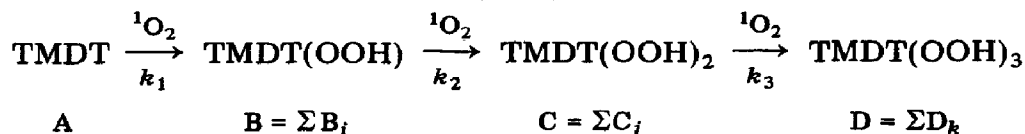
The first group contains eight peaks (several are shoulders or poorly resolved peaks); they all correspond to monosilylethers. The mass spectra obtained by combined VPC—MS all show parent peaks at $m/e = 294$ or $m/e = 279$ ($M - 15$). Thus as expected eight different monohydroperoxides are formed by singlet oxygenation. This result is consistent with that obtained under the same conditions using the diisoprenic model compound 4,8-dimethyl-4,8-dodecadiene for which the six monohydroperoxides expected were identified [8].

The second group also shows eight peaks and groups, all of which are disilylethers (mass spectra with parent peaks at $m/e = 382$ or $m/e = 367$ ($M - 15$)).

The third group contains five peaks including one shoulder which according to the mass spectra (parent peaks at $m/e = 470$, $m/e = 455$ ($M - 15$) or $m/e = 365$ ($M - 15 - 90$)) are those of the trisilylethers.

Thus, as in the case of model compounds containing two units [2, 3, 8], it is probable that all the products which are expected to occur are effectively formed. However, we did not attempt to assign the corresponding structures as this would require better chromatographic resolution than that available in this work to obtain the individual mass spectra.
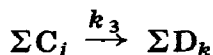
Therefore we did not determine the rate constants for all the possible reactions but used the following simplified scheme:

$$\text{TMDT} \xrightarrow[k_1]{^1O_2} \text{TMDT(OOH)} \xrightarrow[k_2]{^1O_2} \text{TMDT(OOH)}_2 \xrightarrow[k_3]{^1O_2} \text{TMDT(OOH)}_3$$

$$\quad\text{A} \qquad\qquad \text{B} = \Sigma B_i \qquad\qquad \text{C} = \Sigma C_j \qquad\qquad \text{D} = \Sigma D_k$$

By considering the characteristics of the system, it can be shown that the second reaction

$$\Sigma B_i \xrightarrow{k_2} \Sigma C_j$$
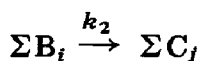
and the third reaction

$$\Sigma C_j \xrightarrow{k_3} \Sigma D_k$$

are first order with respect to $B = \Sigma B_i$ and $C = \Sigma C_j$ respectively and that k_2 and k_3 are functions which depend only on the individual rate constants. Then we can use the relations between the three consecutive first-order reactions to determine k_2 and k_3 (Appendix A).

The disappearance of A and the appearance of the silylethers corresponding to its hydroperoxides were monitored by gas chromatography analysis. The variations with time of the instantaneous molar ratios a, b, c and d of A, B, C and D are shown in Fig. 1. The curves show the behaviour of the consecutive reactions. A plot of $\log(1/a)$ versus time gives a straight line which confirms that the first oxygen addition reaction is first order for $[\text{TMDT}] \ll \beta$ and allows us to obtain the pseudomonomolecular rate constant $k_1[^1O_2]$. The concentration of $^1O_2$ can be obtained because the β value (and therefore k_1) was independently determined. We found $\beta = 0.055$ M or $k_1 = 2.02 \times 10^6$ M^{-1} s^{-1} when the lifetime of $^1O_2$ in methanol is assumed to be 9×10^{-6} s which leads to $[^1O_2] = 3.83 \times 10^{-6}$ M. Then $k_2 k_1^{-1}$ and $k_3 k_2^{-1}$ can be estimated from the coordinates of the maxima of the curves $b = f(t)$ and $c = f(t)$ (Appendix A). Table 1 summarizes the values of the corresponding absolute rate constants.

3.2. 2,6,10,14-tetramethyl-2,6,10,14-hexadecatetraene

TMHT is a model compound containing four isoprenic units in the 1,4 *cis* or *trans* addition mode which adds four oxygen molecules by the reaction of $^1O_2$ at each double bond. Its photo-oxidation gives the monohydroperoxides, dihydroperoxides, trihydroperoxides and tetrahydroperoxides as shown by combined VPC–MC analysis of the corresponding silylethers. Four
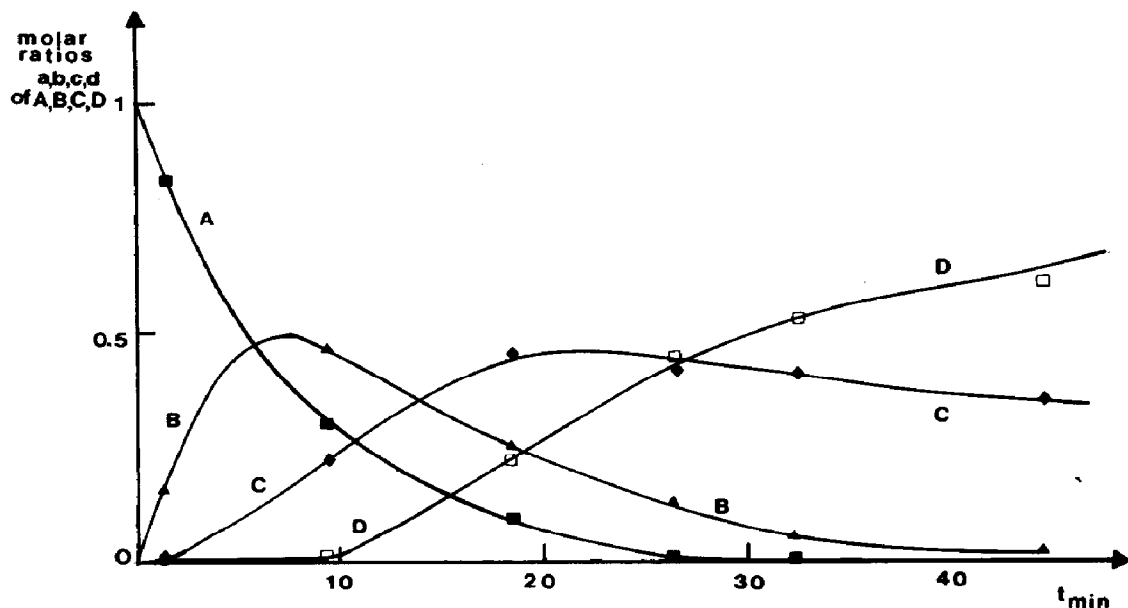
Fig. 1. Photo-oxygenation of TMDT: the variation with time of the instantaneous molar ratios a (substrate), b (sum of the monohydroperoxides), c (sum of the dihydroperoxides) and d (sum of the trihydroperoxides).

TABLE 1

Rate constants for the consecutive addition of $^1O_2$ to 2,6,10-trimethyl-2,6,10-dodecatriene in methanol

Experimental data	
β (M)	0.055 ± 0.005
$[^1O_2]$ (M)	3.83×10^{-6}
$k_2 k_1^{-1}$	0.6 ± 0.05
$k_3 k_2^{-1}$	0.5 ± 0.1
Rate constants	
k_1 (M^{-1} s^{-1})	$(20.2 \pm 2.0) \times 10^5$
k_2 (M^{-1} s^{-1})	$(12.1 \pm 2.2) \times 10^5$
k_3 (M^{-1} s^{-1})	$(6.1 \pm 2.3) \times 10^5$

groups of broad chromatographic peaks are obtained corresponding to mass spectra with parent peaks at $m/e = 362$ or $m/e = 347$ ($M - 15$) (first group), $m/e = 450$ (second group), $m/e = 538$ or $m/e = 448$ (third group) and $m/e = 611$ ($M - 15$) (fourth group). Measurements of oxygen consumption gave a value of $\beta = 0.05$ M for TMHT.

3.3. Squalene

Squalene is a natural model of polyisoprene containing six units; during the photo-oxidation it adds successively six molecules of $^1O_2$. Owing to their

very high molecular weights, silylethers corresponding to each oxidation could not be separated by VPC.

However, MS analysis was effected by direct injection of a mixture of allylic alcohols and the mass spectrum exhibits peaks at m/e values of 420, 422, 424, 436, 438, 440, 452, 454 and 456 which correspond to dehydration (loss of one, two or three water molecules) and originate from the monohydroperoxides, dihydroperoxides, trihydroperoxides, tetrahydroperoxides, pentahydroperoxides and hexahydroperoxides. Measurements of oxygen consumption gave a value of $\beta = 3.1 \times 10^{-2}$ M for squalene in methanol.

3.4. Oligomer PN 20

This oligomer which has a polymerization number of 20 was prepared by anionic polymerization. NMR examination showed that only 60% of the units were in the 1,4 addition mode, the remainder being in the 3,4 or 1,2 addition modes.

NMR spectra and oxygen consumption measurements show that all the 1,4 units react with $^1O_2$ whereas few of the 3,4 and 1,2 units underwent this reaction.

4. Discussion

4.1. Number of oxygen molecules incorporated

The maximum number of oxygen molecules consumed during photo-oxygenation under our experimental conditions is approximately equal to the number of 1,4 units regardless of the polymerization number. The low reactivity of the 1,2 and 3,4 units of the oligomer PN 20 is related to the low reactivity of monosubstituted and disubstituted olefins compared with that of trisubstituted olefins.

The stabilization of oxygen consumption at values slightly greater than the number of units after very long irradiation times is attributed to the possibility of a second addition of $^1O_2$ to the same unit as demonstrated for models containing one [1] and two [8] units.

4.2. Rate constants for the first addition

We showed that the rate constant of the first addition to model compounds of polymerization number 2 could be estimated as the sum of the rate constants of two appropriate olefins [2, 3]. In the same way Table 2 shows that there is excellent agreement between the experimental and calculated rate constants for the first addition of $^1O_2$ to TMDT, TMHT and squalene. Thus in order to predict the reactivity of any oligoisoprene we have only to choose two olefins with a structure analogous to that of the end units of the chain and to take 4-methyl-4-octene to represent the in-chain units.

TABLE 2

Comparison of the experimental and calculated rate constants for the first addition reaction of $^1O_2$ with polyisoprene model compounds in methanol

Model compound	Rate constants of the constituent olefins ($\times 10^{-5}$ M^{-1} s^{-1})			Calculated rate constant k_1 of the model compound ($\times 10^{-5}$ M^{-1} s^{-1})	Experimental rate constant k_1 of the model compound ($\times 10^{-5}$ M^{-1} s^{-1})
TMDT	6.2^a - 6.9^b	3.3^c	5.8^c	15.3	20.2
		5.6^c	9.3^c	21.8	
TMHT	6.2 - 6.9	2×3.3	5.8	18.6	22.2
		2×5.6	9.3	27.4	
Squalene	$2 \times (6.2 - 6.9) + 4 \times 5.6$			34.8 - 36.2	35.8

[a] From ref. 7.
[b] From ref. 9.
[c] From ref. 1.

4.3. Effect of neighbouring oxygenated units on the reactivity of a unit

Comparison of the rate constants k_1, k_2 and k_3 obtained for TMDT (Table 1) shows that the reactivity of a unit is not appreciably modified by the presence of neighbouring hydroperoxidized units. This result is consistent with that obtained with model compounds of polymerization number 2 for which the weak differences observed for the values of k_2/k_1 had been attributed to the effect of the nature of the substituents of the double bonds on their reactivity [3, 10].

4.4. Consequences of $^1O_2$ reactions with polymers

Some of the results for oligoisoprenes can be extrapolated to polymers. For a polydiene M_n of polymerization number n, the rate constant k_{M_n} for the first addition of $^1O_2$ is n times the rate constant k_M relative to one unit: $k_M = nk_M$. At a given photo-oxidation time a fraction p/n of the initial units is hydroperoxidized and the rate constant $k_{M_{n-p}(MOOH)_p}$ for the addition of $^1O_2$ is equal to the sum of the rate constants for the unreacted units:

$$k_{M_{n-p}(MOOH)_p} = k_{M_{n-p}} = (n-p)k_M$$

More generally, it may be possible to use the same approach to estimate the rate constant for the reaction of any polymer with $^1O_2$ if the concentration and the nature of the reactive functional groups are known (thus the residual level of C=C bonds in polypropylene is about 0.05 M [11]). This estimation may allow us to evaluate the importance of a possible participation of singlet oxygen in the initiation step of polymer degradation.

In polymers with many unsaturated bonds such as polydienes in the solid state or in concentrated solutions all the $^1O_2$ will react as long as a sufficient number of unreacted units remain, since the probability ϕ_R for $^1O_2$ to react with an unsaturated double bond is unity if the β value for a unit is much smaller than the local concentration of double bonds [C=C]. This is valid in the present study of polyisoprenes because

$$\phi_R = \frac{[C=C]}{[C=C] + 0.1}$$

Furthermore the importance of the participation of $^1O_2$ in the initiation step of the oxidative degradation of polymers through hydroperoxide formation will depend on the efficiency of its production.

Acknowledgment

References

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Appendix A

We consider the reactions

$$M_3 \xrightarrow[k_1]{^1O_2} M_2(MOOH) \xrightarrow[k_2]{^1O_2} M(MOOH)_2 \xrightarrow[k_3]{^1O_2} (MOOH)_3$$

A   B   C   D
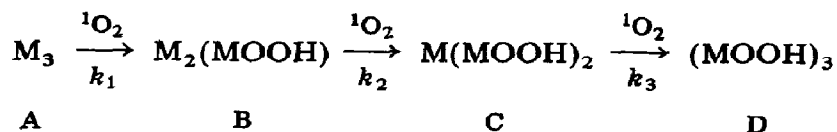
in which the instantaneous molar ratios of A, B, C and D are a, b, c and d respectively. Since each of the reactions is first order with respect to the substrate, we obtain the following differential equations:

$$\frac{da}{dt} = k_1 a$$

$$\frac{db}{dt} = k_1 a - k_2 b$$

$$\frac{dc}{dt} = k_2 b - k_3 c$$

$$\frac{dd}{dt} = k_3 c$$

The solution of these equations leads to

$$a = \exp(-k_1 t)$$

$$b = \frac{k_1}{k_1 - k_2} \{-\exp(-k_1 t) + \exp(-k_2 t)\}$$

$$c = k_1 k_2 \left\{ \frac{\exp(-k_1 t)}{(k_1 - k_2)(k_1 - k_3)} + \frac{\exp(-k_2 t)}{(k_2 - k_1)(k_2 - k_3)} + \frac{\exp(-k_3 t)}{(k_3 - k_1)(k_3 - k_2)} \right\}$$

$$d = k_1 k_2 k_3 \left\{ \frac{1 - \exp(-k_1 t)}{k_1 (k_1 - k_2)(k_1 - k_3)} + \frac{1 - \exp(-k_2 t)}{k_2 (k_2 - k_1)(k_2 - k_3)} + \right.$$

$$\left. + \frac{1 - \exp(-k_3 t)}{k_3 (k_3 - k_1)(k_3 - k_2)} \right\}$$

The rate constant k_2 can then be derived from the coordinates $(t_{mb}, b_{t_{mb}})$ of the curve $b = f(t)$ and from the corresponding $a_{t_{mb}}$ value:

$$\frac{k_2}{k_1} = \frac{a_{t_{mb}}}{b_{t_{mb}}}$$

$$k_2 = \frac{1}{t_{mb}} \ln\left(\frac{1}{b_{t_{mb}}}\right)$$

The rate constant k_3 can be derived from the coordinates $(t_{mc}, c_{t_{mc}})$ of the curve $c = f(t)$ and from the corresponding $b_{t_{mc}}$ value:

$$\frac{k_3}{k_2} = \frac{b_{t_{mc}}}{c_{t_{mc}}}$$

$$k_3 = \frac{k_1 k_2 \exp(-k_2 t_{mc}) - \exp(-k_1 t_{mc})}{c_{t_{mc}}(k_1 - k_2)}$$