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Photo-controlled Degradation of Natural Rubber

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The chain cleavage mechanisms during hydrogen peroxide catalysed photo-oxidative degradation of high molecular weight natural rubber, which was described as producing liquid natural rubber is elucidated. NR is photolysed in toluene solution (2.5 wt.%) in a photoreactor at 30°C under atmospheric air and nitrogen, separately, with a 400 W medium pressure mercury vapour lamp ($\lambda = \geq 290$ nm) with constant stirring in the presence of hydrogen peroxide and/or titanium dioxide. The decrease in viscosity-average molecular weight ($\overline{M}_v$) was determined by viscosity measurements. The photoproducts were characterised by FT-IR, ^1H and ^{13}C NMR spectroscopies. Burfield's and the present results gave indication for chain cleavages resulting from the classical free-radical oxidation process rather than a direct reaction of hydroxy radical at the methylene-methylene bond. The hydrogen peroxide and/or allylic hydroperoxides act as photoinitiator by producing hydroxy radicals and/or alkoxy radicals. Moreover, the concomitant addition of $^1O_2$ (singlet oxygen) via *the well known 'ene' reaction producing hydroperoxides, can not be neglected.*

Reactive oligomers such as terminally functionalised (telechelic) oligomers and macromonomers are attracting interests as intermediates for use in various fields, *viz.* surface coatings, adhesives, reactive injection moulding and synthesis of speciality block and graft copolymers. Numerous investigations have been carried out for the synthesis of telechelic polymers using polymerisation methods. They are also prepared by the cleavage of macromolecular chains of high molecular weight polymers using the well known conventional methods. In recent years, an effective alternative method for the production of telechelic oligomers from high molecular weight polymers has been investigated. Besides, the cleavage of macromolecular chain using specific reactions such as ozonolysis or metathesis[1–3], competition between the control of chain cleavage and/or crosslinking during oxidative degradation was considered[3,4]. Although there are few reported investigations, still the latter method (cleavage of macromolecular chain) *(Scheme I)* was rather explored especially for the control of phenylhydrazine-accelerated thermo-oxidation[5,6] and hydrogen peroxide catalysed photo-oxidation[5–9] of NR with the aim of production of ketone-terminated and hydroxy-terminated telechelic liquid natural rubbers (LNRs), respectively.

In the first method, the improvement in chain cleavage by phenylhydrazine acceleration was explained by the phenyl radical initiation producing phenyl-ketone and methyl-

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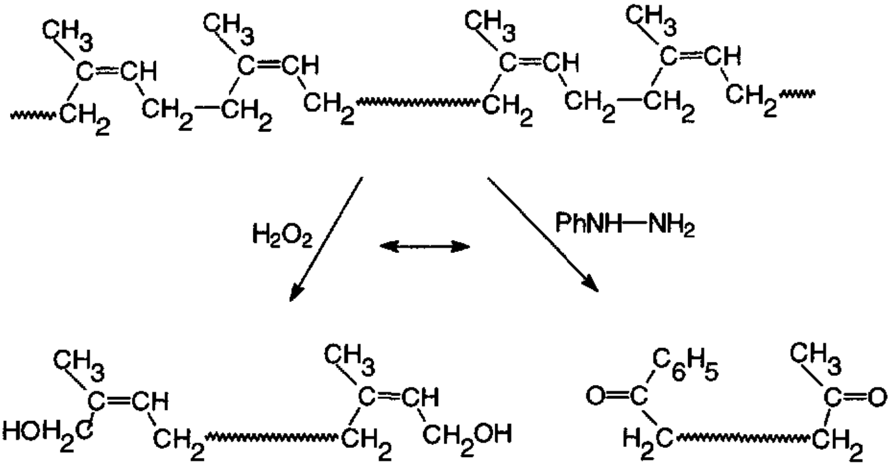


Scheme 1. Photo-oxidation of natural rubber.

ketone chain ends. In the second method, the role of hydrogen peroxide is to generate hydroxy radicals (˙OH) to produce hydroxy-chain ends, but the addition of titanium dioxide (TiO_2) is a new approach in the chain cleavage of NR in the solution. The TiO_2 catalysed photo-oxidation generates hydroxy radicals[8] on its surface which produces hydroxy-terminated end groups. The present work describes some results for photo-oxidative degradation of NR using different systems H_2O_2/THF, TiO_2 and H_2O_2/TiO_2/THF under air and nitrogen using toluene as a solvent.

EXPERIMENTAL

Materials

Natural rubber (NR) ($\overline{M}_v = 2.82 \times 10^5$) was supplied through the courtesy of Dr. S. Thomas, M.G. University, Kottayam, Kerala. H_2O_2 (30 wt%) and TiO_2 (anatase) were supplied by M/s. S.D. Fine Chemicals Ltd. Toluene, acetone and tetrahydrofuran were of reagent grades and used after distillation.

Photo – controlled Oxidation

A 2.5 wt% solution (105 ml) of purified NR was prepared in toluene. The homogeneous NR solution was photolysed in a closed photoreactor (Pyrex glass) under air and nitrogen atmosphere, separately, under constant and efficient stirring (600 r.p.m.) with the help of 400 W medium pressure mercury vapour lamp. The temperature was kept at 30 ± 1°C by a circulating water bath. Aliquots were withdrawn at different time intervals and the rubber precipitated with acetone and dried under vacuum. For photo-controlled degradation, three different experiments were carried out by taking NR solution with H_2O_2 (5 ml) [I], 1w/v % TiO_2 [II] or H_2O_2 (5 ml) + 1 w/v% TiO_2 [III], respectively. When H_2O_2 was present, 25 ml THF was also added to homogenize the solution.

Spectral Analysis

FT-IR spectra were acquired from thin films obtained by evaporating 1.0 wt% solution of the oxidised rubber, which was dried to constant weight, with PERKIN-ELMER 16 PC spectrophotometer at room temperature. ^1H and ^{13}C NMR spectra were recorded using Bruker AC 200 and 300 spectrometers (time acquisition: 22.048 sec., temperature: 24°C, number of transient: 512 *etc.*) operating at 200 MHz and 300 MHz, respectively. $CDCl_3$ (Aldrich 99.8% D) was used as solvent.

Molecular Weight Determination

Viscosity-average molecular weights ($\overline{M}_v$) of controlled and oxidised rubbers were determined in dried toluene (0.016 wt%) at 25 ± 0.1°C using an Ubbelohde viscometer and the Mark-Houwink-Sakurada equation:

$$[\eta] = K.\,\overline{M}_v^{\,a} \qquad \ldots 1$$

where

$K = 5 \times 10^{-4}$ and $a = 0.667$

RESULTS AND DISCUSSION

Viscosity-average molecular weights were determined at different intervals of irradiation time for the control, H_2O_2/ THF, TiO_2 and combination of H_2O_2 and TiO_2 / THF systems *(Table 1)*.

TABLE 1. DEPENDENCE OF MOLECULAR WEIGHT ON IRRADIATION TIME

Serial No.	System	Time (h)	In air	In nitrogen
1	NR (control)	0	2.82×10^5	2.82×10^5
		12	1.13×10^5	1.23×10^5
		36	8.40×10^3	9.90×10^3
		63	7.20×10^3	7.95×10^3
		93	–	3.97×10^3
2	NR with H_2O_2/THF	12	2.40×10^4	1.10×10^5
		24	1.11×10^4	8.74×10^3
		36	1.11×10^3	6.30×10^3
		63	1.00×10^3	3.40×10^3
3	NR with TiO_2/THF	12	2.60×10^5	7.40×10^4
		36	2.23×10^3	3.90×10^3
		63	1.64×10^3	–
4	NR with combination of H_2O_2 and TiO_2	12	2.30×10^4	2.40×10^4
		36	1.00×10^3	6.10×10^3
		63	0.79×10^3	3.20×10^3

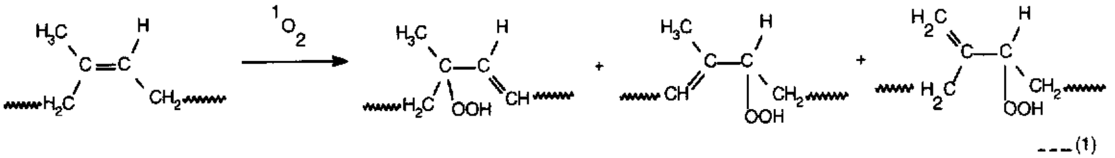
We observed a continuous decrease in $\overline{M}_v$ with irradiation time. It decreased faster under air than under nitrogen. On longer time of irradiation (beyond 63 h), slight crosslinking was observed in air while no crosslinking was observed in nitrogen atmosphere. The corresponding values of $\overline{M}v$ under air (63 h) and under nitrogen (93 h) were found to be 7.20×10^3 and 3.97×10^3, respectively. These values suggest that photo-oxidation is faster in the presence of air and in the I-system (*i.e.* H_2O_2/ THF).

H_2O_2 generates hydroxy radicals upon U.V. irradiation. The hydroxy (3600 cm^{-1} – 3200 cm^{-1}) and carbonyl (1850 cm^{-1} – 1550 cm^{-1}) peaks, in FT-IR spectra (*Figures 1* and *2*), are formed during the depolymerisation process by oxidative cleavage of the rubber molecules. Upon addition of H_2O_2 in NR solution, FT-IR spectra showed the gradual increase in the peak intensity in the hydroxy region with irradiation time. A broad band with a maximum of 3280 cm^{-1} and a shoulder at 3450 cm^{-1} appeared during U.V. irradiation. After 63 h of irradiation, decrease in the peak of hydroxy group is observed which may be due to the simultaneous generation of carbonyl groups and /or crosslinking. A low intensity peak at 1730 cm^{-1} is observed upon 12 h of U.V. irradiation *(Figure 1B)* and it increases slightly on further irradiation. In *Figure 2D*, a broad hump appeared which may be due to adventitious oxidation during isolation of the product.

In nitrogen atmosphere, there is a gradual, but less intense, broad hydroxy region which increases upto 36 h and then decreases, which may be due to the formation of epoxy group in the oxidative degraded polymer chain (*Figures 3* and *4*). No changes were observed in the carbonyl region.

These results are quite similar to those previously observed in the photo-oxidation of rubber in the presence of oxygen in which allylic hydroperoxides[11] (3400 cm^{-1}), which are generated due to singlet oxygen reaction according to the 'ene' reaction mechanism but no evidence of carbonyl absorption *(Scheme 2)*.

In this context, the chain cleavages would be the result of hydroperoxide decomposition through O-O photolysis[12,13] and fragmentation of the resulting alkoxy radicals. However, the classical auto-oxidation involving both alkoxy and hydroxy radicals initiating species would concomitantly occur to produce allylic hydroxy and carbonyl species. In fact, these hydroperoxides would act as photoinitiators. Due to the relative importance of the oxidation by this process, it was not possible to discriminate the eventual terminating –OH groups resulting from the H_2O_2 as a photo-catalysis.

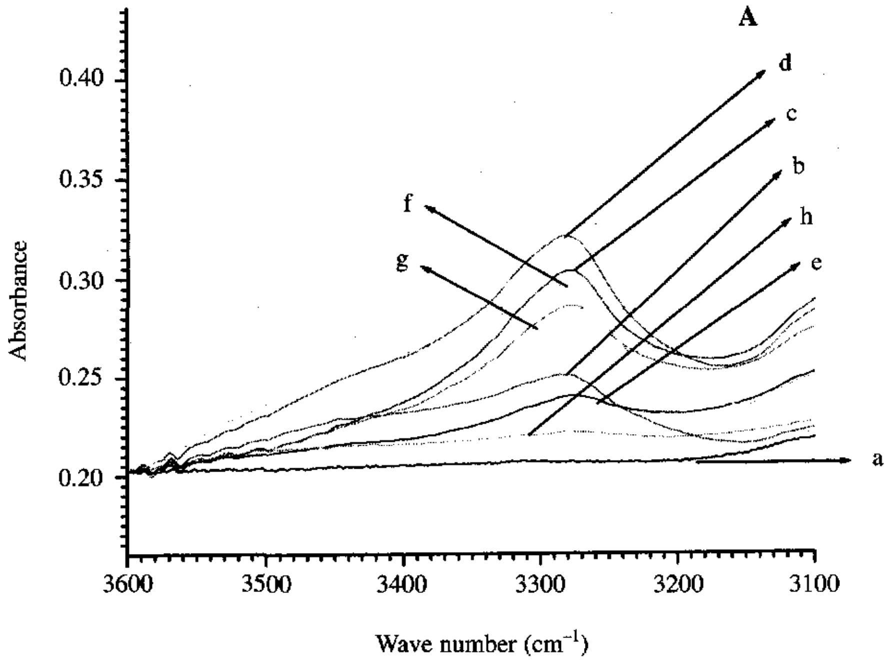


---(1)

A **B** **C**

with possible Z (*cis*) or E (*trans*) configuration

Scheme 2



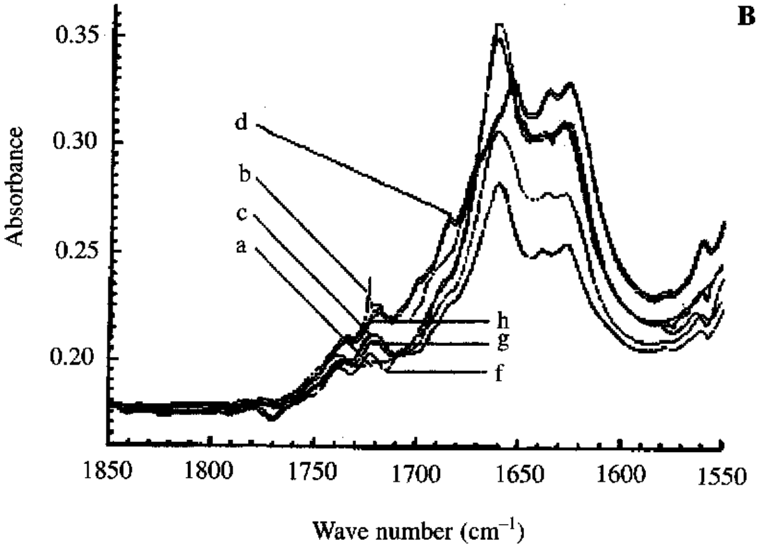


Figure 1. FT-IR spectral changes in the (A) hydroxy and (B) {except e} carbonyl regions of U.V. irradiated natural rubber in presence of hydrogen peroxide [I]: a: control; b: 12 h; c: 48 h; d: 63 h; e: 78 h; and titanium dioxide [II]: f: 12 h; g: 48 h; h: 63 h.

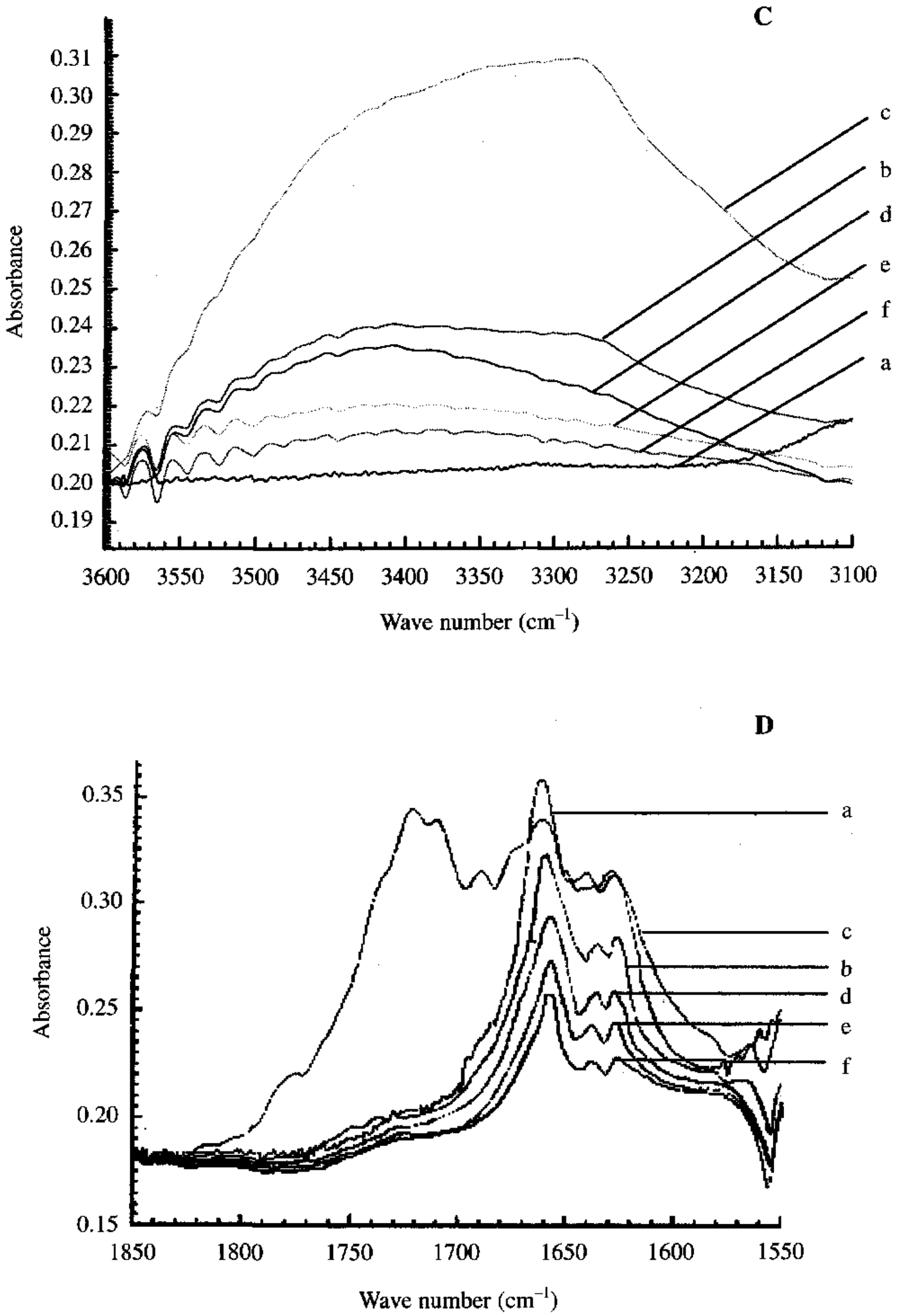
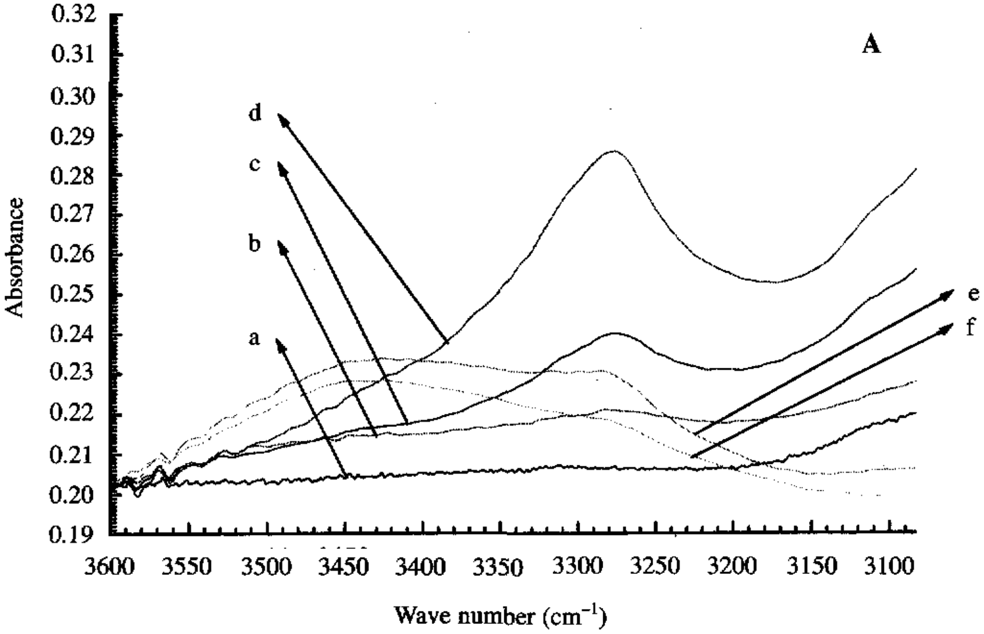


Figure 2. FT-IR spectral changes in the (C) hydroxy and (D) carbonyl regions of U.V. irradiated natural rubber in presence of combination of hydrogen peroxide and titanium dioxide [III]: a: control; b: 12 h; c: 24 h; d: 36 h; e: 48 h; f: 63 h.



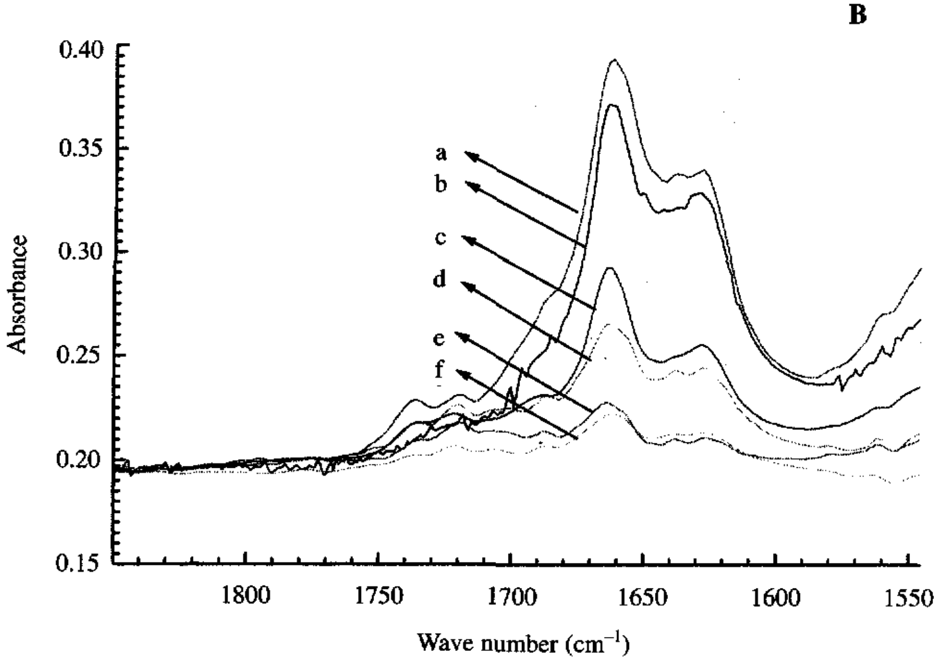


Figure 3. FT-IR spectral changes in the (A) hydroxy and (B) carbonyl regions of U.V. irradiated natural rubber in presence of hydrogen peroxide (under nitrogen atmosphere): a: control; b: 12 h; c: 24 h; d: 36 h; e: 48 h and f: 63 h.

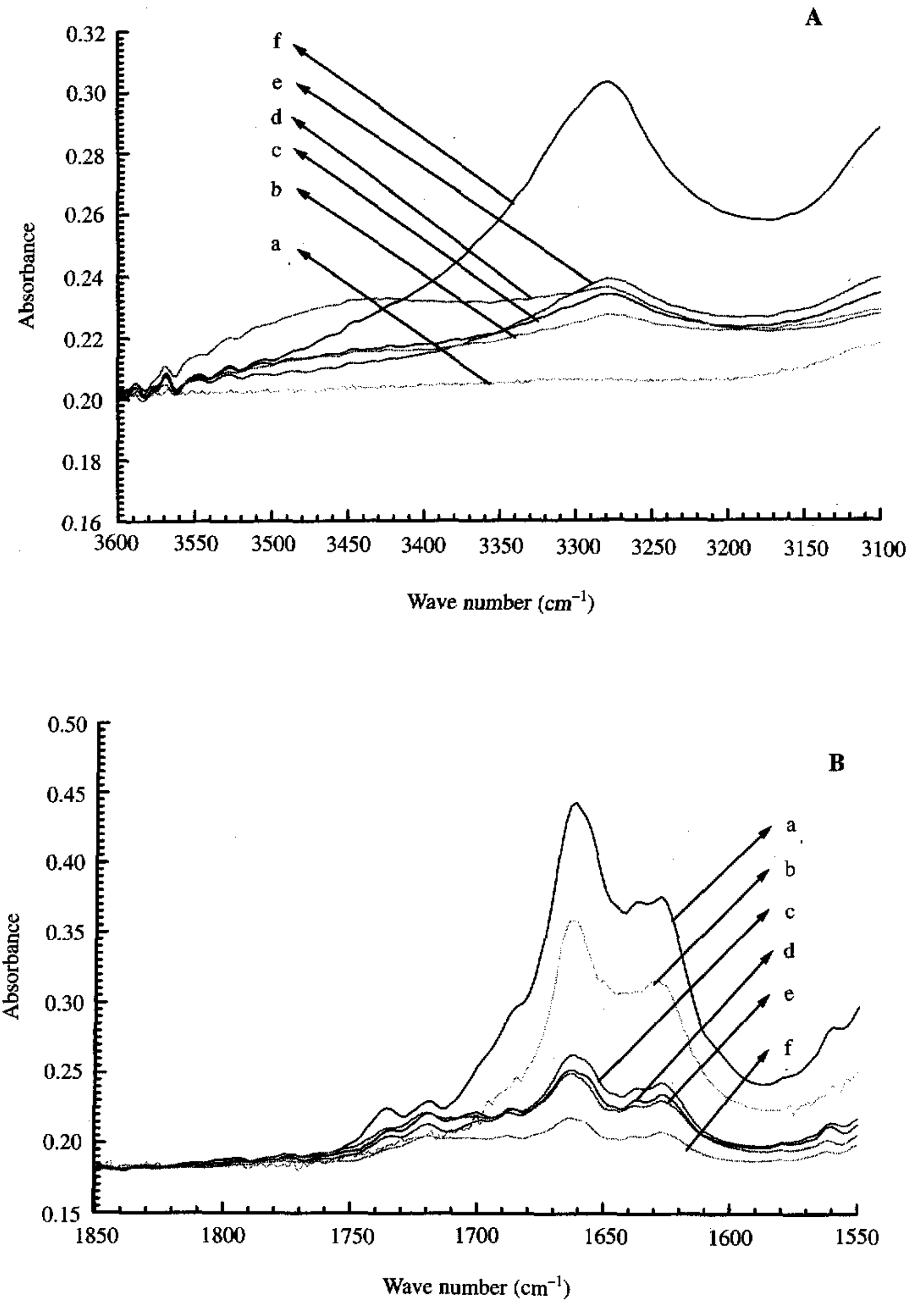


Figure 4. FT-IR spectral changes in the (A) hydroxy and (B) carbonyl regions of U.V. irradiated natural rubber in presence of combination of hydrogen peroxide and titanium dioxide (under nitrogen atmospehere): a: control; b: 12 h; c: 24 h; d: 36 h; e: 48 h and f: 63 h.

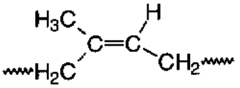
In case of NR solution in II-system, the hydroperoxide accumulates up to 12 h *(Figure 1)* and after that there is the fast decomposition (63 h) due to photocatalytic[14,15] effect of TiO_2. The absorbed U.V. radiation below 370 nm releases electrons and positive holes in the TiO_2 crystals, some of which diffuse into the surface, resulting in the production of free radicals, which can attack the polymer causing the classical oxidative degradation. In this case, the carbonyl peak (1730 cm^{-1}) is maximum due to the fast decomposition of hydroperoxides on longer irradiation (63 h). Under nitrogen atmosphere, we observed continuous increase in hydroxy region *(Figure 5)*, which may be due to the accumulation of hydroxy groups onto TiO_2 surface (due to the screening effect of the pigment)[15] as they are not decomposed due to lack of free hydroxy groups formed in the presence of air.

In case of combined effects of TiO_2 (1% w/v) and H_2O_2 *(Figure 2)*, in system-III the hydroperoxides accumulate up to 24 h due to simultaneous catalysis of H_2O_2 and after that similarly, the fast decomposition was observed. The broad hydroxy region increases (under nitrogen) with irradiation time. A broad band with a maximum at 3280 cm^{-1} and a shoulder at 3448 cm^{-1} *(Figure 4)* appears during U.V. irradiation. There is no change in the carbonyl region, only the peak at 1660 cm^{-1} decreases gradually with irradiation time.

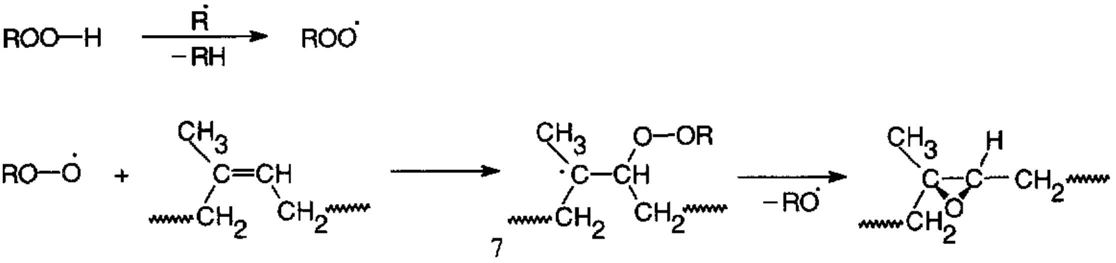
We must notice that the free radical mechanism occurrence makes possible the double bond epoxidation by addition of peroxy radical and elimination of alkoxy radical[5,6,9] *(Scheme 3)*.

The previous detection of epoxidised units in H_2O_2-catalysed photo-degradation of liquid natural rubber[9] is a supplementary argument for a photoinitiated radical oxidation process.

In each case, ^1H and ^{13}C NMR spectra presented preponderantly the *cis* 1,4-polyisoprene signals. The ^1H NMR (*Figures 6, 7* and *8*) and ^{13}C NMR spectra in $CDCl_3$ at 24°C lead further support to the above conclusion. ^1H NMR δ = 1.63 p.p.m. ($-CH_3$, 3 H); δ = 2.05 p.p.m. ($-CH_2-C=C$, 4 H); δ = 5.1 p.p.m



.The signal due to hydroxy proton in the hydroxymethyl group is observed at ~ 4.15 p.p.m.[16], but in our studies this peak is quite clear at 3.5 p.p.m. – 4.0 p.p.m. under air as well as nitrogen atmosphere. In addition to that, two more signals are observed at 1.27 p.p.m. and 2.70 p.p.m, after 48 h exposure (nitrogen), denoting *trans* and *cis*



cis and *trans*

Scheme 3

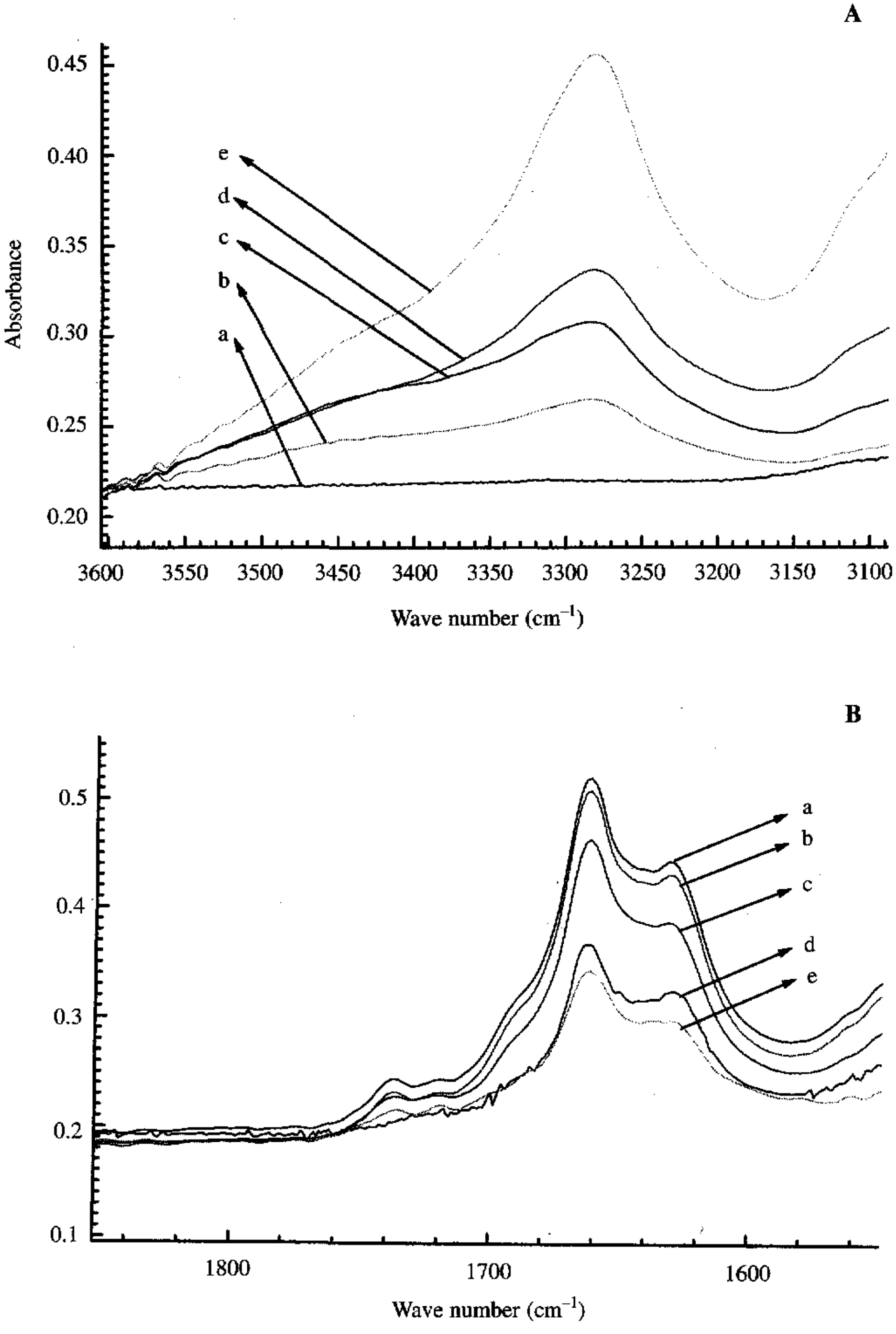


Figure 5. FT-IR spectral changes in the (A) hydroxy and (B) carbonyl region of U.V. irradiated natural rubber in presence of titanium dioxide (under nitrogen atmosphere):
a: control; b: 12 h; c: 36 h; d: 48 h and e: 63 h.

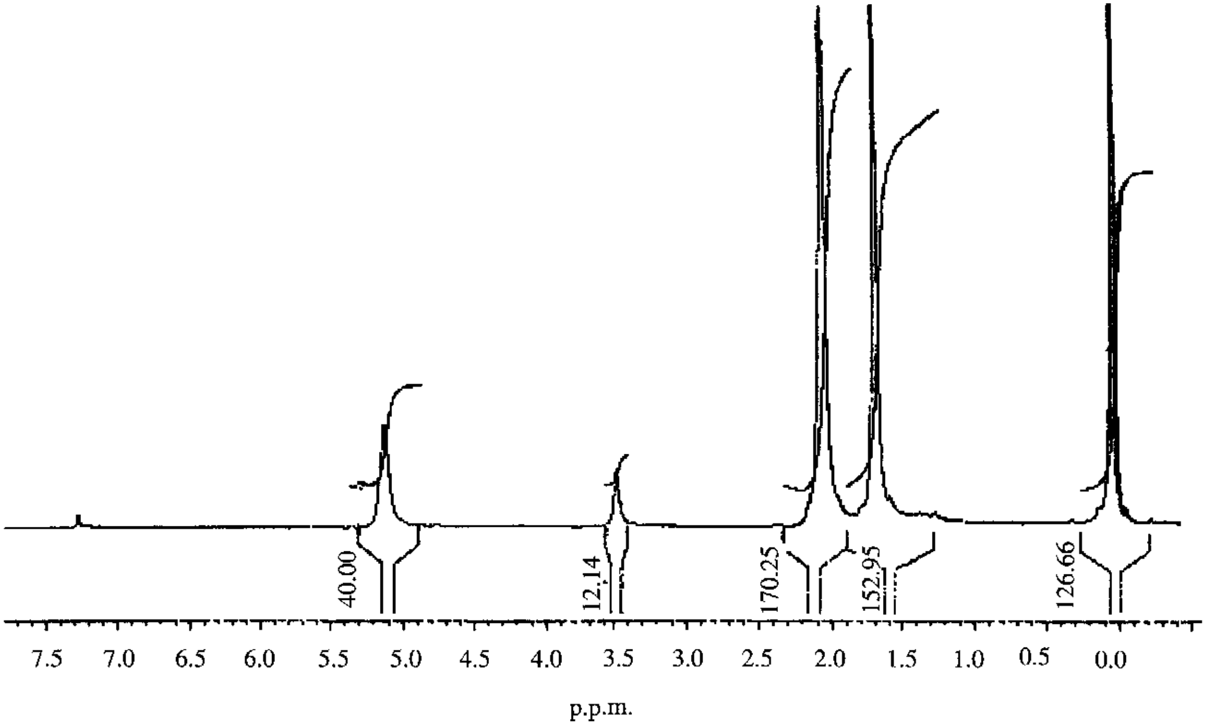


Figure 6. ^1H NMR spectrum of degraded natural rubber after 18 h U.V. exposure (under air) in $CDCl_3$ solution.

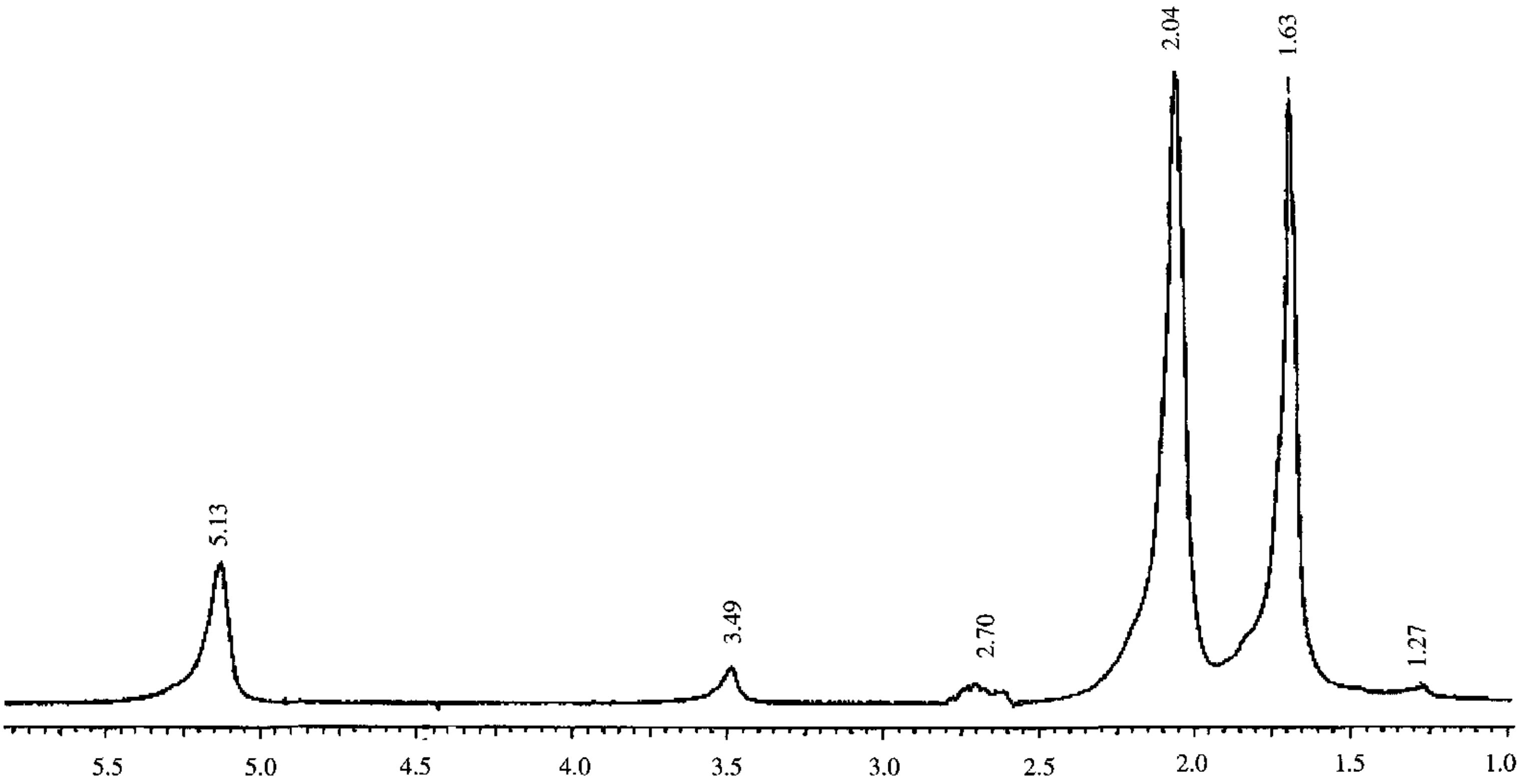


Figure 7. ^{1}H NMR spectrum of degraded natural rubber after 48 h U.V. exposure (under nitrogen) in $CDCl_3$ solution.

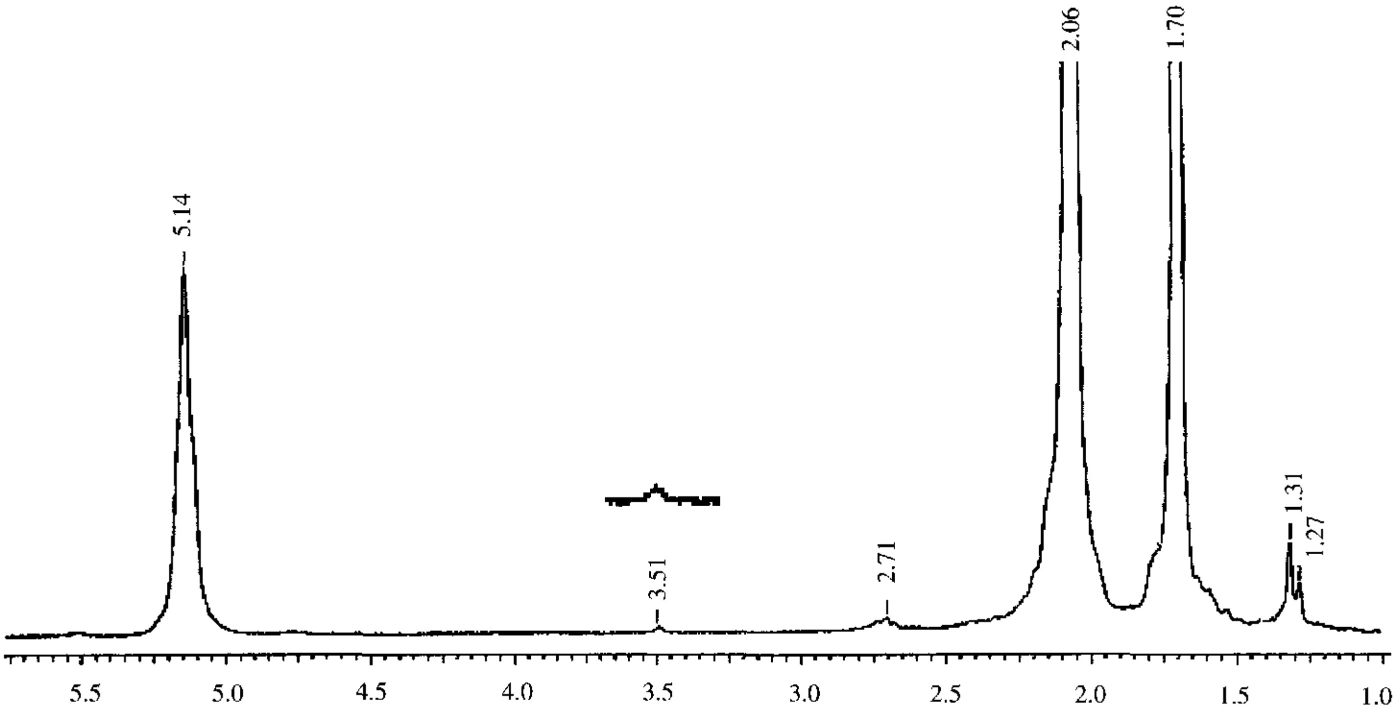
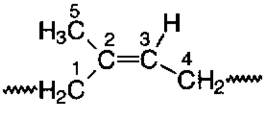


Figure 8. ^1H NMR spectrum of degraded natural rubber after 63 h U V. exposure (under nitrogen) in $CDCl_3$ solution.

epoxides[9], respectively *(Figure 7)* and the intensity of signals increase with irradiation time *(Figure 8)*. The signal at 1.30 p.p.m. increases with irradiation time which is assumed due to some impurities.

The ^{13}C NMR spectra indicate ^{13}C shieldings typical of *cis*-1,4-polyisoprene at the following positions: C^1 $\delta = 32.19$, C^2 $\delta = 135.10$, C^3 $\delta = 125.03$, C^4 $\delta = 26.38$ and C^5 $\delta = 23.27$



We have also noticed the appearance of a small signal at 27.09 p.p.m. *(Figure 9)* upon irradiation for 36 h with combined effect of TiO_2 (1% w/v) and H_2O_2. This mild peak besides the sharp signal of allylic methylene at 26.4 p.p.m. could be due to a small amount of *trans* 1,4- isoprene units. Two signals were observed after 48 h in the case of the combination of H_2O_2 and TiO_2 (nitrogen) at 64.40 p.p.m. and 60.76 p.p.m. *(Figure 10)*, due to partially epoxidised NR.

The peaks at $\delta = 63.49$ (air)[7,8] after 18 h *(Figure 11)* and $\delta = 63.48$ (nitrogen) after 24 h *(Figure 12)* are quite evident which are due to α -carbons (allylic-1 alcohol) attached to the hydroxy groups and hence can correspond to an α-hydroxymethyl group/hydroxy terminated functional groups.

In all the earlier schemes, a free-radical mechanism has been suggested for the degradation of NR. These free radicals interact with the labile α- C-H bond, abstracting the proton and leaving macroradicals behind. The peroxides are formed by the interaction of these radicals with O_2 and decomposed to yield various degradation products containing hydroxy, carbonyl and carboxy groups at the chain ends. We also observed that after purification and drying, further solubilisation of the photoproduct in varying solvents was often difficult and sometimes a part of it was insoluble. This can be explained by crosslinking resulting from subsequent reactions involving hydroperoxide decomposition.

Since, in the presence of atmospheric air, reactions involving oxygen can not be prevented, namely oxidation by singlet oxygen and radical-induced auto-oxidation resulting from hydrogen peroxide and hydroperoxide photolysis, leading to the formation of hydroperoxy, hydroxy, carbonyl and epoxide groups. The segregation/identification of the chain-end-oxidised microstructure is difficult, therefore, the mechanism of the chain cleavage is difficult to propose definitively. Thus, the mechanism through H_2O_2 photolysis and the hydroxy radical-induced chain cleavage[7,8] could not be evidenced and it will be implied to characterise the resulting allylic alcohol chain ends.

Further experiments are in progress, namely, study of the photoinitiated free-radical oxidation process and photo-oxidation by $^1O_2$ and controlled post decomposition of hydroperoxide (oxido-reduction catalysis). Peroxide or hydroperoxide reduction using triphenylphosphine rather than the classical phenolic protection will improve the work-up in order to prevent subsequent auto-oxidation.

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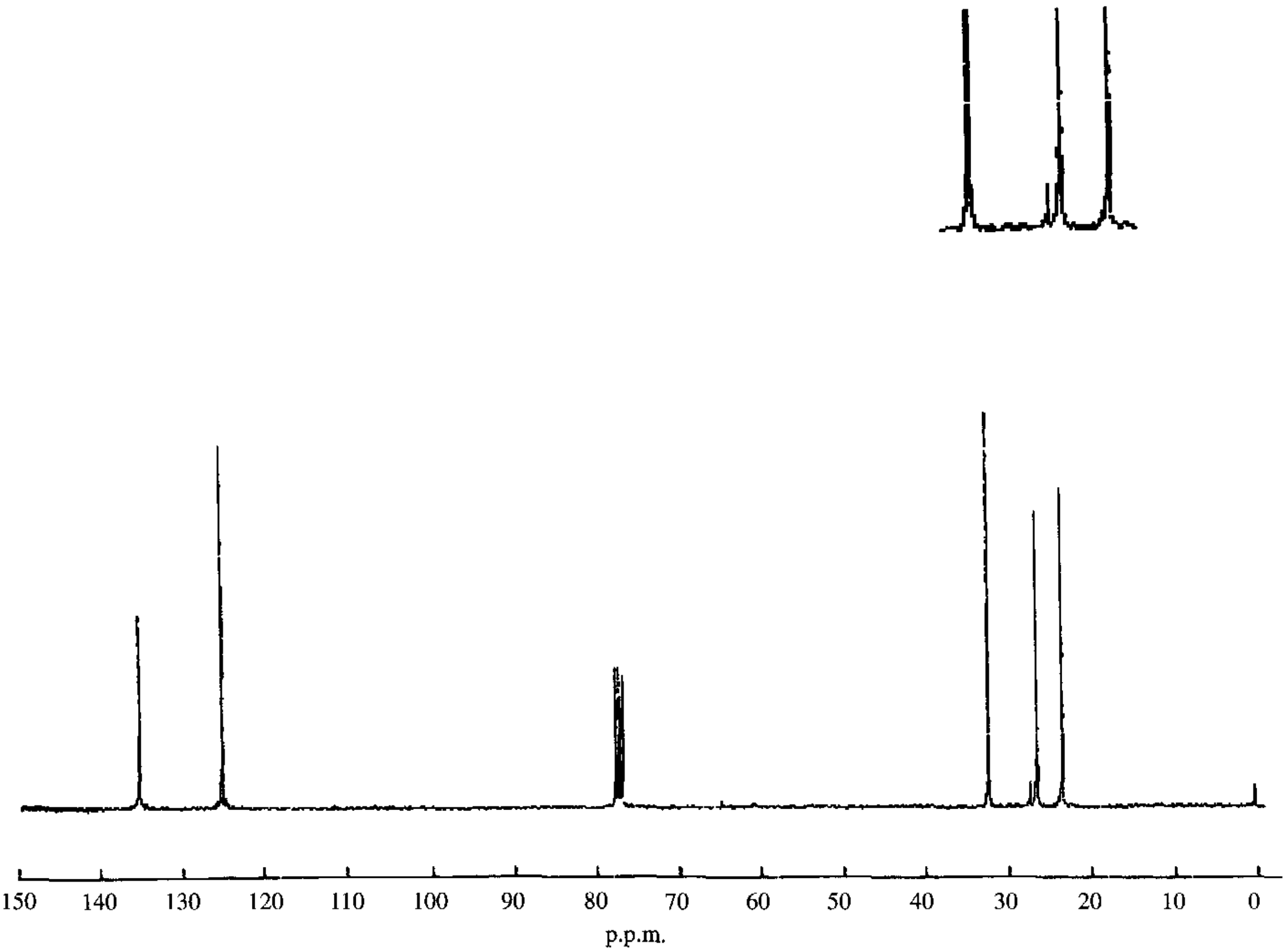

Figure 9. Combined effect of titanium dioxide and hydrogen peroxide on degraded natural rubber after 36 h U.V. irradiation (under air) ^{13}C NMR spectra.

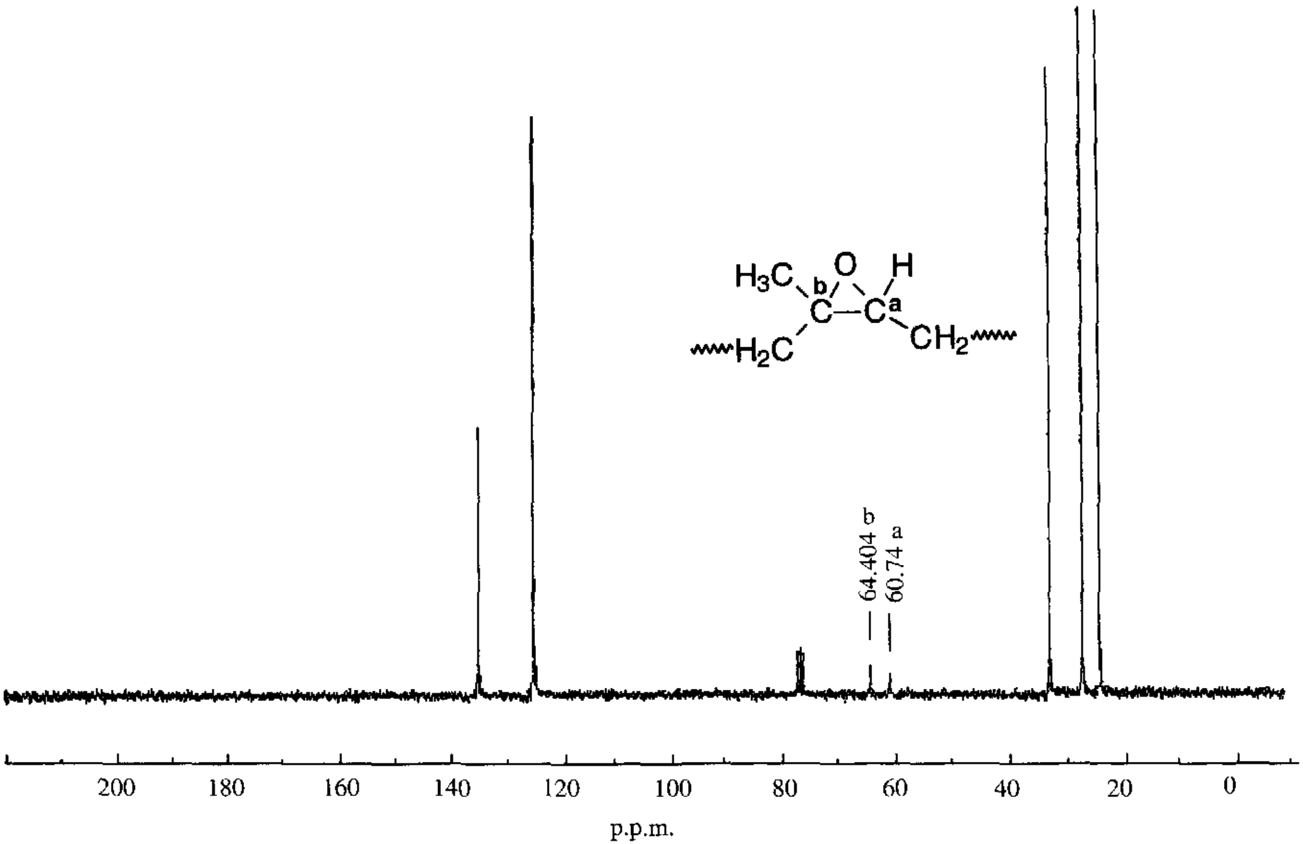

Figure 10. Partially epoxidised natural rubber formation due to combined effect of titanium dioxide and hydrogen peroxide on degraded N.R. after 48 h U.V. irradiation (under nitrogen) ^{13}C NMR spectra.

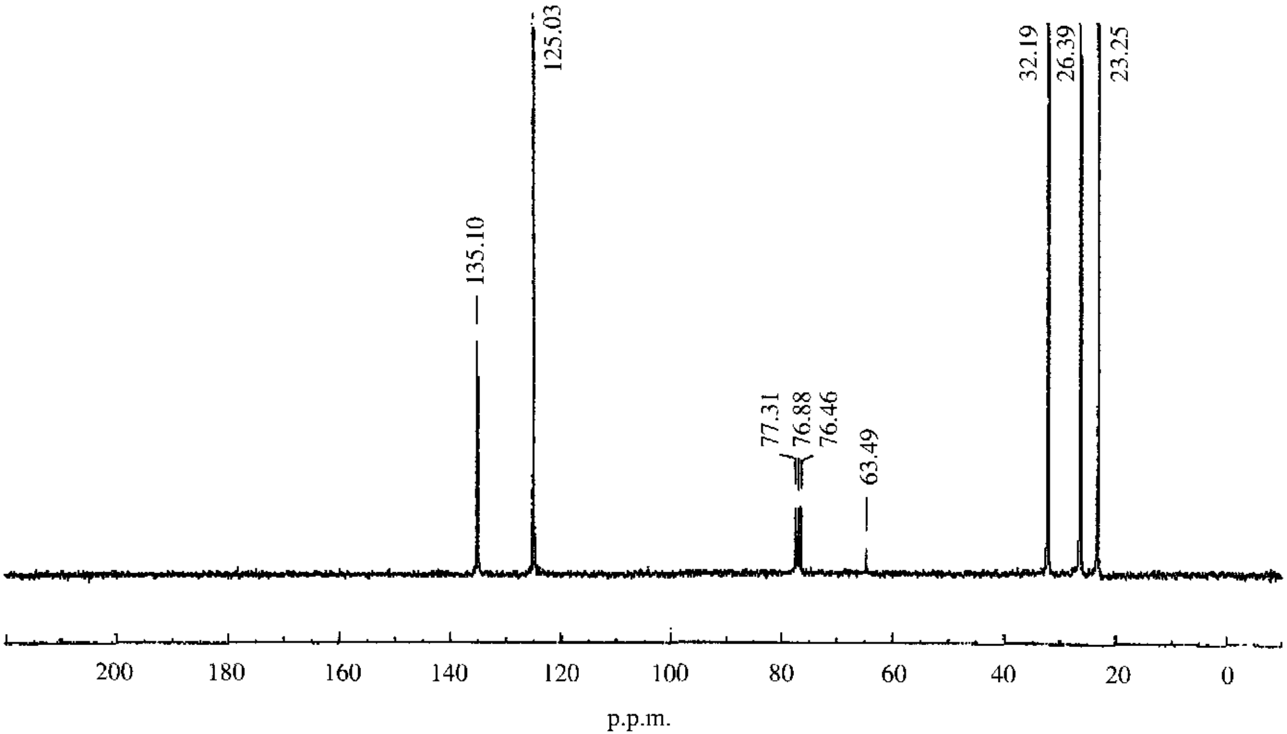

Figure 11. ^{13}C *NMR spectrum of degraded natural rubber after 18 h U.V. exposure (under air) in* $CDCl_3$ *solution.*

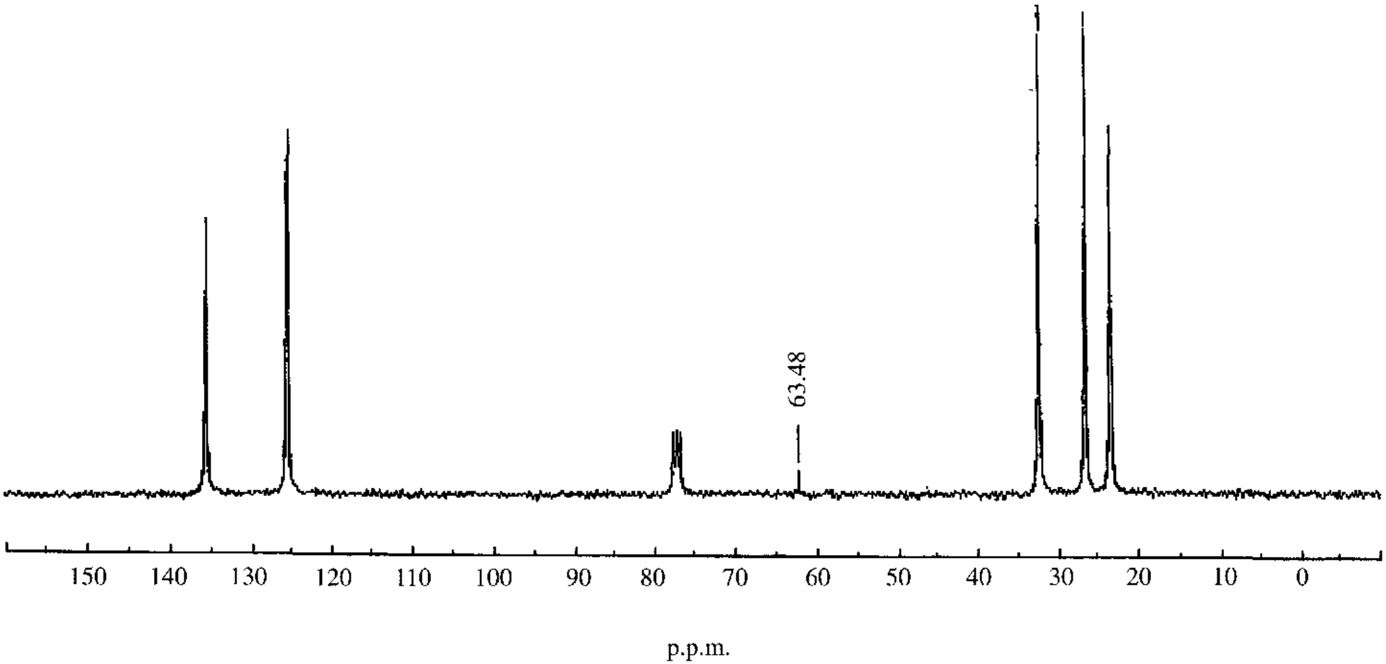

Figure 12. ^{13}C NMR spectrum of degraded natural rubber after 24 h U.V. exposure (under nitrogen) in $CDCl_3$ solution.

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