

Effect of Conjugated Trienes on the Oxidation of Polyisoprenes

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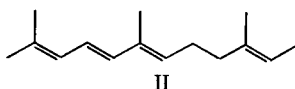
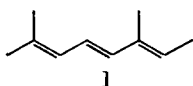
Synopsis

The effect of low concentrations of conjugated triene on the rate of oxidation of polyisoprenes has been investigated. At concentrations similar to those expected to occur in sulfur vulcanizates of NR, conjugated trienes exert a significant accelerative effect on both the uninhibited and the inhibited oxidations of squalene. This accelerative effect is also present, but to a lesser extent, in the inhibited oxidation of carbon-carbon cross-linked NR vulcanizates.

INTRODUCTION

Bateman et al.¹ identified the conjugate triene alloocimene (I) as a minor product of the reaction of sulfur with 2,6-dimethylocta-2,6-diene. More recent work in these laboratories² has shown that conjugated dienes and trienes are also formed when this olefin reacts with sulfur in the presence of vulcanization accelerators. Watson³ has identified conjugated unsaturation products in the reaction of 2-methylpent-2-ene with tetramethylthiuram disulfide and zinc oxide. These results show that formation of conjugated unsaturation is likely to be a common side reaction in the vulcanization of polyisoprenes. There is also evidence⁴ that formation of conjugated unsaturation can occur during oxidative ageing of sulfur-crosslinked polyisoprene networks.

Since conjugated dienes and trienes are considerably more susceptible to oxidation by atmospheric oxygen than are simple olefins,⁵ the presence of such conjugated structures in a vulcanizate is expected to have an adverse effect on its resistance to oxidative ageing. Earlier work⁶ has shown that alloocimene (0.2*M*) has a large accelerative effect on the rate of oxidation of squalene. In the present paper, the oxidation of squalene and of carbon-carbon crosslinked natural rubber (NR) vulcanizates has been studied in the presence of the conjugated triene 3,7,11-trimethyldodeca-2,4,6,10-tetraene (II) at concentrations close to the low levels expected to be present in accelerated sulfur vulcanizates.



Compound II was chosen for this work in preference to alloocimene because of its lower volatility and because its structure is more closely related to that of a conjugated triene function within a polyisoprene chain.

EXPERIMENTAL

Chlorobenzene was fractionated through a 30-cm glass helix column; bp 131°C. Squalene was obtained by molecular distillation of basking shark liver oil and was purified by chromatography on alumina.⁷ Samples of squalene were passed through alumina immediately before use in oxidation experiments. Alloocimene (I) was a commercial product fractionally distilled from hydroquinone under reduced pressure; bp 81.5°C/16 mm, n_D^{20} 1.5454. Gas-liquid chromatographic (GLC) analysis showed the presence of only two components with retention times expected for *trans*, *cis*- and *trans*, *trans*-alloocimene. Alloocimene dioxide was a commercial product (Tenneco Chemicals Inc.) fractionally distilled to give material with bp 103.5–104.5°C/15 mm, containing two major components (28% and 71% by GLC analysis), which could be assigned as *cis* and *trans* isomers of the diepoxide,⁸ and only one minor component. *N*-Isopropyl-*N'*-phenyl-*p*-phenylenediamine was the commercial antioxidant, Nonox ZA, recrystallized several times from ethanol; mp 79–80°C.

3,7,11-Trimethyldodeca-2,4,6,10-tetraene (II) was prepared as follows. Ethyl triphenylphosphonium bromide (40 g) was added to a solution of phenyllithium (0.89*M*, 122 ml) in anhydrous ether under a stream of dry nitrogen, and the mixture was stirred at room temperature for 3 hr. Pseudo ionone⁹ (20.8 g) in anhydrous ether (100 ml) was added, and stirring was continued for 1 hr. The reaction mixture was allowed to stand under a blanket of nitrogen for two days at room temperature and was then washed with water, dried, and the ether removed under reduced pressure. The residue was shaken with petroleum spirit (bp 30–40°C), and the suspension was filtered to remove triphenylphosphine oxide. The filtrate was evaporated under reduced pressure and the residue was fractionally distilled to give a main fraction, bp 99–104°C/1.5 mm, which contained some biphenyl (5% by GLC analysis). Chromatography on Woelm basic alumina, grade I, in petroleum spirit (bp 40–60°C) gave a product with n_D^{20} 1.5447, λ_{\max} 275 m μ , ϵ 43,600 (Found: C, 87.9%; H, 11.8%; C₁₅H₂₄ requires C, 88.2%; H, 11.8%), containing <0.5% biphenyl by GLC analysis and >99% of a group of four components which could be assigned as *cis-trans* isomers of the dodecatetraene. The NMR spectrum was consistent with the assigned structure. The product was stored *in vacuo* at –25°C, and samples were passed through alumina immediately before use in oxidation experiments.

Vulcanizates were prepared as 10 × 10 × 0.02 cm sheets from highly purified NR (U.S. Rubber Co.) and 2 phr dicumyl peroxide. Curing was for 10 min at 100°C, followed by 50 min at 150°C. Oxidation samples, 10 × 0.5 × 0.02 cm, were cut from these sheets. Antioxidant was introduced by swelling the strips in an ethyl acetate solution of the *p*-phenylene-

diamine (1.45 g in 100 ml) overnight. The strips were then removed from the solution and the solvent evaporated under reduced pressure. This procedure gave a final concentration of antioxidant in the dry rubber of $1.03 \pm 0.05\%$ (w/w) as determined by acetone extraction and colorimetric estimation of the Wurster salt of the *p*-phenylenediamine.¹⁰

Oxygen absorption measurements were carried out at an oxygen pressure of 755 ± 10 mm. The automatic recording apparatus¹¹ was developed from that of Dunn and Scanlan.¹² Liquids were oxidized in small round-bottomed silica flasks with integrated water-cooled condensers and were shaken continuously during oxidation. Rubber samples were supported on fine-mesh stainless steel gauze. Oxidation mixtures in chlorobenzene were prepared by weighing reactant directly into the oxidation flask and adding 5.0 ml of solvent. Squalene co-oxidation mixtures were prepared by weight. Rubber samples ($10 \times 0.5 \times 0.02$ cm, containing antioxidant) were impregnated with a carefully measured volume (0.2 ml) of a standard solution of dodecatetraene (II) in methylene chloride containing 1% (w/v) of *p*-phenylenediamine antioxidant, delivered from a micrometer syringe. The methylene chloride evaporated rapidly and the samples were allowed to equilibrate overnight in an atmosphere of nitrogen before oxidation. Additional antioxidant added to the rubber by this procedure was less than 5% of the amount already present.

RESULTS AND DISCUSSION

Autoxidation of Conjugated Triene

The rates of oxidation of carefully purified alloocimene (I) and dodecatetraene (II) (0.17*M*) in chlorobenzene at 25°C were very similar up to the absorption of at least 10 mole oxygen/100 mole triene. The reactions were rapid and autocatalytic, 10 mole-% of oxygen being absorbed in 1 hr. Graphs of oxidation rate versus extent of oxidation gave curves concave to the extent axis, but the same results plotted against the square root of the extent of oxidation gave a straight line up to the absorption of at least 10 mole-% of oxygen. At equal molar concentrations, the two trienes gave coincident rate-extent plots (Fig. 1). This behavior suggests that, at least in the early stages of oxidation, the triene function of compound II undergoes reaction without interference from the adjacent trialkylethylene group.

The dependence of reaction rate on the square root of the extent of reaction indicates autocatalysis by an oxidation product which decomposes unimolecularly to give chain-initiating species, provided the concentration of the labile oxidation product is directly proportional to the extent of the reaction. This type of kinetic behavior has been observed by Allen and Kummerow¹³ for the autoxidation of methyl eleostearate and in the autoxidation of conjugated dienes⁵ and styrene¹⁴ and is in contrast to the behavior of simple olefins where reaction rate is directly proportional to the extent of reaction and catalysis occurs by interaction of two hydroperoxide

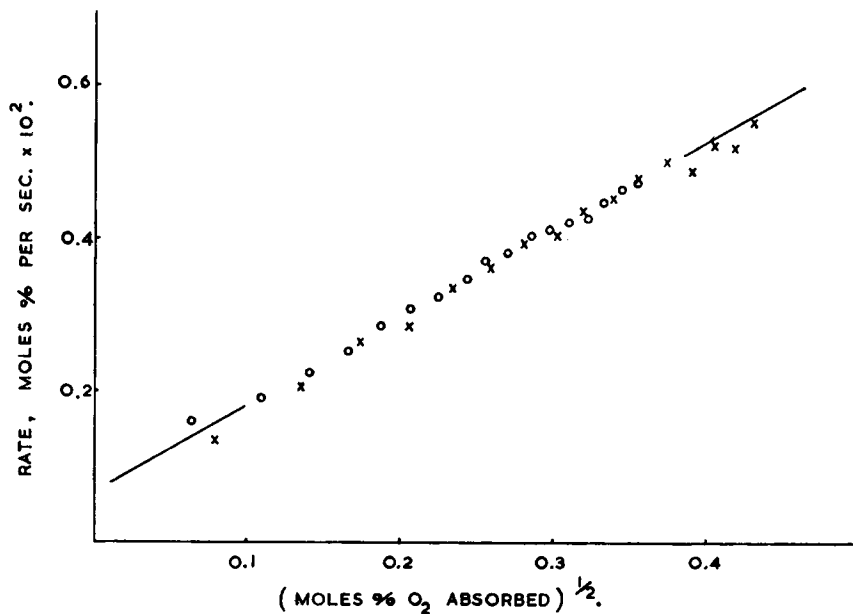


Fig. 1. Reaction rate versus the square root of reaction extent for the oxidation of (O) alloocimene and (X) compound II in chlorobenzene solution (0.17M) at 25°C.

groups to give rise to chain-propagating species.¹⁵ The labile triene oxidation product is probably a polymeric peroxide which undergoes homolytic oxygen-oxygen scission of the peroxide linkage to give two alkoxy radicals capable of initiating further oxidation. Alloocimene is known to give a polymeric peroxide on oxidation¹⁶⁻¹⁹ which decomposes thermally to give the diepoxide, alloocimene dioxide, as a stable end product in the absence of oxygen and oxidizable substrate.⁸

Co-oxidation of Squalene and Conjugated Triene

The oxygen uptake curves of pure squalene and of several mixtures of squalene and compound II at 25°C are shown in Figure 2. The oxidation rate of pure squalene at this temperature was very low and showed only slight autocatalysis. The co-oxidations at different concentrations of conjugated triene were more rapid and showed an initial autocatalytic phase followed by a linear relationship between oxygen uptake and time (representing constant reaction rate) which extended beyond the absorption of 2 mole oxygen/100 mole double bond. This reaction rate was directly proportional to the initial concentration of conjugated triene (Fig. 3) and was operative at oxygen absorption levels beyond those equivalent to absorption of 1 mole of oxygen per mole of triene.

Pre-oxidation of compound II at 25°C, to the absorption of slightly more than 1 mole of oxygen/mole, followed immediately by co-oxidation of this oxidized product with squalene resulted in an oxidation behavior

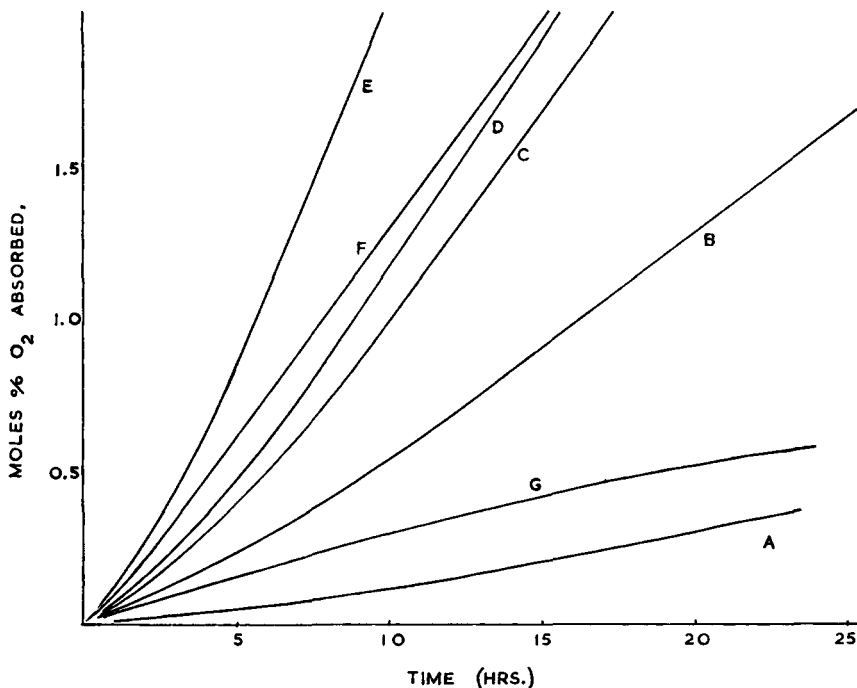


Fig. 2. Co-oxidation of squalene and compound II at 25°C at various concentrations of compound II (moles per 100 moles of squalene double bond): (A) 0; (B) 3.95×10^{-2} mole-%; (C) 1.27×10^{-1} mole-%; (D) 1.47×10^{-1} mole-%; (E) 3.94×10^{-1} mole-%; (F) co-oxidation of squalene and pre-oxidized compound II (1.67×10^{-1} mole-%); (G) co-oxidation of squalene and alloocimene dioxide (2.42×10^{-1} mole-%).

showing very little autocatalysis (Fig. 2) and a constant oxidation rate close to that found in the normal co-oxidation at an equivalent concentration of conjugated triene (Fig. 3). Co-oxidation of squalene and the diepoxide, alloocimene dioxide, showed a slight rate enhancement over pure squalene (Fig. 2), but the effect was small compared with that of the conjugated triene.

The above results show that low concentrations of conjugated triene have a pronounced accelerative effect on the rate of oxidation of squalene. The kinetic behavior of the co-oxidations and of the co-oxidation with pre-oxidized conjugated triene suggests that a product is formed from the triene during the early autocatalytic stage of the reaction which acts as an initiator for the squalene oxidation. This initiator is not a diepoxide similar to the end product of high-temperature oxidation of alloocimene (alloocimene dioxide). It is, most probably, the same polymeric peroxide species as that responsible for autocatalysis in the conjugated triene autoxidations in chlorobenzene solution.

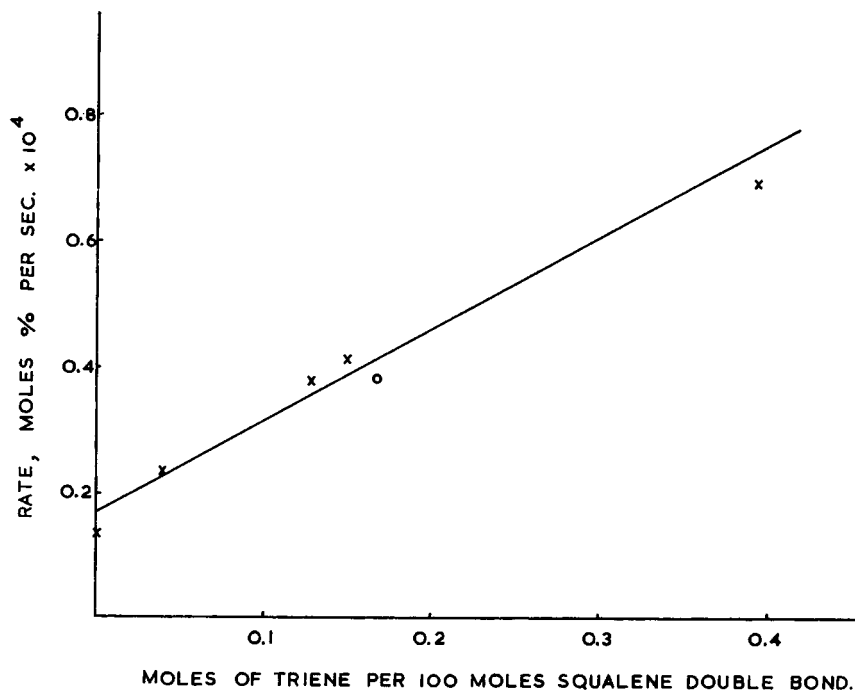


Fig. 3. Squalene oxidation rate at 25°C vs. concentration of (X) compound II and (O) pre-oxidized compound II.

Inhibited Co-oxidation of Squalene and Conjugated Triene

Co-oxidation of squalene and compound II was studied at 100°C in the presence of the efficient antioxidant *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine. The reactions showed initial autocatalysis followed by a period of constant reaction rate (Fig. 4). At higher extents of oxidation there was a decrease in rate to a second constant level. The oxidation rate over the first linear portion of the oxidation curves was directly proportional to the conjugated triene concentration (Fig. 5). Furthermore, this dependence of rate on triene concentration was very similar to that observed for the inhibited reaction, although the rates were, of course, very much slower.

The reaction rates at the later stages of reaction were much less dependent upon initial triene concentration. They were within a factor of two of the inhibited oxidation rate of squalene alone at similar extents of reaction.

The initial autocatalyses and subsequent constant reaction rate for these inhibited oxidations closely resembles the behavior of the uninhibited co-oxidations, but because of the large differences in reaction temperature and time scale for the two sets of oxidations it is doubtful whether the initiating species formed from the conjugated triene can be the same in both cases. The duration of the accelerative effect of the conjugated triene in the inhibited co-oxidations was much more limited in terms of extent of oxida-

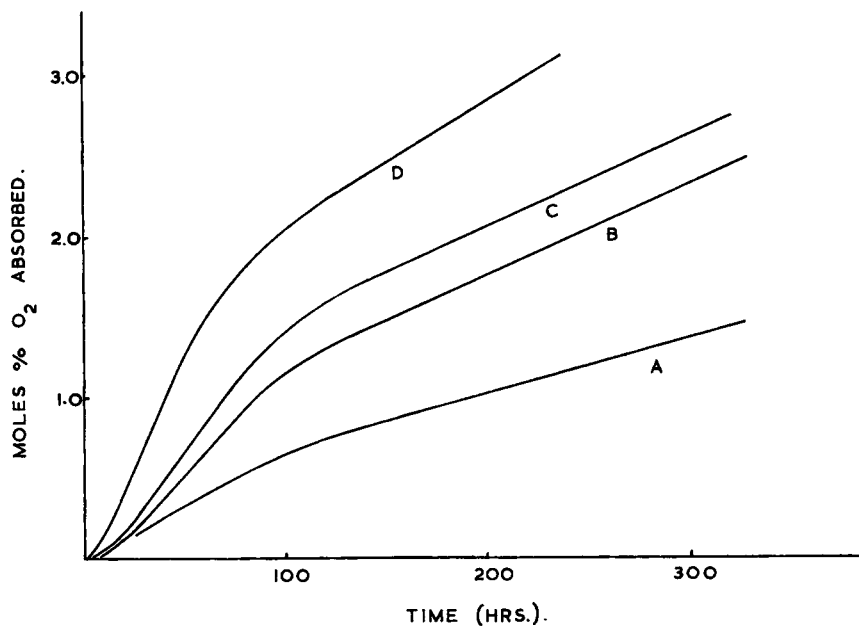


Fig. 4. Co-oxidation of squalene and compound II at 100°C, inhibited by *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine (1.00% w/w) at various concentrations of compound II: (A) 0; (B) 5.30×10^{-2} mole-%; (C) 1.52×10^{-1} mole-%; (D) 4.14×10^{-1} mole-%.

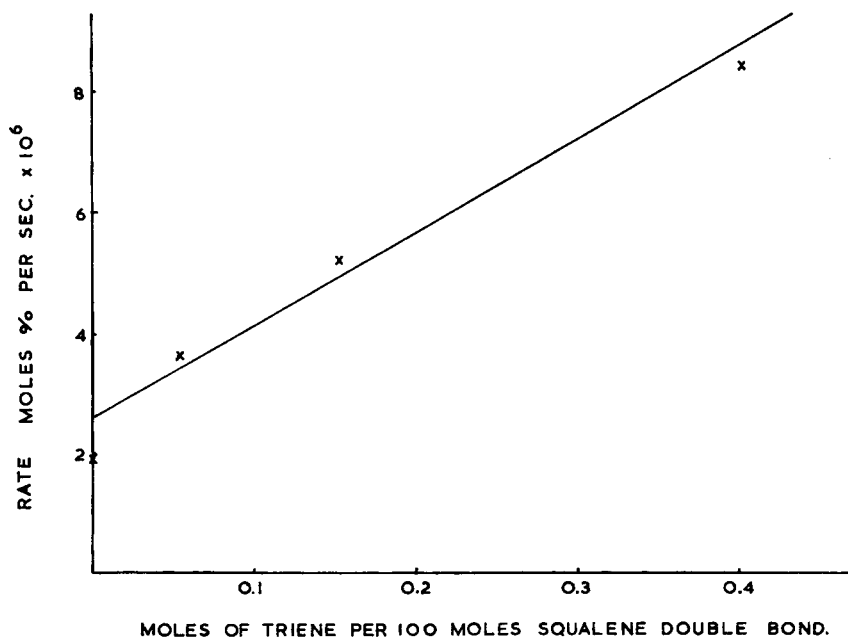


Fig. 5. Squalene oxidation rate vs. concentration of compound II for oxidations at 100°C in the presence of *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine (1.00% w/w).

tion than in the uninhibited co-oxidations. The experimental results for the inhibited co-oxidations were not sufficiently accurate to provide meaningful rate-extent curves from which information could be obtained about the initiation process.

Inhibited Co-oxidation of a Peroxide-Cured NR Network and Conjugated Triene

The oxidation of a carbon-carbon crosslinked NR network was studied in the presence of compound II and *p*-phenylenediamine inhibitor at 100°C. The oxygen uptake curves (Fig. 6) were very similar to those obtained for the inhibited co-oxidation of squalene, but the dependence of rate (over the linear portions of the curves following the initial autocatalysis) on the initial conjugated triene concentration was much less than for the squalene reactions. At the highest conjugated triene concentration used (4.92×10^{-1} mole/100 mole of olefinic double bond) the inhibited oxidation rate was only a factor of two greater than the control, whereas in the inhibited squalene co-oxidation an equivalent conjugated triene concentration increased the rate by a factor of five.

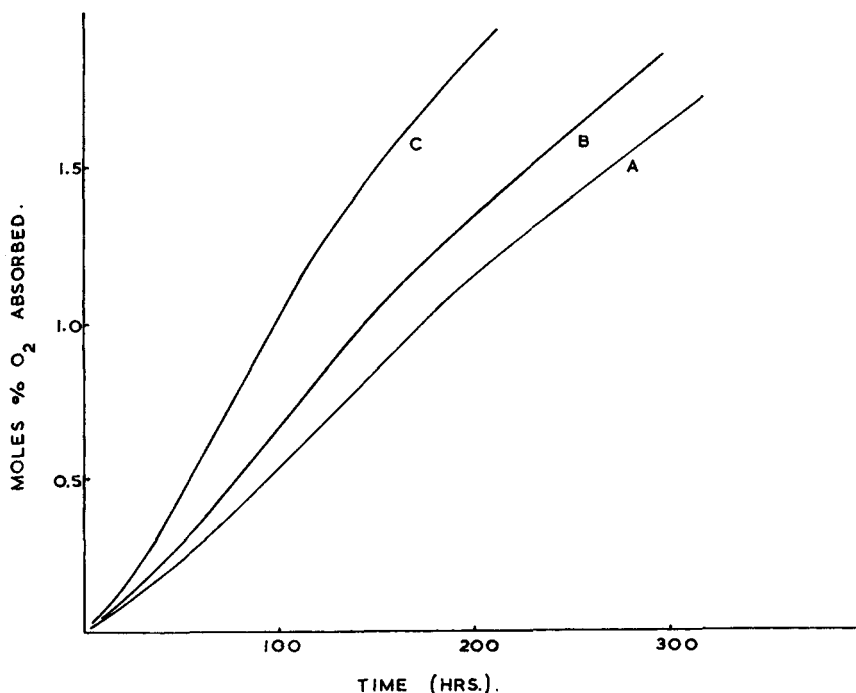


Fig. 6. Co-oxidation of peroxide-cured purified NR and compound II at 100°C in the presence of *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine (1.03% w/w) at various concentrations of compound II: (A) 0; (B) 5.75×10^{-2} mole-%; (C) 4.92×10^{-1} mole-%.

On the basis of work on the sulphuration reactions of model olefins,^{2,3} the ratio of conjugated triene units to chemical crosslinks in accelerated sulfur vulcanizates of NR may vary from 0.1:1 to 1:1 or higher, depending on the particular vulcanization system. Hence, at normal crosslinking levels (approximately 5×10^{-5} mole chemical crosslink/g rubber hydrocarbon) the triene concentration will lie within the range 0.07–0.7 mole/100 mole of olefinic double bond. The concentrations of conjugated triene used in the present work were of this order and the results for the inhibited co-oxidations of carbon-carbon crosslinked vulcanizates therefore provide a realistic picture of the contribution which the conjugated triene function makes towards the oxidative behavior of vulcanizates. Experimental difficulties in the preparation of samples prevented measurement of the uninhibited co-oxidation of a carbon-carbon crosslinked vulcanizate network and conjugated triene, but the picture is probably similar to that for the uninhibited co-oxidation of squalene.

CONCLUSIONS

The uninhibited oxidations of polyisoprenes can be markedly accelerated by the presence of conjugated trienes at concentrations comparable to those expected to be present in accelerated sulfur vulcanizates of NR. In a liquid oxidizing system (squalene) this accelerative effect is also apparent in the presence of an efficient inhibitor, but in a rubber system in the presence of inhibitor the effect, although still present, is considerably diminished. Bell and Cunneen²⁰ have discussed the inhibited and the uninhibited rates of oxidation of various sulfur vulcanizates and have shown that the uninhibited rates fall in the order of expected triene content of the networks, but in the inhibited reactions, this trend is masked by antagonistic effects of various sulfur groups on the inhibitor performance.

The effect of conjugated dienes on the oxidation of olefinic materials has not been investigated in this work. Their oxidative behavior is very similar to that of conjugated trienes,⁵ but they are somewhat less reactive. Their presence in vulcanizates can therefore be expected to have an adverse effect on oxidative behavior, but the effect is likely to be less than that of conjugated triene at the same concentration.

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