Kinetics of Photo-oxidative Degradation of Butyl Rubber by Light Scattering

RAMESH CHANDRA & HARI L. BHATNAGAR

Department of Applied Sciences & Humanities, Kurukshetra University, Kurukshetra

The kinetics of photo-oxidative degradation of butyl rubber at 366 nm and constant intensity flux of 1.68×10^{-8} Einstein sec^{-1} cm^{-2} have been studied in the absence and presence of 0.1% (w/w) phenyl allyl mercury (PAM) dispersed evenly in the matrix of polymer films in the temperature range of 265° to 293°K. The random chain scission processes taking place have been followed experimentally by light scattering technique by observing the changes in molecular weight. It is found that in the initial stages the polymer molecular weight decreases with increase in temperature but on prolonged exposure it increases after reaching a minimum. The data obtained have been interpreted in terms of the cage mechanism operating in random chain scission processes. The effect of UV radiation (366 nm) on PAM has also been studied as a function of time of irradiation at 283°K. It has been shown that the variation of the absorbance of 7.027×10^{-6} molar PAM solution in cyclohexane versus irradiation time is linear in terms of the production of allyl and phenyl radicals. The importance of production of allyl radicals under irradiation conditions and mechanism of photostabilization have been critically discussed.

THE kinetics of chain scission of butyl rubber in solid state by small amounts of nitrogen dioxide and air was reported by Jellinek and coworker[1]. These studies were later extended[2] to photo-oxidation of butyl rubber as a function of nitrogen dioxide, oxygen pressure and temperature. No attempt was made to isolate a particular wavelength of ultravoilet radiation and all studies were conducted using radiations above 280 nm. The average chain lengths were determined by viscosity technique. The data were processed to calculate the Arrhenius energy of activation for photo-degradation.

An important factor to be considered is the insensitivity of the viscosity technique to the formation of branched chains during photo-oxidative degradation. Sarfare *et al*.[3] using light scattering technique have shown that on branch chain formation the molecular weight of the thermally degraded *cis*-rubber increased. Later Bhatnagar and co-workers[4,5] carried out thermal degradation of butyl rubber in solution and followed it by viscosity technique. The increase in molecular weight on prolonged thermal degradation could not be detected due to the insensitivity of the technique. It was, therefore, considered desirable to study the photo-oxidative degradation of butyl rubber in air at a fixed wavelength of 366 nm in the temperature range 265-293°K with and without the presence of phenyl allyl mercury (PAM)[6,7]. The changes in molecular weight corrected for dissymmetry were estimated by light scattering. The data obtained were processed to evaluate the Arrhenius energy, enthalpy, entropy and free energy of activation for degradation process respectively.

Materials and Methods

The butyl rubber (a copolymer of isobutylene and isoprene) (M/s Swastic Rubber Co., Poona) was cut into small pieces and subjected to acetone and methanol extraction for 72 hr in a soxhlet. It was evacuated to a constant weight and kept in contact with pet. ether (40-60°) for four days at room temperature, when a part of the rubber went into solution. The acetone extraction and dissolution in petroleum ether were conducted in dark. The rubber was precipitated from 1% solution in pet. ether with acetone. The precipitated rubber was dried *in vacuo* to a constant weight and preserved in vacuum in dark at room temperature.

The solvents used were purified by the standard techniques.

Preparation of films with and without the stabilizer — The incorporation of the PAM was effected by dissolving the butyl rubber (10% w/v) cyclohexane containing 0.1% of PAM on the basis of the weight of the polymer.

The butyl rubber films of uniform average thickness $(4.58 \times 10^{-2}$ g $cm^{-2})$ were prepared by casting 9 ml of the solution in cyclohexane containing butyl rubber with and without PAM on quartz plates which were sealed with pyrex glass plates having a 5 cm diameter bore. The films were placed in a desiccator over dried silica gel. A freshly filtered solution was used for each casting of a film. The solution was slowly evaporated under standardized[8] conditions for 12 hr. The films were then dried in high vacuum for 24 to 30 hr to a constant weight in dark.

Photo-irradiation — The photo-degradation was carried out in air with a 125-watt (230 V) mercury vapour lamp whose glass casing was removed. The dried butyl rubber films were irradiated by a monochromatic light of wavelength 366 nm for different intervals of time in the temperature range of 265-293°K. The temperature of the system was controlled within ±1°.

The intensity of radiation and quantum yields for polymer chain scissions were quantitatively determined by a chemical actinometer designed and calibrated by the present authors[9].

Refractive index increment — The refractive index increment with concentration of butyl rubber (dn/dc) and the optical constant (H) for the solution in cyclohexane were determined using a Brice-Phoenix differential refractometer (Phoenix Precision Instrument Co., Philadelphia, USA) and the values at 298°K are: $n_0 = 1.4338$; $dn/dc = 0.1248$; and $H = 1.957 \times 10^{-6}$.

Light scattering studies — The stock solutions of butyl rubber were prepared by dissolving the films in a known volume of dittilled cyclohexane. The solutions were filtered to remove any suspended dust particle through an ultra-finepore sintered glass filter. Solutions of different concentrations were obtained by adding a known volume of the stock solution to a known volume of the solvent in the light scattering cell directly. The light scattering investigations were made with a light scattering photometer designed and calibrated by the present authors[10].

Spectrophotometric measurements — Absorption measurements were carried out with a Beckman DU spectrophotometer. The absorption spectra of 7.027 $\times 10^{-6} M$ PAM in cyclohexane induced by the different light doses by changing the time of irradiation at 283°K were measured in a quartz cell (1 cm path length).

Degree of degradation (α) — For a random chain scission process in a polymer, the degree of degradation, α, is given by Eq. (1)

$$\alpha = \frac{s}{p_{w,o}-1} \simeq \frac{s}{p_{w,o}} \qquad \qquad ...(1)$$

where s, the average number of cuts per single original chain, is given[11] by Eq. (2)

$$\frac{p_{w,t}}{p_{w,o}} = (2/s^2)(e^{-s}+s-1) \qquad ...(2)$$

and $p_{w,o}$ and $p_{w,t}$ represent the weight average degree of polymerization initially and at time t of degradation of the polymer respectively.

If the values of $p_{w,t}$ and $p_{w,o}$ are known from experiment, the values of s can be estimated by using Eq. (2). A theoretical graph of $p_{w,t}/p_{w,o}$ versus s can be drawn and the values of s can be read from it by using the experimental values of $p_{w,t}/p_{w,o}$.

Results and Discussion

Variation of 'α' with irradiation time — Fig. 1 gives the variation of photo-degradation rate, α,
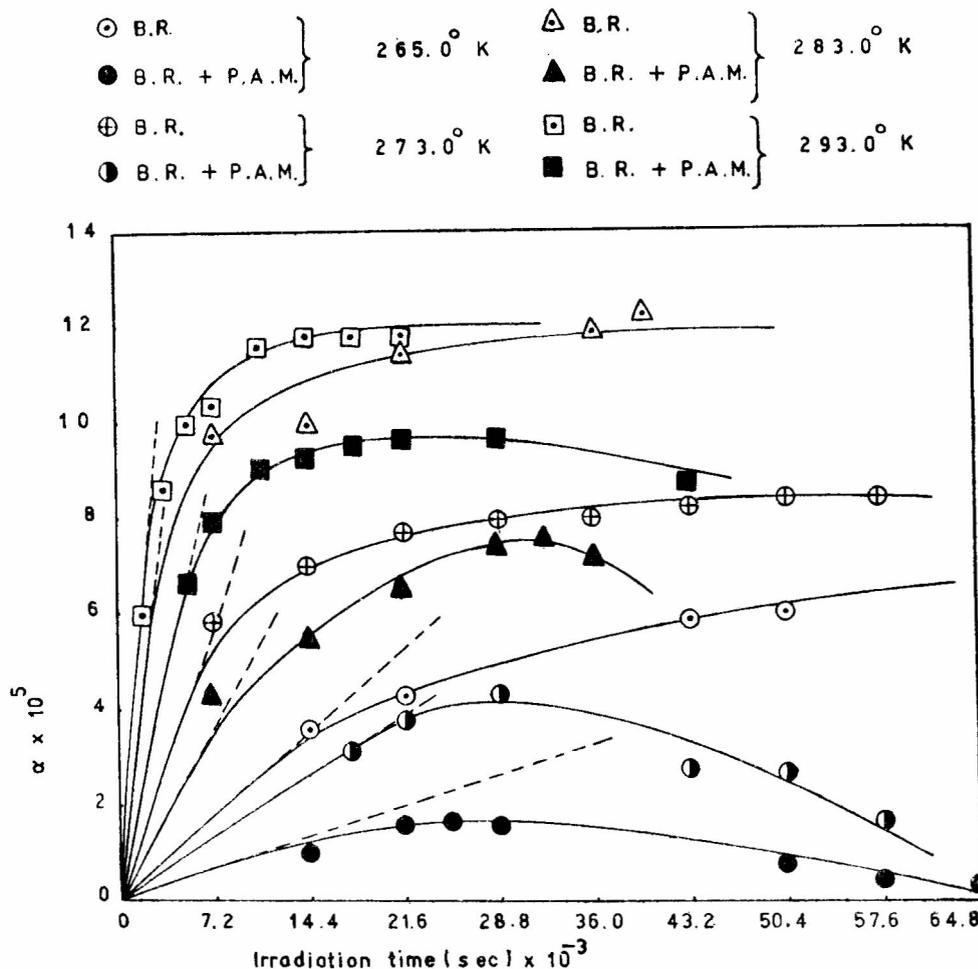
Fig. 1 — Plots of photo-degradation rate (α) versus irradiation time for butyl rubber in the presence and absence of phenyl allyl mercury (PAM)

versus time for butyl rubber irradiated with and without the presence of phenyl allyl mercury. Since, for a random chain degradation process, $\alpha = k_1 t$, the initial slope of α versus t curve which should be linear if only one kind of links are ruptured gives a method of evaluating k_1, the specific rate constant. If the plot is nonlinear, Jellinek[1] has indicated the possibility of more than one rate constants being operative.

The problem is comparatively simple in the case of butyl rubber blanks (in the absence of PAM), where the value of α increases initially and subsequently reach a saturation limit. In such cases, only the role of oxygen attacking weak links consisting of isoprene units is to be considered as proposed by Jellinek[1].

At later stages of degradation in the absence and presence of PAM the problem of simultaneous rupture of weak and normal links as also of cross-linking has to be considered.

Evaluation of ΔE and A — Table 1 gives the values of the weight average molecular weights (M_w) $p_{w,t}/p_{w,o}$, s per original chain length and the α at different irradiation periods. To avoid complications arising out of branching at high degree of degradation, values of the specific rate constants, k_1, have been calculated (Table 2) from the initial slopes of α versus time curves using the relation $\alpha = k_1 t$.

The values of the Arrhenius energy of activation, ΔE and the frequency factor A have been obtained by using the equation[12]

$$\ln k_1 = \ln A - \Delta E / RT \qquad ...(3)$$

The plots of $\ln k_1$ versus $1/T$ are linear and the values of ΔE as well as A can be estimated from the slope and intercept respectively. Alternatively, one may use the method of least squares to estimate the slopes ($-\Delta E/R$) and the intercept ($\ln A$) from the data. The values of ΔE and A obtained using the latter method in the absence and presence of PAM are 13·2442 kcal mole[-1], $2·286 \times 10^2$ sec[-1] and 14·448 kcal mole[-1], $7·263 \times 10^2$ sec[-1] respectively.

It has been shown[4] that polymer degradation is a zero order reaction with respect to polymer and oxygen concentrations under the present conditions, and is governed by Eq. (4)

$$A = e^2(kT/h) \exp(\Delta S^*/R) \qquad ...(4)$$

where e is the exponential and other letters having standard nomenclature. The free energy of activation for the degradation process may be obtained at any convenient temperature by using the relation (5)

$$\Delta F^* = \Delta H^* - T\Delta S^* \qquad ...(5)$$

The values of enthalpy of activation ΔH^*, the entropy of activation ΔS^* and the free energy of activation ΔF^* at 400·0°K for the photo-oxidative degradation of butyl rubber with and without PAM (0·1%) at light intensity flux of $1·68 \times 10^{-8}$ Einsteins sec^{-1} cm^{-2} at $\lambda = 366$ nm are: $-52·31$, $-50·1$ e.u.; 13·24, 14·45 kcal mole[-1]; and 34·16, 34·45 kcal mole[-1] respectively.

TABLE 1 — PHOTO-OXIDATIVE DEGRADATION OF BUTYL RUBBER IN THE ABSENCE AND PRESENCE OF 0·1% PAM IN AIR AT DIFFERENT TEMPERATURES

[Light intensity flux = $1·68 \times 10^{-8}$ Einstein sec^{-1} cm^{-2}; irradiation wavelength (λ) = 366 nm]

Time of irradiation sec $\times 10^{-3}$	$M_w \times 10^{-6}$	$p_{w,t}/p_{w,o}$	s	$\alpha \times 10^5$
BUTYL RUBBER SYSTEM: TEMP. 265°K				
0·0	1·356	1·000	—	—
14·4	1·039	0·766	0·858	3·557
21·6	0·985	0·726	1·046	4·336
43·2	0·888	0·655	1·428	5·920
50·4	0·879	0·648	1·467	6·081
BUTYL RUBBER + 0·1% PAM SYSTEM: TEMP. 265°K				
0·0	1·356	1·000	—	—
14·4	1·251	0·923	0·247	1·024
21·6	1·185	0·874	0·419	1·737
25·2	1·178	0·869	0·437	1·812
28·8	1·201	0·886	0·376	1·559
50·4	1·254	0·925	0·239	0·991
57·6	1·301	0·959	0·125	0·518
64·8	1·303	0·961	0·121	0·502
BUTYL RUBBER SYSTEM: TEMP. 273°K				
0·0	1·356	1·000	—	—
7·2	0·897	0·662	1·390	5·762
14·4	0·826	0·609	1·710	7·088
21·6	0·799	0·589	1·845	7·648
28·8	0·786	0·580	1·913	7·930
36·0	0·779	0·575	1·950	8·083
43·2	0·773	0·570	1·982	8·216
50·4	0·772	0·569	1·990	8·249
57·6	0·766	0·565	2·020	8·374
BUTYL RUBBER + 0·1% PAM SYSTEM: TEMP. 273°K				
0·0	1·356	1·000	—	—
21·6	1·021	0·753	0·919	3·810
28·8	0·989	0·729	1·031	4·274
36·0	0·956	0·705	1·154	4·784
43·2	1·099	0·811	0·666	2·761
50·4	1·105	0·815	0·648	2·686
57·6	1·185	0·874	0·419	1·737
BUTYL RUBBER SYSTEM: TEMP. 283°K				
0·0	1·356	1·000	—	—
7·2	0·708	0·522	2·362	9·791
14·4	0·701	0·517	2·406	9·969
21·6	0·646	0·476	2·783	11·536
36·0	0·634	0·468	2·872	11·905
39·6	0·623	0·459	2·960	12·270
BUTYL RUBBER + 0·1% PAM SYSTEM: TEMP. 283°K				
0·0	1·356	1·000	—	—
7·2	0·989	0·729	1·031	4·274
14·4	0·911	0·672	1·332	5·522
21·6	0·851	0·628	1·593	6·603
28·8	0·806	0·594	1·810	7·503
32·4	0·802	0·592	1·830	7·586
36·0	0·824	0·608	1·720	7·130
BUTYL RUBBER SYSTEM: TEMP. 293°K				
0·0	1·356	1·000	—	—
1·8	0·887	0·654	1·433	5·940
3·6	0·757	0·558	2·070	8·581
5·4	0·702	0·518	2·400	9·949
7·2	0·691	0·510	2·470	10·239
10·8	0·643	0·474	2·805	11·628
14·4	0·639	0·471	2·835	11·752
18·0	0·638	0·471	2·843	11·785
21·6	0·638	0·471	2·843	11·785

TABLE 1 — PHOTO-OXIDATIVE DEGRADATION OF BUTYL RUBBER IN THE ABSENCE AND PRESENCE OF 0·1% PAM IN AIR AT DIFFERENT TEMPERATURES — Contd

[Light intensity flux $= 1\cdot68 \times 10^{-8}$ Einstein sec^{-1} cm^{-2}; irradiation wavelength (λ) $= 366$ nm]

Time of irradiation sec $\times 10^{-3}$	$M_w \times 10^{-6}$	$p_{w,t}/p_{w,o}$	s	$\alpha \times 10^5$
BUTYL RUBBER + 0·1% PAM SYSTEM: TEMP. 293°K				
0·0	1·356	1·000	—	—
5·4	0·852	0.628	1·588	6·583
7·2	0·788	0·581	1·903	7·889
10·8	0·739	0·545	2·174	9·012
14·4	0·726	0·535	2·250	9·327
18·0	0·720	0·531	2·287	9·480
21·6	0·714	0·527	2·323	9·630
28·8	0·714	0·527	2·323	9·630
43·2	0·747	0·551	2·127	8·817

Thus k_1 for photo-oxidative degradation of butyl rubber alone and in the presence of 0·1% PAM can be represented by Eqs. (6) and (7) respectively

$$k_1 = 2\cdot29 \times 10^2 \exp(-13244/RT) \qquad \ldots(6)$$
$$k_1 = 7\cdot26 \times 10^2 \exp(-14448/RT) \qquad \ldots(7)$$

It can be seen that the values of ΔS^* are negative and ΔE values in the absence and presence of 0·1% PAM are 13·24 and 14·45 kcal mole^{-1} respectively. The higher value of ΔH^* in the presence of PAM indicates that the stabilizer retards the rate. Moreover, irrespective of the variations in the values of ΔH^* and ΔS^* the values of ΔF^* remain almost constant around 34·31 kcal mole^{-1}, indicating that the rate determining step is the same for both the systems.

Mechanism of photo-oxidative degradation of butyl rubber — One may calculate the energy of hydroperoxidation in the following manner:

$$PH + O_2 \xrightarrow{k_0} P^\cdot + HOO^\cdot + q \qquad \ldots(8)$$
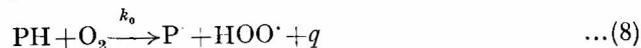
where

$$-q = Q_{C-H} - Q_{H-O-O^\cdot} \qquad \ldots(9)$$

Since, $Q_{H-O-O^\cdot} = 47$ kcal mole^{-1}, $q = (47 - Q_{C-H})$ kcal mole^{-1}.

The rate of initiation $W_0 = k_0[PH][O_2]$, which is a bimolecular process and is given by

$$W_0 = e^2(kT/h) \exp(\Delta S^*/R) \exp -(\Delta H^*/RT)[PH][O_2] \qquad \ldots(10)$$

where [PH] and [O$_2$] are the active concentrations of the polymer and oxygen per chain. To evaluate q, one may speculate regarding the possible value of Q_{C-H}. This depends upon the nature of the site available for hydroperoxidation on the chain skeleton. It has been shown that the Q_{C-H} for site available adjacent to an aliphatic double bond[13] would be approximately 77 kcal mole^{-1} or less.

P—O—O—H dissociates unimolecularly at the oxygen molecule diradical ·Ö—Ö· link. The enthalpy of activation of the ·Ö—Ö· bond in a peroxide requires about 40 kcal mole^{-1}. The decomposition of a polymer hydroperoxide can occur in a reaction when either energy transfer process occurs[14-17] or the sensitizer can propagate the free radical induced

TABLE 2 — DATA FOR THE EVALUATION OF ARRHENIUS ACTIVATION ENERGY AND FREQUENCY FACTOR OF PHOTO-OXIDATIVE DEGRADATION OF BUTYL RUBBER IN AIR

[Light intensity flux $= 1\cdot68 \times 10^{-8}$ Einstein sec^{-1} cm^{-2}; irradiation wavelength (λ) $= 366$ nm]

$T°K$	$1/T \times 10^3$	$1/T^2 \times 10^6$	$k_1 \times 10^9$ (sec^{-1})	$-\ln k_1$	$-1/T \ln k_1 \times 10^3$
BUTYL RUBBER SYSTEM					
265	3·7735	14·2393	2·402	19·8505	74·9059
273	3·6630	13·4176	7·843	18·6669	68·3769
283	3·5335	12·4856	22·222	17·6233	62·2719
293	3·4129	11·6479	32·778	17·2366	58·8268
BUTYL RUBBER + 0·1% PAM SYSTEM					
265	3·7735	14·2393	0·926	20·8039	78·5035
273	3·6630	13·4176	1·794	20·1423	73·7813
283	3·5335	12·4855	5·382	19·0435	67·2902
293	3·4129	11·6479	12·037	18·2384	62·2458

TABLE 3 — ENERGY OF HYDROPEROXIDATION AT VARIOUS SITES

C—H bond	Q_{C-H} (kcal mole^{-1})	$-q \simeq \Delta E$ (kcal mole^{-1})
Tertiary	89	$(89+40-116) = 13$
Secondary (long chain alkane)	88	$(88+40-116) = 12$
Tertiary (long chain alkane)	<88	<12

decomposition of the peroxide[18]. Therefore, it can be reasonably postulated that the rate controlling step for the photo-oxidative degradation process at $\lambda = 366$ nm would be the initiation step. Assuming it to be the rate determining step, an inspection of Table 3 indicates that hydroperoxidation takes place at a secondary carbon atoms with $Q_{C-H} \simeq 88$ kcal mole^{-1}, so that $q = (88+40-116) \simeq 12$ kcal mole^{-1}. This value is close to the experimental values of ΔE observed for the photo-oxidative degradation process taking place either in the absence or presence of PAM.

Therefore, the hydroperoxidation at alpha position appears to be the rate controlling reaction. This is a bimolecular reaction, involving oxygen molecule diradical (·Ö—Ö·) and a secondary hydrogen, resulting in the formulation of an hydroperoxide.

The thermo-chemical data on diallyl mercury or on PAM are not available in literature and, therefore, approximate values of bond dissociation energies of propyl and isopropyl groups may be used as representative values. The nearest bond dissociation energies of Hg—C bonds for the present system are given below[19].

Compound		Mean dissociation energy (kcal mole^{-1})
Hg-propyl	⎫	24·5 ± 2·2
Hg-isopropyl	⎬ Hg-allyl	21·0 ± 2·2
Hg-phenyl	⎭	32·4 ± 2·1

It can be seen that even the highest value of the energy required for bond scission is much less than
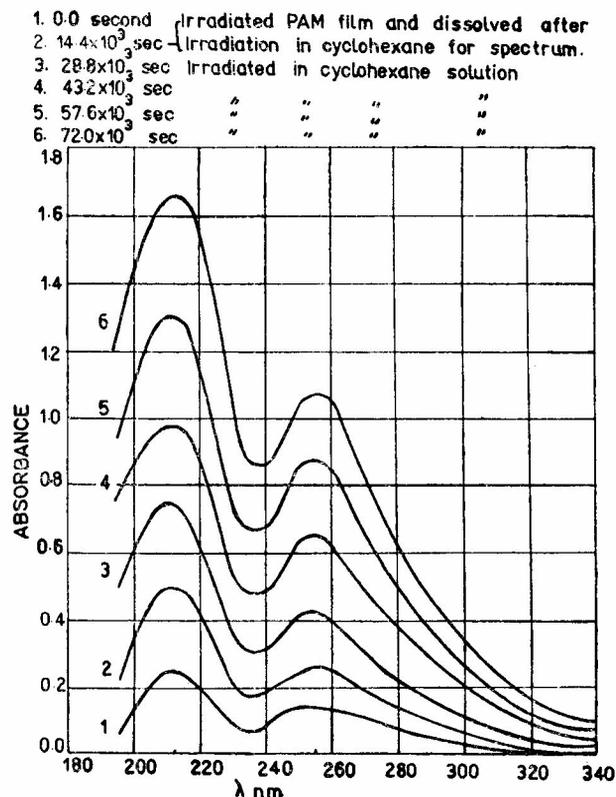
Fig. 2 — Absorption spectra of irradiated PAM in cyclohexine at different intervals of time

the energy carried by a photon of wavelength 366 nm (equivalent to 78·33 kcal mole⁻¹). The net result of incorporation of PAM is the production of allyl and phenyl radicals in the polymer film in addition to ·Hg-allyl or ·Hg-phenyl radicals on irradiation.

From the absorption spectra of irradiated PAM, one can see that with increasing period of irradiation, the concentration of both allyl (λ_{max} = 213 nm) and phenyl (λ_{max} = 255 nm) radicals increase in cyclohexane solution. The increase in absorbance is linear with the dose indicating the absence of reverse reactions. The kinetics of photo-chemically induced change of PAM solution in cyclohexane in air is given in Fig. 2.

These hot radicals would tend to react with radicals formed by the chain scission due to the decomposition of P—O—O—H. All kinds of possibilities exist.

Let A be any of the free radicals formed by the photolysis of PAM, then the formation of inert products can be visualized as shown in Scheme 1.

In solid state the excited species P˙ and A˙ would be energetic and long-lived, particularly where bimolecular collisions are required. Thus, in the
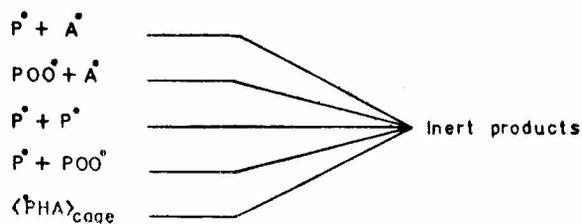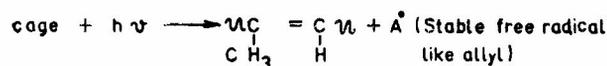
present case where the reactions have been carried out in solid state, radicals may be unable to escape through the closely packed molecules that surrounded them. Most of them may recombine, dissipating the energy of recombination as heat and producing no overall chemical change. The caging and recombination of free radicals from excited molecules before they have become separated is known as the Frank-Rabinowitch[20] or cage effect. This is schematically shown in Scheme 2.

Therefore, it appears that PAM acts via the mechanism of production of free radicals which terminate the chain reaction through radical-radical reaction. Since termination step cannot be the rate detemining step due to its fast rate, one has to go back to the slowest reaction, namely the secondary hydroperoxidation site to a double bond in the isoprene units of butyl rubber. This site of reaction has also been suggested by Bhatnagar et al.[21,22] earlier in their studies on thermal degradation of butyl rubber in solution.

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Scheme 1