Tetrahedron Vol. 41, No. 11, pp. 2139 to 2146, 1985
Printed in Great Britain.

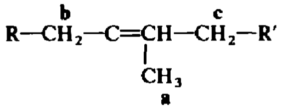
0040-4020/85 \$3.00 + .00

REACTIONS OF SINGLET OXYGEN WITH POLYISOPRENE AND MODEL COMPOUNDS

C. TANIELIAN* and R. MECHIN
Laboratoire de Photochimie, Ecole Nationale Supérieure de Chimie, 1 rue Blaise Pascal, 67008 Strasbourg Cedex, France

(*Received in Japan* 23 *April* 1984)

Abstract—Results from the study of singlet oxygen reaction with *cis*-1,4-polyisoprene and with various models are compared. The nature of the products and their reactivity are discussed for two kinds of models, namely oligodienes and trisubstituted mono-olefins with various substituent length. The reactivity of the double bond decreases with lengthening of the alkyl substituents but the reactivity of 4-methyl-4-octene is close to that of the polymer. The hydroperoxidation of a unit in an oligodiene does not deactivate significantly the adjacent units towards singlet oxygen addition. The reactivity of the allylic hydrogen a, b, and c in the olefin



$$\overset{b}{R{-}CH_2{-}}\underset{\underset{a}{CH_3}}{C}{=}CH{-}\overset{c}{CH_2}{-}R'$$

depends on both the position and the length of the substituents and follows the sequences $k_c > k_b > k_a$. The principle of syn-ene addition can be extrapolated to polyisoprene. The rate constant determined for the *cis*-1,4-polyisoprene–$^1O_2$ reaction allows the conclusion that the probability of reaction of $^1O_2$ with the solid polymer may be high. Similarity in the behaviour of polymer and models in this reaction allows for the estimation of the reactivity of other unsaturated or reactive polymers towards $^1O_2$.

An important amount of work has been devoted to the reactions of singlet molecular oxygen $O_2(^1\Delta_g)$ with olefins over the past 15 years and the subject has been periodically reviewed.[1–5] Most of these studies concern low molecular weight olefins, but some of them deal with unsaturated polymers and this aspect has been reviewed by Golub.[6]

However, the study of polymers suffers many disadvantages if one wishes to distinguish the elementary processes, characterize the reaction products and determine the reactivities of the various unsaturations. It is necessary, therefore, to work in some cases with model compounds. Tanielian and Chaineaux[7–13] have carried out an extensive study of the reactions of singlet oxygen with oligoisoprenes and model compounds of *cis*- and *trans*-1,4-polyisoprenes. The purpose of the present study is to determine the extent to which conclusions arising from work with model compounds can be extrapolated to polyisoprene and in a second step, generalized to other polymers. This involves repeating the previous results as well as the new comparative study including *cis*-1,4-polyisoprene, presented in this report.

REACTION PRODUCTS

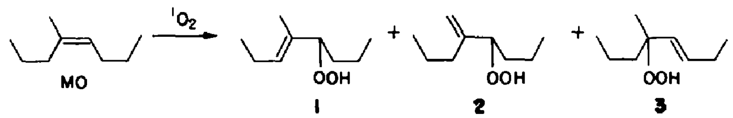
Photo-oxygenation of model compounds. The photo-oxygenation of a number of trisubstituted olefins was studied in the presence of methylene blue or Rose Bengal as sensitizers. Under these conditions the reaction is known to proceed via a type II mechanism involving singlet oxygen $O_2(^1\Delta_g)$ or $^1O_2$.[2]

All the investigated trisubstituted mono-olefins contain an isoprenic unit and lead only to allylic hydroperoxides, but they do not have the same value as models. 2-Methyl-2-butene and 2-methyl-2-pentene give only two photo-oxygenation products and, therefore, are poor models; 3-methyl-2-pentene leads to three products but the environment of the double bond is different from that of a polymer; 4-methyl-4-octene (MO), which consists of an isoprenic unit on which two Et groups are branched, is a better model compound. These Et groups introduce methylene groups on each side of the unit and ensure conditions of quasi-neutrality because of their low inductive and electromer powers.

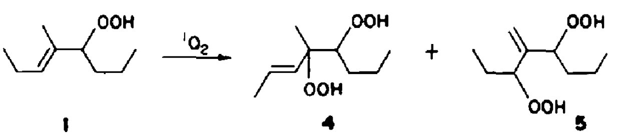
For the MO–$^1O_2$ reaction (reaction 1), the distribution of the shifted double bonds varies with the stereochemistry of the starting olefin, the tertiary hydroperoxide, 3, always being the major product.[10]

A second addition of $^1O_2$ (reaction 2) can occur in MO but only through the intermediacy of the monohydroperoxide having the trisubstituted double bond (1). The disubstituted and exomethylene double bonds (in 3 and 2) are considerably less reactive.[10]

The reactions of singlet oxygen with 4,8-dimethyl-

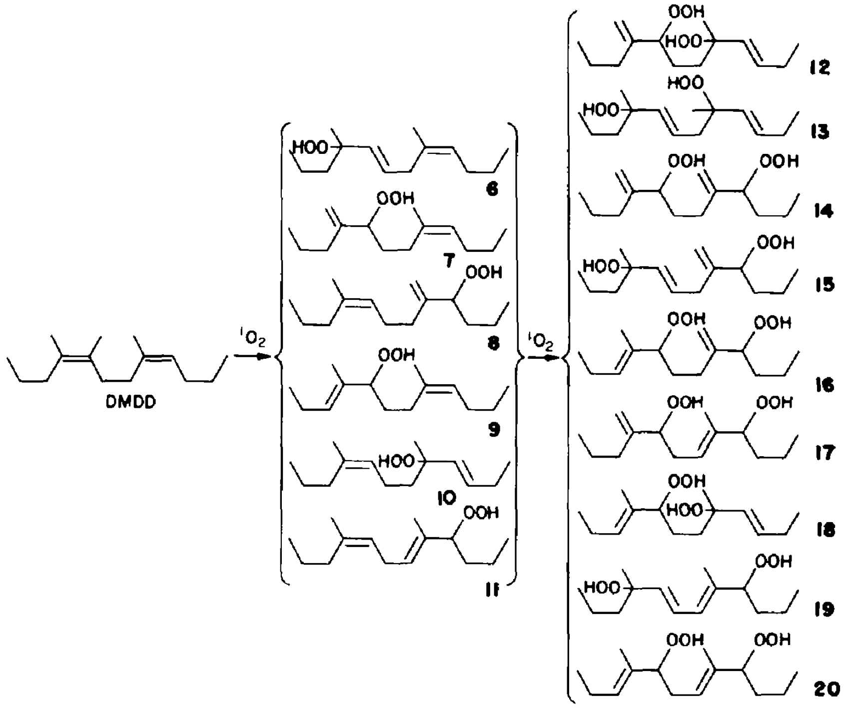


(1)



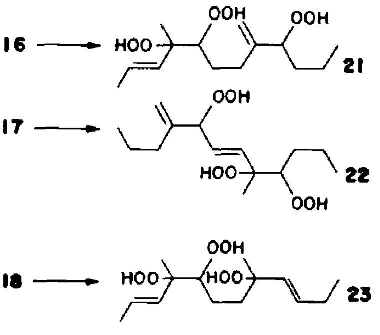
(2)

4,8-dodecadiene (DMDD), 2,6-dimethyl-2,6-octadiene (DHM) and 2,7-dimethyl-2,6-octadiene (DMOD) as polyisoprene model compounds containing two units in head-to-tail or head-to-head arrangement were studied.[7–9] The singlet oxygenation of DMDD yielded all six possible monohydroperoxides (**6**–**11**).[7] Furthermore, on the assumption that the trisubstituted double bonds in these products are the only ones likely to react with additional $^1O_2$, there are nine possible dihydroperoxides from DMDD, of which four were positively identified (**12**–**15**) and three were presumed to have been formed (**16**–**18**) on the basis that the trihydroperoxides **21**–**23** were recovered from extended photosensitized oxidation of DMDD[7] (reaction 3).



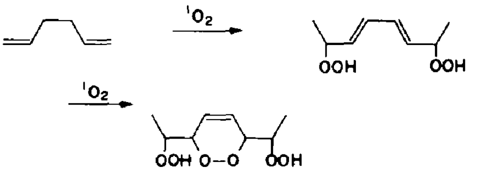
(3)

In every one of the hydroperoxidized products identified, the new disubstituted double bonds where present, were in the *trans* configuration. Reactions (4)



(4)

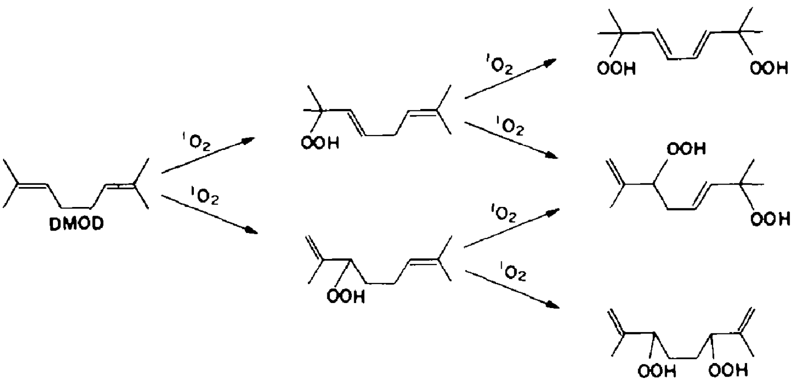
showed that diaddition of $^1O_2$ to the same isoprene unit is possible but only to a hydroperoxidized monomer unit that contains a trisubstituted double bond. However, no dihydroperoxides were obtained from DMDD in which the diaddition of $^1O_2$ occurred in the same isoprene unit while the other unit was left unreacted. This result is in keeping with the deactivation of a double bond by an allylic OOH group.



(5)

It has also been shown, using DMDD[7] and DMOD,[8] that the mechanism proposed by Kaplan and Kelleher[14] for singlet oxygenation of 1,4-polybutadiene (reaction 5) is very unlikely. Thus, the dihydroperoxide, **19**, has a conjugated diene structure appropriate for undergoing reaction (5) but no dihydroperoxyendoperoxide of DMDD was detected. Likewise, in the singlet oxygenation of DMOD (reaction 6), the dihydroperoxide **24** (with a conjugated diene structure), was obtained in fair yield, yet it could not be further singlet oxygenated to an endoperoxide. The failure of the dihydroperoxides **19** and **24** to form endoperoxides was attributed to their acyclic structure and to the deactivation effect of the allylic OOH groups.[8] Results analogous to those of DMDD and DMOD were also reported for DHM.[9]

Some of the conclusions drawn from the study of model compounds containing one or two units are valid for longer oligoisoprenes M_n (with $n = 3$, 4 and 6).[13] Thus, the number of oxygen molecules incorporated slightly exceeds the number of 1, 4 units and gas chromatographic–mass spectral data show that the monohydroperoxidation of each double bond



24

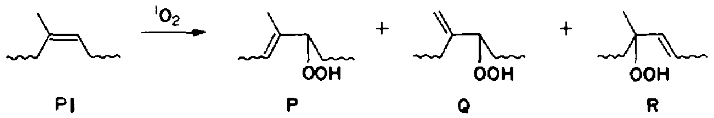
25

26

(6)

is favoured with respect to dihydroperoxidation of the same double bond (as will be confirmed in the kinetics study). Thus, all the possible reactions of singlet oxygen with polyisoprene models are shown in Scheme 1.

Photo-oxygenation of polyisoprene. Within the frame of the present work, the methylene blue sensitized photo-oxygenation of *cis*-polyisoprene (PI) in pure chloroform was followed by oxygen uptake up to 0.5 mol O_2 per monomer unit and this value was confirmed by iodometry. The IR spectrum of oxidized *cis*-PI is identical to those previously published for the product of singlet oxygenation of this polymer under other conditions by Golub *et al.*[15] and Rabek and Ranby.[16] The reaction leads to all of the three possible hydroperoxidized units with a shifted double bond (reaction 7). Qualitative analysis of the spectrum provides evidence that the tertiary hydroperoxide, **R** which possesses a disubstituted double bond is the major product; however, as the photo-oxygenation does not go to completion, the distribution of the hydroperoxides cannot be accurately determined.



(7)

KINETICS

The Rose Bengal or methylene blue sensitized photo-oxygenation of olefins can be summarized as in Scheme 2[1,17] where S is the sensitizer and ^1S and ^3S its first excited singlet and triplet states, respectively.

In these conditions the steady state treatment shows that the quantum yield of oxygen consumption is given by:

$$\phi_{O_2} = \gamma_A k_A[A]/(k_A[A] + k_D)$$

where γ_A is the quantum yield of singlet oxygen formation. Then,

$$(\phi_{O_2})^{-1} = (\gamma_A)^{-1}(1 + \beta[A]^{-1})$$

with

$$\beta = \frac{k_D}{k_A}.$$

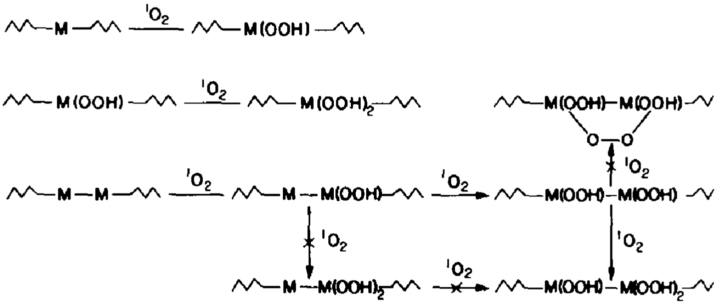
Values of β can be obtained either as

$$\left(\frac{\gamma_A}{\phi_{O_2}} - 1\right)[A]$$

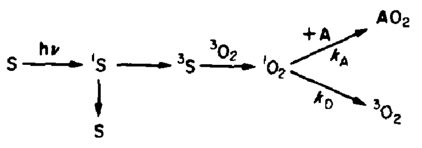
or as the ratio of slope–intercept of the linear plots $(\phi_{O_2})^{-1}$ vs $[A]^{-1}$.

Moreover, successive additions of singlet oxygen were followed by gas chromatographic analysis of the corresponding hydroperoxides.

Reactivity of model compounds of polyisoprene towards singlet oxygen. In order to measure the



Scheme 1.



Scheme 2.

importance of all the reactions depicted above the photo-oxygenation of the oligomers was followed by both oxygen consumption and products formation (solvent: methanol; sensitizer: Rose Bengal).[8–10,13]

Successive additions of singlet oxygen to the same unit.

$$\sim\text{M}\sim \xrightarrow{k_1} \sim\text{M(OOH)}\sim \xrightarrow{k_1'} \sim\text{M(OOH)}_2\sim$$

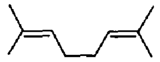
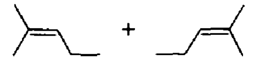
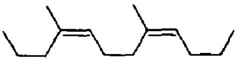
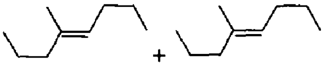
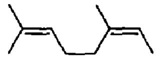
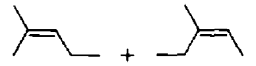
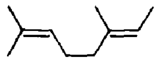
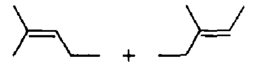
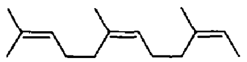
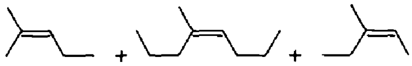
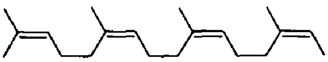
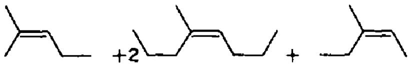
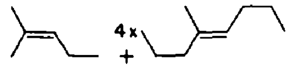
The possibility of the dihydroperoxidation of the same unit was demonstrated above but only through the intermediacy of the monohydroperoxide having the trisubstituted double bond. But the allylic OOH group induces a strong deactivating effect such that reaction (2) (yielding **4** and **5** in that ratio of 1 : 4) is *ca* 20 times slower than reaction (1).[10] A similar effect was shown to be exerted by OH groups and related to the electrophilic nature of singlet oxygen.[12]

First addition of singlet oxygen to an oligomer.

$$\sim\text{M—M—M}\sim \xrightarrow{k_1} \sim\text{M—M(OOH)—M}\sim$$

The rate constant k_1 was measured for a variety of oligomers M_n with $n = 2$–4 and 6 and the values compared to those obtained for mono-olefins in the same conditions. The results are presented in Table 1. It can be seen that the reactivity of an oligomer may be considered as the sum of the reactivities of appropriate constituent mono-olefins: the contribution of terminal units may be represented by 2-methyl-2-pentene or 3-methyl-2-pentene, whereas 4-methyl-4-octene represents the in-chain units. Accordingly, the value of k_1/n (Table 1) is intermediate between that of the most reactive (*E*)-3-methyl-2-pentene (rate constant 9.3 × 10^5 M^{-1} s^{-1}) and the least reactive (*Z*)-4-methyl-4-octene (rate constant 3.3 × 10^5 M^{-1} s^{-1}). This means also that for a longer oligodiene or polydiene M_n the

Table 1. Comparison between the experimental and calculated rate constants k_1 for the first addition of singlet oxygen on oligoisoprenes (in methanol)

Oligoisoprene	Rate constants $k_1 \times 10^{-5}$ ($M^{-1}s^{-1}$)				
		k_1 (oligoisoprene)			
	k_1 (constituent olefin)	Calculated	Experimental	k_1/n	Reference
	 6.2 6.2	12.4	17	8.5	9
 *E-E*	 5.6 5.6	11.2	11.1	5.55	9
	 6.2 5.8	12.0	11.1	5.55	9
	 6.2 9.3	15.5	18.5	9.25	9
	 6.2 *Z* 3.3 5.8 *E* 5.6	15.3 21.8	20.2	6.7	13
	 6.2 *Z* 3.3 5.8 *E* 5.6	18.6 27.4	22.2	5.5	13
Squalene	2  6.2 5.6	34.8	35.8	5.8	13

rate constant k_{M_n} for the first addition of $^1O_2$ is n-times the rate constant k_M relative to a unit:

$$k_{M_n} = nk_M.$$

Addition of singlet oxygen to a unit contiguous to an hydroperoxidized unit.

$$\sim M-M(OOH)-M\sim \xrightarrow{k_2} \sim M-M(OOH)-M(OOH)\sim \xrightarrow{k_3} \sim M(OOH)-M(OOH)-M(OOH)\sim$$

Analysis of the disappearance of the model compound and of the appearance of the hydroperoxides allowed the determination of the rate constants k_2 for DMOD,[8] DMDD, DHM[9] and k_2 and k_3 for 2,6,10-trimethyl-2,6,10-dodecatriene,[13] the triisoprenic model compound. The rate constants obtained for different oligomers are listed in Table 2. Comparison of k_2 with $k_1/2$ for a dimer, and of $k_2/2$ or k_3 with $k_1/3$ for a trimer shows that there is practically no deactivation of a unit by the neighbouring oxygenated units. This means that, in the further steps of the photooxygenation, when a ratio p/n of the unsaturated units is hydroperoxidized the rate constant for the addition of singlet oxygen is equal to the sum of the rate constants for the unreacted units:

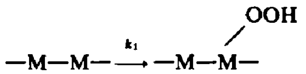
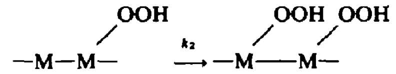
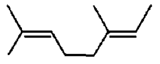
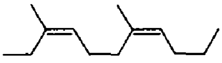
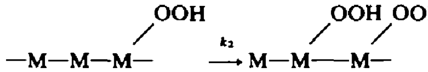
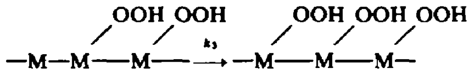
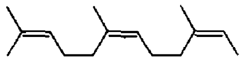
$$k_{M_{n-p}MOOH_p} = (n-p)k_M.$$

Relative reactivities of (E) *and* (Z) *isomers.* It should be added that, for model compounds of polymerization numbers 1 and 2, the (E) isomers are more reactive than the (Z) isomers: $k_{1_E}/k_{1_Z} = 1.6–1.7$ for 3-methyl-2-pentene, 4-methyl-4-octene[10] and dihydromyrcene;[9] for DMDD $k_{1_{E-E}}/k_{1_{50\%Z}} = 1.6$.[9] This result agrees very well with the corresponding ratio of *ca* 1.5 obtained by Golub *et al.*[15] for *trans*- and *cis*-polyisoprene.

Comparison with the polymer. In order to compare directly the reactivity of model compounds with that of the polymer the kinetics of singlet oxygenation of the following substrates have been reinvestigated in chloroform, for solubility reasons, in the presence of methylene blue: 2-methyl-2-pentene, (Z)-3-methyl-2-pentene, (Z)-4-methyl-4-octene and *cis*-1,4-polyisoprene. The plots of the reciprocal of the quantum yield of oxygen consumption vs the reciprocal of concentration are shown in Fig. 1. The β-values calculated from these plots are corrected to take into account the slight influence of the physical quenching of $O_2(^1\Delta_g)$ by methylene blue at the concentration used.[18] The corrected β-values and rate constants, k_A, are derived by choosing for the singlet oxygen lifetime $\tau_\Delta = k_D^{-1}$ a value of 230 μs among recently reported values: 60 μs,[19] 210 μs,[20] 240–265 μs,[21] 228 μs,[22] 250 μs[23] and 415 μs.[24] These results are given in Table 3.

As above, one observes that the reactivity decreases when the substituent chains lengthen; the value corresponding to MO is close to that of the polymer. The conclusion that MO is the best model for PI is coherent with that drawn for oligodienes. Thus, in PI the effect exerted on the reactivity of a double bond is the same as that exerted by sufficiently long alkyl groups in a mono-olefin. A similar conclusion can be

Table 2. Rate constants for the consecutive addition of singlet oxygen to a double bond adjacent to a hydroperoxidized monomer unit in an oligoisoprene M_n (in methanol). Comparison with the rate constant for the first addition

	Rate constants × 10^5 (M^{-1} s^{-1})			
	 $-M-M-\xrightarrow{k_1}-M-\overset{OOH}{M}-$		 $-M-\overset{OOH}{M}-\xrightarrow{k_2}-\overset{OOH}{M}-\overset{OOH}{M}-$	
	k_1	k_1/n	k_2	$\frac{k_2}{k_1/2}$
	18.5	9.2	7.4	0.8
	6.9	3.5	3.8	1.1
			 $-M-M-\overset{OOH}{M}-\xrightarrow{k_2}M-\overset{OOH}{M}-\overset{OOH}{M}-$	
			 $-M-\overset{OOH}{M}-\overset{OOH}{M}-\xrightarrow{k_3}-\overset{OOH}{M}-\overset{OOH}{M}-\overset{OOH}{M}-$	
	20.2	6.8	k_2: 12 k_3: 6	$\frac{k_2/2}{k_1/3}$: 0.9 $\frac{k_3}{k_1/3}$: 0.9

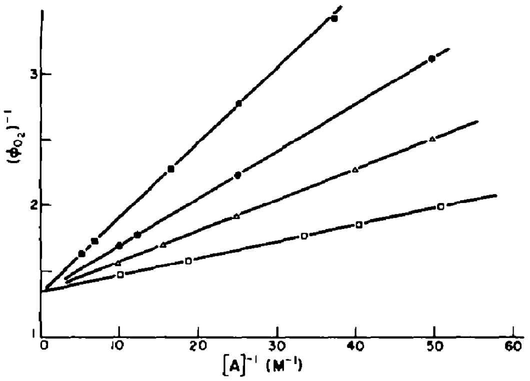


Fig. 1. Methylene blue sensitized photo-oxygenation in chloroform of: *cis*-1,4-polyisoprene (■); 4-methyl-4-octene (54% *Z*–46% *E*) (●); (*Z*)3-methyl-2-pentene (△); 2-methyl-2-pentene (□); Φ_{O_2}, quantum yield of oxygen consumption; [A], substrate concentration.

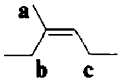
made from recent work[25] in which it is shown that the reactivity of *cis*-9-tricosene is practically the same as that of *cis*-1,4-polybutadiene.

The whole of these results allows estimation of the probability of reaction of $^1O_2$ with PI. In concentrated solutions or in the solid state 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 a double bond is close to 1 if the β-value is much smaller than the local concentration of double bonds [C=C]. This is valid in the case of polyisoprene because

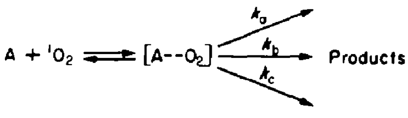
$$\phi_R = \frac{[C{=}C]}{[C{=}C]+0.4}$$

by assuming $\tau_\Delta = 20$ μs in hydrocarbons. Thus, the importance of the participation of $^1O_2$ in the initiation step of the oxidative degradation of PI will depend on the efficiency of its production.

Relative reactivity of different allylic hydrogens. Both the knowledge of hydroperoxide distribution and reactivity of olefins towards $^1O_2$ are necessary to understand the factors governing the reactivity of allylic hydrogen in various environments. The percentage of H abstraction at sites a, b and c of various olefins



are given in Table 4. Inspection of these data shows that two factors must be distinguished.

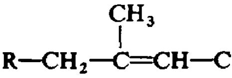


Scheme 3.

(1) *The effect of the position is preponderant.* The percentage of H abstraction at each side follows the order %c > %b > %a. This is in accordance with the syn-ene addition principle formulated by Schulte-Elte *et al.*[26] and Orfanopoulos *et al.*[27] This principle postulates that the major products result from H abstraction on the more crowded disubstituted side of the olefin (syn-addition) and the minor product from H abstraction on the monosubstituted side (anti-addition). In terms of partial rate constants for the positions a, b and c we have: $k_c > k_b > k_a$.

(2) *The effect of chain lengthening appears on the reactivity of the three sites of hydrogen abstraction.* It is slightly more important for position b than position c and it is the weakest for position a.

Thus, the reactivity of a trisubstituted olefin results from the superposition of these two effects. But, for the olefin



$$R{-}CH_2{-}\overset{\overset{\large CH_3}{|}}{C}{=}CH{-}CH_2{-}R'$$

the order of reactivity $k_c > k_b > k_a$ remains valid for any length of the substituents R and R′, for either isomer (*Z*) or (*E*). The resulting product distribution will be %R > %P > %Q (olefin *Z*) or %R > %Q > %P (olefin *E*). These conclusions are valid in the case of *cis*- or *trans*-polyisoprene according to Golub's results.[6]

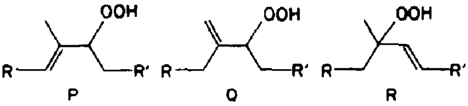
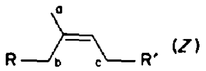
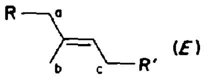
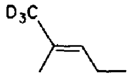
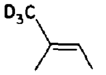
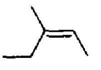
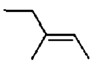
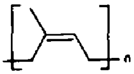
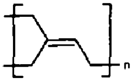
As seen above, the ratio k_Z/k_E was observed for different pairs of isomers containing the isoprenic unit. This effect may be easily explained by the preceding discussion: it mainly originates in the enhancement of k_B in the (*E*) compound.

The origin of the reactivity differences of allylic H in trisubstituted olefins has been recently discussed by several authors.[28–30] Houk *et al.*[31] have attributed such differences to the difference in enthalpy required for the allylic H being abstracted to become nearly perpendicular to the alkene plane. Most recent papers rather favour the initial rapid and reversible formation of an exciplex followed by an entropy-controlled rate determining step.[32–34] The features of the reaction of $^1O_2$ with trisubstituted olefins (A) are not inconsistent with the reaction shown in Scheme 3 where [A–O$_2$] is an exciplex in which the allylic hydrogens are not in the required geometry. But, it seems difficult to assign the

Table 3. Reactivity index, β, and rate constant, k_A, for the reaction of singlet oxygen with *cis*-1,4-polyisoprene and its model compounds in chloroform

	$\beta \times 10^2$(M)	$k_A \times 10^{-5}$(M^{-1} s^{-1})
cis-1,4-Polyisoprene	3.6 ± 0.2	1.2 ± 0.1
(*Z*) 4-Methyl-4-octene	2.75 ± 0.2	1.6 ± 0.1
(*Z*) 3-Methyl-2-pentene	1.5 ± 0.1	2.9 ± 0.2
(*Z*) 2-Methyl-2-pentene	0.85 ± 0.05	5.1 ± 0.3

Table 4. Reaction of singlet oxygen with various trisubstituted olefins: rate constants k_A hydroperoxides distribution (in parentheses partial reactivity for positions a, b and c)

Olefin	Products				
					
		a → Q	b → P	c → R	
		a → P	b → Q	c → R	
	$k_A \times 10^5 (M^{-1} s^{-1})$	%a (k_a)	%b (k_b)	%c (k_c)	Reference
	7.7	7 (0.5)	40 (3)	53 (4)	27
	5.2	7 (0.36)	43 (2.2)	50 (2.6)	27
	2.9	16 (0.46)	27 (0.8)	57 (1.65)	This work
	5.3	12 (0.6)	43 (2.3)	45 (2.4)	This work
	1.2	6 (0.1)	47 (0.56)	47 (0.56)	6
	1.8	26 (0.46)	26 (0.46)	48 (0.86)	6

slight differences in reactivity observed (between one site and another or at a given site when lengthening the chain) either to an enthalpy barrier or to the entropy variation between [A--O_2] and the products. Further discussion on the mechanism of the reaction of $^1O_2$ with olefins appears in this issue.[35]

CONCLUSION

This work provides further information on the reactivity and product distribution resulting from the reaction of trisubstituted olefins with singlet oxygen including the case where two of the substituents are long hydrocarbon chains. Most of the features of this reaction concerning low molecular weight olefins may be extended to polyisoprene. The results of the kinetic studies allow estimation that the probability of singlet oxygen reaction with a polydiene is high. More generally, it seems possible to estimate the reactivity towards $^1O_2$ and the nature of the products for any polymer containing unsaturations or other reactive groups of known structure and concentration [X]. Thus, provided that the β-value is measured for a suitable model containing the reactive group (e.g. 4-methyl-4-octene for polyisoprene), the probability of the polymer $^1O_2$ reaction will be

$$\phi_R = \frac{[X]}{[X]+\beta}.$$

The use of this methodology for the evaluation of the participation of $^1O_2$ in the photodynamic effect on complex natural macromolecular substrates may be of interest.

EXPERIMENTAL

cis-PI (Aldrich) was purified by two redissolutions and reprecipitations in benzene in the dark. 4-Methyl-4-octene was synthesized via a Wittig reaction;[36] other olefins were obtained from Fluka. Methylene blue Merck and Rose Bengal Fluka were used as sensitizers.

The photoreactions were performed in an external cylindrical photoreactor equipped with a gas burette. Irradiation was provided by a high pressure mercury-halogen lamp HANAU TQ 150W Z2 (most intensive ray at 535 nm). Short wavelength rays were filtered by a $NaNO_2$ filter 200 g/l. ($\lambda > 400$ nm).

The initial rates of photo-oxygenations were followed by O_2 consumption; consecutive reactions were followed by gas chromatographic analysis of the products as previously described.[10] The quantum yields of O_2 consumption were measured by the method described in recent work.[17]

The IR spectra were performed on films on a Perkin–Elmer 180 spectrometer.

The molar ratio of the hydroperoxides resulting from the photo-oxygenation of 2-methyl-2-pentene were calculated from the ^{1}H-NMR spectra of the mixture run in $CDCl_3$ on a Perkin–Elmer R12B spectrometer.

Acknowledgement—We are indebted to Dr. M. A. Golub for many useful discussions on polyisoprene photo-oxygenation.

REFERENCES

[1] K. Gollnick, *Adv. Photochem.* **6**, 1 (1968).

[2] K. Gollnick, *Singlet Oxygen* (Edited by H. H. Wasserman), p. 287. Academic Press, New York (1979).

[3] R. W. Denny and A. Nickon, *Org. React.* **20**, 133 (1973).

[4] P. A. Schaap, *Singlet Molecular Oxygen.* Hutchinson and Ross, Stroudsbourg (1976).

[5] A. A. Frimer, *Chem. Reviews* **79**, 359 (1979).

[6] M. A. Golub, *Pure Appl. Chem.* **52**, 305 (1980).

[7] C. Tanielian and J. Chaineaux, *Singlet Oxygen Reactions of Organic Compounds and Polymers* (Edited by B. Ranby and J. F. Rabek), p. 164. Wiley, Chichester (1978).

[8] C. Tanielian and J. Chaineaux, *Photochem. Photobiol.* **28**, 487 (1978).

[9] C. Tanielian and J. Chaineaux, *J. Photochem.* **9**, 19 (1978).

[10] C. Tanielian and J. Chaineaux, *J. Polym. Sci. (Pol. Chem.)* **17**, 715 (1979).

[11] C. Tanielian and J. Chaineaux, *J. Appl. Polym. Sci. (Appl. Polym. Symp.)* **35**, 337 (1979).

[12] C. Tanielian and J. Chaineaux, *Eur. Polym. J.* **16**, 619 (1980).

[13] C. Tanielian and J. Chaineaux, *J. Photochem.* **21**, 265 (1983).

[14] M. L. Kaplan and P. G. Kelleher, *J. Polym. Sci (A1)* **8**, 3163 (1970).

[15] M. A. Golub, M. L. Rosenberg and R. V. Gemmer, *Rubb. Chem. Technol.* **50**, 704 (1977).

[16] J. F. Rabek and B. Ranby, *Photochem. Photobiol.* **30**, 133 (1979).

[17] C. Tanielian, L. Golder and C. Wolff, *J. Photochem.* **25**, 117 (1984).

[18] C. Tanielian and R. Mechin, unpublished results.

[19] P. B. Merkel and D. R. Kearns, *J. Am. Chem. Soc.* **94**, 7244 (1972).

[20] A. A. Krasnovsky, *Chem. Phys. Lett.* **81**, 443 (1981).

[21] J. R. Hurst, J. D. MacDonald and G. B. Schuster, *J. Am. Chem. Soc.* **104**, 2065 (1982).

[22] R. H. Young and D. R. Brewer, *Singlet Oxygen Reactions of Organic Compounds and Polymers* (Edited by B. Ranby and J. F. Rabek), p. 36. Wiley, Chichester (1978).

[23] K. I. Salokhiddinov, I. M. Byteva and B. M. Dzhagarov, *Opt. Spektrosk.* **47**, 881 (1979).

[24] G. Peters and M. A. J. Rodgers, *J. Am. Chem. Soc.* **103**, 6759 (1981).

[25] C. Tanielian, R. Mechin and M. Esch, *Oxygen Radicals in Chemistry in Biology* (Edited by W. Bors, M. Saran and D. Tait), p. 527. Walter de Gruyter, Berlin (1984).

[26] K. H. Schulte-Elte, B. L. Muller and V. Rautenstrauch, *Helv. Chim. Acta* **61**, 2777 (1978).

[27] M. Orfanopoulos, M. J. Grdina and L. M. Stephenson, *J. Am. Chem. Soc.* **101**, 275 (1979).

[28] L. M. Stephenson, *Oxygen and Oxy-radicals in Chemistry and Biology* (Edited by M. A. J. Rodgers and E. L. Powers), p. 371. Academic Press, New York (1981).

[29] K. Gollnick, *Oxygen and Oxy-radicals in Chemistry and Biology* (Edited by M. A. J. Rodgers and E. L. Powers), p. 379. Academic Press, New York (1981).

[30] K. H. Schulte-Elte and V. Rautenstrauch, *J. Am. Chem. Soc.* **102**, 1738 (1980).

[31] K. N. Houk, J. C. Williams Jr., F. A. Mitchell and K. Yamaguchi, *J. Am. Chem. Soc.* **103**, 949 (1981).

[32] A. A. Gorman, I. R. Gould and I. Hamblett, *J. Am. Chem. Soc.* **104**, 7098 (1983).

[33] J. R. Hurst and G. B. Schuster, *J. Am. Chem. Soc.* **104**, 6854 (1982).

[34] L. E. Manring and C. S. Foote, *J. Am. Chem. Soc.* **105**, 4710 (1983).

[35] J. R. Hurst, S. L. Wilson and G. B. Schuster, *Tetrahedron* **41**, 2191 (1985).

[36] C. Pinazzi and D. Reyx, *Bull. Soc. Chim. Fr.* **10**, 3930 (1972).