

## Radiation Crosslinking of Rubber. IV. Ultraviolet and Infrared Absorption Spectra

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No previous work has been reported on the ultraviolet absorption spectra of irradiated rubber. Infrared studies have resulted in apparently conflicting conclusions concerning decreases in unsaturation.

In the present work purified natural rubber was irradiated *in vacuo* and changes in absorption recorded over a wide range of frequencies. The results are here considered in relation to the mechanisms of formation of hydrogen and crosslinks.

### EXPERIMENTAL MATERIALS AND METHODS

A benzene solution of acetone extracted deproteinized crepe rubber (ca. 0.15% O, 0.03% N) was injected into glass rings floating on mercury. The bulk of the solvent was removed with a stream of nitrogen and in the later stages the films were exposed to an infrared lamp. Finally, the films were removed on their glass supports and degassed *in vacuo*.

Ultraviolet absorption was measured with a Hilger Uvispec Spectrophotometer and infrared spectra on a Hilger H.800 double beam spectrometer fitted with a sodium chloride prism. The films were again thoroughly degassed and sealed in glass tubes at ca.  $10^{-5}$  mm. Hg. The tubes were cooled in an air blast during exposure to an electron beam at 5 Mrad/min. from a 4 Mev linear accelerator at the Wantage Radiation Laboratory. After irradiation the spectra were again recorded.

The thickness of the films was estimated by mounting sections in plasticine and viewing their edges against the calibrated eyepiece of a microscope. A typical film had a thickness ranging from about 20  $\mu$  near the edge to about 15  $\mu$  in the center. These measurements were kindly undertaken by Mr. E. H. Andrews.

### EXPERIMENTAL RESULTS AND DISCUSSION

#### Ultraviolet Absorption—Conjugated Diene and Triene Groups

Figure 1 shows typical absorption curves before and after irradiation. The difference in absorption reveals two maxima at about 245 and 290  $m\mu$ . Both maxima increase with dose and are probably due, respectively, to conjugated diene and triene groups.

The concentration of a chromophone C, in moles per gram, has been calculated using Beer's law as

$$C = \Delta E / 1000 l e$$

where  $\Delta E$  is the observed difference in optical density,  $l$  is the thickness of the rubber in cm., and  $e$  its density (0.92). The values used for the molar extinction coefficient,  $\epsilon$ , in the case of conjugated diene, were those reported for 2,5-dimethylhexa-2,4-diene, *viz.*, 21,500 at  $\lambda_{\max.} = 242 m\mu^1$  and 22,500 at  $\lambda_{\max.} = 241 m\mu^2$ . These two values were used in conjunction with the range of values for film thick-

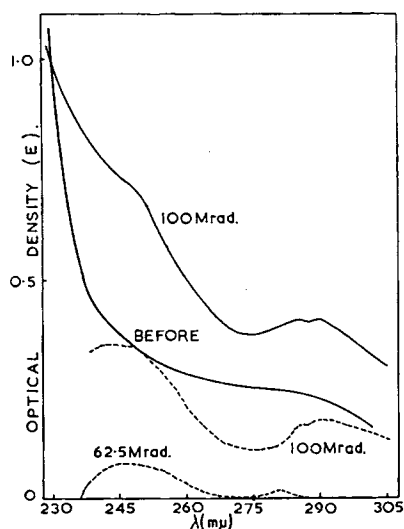


Fig. 1. Effect of irradiation on ultraviolet absorption spectra of rubber. The broken curves show the difference in absorption resulting from irradiation.

TABLE I  
Estimation of Conjugated Diene and Triene Groups

Mrad	Moles per gram of product $\times 10^6$			
	Conjugated diene	Conjugated triene	Hydrogen	Chemical crosslinks
62.5	2.1-4.2	0.3-0.6	42	85
100	8.8-12.1	2.3-3.3	67	136
175	13.2-16.4	1.7-3.4	117	238

TABLE II  
Estimation of Conjugated Triene

Dose (Mrad)	92.3	159.5	216	274	326
Moles/g. $\times 10^6$	1.7-3.0	1.6-4.1	1.6-3.0	2.2-5.8	<sup>a</sup>

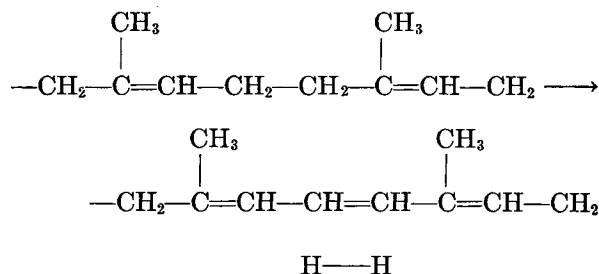
<sup>a</sup> Absorbed too strongly to measure.

ness,  $l$ , to calculate upper and lower limits for the concentration of conjugated diene groups formed on irradiation. Similar limits were calculated for conjugated triene groups using  $\epsilon$  values for 2,6-dimethylocta-2,4,6-triene<sup>3</sup> of 39,900 at  $\lambda_{\max.} = 278$   $m\mu$  (*trans* C<sub>4</sub>-*trans* C<sub>6</sub>) and of 42,900 at  $\lambda_{\max.} = 273$   $m\mu$  (*trans* C<sub>4</sub>-*cis* C<sub>6</sub>). These values of  $\epsilon$  were used in the absence of more pertinent values for the various possible conjugated chromophores in rubber hydrocarbon itself which, however, are unlikely to differ by more than 10% from the above values.

Results are given in Table I together with the yields of hydrogen and chemical crosslinks which were calculated from the dose and values of  $G(H_2) = 0.64$  and  $G(X, \text{chem.}) = 1.3$ .<sup>4</sup> In a second series of exposures rather thicker films (30-70  $\mu$ ) were cast primarily for infrared examination. These absorbed too strongly to provide data on conjugated diene but gave the further estimates of conjugated triene groups shown in Table II.

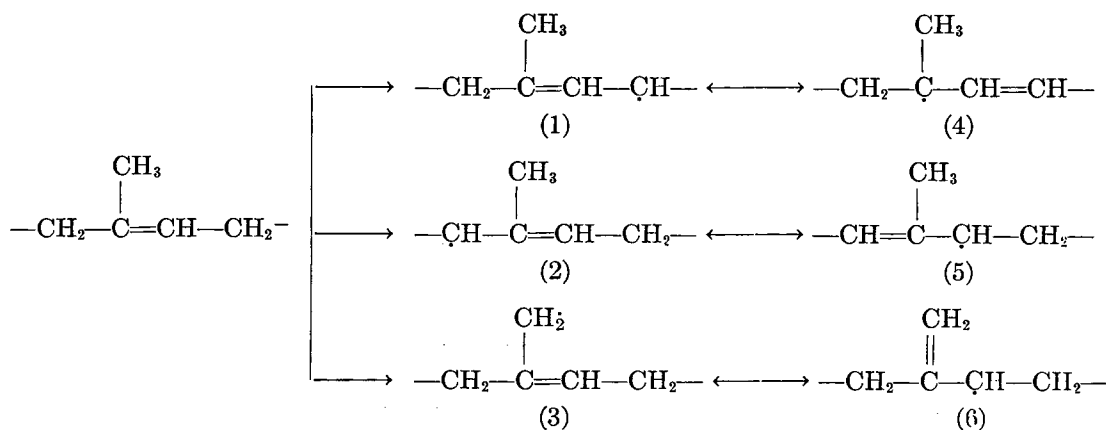
The yield of triene groups is of importance in relation to the mechanism of hydrogen formation and

its correlation with crosslink formation. For example, in the radiation crosslinking of polyethylene about 40% of the hydrogen is reported to be accounted for by formation of *trans*-vinylene unsaturation.<sup>5</sup> This "molecular" elimination would have no concomitant crosslinking potential such as would be the case when hydrogen is formed as a result of the elimination of hydrogen atoms. In the case of rubber hydrocarbon molecular elimination of hydrogen would presumably result in the formation of a conjugated triene, *viz.*:



Even if all the conjugated triene detected is formed by this reaction, it would only account for from 0.7-3.5% of the yield of hydrogen (calculated from Table I). As will be discussed later, conjugated triene is likely to be formed by another reaction and therefore it can be concluded that the above mechanism of hydrogen formation is of negligible importance. It is worth noting that, similarly, hydrogen atoms are regarded as precursors of hydrogen molecules in the photolysis of olefins which contain  $\alpha$ -methylene hydrogen atoms.

The formation of conjugated groups is also of considerable importance because of its implication that disproportionation of allylic radicals occurs as well as their combination with crosslink formation. Hydrogen abstraction from rubber hydrocarbon can lead to three mesomeric radicals<sup>6</sup>



It can be seen that disproportionation reactions involving the structures marked as (4), (5), and (6) would result in the formation of conjugated diene while, similarly, structures (1) and (2) would lead to conjugated triene. An estimate of the percentage of allylic radicals which disproportionate can be obtained from the expression

$$\frac{100 ([\text{diene}] + [\text{triene}])}{[\text{diene}] + [\text{triene}] + [\text{crosslinks}]}$$

On this basis only 2.5–10% of the allylic radicals disproportionate. As a chain fracture reaction is a further possible source of conjugated diene groups, it may be concluded that wastage of the crosslinking potential of allylic radicals by disproportionation is relatively unimportant.

### Infrared Absorption

Infrared studies have proved helpful in considerations of the radiation crosslinking of polyethylene. In particular, small changes of unsaturation show

et al.<sup>7</sup> that a sulfur-based vulcanizate on irradiation in nitrogen showed a decrease in trialkyl ethylene unsaturation of approximately 2% after a dose of about 100 Mrad and of approximately 15% after about 1000 Mrad. This was estimated by reference to absorption at 830  $\text{cm}^{-1}$ . Completely different results were reported by Dogadkin et al.<sup>8</sup> for an acetone-extracted butadiene–styrene copolymer (SKS-30) which was irradiated in air. Infrared absorption spectra were interpreted to indicate practically complete disappearance of unsaturation after a dose of about 55 Mrad.

Independently, Kuzminsky et al.<sup>9</sup> reported similar results for various elastomers, and in the case of an unpurified natural rubber (smoked sheet) claimed a decrease of unsaturation of 50% after a dose of about 220 Mrad. The reported data was obtained chemically by titration with iodine monobromide and apparently checked by infrared studies, although, unfortunately, no experimental results were presented. Of course, in all these studies there is the possible complication of radiation-

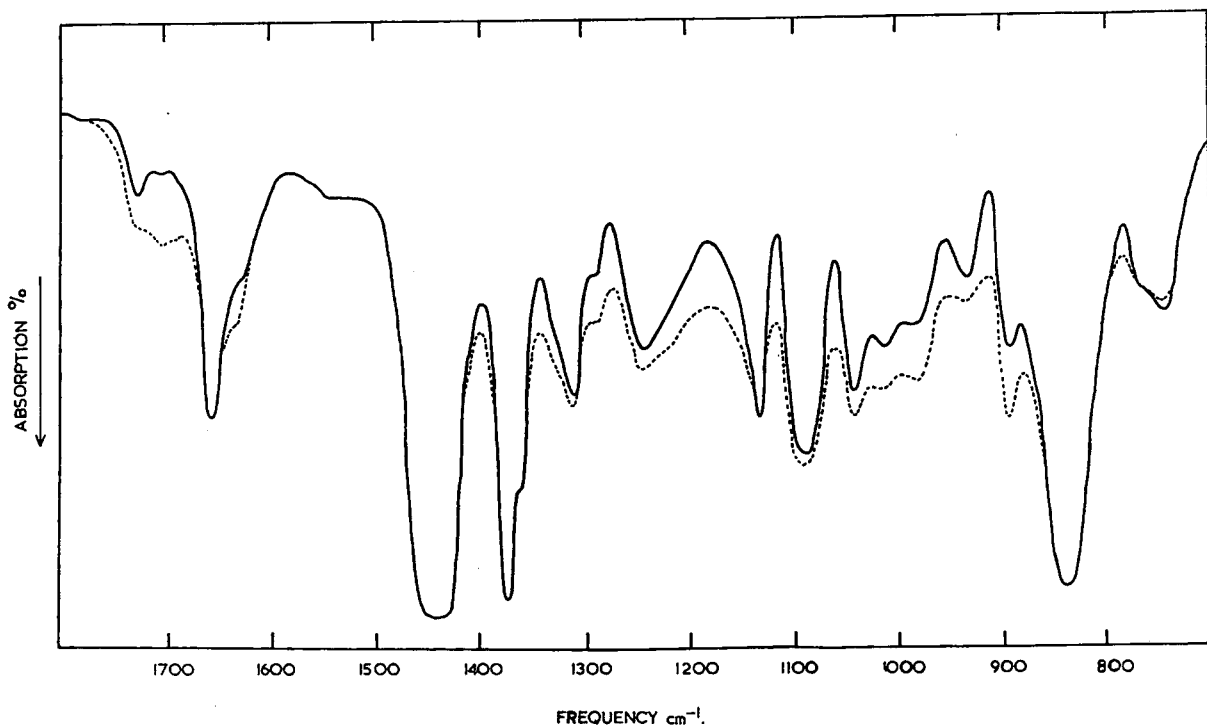


Fig. 2. Effect of irradiation on infrared absorption spectra of rubber. Full curve: before irradiation. Broken curve: after a dose of 326 Mrad.

up well against the background of saturated hydrocarbon, but in the case of natural rubber changes of similar magnitude would be more difficult to detect. Nevertheless, it has been reported by Loughborough

induced oxidation, but the latter authors also reported an even greater consumption of double bonds when a polybutadiene was irradiated *in vacuo*. The data obtained in the present experiments does not

justify quantitative conclusions on account of the observed variations in film thickness and the difficulty of examining the same area before and after irradiation. However, it can be seen from Figure 2 that any changes in absorption at the frequencies 830 and 1655  $\text{cm.}^{-1}$ , which are characteristic of the  $\text{R}_2\text{C}=\text{CHR}$  group, are not great and therefore there is qualitative agreement with the results of Loughborough et al. rather than with the extensive decrease of unsaturation suggested by the work of Kuzminsky et al. The present data is certainly not suitable for estimating any small changes in unsaturation incidental to the crosslinking reaction because even after a dose of 326 Mrad only about 6% of the isoprene units are crosslinked. Nor would it be justifiable to comment on the general possibility, suggested by Moore and Watson,<sup>6</sup> that some decrease in unsaturation may occur due to radical cyclization reactions.

The observation that the intensity of a band at 890  $\text{cm.}^{-1}$  increased on irradiation, coupled with the appearance of a shoulder near 1645  $\text{cm.}^{-1}$ , indicates a slight increase of vinylidene unsaturation. This might be anticipated in view of the proposed participation of the radical structure previously marked as (6). The reverse effect has been observed on irradiation of polyethylene in that initial vinylidene unsaturation rapidly disappears.<sup>5</sup>

Slight changes in the infrared spectra between 1100 and 1300  $\text{cm.}^{-1}$  may indicate some *cis-trans* isomerization.<sup>10</sup> Charlesby<sup>11</sup> has reported that both *cis* and *trans* isomers of various octadecenes gave a mixture which contained 35% *trans* after a dose of about 450 Mrad in an atomic pile, there being little change in total unsaturation. Specification of the temperature of irradiation may be important in these experiments on account of the temperature dependence of radical catalyzed *cis-trans* isomerization. The temperature in the present experiments was probably about 40°C. but unfortunately the temperature for the pile irradiations was not reported. It should be noted that any change in the *cis-trans* ratio would affect absorption at about 830  $\text{cm.}^{-1}$  and would need to be taken into account in estimates of  $\text{R}_2\text{C}=\text{CHR}$ .

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## Synopsis

When purified rubber is exposed *in vacuo* to high energy radiation, very few conjugated triene groups are formed relative to the number of molecules of hydrogen evolved. This indicates that less than 4% of the hydrogen is evolved from adjacent carbon atoms in the same molecule, a reaction which would have no immediate crosslinking potential. Rather more conjugated diene groups have been detected, but when these are compared together with triene groups relative to the yield of chemical crosslinks it can be calculated that less than 10% of the allylic radical precursors disproportionate. Infrared absorption spectra do not indicate the marked decrease in unsaturation reported by some previous workers. Slight changes in the infrared spectra may indicate some *cis-trans* isomerization. There is qualitative evidence for a small increase in vinylidene unsaturation.

## Résumé

Quand le caoutchouc purifié est exposé sous vide à une radiation d'énergie élevée il se forme très peu de groupes triéniques conjugués si on les compare au nombre de molécules d'hydrogène dégagé. Ceci indique que moins de 4% de l'hydrogène est dégagé au départ des atomes de carbone voisins dans une même molécule, réaction qui ne présentait pas de potentiel de pontage immédiat. On a trouvé des groupes diéniques plus nombreux; toutefois quand ceux-ci sont comparés ensemble avec les groupes triéniques au taux de pontage, on peut calculer que moins de 10% des radicaux allyliques précurseurs disproportionnent. Les spectres d'absorption infra-rouge n'indique pas de diminution notable de l'insaturation signalée par quelques chercheurs précédents. De faibles changements dans les spectres infrarouges pouvant indiquer quelque isomérisation *cis-*

*trans.* Il y a une évidence qualitative d'une faible augmentation d'insaturation vinyliénique.

### Zusammenfassung

Bei der Einwirkung hochenergetischer Strahlung auf gereinigten Kautschuk im Vakuum werden in Verhältnis zur Anzahl der entwickelten Wasserstoffmoleküle nur sehr wenige konjugierte Triengruppen gebildet. Das spricht dafür, dass weniger als 4% des Wasserstoffs von benachbarten Kohlenstoffatomen im gleichen Molekül abgespalten wird, bei welcher Reaktion keine unmittelbare Möglichkeit zur Vernetzung bestünde. Dagegen wurden mehr kon-

jugierte Diengruppen gefunden; aus dem Verhältnis dieser Gruppen, zusammen mit den Triengruppen, zu den gebildeten chemischen Vernetzungsstellen kann man jedoch berechnen, dass weniger als 10% der primär gebildeten Radikale vom Allyltyp disproportionieren. Die Infrarotabsorptionsspektren lassen keine so ausgeprägte Abnahme des ungesättigten Charakters erkennen, wie sie von einigen Autoren früher berichtet wurde. Schwache Änderungen der Infrarotspektren sprechen für eine gewisse *cis-trans*-Isomerisierung. Es bestehen qualitative Hinweise auf eine kleine Zunahme an Vinylidengruppen.

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