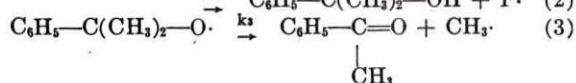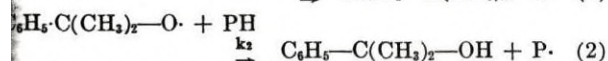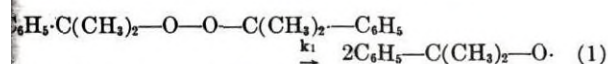# Crosslinking Efficiency of Dicumyl Peroxide in Natural Rubber

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Introduction

Ostromislensky[1] first proposed organic peroxides as crosslinking agents in natural rubber. A peroxide possessing many of the properties desirable in a crosslinking agent is dicumyl peroxide, and studies of its behavior in natural rubber[2,3] and synthetic polymers[3,4] have been made. The mechanism proposed for the crosslinking reaction is a very simple one[2] leading finally to the formation of a carbon to carbon crosslink between polymer molecules. The initial step involves the thermal decomposition of the peroxide [eq. (1)]; the cumyloxy radicals formed may abstract hydrogen from the polymer [eq. (2)] or decompose further to give methyl radicals [eq. (3)] which may also abstract hydrogen from the polymer. A crosslink is then formed by combination of two polymer radicals.

$$C_6H_5 \cdot C(CH_3)_2—O—O—C(CH_3)_2—C_6H_5$$
$$\xrightarrow{k_1} 2C_6H_5—C(CH_3)_2—O \cdot \quad (1)$$

$$C_6H_5 \cdot C(CH_3)_2—O \cdot + PH$$
$$\xrightarrow{k_2} C_6H_5—C(CH_3)_2—OH + P \cdot \quad (2)$$

$$C_6H_5—C(CH_3)_2—O \cdot \xrightarrow{k_3} C_6H_5—C{=}O + CH_3 \cdot \quad (3)$$
$$\underset{CH_3}{|}$$

No quantitative determination of the crosslinking efficiency has been made, but in a few cases[3] the relative importance of the cumyloxy and methyl radicals has been deduced from the amounts of cumyl alcohol and acetophenone produced. In those cases in which analytical work has been carried out[3,4] the results show that the bulk of the decomposed peroxide has been converted to cumyl alcohol and acetophenone, but they are not conclusive in showing that no cumyloxy radicals become incorporated in the crosslinked polymer.

In the present work the rate of decomposition of dicumyl peroxide and the rates of formation of cumyl alcohol and acetophenone are determined over a range of temperature. A quantitative determination of crosslink density in vulcanized specimens is also made, and these in conjunction with the rate data lead to values for the efficiency of the crosslinking reaction.

Experimental

Crepe rubber was extracted with acetone under nitrogen for 16 hr. and was then dried *in vacuo*. It was then mixed with 1.5 wt.-% dicumyl peroxide on a roll mill at 50°C. All work was carried out with samples from the same stock supply.

Rate Measurements

Three gram samples of rubber were thoroughly outgassed by repeated freezing, thawing, and pumping and were finally sealed in Pyrex tubes at a pressure of 10^{-6} cm. They were then heated in an oil bath at a temperature controlled to ±0.1°C. for known times. The decomposition of the peroxide was quenched by immersing the tube in cold water. The reaction products were extracted immediately after the seal was broken.

Analytical Procedures

Cold extraction of the reaction products from the crosslinked rubber was carried out by swelling in a suitable solvent, which was carbon tetrachloride for infrared analysis and isooctane for ultraviolet analysis. In both cases 0.5 g. of crosslinked material was immersed in 25 cc. of solvent, the time for extraction being 4 hr. in the former and 24 hr. in the latter solvent.

Cumyl alcohol was determined by infrared analysis using a Grubb-Parsons double beam instrument with a rock salt prism; the intensity of absorption due to the O-H fundamental vibrational mode was found to obey Beers' law over the concentration range encountered in the present work and was not influenced by the presence of acetophenone. Knowing the concentration of cumyl alcohol the amount of acetophenone and residual peroxide was determined from the ultraviolet absorption at 2390 and 2580 A. It had been pre-

viously verified that all three compounds obeyed Beers' law independently and in admixture in isooctane.

Estimation of Crosslink Density

For estimates of crosslinking efficiency 6 g. samples were vulcanized in a press at 1500 psi; the fraction of peroxide decomposed was evaluated from the time and temperature of vulcanization and the rate data for decomposition. The crosslink density was obtained from the value of the equilibrium swollen volume in n-decane at 25°C.

A strip of the vulcanizate of known weight was immersed in n-decane at 25 ± 0.02°C. for 48 hr.; it was then removed, surface-dried, and weighed in a stoppered bottle. Finally the strip was dried to constant weight *in vacuo*. From this final weight, the weight of decane in the material at equilibrium, and the densities of rubber (0.91) and decane (0.725) at 25°C., the volume fraction of rubber (V_r) in the swollen vulcanizate is calculated.

The crosslink density $(1)/(2\bar{M}_c)$, where $\bar{M}_c$ is the average molecular weight of the network chains between crosslinks, is obtained by using the correlation between crosslink density and equilibrium swelling established by Mullins[5] and Moore and Watson.[6] The elastic constant C_1 is related to V_r by the equation

$$-\ln(1 - V_r) - V_r - V_r^2\mu$$
$$= 2V_0 C_1 R^{-1}T^{-1}[V_r^{1/3} - (V_r/2)]$$

where V_0 is the molar volume of the swelling liquid, and μ the interaction constant for rubber and decane has a value of 0.425.

Corrections for chain entanglements and network flaws are given[5] by

$$C_1 = (C_1^* + 0.78 \times 10^6)\left(1 - 2.3\frac{\bar{M}_c}{M}\right)$$

where C_1^* is the corrected value of C_1, $\bar{M}_c$ is the molecular weight between crosslinks, and M is the initial molecular weight of the polymer. Finally C_1^* and $\bar{M}_c$ are related by

$$C_1^* = \frac{\rho RT}{\bar{M}_c}$$

ρ being the density of the polymer. The initial molecular weight (M) of the rubber was obtained by measuring the limiting viscosity number of its benzene solution at 25°C. and substituting for $[\eta]$ in the equation $[\eta] = 2.29 \times 10^{-7} \cdot M^{1.33}$ found for benzene solutions of masticated rubber.[7]

Results

The analyses of specimens heated at four different temperatures are shown in Table I; C_p, C_A, and C_k are the concentrations in gram moles/liter of extract of dicumyl peroxide, cumyl alcohol, and acetophenone. Examination of the infrared spectra of the extracts did not reveal any other products.

The rate of decomposition is conveniently ex-

TABLE I
Results of Analytical Work on Natural Rubber–Dicumyl Peroxide Mixtures

T, °C.	Heating time	C_p initial $\times 10^4$	C_p final $\times 10^4$	$\frac{1}{2}C_A \times 10^4$	$\frac{1}{2}C_k \times 10^4$	C_k/C_A	Recovery, %
140	20 min.	11.0	8.4	2.5	0.28	0.11_2	101
	50 min.	11.2	5.2	5.4	0.60	0.11_0	100
	90 min.	12.9	3.2	9.3	1.0	0.11_2	104
	150 min.	12.8	1.34	9.4	1.1	0.11_8	92
130	1.5 hr.	11.4	7.0	4.0	0.36	0.08_8	100
	3 hr.	10.0	3.7	5.4	0.49	0.09	96
	4 hr.	11.1	2.9	8.0	0.74	0.09_4	105
	6 hr.	11.1	1.1_4	9.0	0.85	0.09_4	99
120	3 hr.	11.2	8.4	3.0	0.18	0.06	103
	5 hr.	9.6	5.0	3.7	0.23	0.06_2	95
	7 hr.	10.0	4.4	5.0	0.30	0.06_1	97
	8 hr.	10.9	4.0	5.9	0.34	0.05_7	95
110	8 hr.	11.2	8.06	3.0	0.12	0.04	100
	22 hr.	10.4	3.96	6.0	0.26	0.04_4	98
	30 hr.	10.9	3.07	7.3	0.30	0.04_2	97

TABLE II
Half-lives for Decomposition of Dicumyl Peroxide

T, °C	Present work in natural rubber	Mineral oil[a]	Paraffin oil[b]	Dodecane[c]	Cumene[d]
150	—	12 min.	20 min.	14.7 min.	—
140	44 min.	36 min.	51 min.	40.2 min.	49.3 min.
130	2.1 hr.	1.8 hr.	2.2 hr.	1.95 hr.	2.3 hr.
120	5.8 hr.	5.4 hr.	5.0 hr.	—	7.0 hr.
110	16 hr.	16 hr.	—	—	—
Activation energies kcal./mole	32.5	—	32.4	35.2	34.5

[a] Data taken from ref. 3. [b] Data taken from ref. 4. [c] Data taken from ref. 8. [d] Data taken from ref. 9.

essed in terms of the half-life of the peroxide at e temperatures studied; these values are shown Table II together with those obtained by other orkers in different solvents. The decomposition llows first-order kinetics, and a plot of ln k against T is linear. A value of 32.5 kcal./mole is tained for the activation energy of decomposition.

TABLE III
Efficiency of the Crosslinking and Its
Variation with Temperature

T, °C.	Crosslinking efficiency, %
110	95
120	95
125	92
130	102
135	98
140	102

TABLE IV
Variation of Crosslinking Efficiency with
Time of Vulcanization at 140°C.

Time of cure, min.	Crosslinking efficiency, %
50	96
65	102
98	94
120	98
144	97

The values obtained for the efficiency of the osslinking reaction, defined as the ratio of the umber of crosslinks formed to the number of olecules of peroxide decomposed, are shown in ables III and IV.

Discussion

Studies[8,9] of the thermal decomposition of dicumyl peroxide in a number of hydrocarbons have shown that the rate of decomposition is largely unaffected by the nature of the solvent, as can be seen from Table II. Discrepancies occur above 130°C.; although they are not sufficiently great to affect the procedure for practical vulcanization, they become significant when making quantitative estimates of crosslinking efficiency and when trying to account for the decomposed peroxide. No two workers have carried out their experiments under exactly the same conditions and with similar analytical procedures. It seems reasonable therefore to ascribe the variations in half-lives determined to experimental factors rather than to changes of decomposition rate with solvent. The results of the present work in natural rubber give a first-order decomposition of the peroxide; the Arrhenius plot of log k against $1/T$ leads to the rate expression $k = 3.9 \times 10^{13}\ e^{-32500/RT}$. If decomposition of the peroxide occurs in a hydrocarbon medium, the production of cumyl alcohol indicates hydrogen abstraction by the cumyloxy radicals. Acetophenone will be produced by decomposition of cumyloxy radicals and therefore analysis of the reaction products for acetophenone and cumyl alcohol allows the fate of the cumyloxy radicals to be ascertained. From eqs. (2) and (3) it follows that

$$C_K/C_A = K_3/K_2 \cdot [PH] \qquad (4)$$

The values of the ketone to alcohol ratios are shown in Table I and they appear to be constant within the limits of experimental error at any one temperature of reaction; a plot of log C_k/C_A against $1/T$ is linear and gives a value of 11 kcal./

mole for the difference between the activation energies for reactions (3) and (2).

The efficiency of the crosslinking reaction can be determined from a knowledge of the number of crosslinks formed and the number of molecules of peroxide decomposed; the values so obtained are shown in Tables III and IV. It should be stressed that the measurement of crosslink density is based upon the correlation found between the chemically and physically determined crosslink densities in the di-*tert*-butyl peroxide–natural rubber system,[6] and insofar as this is so the values in Tables III and IV are correct only if the assumption of exclusive combination of rubber radicals to give elastically effective crosslinks, made in the di-*tert*-butyl work,[6] is valid. The arguments given in support of this assumption in the di-*tert*-butyl peroxide system[6] concern only the rubber radicals and are therefore applicable to the present work.

The mean value obtained for the crosslinking efficiency is 97%, and there is no obvious trend with temperature. As the temperature of reaction is increased the fraction of cumyloxy radicals decomposing to methyl radicals will increase; this does not seem to affect the crosslinking efficiency in any way, and at 140°C. the crosslinking efficiency is still virtually 100%, although 11% of the cumyloxy radicals undergo further decomposition. Hence the methyl radicals are also effective in producing crosslinks, although owing to the limiting factor of experimental accuracy it cannot be claimed that their efficiency is unity.

The high value obtained for the crosslinking efficiency does not exclude the possibility that cumyloxy radicals become incorporated in the crosslinked polymer, although it does show that no wastage occurs through side reactions not leading to the formation of crosslinks. Infrared analysis showed that the only soluble reaction products were acetophenone and cumyl alcohol and hence, a quantitative estimation of these two materials together with that of the undecomposed peroxide when compared with the initial peroxide concentration should indicate whether cumyloxy radicals become attached to the rubber. The results obtained are shown in the last column of Table I, and they show that within the limits of experimental accuracy none of the cumyloxy radicals is attached to the crosslinked polymer. In this respect dicumyl peroxide resembles di-*tert*-butyl peroxide. From the chemical standpoint it is a very efficient crosslinking agent in natural rubber.

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Synopsis

The rate of decomposition of dicumyl peroxide in natur rubber has been measured at four temperatures and th results lead to the expression $k = 3.9 \times 10^{13} e^{-32500/RT}$ for th rate constant. The crosslinking efficiency is high and i constant over the range 110 to 140°C. The low value found for the ratio of acetophenone to cumyl alcohol in th reaction products indicate that hydrogen abstraction i brought about mainly by cumyloxy radicals, although i seems likely that methyl radicals present are also effectiv in producing crosslinks. No cumyloxy radicals becom attached to the polymer during the crosslinking reaction.

Résumé

La vitesse de décomposition du peroxyde de décumyl dans le caoutchouc naturel a été déterminée à 4 températures différentes et les résultats nous donnent la relation suivante $k = 3.9 \times 10^{13} e^{-32500/RT}$ pour la constante de vitesse. L'efficacité de pontage est élevé et est constante pour des températures de l'ordre de 110°C à 140°C. Les faibles valeurs trouvées par le rapport de l'acétophénone à l'alcool cumylique dans les produits de réaction indiquent que l'abstraction d'un hydrogène est due principalement aux radicaux cumyloxy, cependant il apparaît de la même manière que les radicaux méthyle présents sont également efficaces pour la production des ponts. Aucun radical cumyloxy n'est attaché au polymère pendant la réaction de réticulation.

Zusammenfassung

Es wurde die Zersetzungsgeschwindigkeit von Dicumylperoxyd in Naturkautschuk bei vier Temperaturen gemessen; die Ergebnisse führen zu folgendem Ausdruck für die Geschwindigkeitskonstante: $k = 3.9 \times 10^{13} e^{-32500/RT}$. Die Vernetzungsausbeute ist gross und im Bereich von 110 bis 140°C konstant. Die kleinen Werte für das Verhältnis von Acetophenon zu Cumylalkohol in den Reaktionsprodukten zeigen, dass die Wasserstoffabspaltung hauptsächlich durch die Cumyloxyradikale hervorgerufen wird, obwohl wahrscheinlich die vorhandnen Methylradikale auch Vernetzungsstellen erzeugen. Während der Vernetzungsreaktion werden keine Cumyloxyradikale an das Polymere gebunden.