

SINGLET OXYGEN REACTIONS WITH MODEL COMPOUNDS OF *CIS* AND *TRANS* POLYISOPRENE CONTAINING TWO UNITS

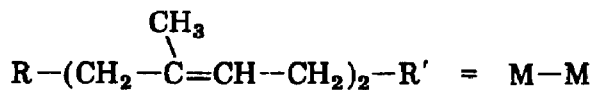
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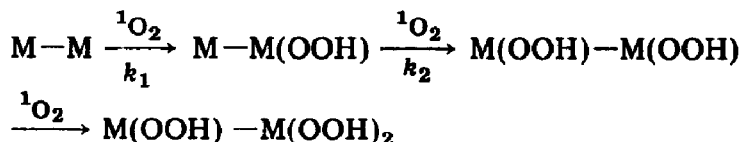
Summary

We have studied the rose bengal sensitized photo-oxygenation of *cis*-polyisoprene and *trans*-polyisoprene model compounds containing two units

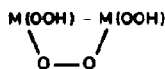


in methanolic solutions.

The following reactions have been observed:



but a dihydroperoxy-endoperoxide



has never been detected.

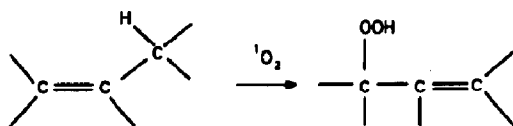
The reactivity of M—M is twice that of M and a *trans* unit is 1.6 - 1.7 times more reactive than a *cis* unit. Moreover, the photo-oxygenation of one unit can induce a slight deactivation of the remaining double bond $k_2/k_1 \leq 0.5$. A kinetic study has allowed us to determine the rate constants k_1 and k_2 .

1. Introduction

It is well known that hydroperoxides are key initiators in the oxidative degradation of polymers. Hydroperoxides may indeed decompose under the effect of heat or light to yield radicals which are able to initiate the autoxidative destruction of the chains. Thus, it is important in the field of oxidative

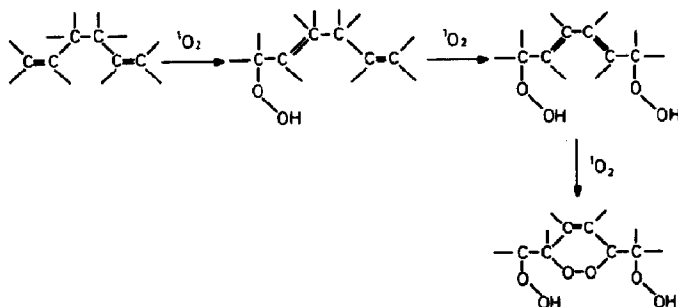
degradation of polymers to know the kinetics and the mechanism of the hydroperoxidation of macromolecules.

Several modes of formation of these hydroperoxides are possible. It has recently been suggested [1] that singlet oxygen may play an important part in these processes since it reacts with olefins having at least one allylic hydrogen to give hydroperoxides:



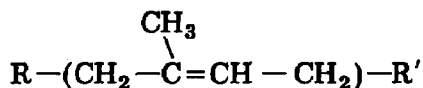
The unsaturated sites pre-exist in the macromolecular chain or may have been created in the course of a previous degradation.

In such a study it is interesting to observe the reactions of ${}^1\text{O}_2$ with elastomers which have the advantage of containing a number of double bonds in well-defined positions along the macromolecular chain. Thus, Mill *et al.* [2] have indicated that solutions of polyisoprene in chlorobenzene undergo an attack by ${}^1\text{O}_2$ under UV irradiation in the presence of methylene blue. Other works [3 - 11] have pointed out that polydienes and other unsaturated polymers react with singlet oxygen produced by various techniques. For the oxygenation of *cis*-polybutadiene by ${}^1\text{O}_2$ Kaplan and Kelleher [7] have proposed the following mechanism:



This scheme involves several steps and we propose to analyse them successively for the case of polyisoprene. Unfortunately it is almost impossible to use polymers directly for several reasons. As a matter of fact, with macromolecular compounds the separation and analysis of the oxidation products is very complex, if not unrealizable. Moreover, small amounts of compounds such as initial impurities or additives tend either to modify the nature and the rate of formation of the oxidation products or to induce a fast and competitive deactivation of ${}^1\text{O}_2$, thus inhibiting any effect on the polymer.

Therefore, we have chosen to work on model compounds that will allow identification of the elementary processes, characterization of the reaction products and determination of the reactivities of the various unsaturations. In a previous paper [12] we reported the results concerning the reactions of singlet oxygen with model compounds containing one unit



in methanolic solutions. The main results, related to the present work, were as follows.

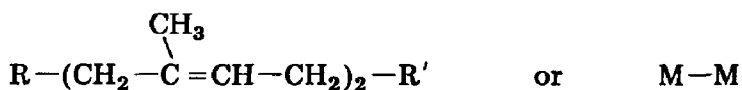
(a) As expected, considering the number of allylic hydrogens, three different monohydroperoxides are formed in the case of 4-methyl-4-octene and 3-methyl-2-pentene; their distribution is dependent upon the stereochemistry of the double bond, but the hydroperoxide which has a trisubstituted double bond is always present in small amounts.

(b) A second addition of singlet oxygen to the same unit is possible, but only for the hydroperoxide containing precisely a trisubstituted double bond.

(c) The reactivity of the *trans* isomer towards $^1\text{O}_2$ is 1.6 - 1.7 times that of the *cis* isomer.

(d) The second addition of singlet oxygen on the same unit is much slower than the first addition; the reactivity of 5-methyl-4-hydroperoxy-5-octene towards $^1\text{O}_2$ is about 20 times weaker than the reactivity of 4-methyl-4-octene.

Consider now a model compound containing two isoprenic units



One may anticipate a series of reactions leading to monohydroperoxides, dihydroperoxides, trihydroperoxides and tetrahydroperoxides as well as to a dihydroperoxy-endoperoxide (Fig. 1). Do all these reactions really take place?

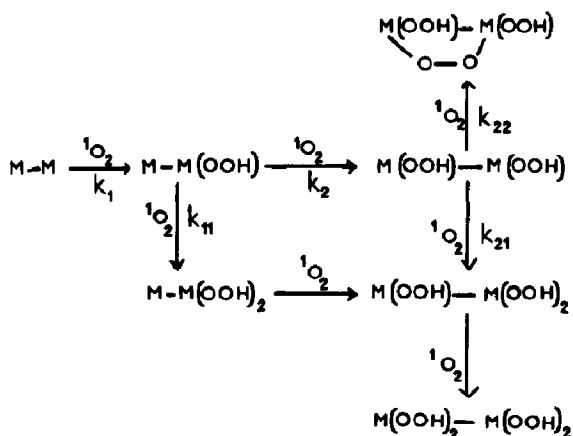


Fig. 1. Possible singlet oxygen reaction with model compounds of *cis*- and *trans*-polyisoprene containing two units:



For the reactions that effectively occur, what are the rate constants (for example, what is the effect of the addition of $^1\text{O}_2$ to a unit on the reactivity of a neighbouring unit)? One of the major aims of the present work is to give some answers to these questions.

2. Experimental

2.1. Synthesis of model compounds

A mixture of the four isomers of 4,8-dimethyl-4,8-dodecadiene (DMDD) ($\text{cis-cis}/(\text{cis-trans} + \text{trans-cis})/\text{trans-trans} = 24/52/24$) was synthesized by using a procedure [13] based on Carroll and Wittig reactions. From this initial mixture we have obtained the pure *trans-trans* isomer and a mixture enriched in *cis-cis* isomer (70/20/10) using preparative gas chromatography (Varian Autoprep 700; column SE 30 20% on Chromosorb W, 45/60 mesh, 4 m long, $\frac{1}{4}$ in internal diameter, flow rate 60 ml min^{-1} , 50 - 200 °C). 2,7-Dimethyl-2,6-octadiene (DMOD) was obtained by reducing linalol or geraniol by sodium in liquid ammonia. In the case of geraniol the pure *trans* isomer is formed, whereas linalol leads to a mixture containing 60% *trans* isomer.

2.2. Irradiations

The reactions were performed at -20 °C in methanolic solutions in the presence of rose bengal (3 g l^{-1}). We used an immersion photoreactor equipped with a high pressure mercury vapour lamp (Philips HPK 125 W) with a device which allowed us to follow 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) the yield of singlet oxygen formation is constant during the course of the kinetic runs.

2.3. Measurements

β values (ratio of the decay rate of singlet oxygen to its rate of reaction) were obtained by using Schenck's [14] method based on the comparison of the maximum consumption rate of oxygen of the substrate with that of α -terpinene in the same conditions. The absolute rate constants k_1 of the first addition of $^1\text{O}_2$ were obtained by taking $9 \times 10^{-6} \text{ s}$ as the lifetime of singlet oxygen in methanol.

The kinetic study was completed by following by vapour phase chromatography (VPC) the disappearance of substrate and appearance of products (see Section 3) as a function of time; this allowed us to obtain the pseudo-monomolecular rate constants $k_1[^1\text{O}_2]$ and $k_2[^1\text{O}_2]$. The knowledge of k_1 allows us to determine the $^1\text{O}_2$ yield under our experimental conditions and then the overall absolute rate constant k_2 of the second addition.

2.4. Characterization of the products.

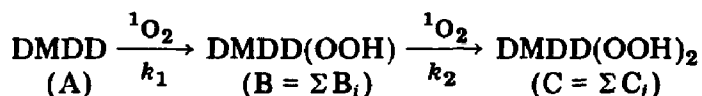
Since the usual analysis techniques of the oxidized products have been shown to be ineffective, we used an original method based on analysis of the trimethyl silyl ethers corresponding to the resulting hydroperoxides [12] by VPC, mass spectrometry (MS) and a coupled VPC-MS system.

3. Results

3.1. 4,8-dimethyl-4,8-dodecadiene (cis-cis/(cis-trans + trans-cis)/trans-trans = 24/52/24)

The photo-oxygenation of a mixture of the four isomers of DMDD leads to the formation of monohydroperoxides and dihydroperoxides corresponding to the attack of one unit and of two units [15]. Each of the six expected monohydroperoxides is produced, hydroperoxides having a trisubstituted double bond formed in smaller quantities. Among the nine diaddition products, most of the possible dihydroperoxides were identified directly or by their photo-oxygenation products.

The kinetic scheme is complex and the chromatographic resolution of the silyl ethers, although allowing the determination of overall products of monoaddition and diaddition, is not sufficient to follow the variation of molar ratio with time for each of them. Hence, we did not attempt to determine the rate constants for all the possible reactions and we used the following simplified scheme:



Considering the particular characteristics of the system, the calculations show that the second reaction $\Sigma B_i \xrightarrow{k_2} \Sigma C_j$ is first order with respect to $B = \Sigma B_i$ and that k_2 is a function which depends only on the individual rate constants of the first and the second addition reactions. Then, we can use the classical relations of consecutive first order reactions to determine k_2 .

Figure 2 shows the plot of time *versus* the molar ratios a , b and c of A, B and C and of $\log(1/a) = f(t)$. The curves show the classical aspects of consecutive reactions and the straight line observed for $\log(1/a)$ confirms that the first oxygen addition reaction is first order. This allows us to obtain the constant k_1 ; k_2 is then calculated from the coordinates of the maximum of the curve $b = f(t)$.

We find $k_1 = 6.94 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and $k_2 = 3.82 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. This means that all the monoaddition products have an overall reactivity which is about half that of the initial DMDD.

For the *trans-trans* isomer we find $k_1 = 11.11 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. We observe, as in the cases of 4-methyl-4-octene and of 3-methyl-2-pentene, that the pure *trans-trans* isomer is 1.6 times as reactive as the isomer mixture (50% *trans*).

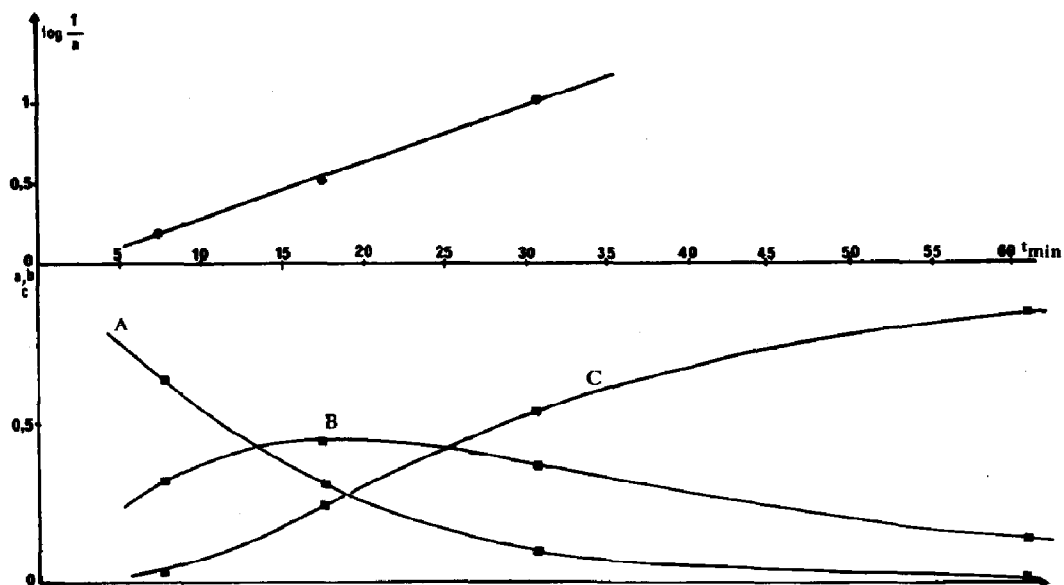


Fig. 2. Photo-oxygenation of 4,8-dimethyl-4,8-dodecadiene: variation with time of a , b , c and $\log(1/a)$ (see text for definition of symbols).

3.2. 2,6-dimethyl-2,6-octadiene

As with DMDD, the chromatogram of the silyl ethers corresponding to an incomplete photo-oxygenation of *trans* 2,6-dimethyl-2,6-octadiene presents two groups of bulky peaks due to the monoaddition and diaddition products.

2,6-Dimethyl-2,6-octadiene (DHM) is capable of giving five monohydroperoxides and six dihydroperoxides having two possible origins (there are 17 different reactions). We could confirm the formation of the products I, II, III, IV, V, VI, VII, VIII and IX (Fig. 3)[†], but because of the poor chromatographic resolution of the peaks of the silyl ethers (those of II and III coincide) and because some isomers must present identical fragmentations we cannot exclude the formation of small quantities of compounds V, X and XI.

By using the same simplified scheme and the same notation as for DMDD we obtain the variations of a , b and c and of $\log(1/a)$ (Fig. 4). Similarly, we find that $k_1 = 18.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and $k_2 = 7.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ which indicates that all the monoaddition products have an overall reactivity slightly less than half that of the initial DHM ($k_2/(k_1/2) = 0.8$).

For *cis*-DHM we obtain the value $k_1 = 11.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ which again confirms the greater reactivity of the *trans* isomer ($k_{1 \text{ trans}}/k_{1 \text{ cis}} = 1.7$).

[†]The identification of products was facilitated by the fact that the photo-oxidation products of linalol (2,6-dimethyl-2,7-octadiene-6-ol) after reduction to alcohols and linalol itself are three of the expected reduction products corresponding to VI, VII and II in a DHM photo-oxygenation mixture.

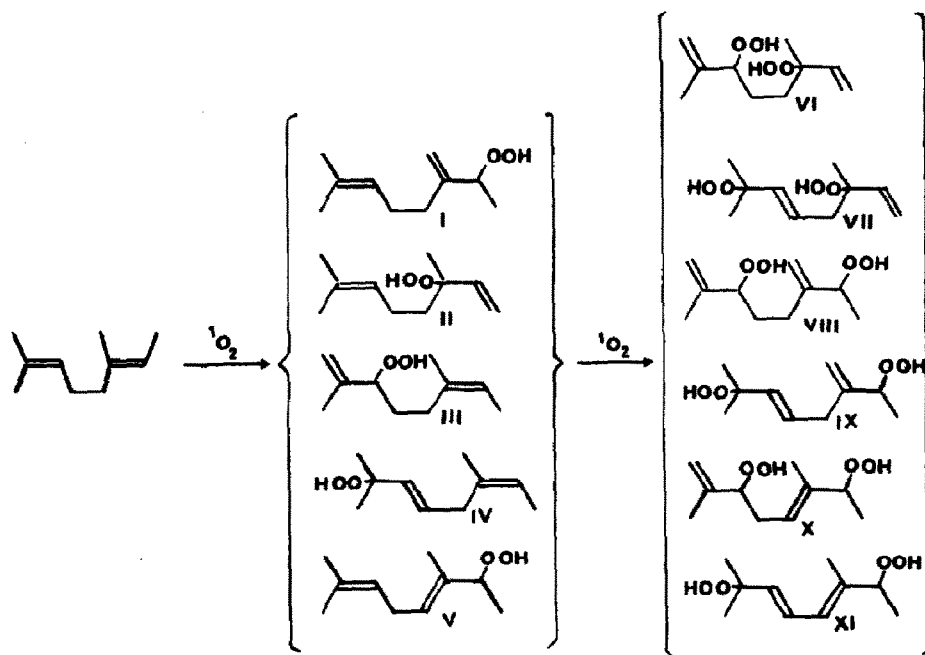


Fig. 3. Reaction products of the photo-oxygenation of 2,6-dimethyl-2,6-octadiene.

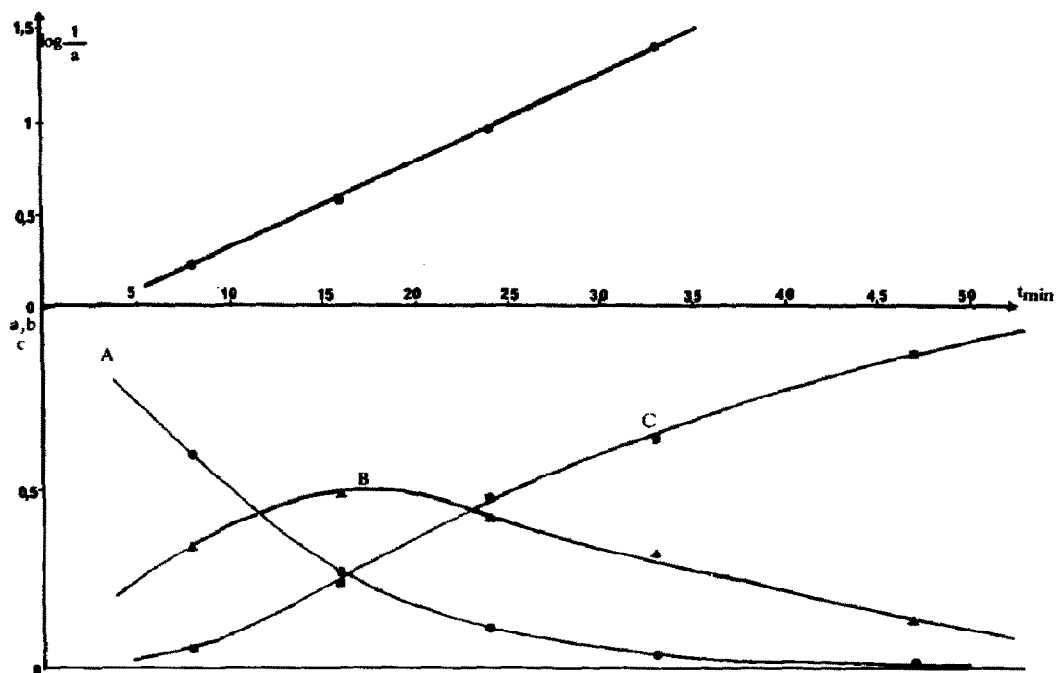


Fig. 4. Photo-oxygenation of 2,6-dimethyl-2,6-octadiene: variation with time of a , b , c and $\log (1/a)$ (see text for definition of symbols).

3.3. 2,7-dimethyl-2,6-octadiene

This diene may be considered to be a model compound of polymerization number 2 for polyisoprene with a 1,4-4,1 addition mode in contrast to the previous substrates which displayed 1,4-1,4 addition. Because of its symmetry the number of photo-oxygenated products is limited and the kinetic scheme is relatively simple. This permits the determination of rate constants for the different reactions [16]. The main results are summarized in Fig. 5. We observe that the deactivating effect of the photo-oxygenation of one unit upon the untouched double bond, although again weak, is more important than for the preceding models since $k_2/(k_1/2) = 0.58$ (see Section 4).

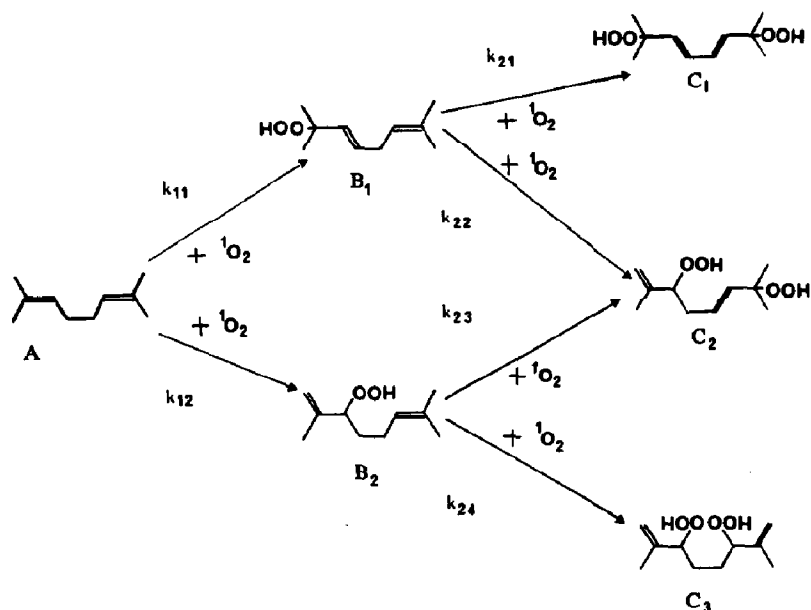
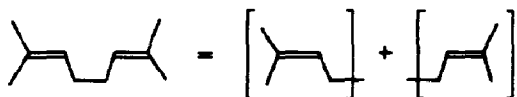


Fig. 5. Photo-oxygenation of 2,7-dimethyl-2,6-octadiene showing the reaction products. The rate constants ($M^{-1} s^{-1}$) are: $k_{11} = 9.0 \times 10^5$; $k_{21} = 1.9 \times 10^5$; $k_{23} = 1.9 \times 10^5$; $k_{12} = 8.1 \times 10^5$; $k_{22} = 2.2 \times 10^5$; $k_{24} = 4.1 \times 10^5$; $k_1 = 17.1 \times 10^5$; $k_2 = 5.0 \times 10^5$; $k_2(B_1) = 4.1 \times 10^5$; $k_2(B_2) = 6.0 \times 10^5$.

4. Discussion

4.1. Reactions $M-M \xrightarrow[k_1]{^1O_2} M-M(OOH) \xrightarrow[k_2]{^1O_2} M(OOH)-M(OOH)$

The model compounds of polymerization number 2 can be considered to be formed by juxtaposition of two molecules of polymerization number 1, or as their "dimer", and it might be wondered whether their reactivity towards singlet oxygen is twice that of a single unit. For example, DMOD may be considered as the sum of two molecules of 2-methyl-2-pentene

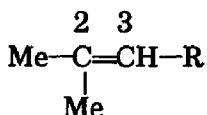


and effectively its reaction rate with $\Delta_g \text{}^1\text{O}_2$ is practically twice as great as that of 2-methyl-2-pentene. Moreover, the rate constants k_{11} and k_{12} of formation of the tertiary hydroperoxide B_1 and of the secondary hydroperoxide B_2 lead to an initial distribution of B_1 and B_2 of 52.5% and 47.5% respectively. Now when DMOD is considered as the sum of two molecules of 2-methyl-2-pentene, we expect the proportions of B_1 and B_2 to be approximately 51% and 49% respectively. In the same way, the reactivities of DMDD and of DHM may be considered as the sum of the reactivities of the two constituent olefins (Table 1).

We find again that, as with compounds of polymerization number 1, the *trans* isomers are more reactive than the *cis* isomers ($k_{1 \text{ trans}}/k_{1 \text{ cis}} = 1.6 - 1.7$) for 3-methyl-2-pentene, 4-methyl-4-octene and dihydromyrcene; for DMDD $k_{1 \text{ trans-trans}}/k_{1 \text{ 50\% trans}} = 1.6$.





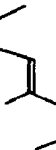

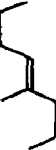




If we observe the values of k_2/k_1 , the ratio of the overall reactivities (Table 2), we see that this value decreases from about 0.5 for DMDD to 0.4 and 0.3 for DHM and DMOD respectively. If these models are considered as the sum of two units, we ascertain that the two units of DMDD react with the same rate. For DHM and DMOD, however, the photo-oxygenation of one of the two double bonds induces a deactivation of the other.

In order to explain this observation it is necessary to reconsider the case of monosubstituted olefins. Several works [16 - 24] have been devoted to the study of the addition reaction of ${}^1\text{O}_2$ with olefins containing allylic hydrogen atoms, and the stereoelectronic effects of alkyl groups attached to the carbon atoms of the double bond, the requirement of "axial-positioned" allylic hydrogen atoms and the steric effects shown by bulky groups towards an attack of singlet oxygen as well as in the expected product have been discussed. The data in Table 2 indicate that the effect of the nature of the alkyl group R in the series



is quite important as can be seen by comparing 2-methyl-2-butene and 2-methyl-2-pentene; this effect is confirmed by *cis*- and *trans*-4-methyl-4-octene. According to Gollnick [17] the decrease of the value of the constant k_1 in the case of 2,4,4-trimethyl-2-pentene is due to the steric hindrance exerted by the tert-butyl group on the attack of ${}^1\text{O}_2$ on the C_3 carbon atom. With 2,4-dimethyl-2-pentene the conformation of the allylic hydrogen of the isopropyl group is unfavourable for the formation of the tertiary hydroperoxide and a decrease of the reactivity of this olefin compared with 2-methyl-2-butene is also observed.

TABLE 1
Rate constants of the first addition reaction of singlet oxygen with model compounds of polyisoprene containing two units

Polymerization number 2 model compounds and rate constants ^a $k_1 \times 10^{-5}$ ($M^{-1} s^{-1}$)		Constituent olefins ol ₁ and ol ₂ and rate constants ^a $k_1 \times 10^{-5}$				
		ol ₁	ol ₂	$k_1(ol_1)$ ($M^{-1} s^{-1}$)	$k_1(ol_2)$ ($M^{-1} s^{-1}$)	$k_1(ol_1) + k_1(ol_2)$ ($M^{-1} s^{-1}$)
	17.1			6.2 ^c - 8.6 ^d	6.2 - 8.6	12.4 - 17.2
DMDD 50% trans	6.94			3.3 ^e	5.6 ^e	8.9
DMDD trans	11.1			5.6	5.6	11.2
DHM cis	11.1			6.2 - 8.6	5.8 ^e	12.0 - 14.4
DHM trans	18.5			6.2 - 8.6	9.3 ^e	15.5 - 17.9





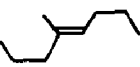
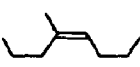


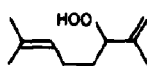

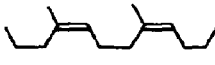
^aWhen taking $\tau(^1O_2) = 9 \times 10^{-6}$ s.

^bData for 4-methyl-3-heptene not being available, we have considered 4-methyl-4-octene as more representative than 2-methyl-2-pentene.

^cFrom ref. 17. ^dFrom ref. 25. ^eFrom ref. 12.

TABLE 2

Effect of the nature of the alkyl group R on the reactivity of $(\text{CH}_3)_2\text{C}=\text{CHR}$ towards singlet oxygen

Substrate	$k_1 \times 10^{-5}$ ($\text{M}^{-1} \text{s}^{-1}$)	$k_2 \times 10^{-5}$ ($\text{M}^{-1} \text{s}^{-1}$)	k_2/k_1
	20.2 ^a 11.1 ^b 10.1 ^c		
	8.6 ^d 6.9 ^d 6.2 ^a		
	0.86 ^a		
	0.26 ^a		
	5.6 ^e		
	3.3 ^e		
 DHMt	18.5		
DHM(OOH)		7.4	0.40
	17.1 ^f		
 HOO		6.0 ^f	0.35
 OOH		4.1 ^f	0.24
DMDD	6.94		
 DMDD(OOH)		3.82	0.55

^aFrom ref. 17. ^bFrom ref. 26. ^cFrom ref. 18. ^dFrom ref. 25.
^eFrom ref. 12. ^fFrom ref. 16.

Such effects may explain the fact that for the compounds B_1 and B_2 derived from DMOD and corresponding to



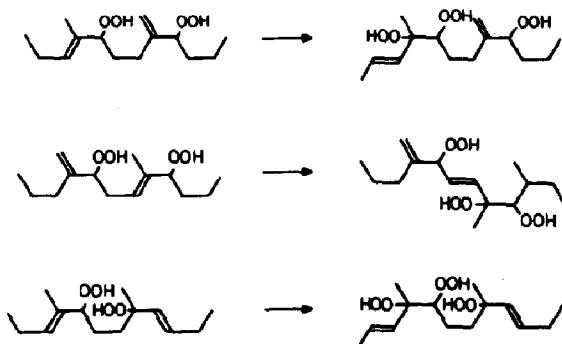
the value of the rate constant is lower than that of 2-methyl-2-pentene although it is much higher than that of 2,4,4-trimethyl-2-pentene for which steric hindrance is prevalent. In fact we note that it is nearly that observed in the case of 4-methyl-4-octene for which the approach of the double bond at the time of the lateral attack of singlet oxygen is at least partially hindered by the presence of the alkyl groups. In the case of DMDD the presence of the propyl groups induces an initial decrease in activity with respect to the other models ($7 \times 10^5 - 18 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) so that an additional deactivating effect connected with the photo-oxygenation of a unit is not observed.

Electronic effects cannot be excluded, however. Thus, for the derivatives of DMOD, the monohydroperoxide B_1 is less reactive than B_2 . This can be attributed to an electro-attractive deactivating effect of the unsaturation located in β - γ with respect to the untouched trisubstituted double bond enhanced owing to the presence of the ---OOH group in the allylic position. In the case of the product B_2 it can be estimated that the hydroperoxy function and the unsaturation of the substituent cannot generate an electronic effect because of their remote position.

4.2. Reactions $M(\text{OOH})\text{---}M(\text{OOH}) \rightarrow M(\text{OOH})\text{---}M(\text{OOH})_2$

The situation depends on the substrate investigated.

Photo-oxygenation of DMDD was carried out until oxygen consumption was no longer observable [15]. The yield was slightly higher than that corresponding to 1 mol O_2 by isoprenic units, and the following trihydroperoxides, which may be formed in the same way as in the case of 4-methyl-4-octene [12], were observed:



Thus a diaddition on the same unit is possible but, as might be expected, only with a hydroperoxide having a trisubstituted double bond, which is formed in relatively small quantities.

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