53.8°. The aryloxyacetic acid of this phenol melted at 157.4–158.8°. These values are identical with those previously reported[17] for 5-indanol and 5-indanyloxyacetic acid, respectively.

Neutral equivalent, calcd. 192. Found: 192.

Selective Extraction of Fraction 105.—An extraction experiment similar to that for fraction 99, yielded an oil which could not be crystallized. The ultraviolet spectrum of this material was almost identical with that of 5-indanol but its aryloxyacetic acid had a neutralization equivalent of 207, which agrees with that of a methyl-5-indanol. Repeated crystallization of this derivative did not yield a constant-melting compound.

Selective Extraction of Fraction 117.—An extraction experiment analogous to that carried out for fraction 99, yielded crystalline material melting after repeated crystallization from petroleum ether at 49.4–55°. The substance had an ultraviolet spectrum typical of a 5-indanol but was obviously impure. Insufficient material was at hand for further purification.

Isolation of *p*-Phenylphenol from Fraction 135.—A portion of this fraction was dissolved in petroleum ether (b. p. 30–60°) and cooled at 0°. The crystalline material which separated was recrystallized from petroleum ether and finally from benzene–cyclohexane. The melting point of this substance, 163–165° was not depressed upon admixture with the authentic compound.

Acknowledgments.—The authors are indebted to Mr. George Goldbach for technical assistance and to Miss Marion Springer for infrared measurements.

Summary

A procedure, based on the countercurrent method, is presented for separation and characterization of complex phenolic mixtures. By this means, 4- and 5-indanol were isolated from a coal hydrogenation oil.

BRUCETON, PA. RECEIVED SEPTEMBER 29, 1949

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[17] O. Kruber and A. Marx, *Ber.*, **73B**, 1175 (1940).

[CONTRIBUTION FROM THE INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Low Temperature Autoxidation of Hydrocarbons: the Phenomenon of Maximum Rates[1,2]

BY ARTHUR V. TOBOLSKY,[3] DONALD J. METZ AND ROBERT B. MESROBIAN

Introduction

Recent chemical researches in the field of hydrocarbon oxidations have demonstrated that hydroperoxides appear as one of the first products of reaction.[4–6] Kinetic studies have shown that subsequent oxidation of the parent hydrocarbon is autocatalyzed by the decomposition of hydroperoxides which produces radical chain carriers for the chain reaction.[7–11] The decomposition of hydroperoxides also leads to the formation of secondary oxidation products such as ketones, aldehydes, acids, alcohols, water, carbon dioxide, etc.[10–12]

One of the simplest and most completely worked out autoxidation mechanisms is the one proposed by Bolland and Gee[9] for the oxidation of ethyl linoleate. At sufficiently high pressures of oxygen (greater than 40 mm.) and in the range where a sufficiently high concentration of hydroperoxide has been built up so that hydroperoxide decomposition is the important chain initiation step, they proposed the mechanism

$$2\text{ROOH} \xrightarrow{k_1} \text{R}\cdot + \text{RO}_2\cdot + \text{H}_2\text{O} \qquad (1\text{A})^{12a}$$

$$\text{R}\cdot + \text{O}_2 \xrightarrow{k_2} \text{RO}_2\cdot \qquad (\text{A}) \quad (2\text{A})$$

$$\text{RO}_2\cdot + \text{RH} \xrightarrow{k_3} \text{ROOH} + \text{R}\cdot \qquad (3\text{A})$$

$$\text{RO}_2\cdot + \text{RO}_2\cdot \xrightarrow{k_6} \text{ROOR} + \text{O}_2 \qquad (4\text{A})$$

(where RH represents ethyl linoleate—C=C—CH—C=C— and the H in question is the one that detaches most easily, due to the activating influence of the double bonds).

The rate of oxidation of ethyl linoleate was taken by Bolland and Gee to be identical with the rate of step 3A, since under their mild conditions of oxidation, every molecule of oxygen absorbed by the substrate could be identified as hydroperoxide

$$d[\text{ROOH}]/dt = k_3[\text{RO}_2\cdot][\text{RH}] \qquad (1)$$

Although we shall find it necessary to modify equation (1) to account for results obtained under relatively severe oxidation conditions (high temperatures, presence of activators, strong light

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(1) Presented before the Division of Petroleum Chemistry at the 115th, April, 1949, meeting of the American Chemical Society in San Francisco.

(2) The work described in this paper first began during the tenure of sponsorship by the Office of the Quartermaster General under Contract QM·1180 with the Polytechnic Institute of Brooklyn and was completed during sponsorship by the Office of Naval Research under Contract N6onr·26309.

(3) Assistant Professor of Chemistry, Princeton University and Adjunct Professor of Chemistry, Polytechnic Institute of Brooklyn.

(4) H. Hock and H. Schrader, *Naturwissenschaften*, **24**, 159 (1936).

(5) R. Criegee, H. Pilz and H. Flygare, *Ber.*, **72**, 1799 (1939).

(6) E. H. Farmer and D. H. Sutton, *J. Chem. Soc.*, 119 (1943); 10 (1946).

(7) P. George, E. R. Rideal and A. Robertson, *Proc. Roy. Soc.* (*London*), **42**, 201 (1946).

(8) R. Robertson and W. A. Waters, *Trans. Fraday Soc.*, **42**, 236, 244 (1946).

(9) J. L. Bolland and G. Gee, *ibid.*, **42**, 236, 244 (1946).

(10) F. F. Rust and W. E. Vaughan, U. S. Patents Nos. 2,396,206 and 2,396,217.

(11) P. George and A. D. Walsh, *Trans. Faraday Soc.*, **42**, 94 (1946).

(12) H. Zuidema, *Chem. Rev.*, **38**, 197 (1946).

(12a) The R· shown on the right side of Eq. 1A is assumed to result from either a chain transfer step of RO· with RH or by self dismutation of the RO· to R·.

intensities, long times), the experimental conditions under which Bolland and Gee performed their oxidations justify their use of equation (1). Under mild conditions of oxidation the chain lengths of oxidation reaction are long and neglect of step 1A in writing the expression for d[ROOH]/d*t* is valid. On the other hand, by using the steady state condition for [R·] and [RO$_2$·], one can derive the following expression for the rate of oxygen absorption

$$-\,d[O_2]/dt = k_3[RO_2\cdot][RH] = k_3(k_1/k_6)^{1/2}[ROOH][RH] \quad (2)$$

Whereas equation (1) is valid only at the beginning of the reaction where hydroperoxide decomposition is slow compared to the chain propagating steps 2A and 3A, equation (2) holds even when the decomposition of hydroperoxide is not negligibly slow.

In this paper we shall discuss the autoxidation of hydrocarbons with particular emphasis upon the phenomenon of maximum rates of oxidation. The paper will be divided into three parts. In Part I, we shall show that a straightforward mathematical extension of the mechanism of Bolland and Gee predicts the occurrence (at sufficiently advanced stages of autoxidation) of steady states of hydroperoxide concentration and steady rates of oxygen absorption. We shall also discuss activated autoxidations such as occur when light or heavy metal ions are used to accelerate the decomposition of hydroperoxides. The theory predicts that agencies which hasten the decomposition of hydroperoxides will accelerate the initial phases of autoxidation, but that the maximum rate of autoxidation is a function of temperature *alone*, and is independent of the presence of activator.

In Part II experimental evidence for the phenomenon of maximum rates of oxidation in vulcanized rubber is presented. It is shown that at low temperatures, light will accelerate the rate of oxygen absorption by vulcanized rubbers until at each temperature a critical light intensity is reached, at which point further increase in light intensity has no effect. Furthermore, it is shown that at sufficiently high temperatures, light will not accelerate the rate of oxidation of vulcanized rubber.

In Part III a theory is developed by which one can calculate the number of chain cleavages per gram of vulcanized rubber from stress relaxation measurements. By comparing scission with oxygen absorption data, it is also possible to calculate the number of oxygen molecules absorbed per cut. At low temperatures (in the absence of light or at sufficiently low light intensities) the number of oxygen molecules absorbed per chain cleavage is large. Under conditions of maximum rate of oxidation, however, the number of oxygen molecules absorbed per chain cleavage is approximately unity.

Part I. Theoretical

An Extension of the Mechanism of Bolland and Gee to Advanced Stages of Autoxidation.—If in writing the equation for the rate of change of hydroperoxide concentration with time based on mechanism A, we include the disappearance of hydroperoxide due to 1A assuming bimolecular thermal decomposition of the hydroperoxide, then

$$\frac{d[ROOH]}{dt} = k_3\sqrt{\frac{k_1}{k_6}}\,[ROOH][RH] - k_1[ROOH]^2 \quad (3)$$

This equation can be integrated, assuming [RH] to be constant, to give

$$[ROOH] = \frac{[ROOH]_\infty}{1 - \left(1 - \frac{[ROOH]_\infty}{[ROOH]_0}\right)\exp(-\,at)} \quad (4)$$

where [ROOH]$_\infty$ is the steady state value of hydroperoxide (the concentration approached at time $t = \infty$, and [ROOH]$_0$ is the initial concentration of hydroperoxide, and where

$$[ROOH]_\infty = \frac{k_3}{\sqrt{k_1k_6}}[RH];\ a = k_3\sqrt{\frac{k_1}{k_6}}\,[RH] \quad (5)$$

From equation (5) it appears that the value of [ROOH]$_\infty$ during the thermal autoxidation is a function of temperature and the concentrations of substrate alone. Upon integration of equation (2) one obtains for the total amount of oxygen absorbed as a function of time

$$-\,[O_2] = [ROOH]_\infty\,at + [ROOH]_\infty \ln\left\{\frac{1 - \left(1 - \frac{[ROOH]}{[ROOH]_0}\right)\exp(-\,at)}{1 - \left(1 - \frac{[ROOH]_\infty}{[ROOH]_0}\right)}\right\} \quad (6)$$

which when $t \rightarrow \infty$ approaches the limiting value

$$-\,[O_2] = [ROOH]_\infty\,at - [ROOH]_\infty \ln\frac{[ROOH]_\infty}{[ROOH]_0} \quad (7)$$

Graphs of equations (4) and (6) are shown in Figs. 1 and 2 where [ROOH]/[ROOH]$_\infty$ and $-$ [O$_2$]/[ROOH]$_\infty$ are plotted as functions of *at* for various values of [ROOH]$_\infty$/[ROOH]$_0$. If the initial concentration [ROOH]$_0$ is larger than [ROOH]$_\infty$, there will, of course, be a decrease of hydroperoxide concentration with time as shown in Fig. 1, and the $-$ [O$_2$]/[ROOH]$_\infty$ curves will exhibit a continually decreasing slope until a steady rate is asymptotically reached as shown in Fig. 2. The curves for ratios [ROOH]$_\infty$/[ROOH]$_0$ less than unity are drawn as dotted lines.

The chain length (γ) at any time during the oxidation may be defined as the rate of oxidation divided by the rate of initiation

$$\gamma = \frac{k_3[RO_2\cdot][RH]}{k_1[ROOH]^2} = \frac{k_3\sqrt{\frac{k_1}{k_6}}\,[ROOH][RH]}{k_1[ROOH]^2} = \frac{[ROOH]_\infty}{[ROOH]} \quad (8)$$

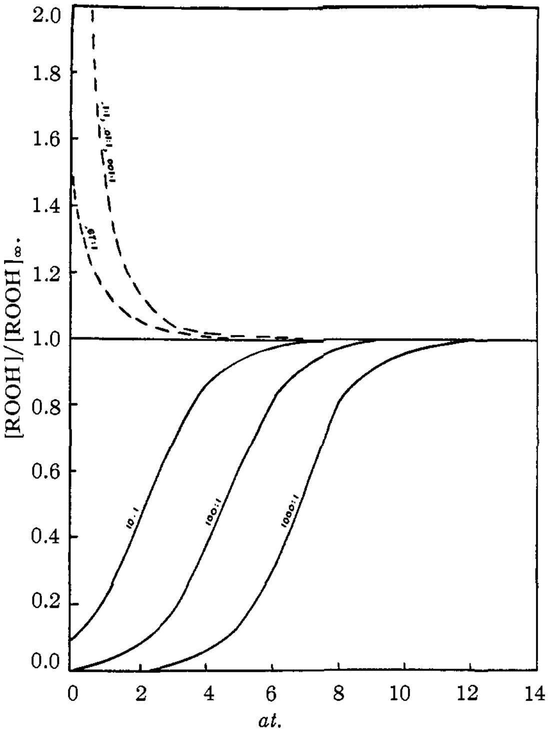

Fig. 1.—Theoretical curves of hydroperoxide content as a function of time (unactivated systems) for indicated ratios of [ROOH]$_\infty$/[ROOH]$_0$ (Eq. 4.).

From equation (8) it is clear that when the steady-state concentration of hydroperoxide has been reached, the chain length of the reaction is unity even though the chain length may have been very large during the initial stage of autoxidation. At the point where ν is unity the propagation step 3A in the chain reaction proceeds at the same rate as the initiation step, and the rate of oxidation approaches a steady state value which is a maximum value if $[\text{ROOH}]_0 < [\text{ROOH}]_\infty$. If we define the velocity of the oxidation as equal to $-\text{d}[\text{O}_2]/\text{d}t = k_3[\text{RO}_2\cdot][\text{RH}]$, then the steady-state rate of oxidation (when the hydroperoxide has reached its limiting concentration) is

$$-\left[\frac{\text{d}[\text{O}_2]}{\text{d}t}\right]_\infty = \frac{k_3^2[\text{RH}]^2}{k_6} \qquad (9)$$

When $[\text{ROOH}]_\infty/[\text{ROOH}]_0$ is considerably greater than unity, the time $t_{1/2}$ required for the hydroperoxide concentration to reach one half its maximum value is

$$t_{1/2} = \frac{1}{a}\ln\left(\frac{[\text{ROOH}]_\infty}{[\text{ROOH}]_0} - 1\right) \qquad (10)$$

From equation (5) for $[\text{ROOH}]_\infty$ it is clear that the maximum concentration of hydroperoxide will vary with temperature according to the magnitude of the expression given below

$$E_3 - \frac{1}{2}(E_1 + E_6) \qquad (11)$$

where E_3 E_1 and E_6 are the activation energies of steps 3A, 1A and 4A, respectively.

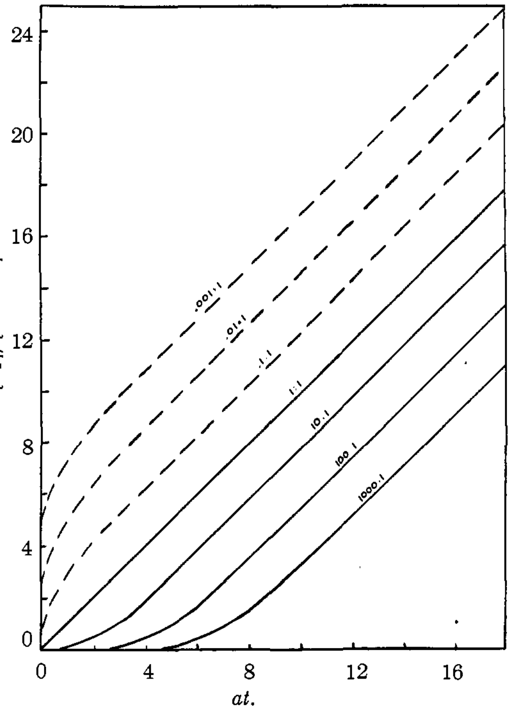

Fig. 2.—Theoretical curves of oxygen absorption as a function of time (unactivated systems) for indicated ratios of [ROOH]$_\infty$/[ROOH]$_0$ (Eq. 6).

If this quantity is negative, as is the case in Bolland and Gee's investigation of ethyl linoleate, then the steady state concentration of hydroperoxide will decrease with increasing temperature, and also $t_{1/2}$ from equation (10) will decrease very rapidly with increasing temperature.

First Order Decomposition of Hydroperoxide and Activated Autoxidation.—Mechanism A has been shown by Bolland and Gee to be valid for ethyl linoleate, though, as they point out, the exact nature of the products in 1A and 4A are unknown. For long oxidation chains the exact formulation of the products in 1A and 4A is not important, but for chains of unit length as proposed in this paper, the derived rate expression depends (within a small numerical factor) on the type and number of radicals produced in 1A and on whether oxygen is evolved in 4A. Furthermore, ethyl linoleate hydroperoxide is the only published example of bimolecular peroxide or hydroperoxide decomposition. For example, tetralin hydroperoxide decomposition is first order plus some chain decomposition.[13]

We shall consider below a particular autoxidation mechanism in which the decomposition of hydroperoxide is activated by an agency such as light or heavy metal ion and breaks into two radicals, X and Y. We shall also suppose that X and Y are each converted almost immediately to [R·] by radical transfer with the substrate [RH]. The kinetic equations are

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(13) R. Robertson and W. A. Waters, *J. Chem. Soc.*, 1578 (1948).

$$\mathrm{ROOH} + \mathrm{Act} \xrightarrow{k_1'} \mathrm{X} + \mathrm{Y} \longrightarrow 2\mathrm{R}\cdot \quad (1\mathrm{B})$$

$$\mathrm{R}\cdot + \mathrm{O_2} \xrightarrow{k_2} \mathrm{RO_2}\cdot \quad (2\mathrm{B})$$

$$\mathrm{RO_2}\cdot + \mathrm{RH} \xrightarrow{k_3} \mathrm{ROOH} + \mathrm{R}\cdot \quad (\mathrm{B}) \quad (3\mathrm{B})$$

$$\mathrm{RO_2}\cdot + \mathrm{RO_2}\cdot \xrightarrow{k_6} \mathrm{RO_2R} + \mathrm{O_2} \quad (4\mathrm{B})$$

The kinetic expressions for d[ROOH]/dt and for $-$ d[O_2]/dt after insertion of the steady state conditions for [R·] and [RO_2·] are

$$\mathrm{d[ROOH]/d}t = k_3(2k_1'/k_6)^{1/2}\,[\mathrm{Act}]^{1/2}[\mathrm{ROOH}]^{1/2}[\mathrm{RH}] - k'[\mathrm{Act}]\,[\mathrm{ROOH}] \quad (12)$$

$$-\,\mathrm{d[O_2]/d}t = k_3(2k_1'/k_6)^{1/2}[\mathrm{Act}]^{1/2}[\mathrm{ROOH}]^{1/2}[\mathrm{RH}] + k'[\mathrm{Act}]\,[\mathrm{ROOH}] \quad (13)$$

From equation (12), the steady state value of hydroperoxide concentration is

$$[\mathrm{ROOH}[_\infty = \frac{2k_3^2[\mathrm{RH}]^2}{k_1'k_6[\mathrm{Act}]} \quad (14)$$

The maximum rate of oxidation

$$-\left[\frac{\mathrm{d[O_2]}}{\mathrm{d}t}\right]_{\max} = \frac{4k_3^2[\mathrm{RH}]^2}{k_6} \quad (15)$$

Because of the fact that in mechanism (B) two radicals of [R·] appear for every molecule of hydroperoxide that disappears, whereas in mechanism A in the previous reaction, *a* [R·] and a [RO_2·] radical appear for every *two* molecules of hydroperoxide that decompose, the maximum rate of oxidation for mechanism (B) is four times the maximum rate predicted by mechanism (A) (compare equations (15) and (9)).

The integrated equations for [ROOH] and $-$ [O_2] are

$$\frac{[\mathrm{ROOH}]}{[\mathrm{ROOH}]_\infty} = \left[1 - \left(1 - \frac{[\mathrm{ROOH}]_0{}^{1/2}}{[\mathrm{ROOH}]_\infty{}^{1/2}}\right)\exp\,(-\ k_1'[\mathrm{Act}]t)\right]^2 \quad (16)$$

$$\frac{-[\mathrm{O_2}]}{[\mathrm{ROOH}]_\infty} = 2k_1'[\mathrm{Act}]t + 6\left(1 - \frac{[\mathrm{ROOH}]_0{}^{1/2}}{[\mathrm{ROOH}]_\infty{}^{1/2}}\right)\exp\left(-\frac{k_1'[\mathrm{Act}]t}{2}\right) - \left(1 - \frac{[\mathrm{ROOH}]_0{}^{1/2}}{[\mathrm{ROOH}]_\infty{}^{1/2}}\right)_2\exp\,(-\ k_1'[\mathrm{Act}]t - 1) \quad (17)$$

Equations (12–17) can be modified to include the case of spontaneous (unactivated) first order decomposition of hydroperoxide by formally replacing k_1'[Act] in these equations by k_1''; where k_1'' is defined as the specific rate constant for unactivated first order disappearance of the hydroperoxide (into two radicals X and Y which convert to 2R· by radical transfer).

It should be pointed out that from equation (14) it appears that the steady state hydroperoxide concentration varies inversely with the activator concentration. On the other hand the maximum rate of oxidation is independent of activator concentration and also is the same whether the decomposition is activated (rate of hydroperoxide decomposition = k_1'[Act][ROOH]) or whether the decomposition of hydroperoxide is a spontaneous first order reaction (rate of hydroperoxide decomposition = k_1''[ROOH]).

When [ROOH]$_\infty$/[ROOH]$_0$ is considerably greater than unity, the time required to reach one-half the maximum hydroperoxide concentration for the activated reaction is

$$t_{1/2} = \frac{2}{k_1'[\mathrm{Act}]}\ln\left\{\frac{1 - \dfrac{[\mathrm{ROOH}]_0{}^{1/2}}{[\mathrm{ROOH}]_\infty{}^{1/2}}}{1 - \sqrt{1/2}}\right\} \quad (18)$$

From (18) it is apparent that the faster the rate of initiation, *i. e.*, the higher the temperature or the higher the activator concentration, the shorter will be the time necessary to attain one-half the maximum concentration of hydroperoxide.

For activated autoxidation the steady state concentration of hydroperoxide will depend on

$$2E_3 - (E_1' + E_6) \quad (19)$$

where E_1' is the energy of activation for step 1B.

When this is positive, as is quite likely since E_1' will be small for activated systems, the steady state hydroperoxide concentration will increase with increasing temperature.

Since the steady or limiting rate of autoxidation (when [ROOH]$_0$ < [ROOH]$_\infty$) is the same for thermal as well as for activated autoxidations, the temperature dependence will be the same in both cases, and will vary according to

$$2E_3 - E_6 \quad (20)$$

We have not attempted to carry through here the complete kinetic treatment of photoactivated autoxidation. It seems very reasonable to assume, however, that the direct effect of light is to accelerate the decomposition of hydroperoxides, so that in many respects a photoautoxidation would bear an over-all similarity to an activated autoxidation. In particular equation (15) for the steady rate of autoxidation ought to be valid for photoautoxidation, too, provided that the same number and type of radicals are produced in the initiating step.

Discussion

There are only a small number of cases in which simultaneous studies of hydroperoxide formation and oxygen absorption have been reported in the literature. Of these, evidence of approach to a maximum concentration of hydroperoxide and a maximum rate of oxygen absorption appears in the paper by Almquist and Branch[14] on benzaldehyde oxidation, and in the papers of George, Rideal and Robertson,[7] and Robertson and Waters[8] on tetralin oxidation. In particular, the general features of the hydroperoxide–time curves and oxygen absorption curves of the latter authors bear an over-all similarity to those predicted by equations (5), (6), or (16) and (17).

In any attempt to apply the results of the

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[14] H. J. Almquist and G. E. K. Branch, THIS JOURNAL, **54**, 2293 (1932).

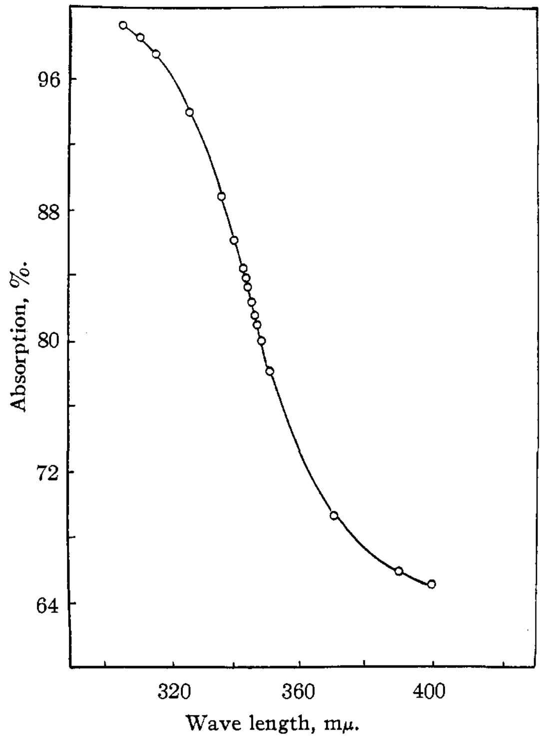

Fig. 3.—Per cent. light absorption (relative to air) Hevea vulcanizate, 2 mils thick.

theoretical treatment presented here to actual cases of oxidation, the following complications must be borne in mind: the extent of oxidation may proceed so far that the assumption that [RH] is a constant may be invalid; the products of oxidation (arising from the initiation and termination steps) may play an important role as inhibitors or activators of the oxidation chain as well as themselves being subject to further oxidation; adventitious impurities may be very important as inhibitors or activators; a side reaction causing destruction of the hydroperoxide (but which may not produce radicals) would also bring about the phenomenon of steady states of hydroperoxide concentration; the chain carrying radicals may themselves induce decomposition of the hydroperoxide.

If the products of oxidation help decompose the hydroperoxide, then the hydroperoxide concentration having reached a maximum will show a steady decline as seems to be the case in some of the reported experimental work.[8,14]

Part II. The Phenomenon of Maximum Rates in the Autoxidation of Vulcanized Natural Rubber

In Part I it was shown that relatively simple autoxidation schemes lead to the prediction of maximum rates of autoxidation at each temperature. In this part data will be presented which show that maximum rates of autoxidation occur in vulcanized natural rubber.

The work of Farmer and Sutton[6] leaves little doubt that hydroperoxide formation plays an important role in the oxidation of natural rubber. Nevertheless it would go far beyond our intention to imply that mechanism (A) and mechanism (B) presented in Part I apply to the case of vulcanized rubber without major or even fundamental modification. The establishment of a mechanism for oxidation of vulcanized rubber is particularly difficult because isolation of products is impossible and even the determination of functional groups (*e. g.* hydroperoxides) which appear during oxidation, presents serious difficulties. Furthermore, various compounds incorporated into rubber to effect vulcanization undoubtedly play an important role in the oxidation mechanism. However, the phenomenon of maximum rates observed in the present studies should be a valuable tool in the elucidation of the reaction mechanism, and the theoretical discussion in Part I may provide some useful clues and orientation.

Experimental Details

For studies of oxygen absorption and the phenomenon of maximum rates of autoxidation a commercially available natural rubber gum vulcanizate obtained from the Young's Rubber Company was used. Although its composition is unknown to us, the material was particularly suitable for photoautoxidation because it is translucent and has a uniform thickness of 2 mils. Although the presence of vulcanizing agents is undesirable since they no doubt affect the oxidation of the rubber hydrocarbon, the use of a vulcanizate enabled us to measure chain scission by stress relaxation studies as discussed in Part III. Data on the transmission curve of the rubber relative to air in the

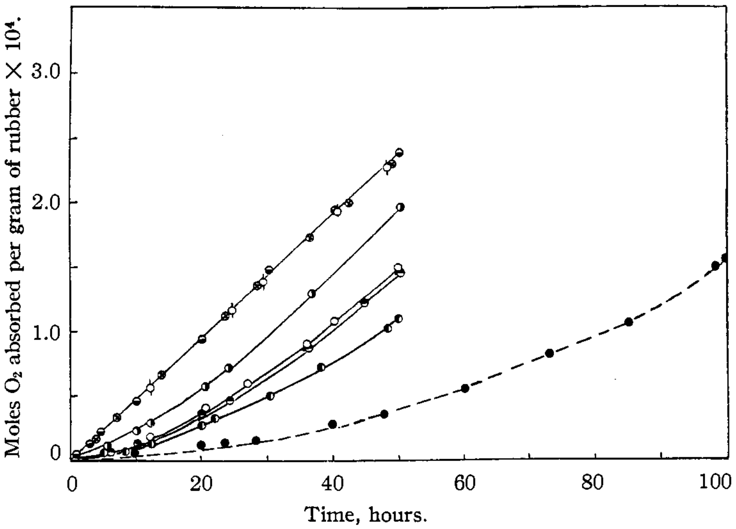

Fig. 4.—Oxygen absorption *vs.* time for natural rubber vulcanizate at 50°; relative light intensities × 6.6 × 10^{13} quanta/sec./sq. cm.: ●, thermal; ◐, 1.0; ○, 1.5; ◑, 2.5; ⊗, 4.5; ⊖, 10.0; ◓, 2.5*; ϕ, 10.0* (rotating half sector interposed).

wave length region 3000–4000 Å. were obtained with a Beckmann Spectrophotometer. From Fig. 3 it may be seen that there is almost complete absorption at the low wave length region decreasing to approximately 60% at 4000 Å.

The light source used in studies of photoactivated oxidation was a 100-watt H-4 mercury arc, operated from a stabilized voltage supply. Filtered radiation between 3100 and 4000 Å. was obtained with a Corning 5970 glass filter giving approximately 90% transmission in this wave length region. To measure light intensities a Weston photronic cell, Model 594 was used. This was calibrated against a uranyl oxalate actinometer for the same light source.

To measure volumetrically the amount of oxygen chemically absorbed by the rubber vulcanizate a static, horizontal tube apparatus[15] similar to that previously reported was employed. Data were calculated in terms of moles of oxygen absorbed per gram of vulcanizate.

Experimental Results

In Fig. 4 are shown data on oxygen absorption as a function of time for the natural rubber vulcanizate at 50°. Both thermal and photoautoxidation runs at various light intensities are represented. It is clearly evident from this graph that at sufficiently high light intensities the rate of oxidation reaches a maximum and does not increase further with increasing light intensity. Furthermore, at an incident light intensity of 10 × 6.6 × 10^{13} quanta/sec./sq. cm. the interposition of a rotating half sector (period ~0.01 second) *has no effect whatsoever* on the rate of oxygen absorption. The interposition of this same sector for a run carried out at a light intensity of 2.5 × 6.6 × 10^{13} quanta/sec./sq.cm. reduced the rate of oxidation to approximately 0.7 the rate in the absence of the sector.

In Fig. 5 are plotted oxygen absorption curves for thermal and photo runs at four temperatures, 50, 75, 100 and 120°. The photoactivated experiments (solid lines) correspond to the maximum attainable rates at each temperature. It is apparent that at the higher temperatures light has no appreciable effect on the rate of oxidation as compared to the thermal rate.

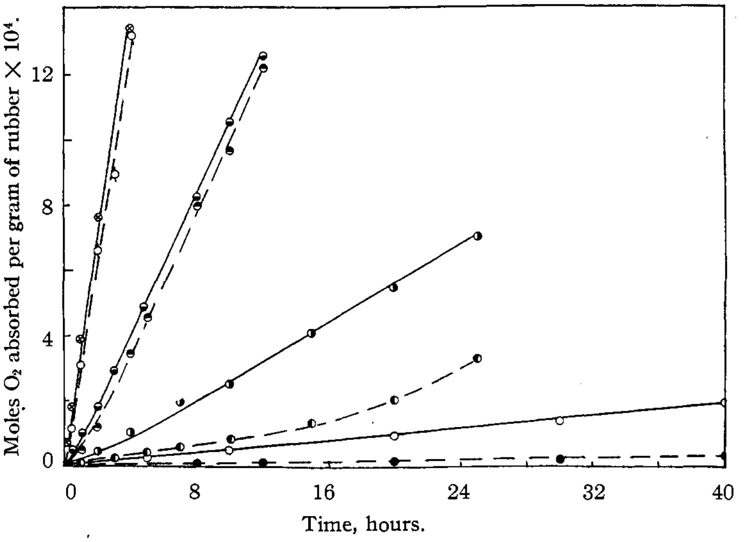

Fig. 5.—Oxygen absorption *vs.* time for natural rubber vulcanizate: ●, thermal 50°; ○, photo 50°; ◐, thermal 75°; ◑, photo 75°; ◓, thermal 100°; ◒, photo 100°; ⌽, thermal 120°; ⊗, photo 120°.

Oxygen absorption curves under conditions of maximum rates are linear with respect to time. In Fig. 6 the logarithm of the rate constants for oxygen absorption (obtained from the maximum rates) are plotted against the reciprocal of absolute temperature. The points lie on a straight line and from its slope an energy of activation of 15 ± 0.3 kcal. is calculated.

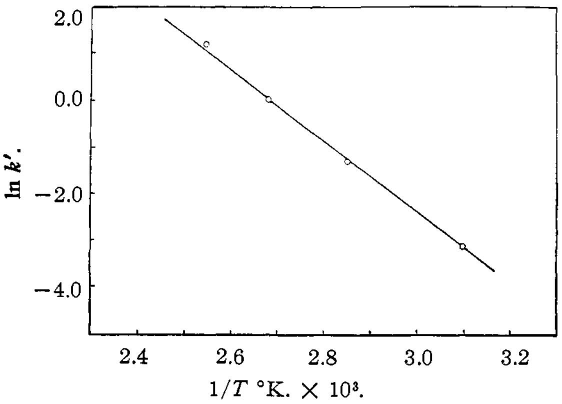

Fig. 6.—Temperature dependence of maximum rates of oxidation of natural rubber vulcanizate, $E_{\text{act.}}$ = 15 kcal.

To determine the extent that diffusion of oxygen into the rubber specimen might affect the observed results, experiments at 50 and 120° were made with samples of varying surface area to weight ratios[16] (Fig. 7). All studies were made under conditions that corresponded to maximum rates of oxygen absorption. At 50° with surface area to weight ratios of 207 and 121 sq. cm./g. no differences in oxygen absorption rates could be detected. For ratios of 71 and 44 the rates of oxidation do appear to be diffusion controlled as particularly noted for the smallest ratio. At 120° no appreciable variation in absorption rate could be detected for ratios of 207 and 71.

Since the rubber samples used throughout the studies reported here were of the highest surface area to weight ratio (207 sq. cm./g.), there is no evidence to indicate that the problem of the diffusion of oxygen into the rubber should invalidate our results. As further supporting evidence it should be added that the energy of activation of 15 kcal. calculated for the over-all oxidation reaction is on the order of 5 kcal. larger than might be expected for an oxygen diffusion controlled process.

Discussion and Summary

The experimental data presented in the previous section leads to the following conclusions:

1. For the thermal oxidation of the natural rubber vulcanizate studied here, a typical autocatalytic curve is obtained for oxygen absorbed *versus* time at 50°, and a steady rate of oxidation appears to be reached only after a very long time. At 120° a steady rate of oxidation is observed from the experimentally measurable beginning of the reaction.

2. At temperatures sufficiently low such that the unactivated thermal autoxidation has the characteristic autocatalytic form, the presence of light accelerates the rate of approach to a steady rate of oxidation.

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(15) R. B. Mesrobian and A. V. Tobolsky, *J. Polym. Sci.*, **2**, 463 (1947).

(16) Varying thicknesses of the gum vulcanizate were obtained by pressing together a number of 2 mil thick sheets under high pressure.

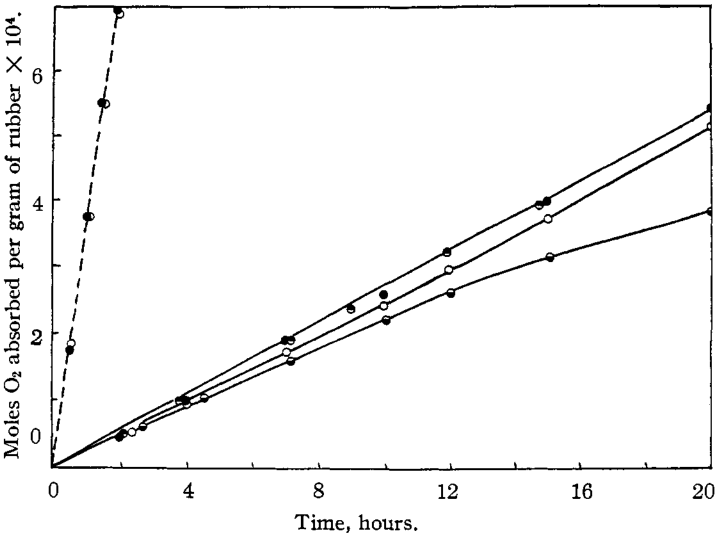

Fig. 7.—Effect of sample thickness on oxygen absorption of natural rubber vulcanizate: —, 75°; – –, 120°; area (sq. cm.)/gram: ●, 207; ◓, 121; ○, 71; ◒, 44.

3. With increasing temperature the effect of photoactivation upon the oxidation becomes progressively less pronounced. At 120° the rate of photoactivated oxidation is almost identical with the purely thermal rate.

4. At low and intermediate temperatures steady rates of oxidation are attained from the beginning of reaction if a sufficiently strong light intensity is present to serve as an activator. If the light intensity is further increased there is no change in the steady rate of oxidation.

5. With a sufficiently rapid rotating half sector, the effect of the interposition of the sector is to reduce the light intensity by half. It was shown that at intensities which were more than twice the intensity required to produce a steady rate of oxidation at 50°, the interposition of a rapidly rotating half sector had no effect on the oxidation rate. At low light intensities, the interposition of a rapidly rotating half-sector (period approximately 0.01 seconds) reduced the rate by a factor of 0.3. This means that in the autocatalytic range of low light intensities (at 50°) the life of the oxidation chain is greater than 0.01 seconds.

From these results one must conclude that at a given temperature there exists a steady rate of oxidation which under the experimental conditions is also a maximum rate. In addition this maximum steady rate of oxidation is unchanged by the presence of light, since the latter merely serves to accelerate the rate of approach to the maximum steady rate. These results are consistent with the predictions of the theory discussed in Part I, but by themselves do not constitute a proof that vulcanized rubber is a system obeying equations (A) or (B).

Part III. The Scission Reaction

During the oxidation of hydrocarbons there are always accompanying reactions of scission of the hydrocarbon chains and linkage of neighboring chains. For macromolecular hydrocarbons, these reactions play a very important role in the changes in mechanical properties that take place during oxidations (such as occur, for example, in natural or artificial aging). For vulcanized rubbers, we have previously developed methods for studying rates of scission and cross-linking.[17–20] It is the purpose of this section to present a quantitative comparison between the number of moles of chain cleavages and the number of moles of oxygen chemically absorbed in rubber vulcanizates.

Theoretical

Rubber vulcanizates have been shown to be three dimensional structures in which the original linear molecules have largely lost their identity through the process of cross linkage occurring during vulcanization. New parameters, M_c and N_0 have been used to describe these three dimensional structures. M_c is defined as the "effective" molecular weight between cross links, and N_0 is the "effective" number of moles of these "chains" between cross links per gram of rubber.[21] The relationship between M_c and N_0 is obviously

$$N_0 = 1/Mc \qquad (21)$$

The two parameters can be obtained from the theoretically derived equation of state,[22–25] relating stress f based on original cross section and relative length α which is the ratio of stretched to unstretched length

$$f_0 = \rho N_0 RT \left[\alpha - \left(\frac{1}{\alpha}\right)^2\right] = \frac{\rho RT}{M_c}\left[\alpha - \left(\frac{1}{\alpha}\right)^2\right] \qquad (22)$$

where ρ is the density of the rubber.

In order to determine the number of chain cleavages in a rubber network during air oxidation we have measured stress in a rubber vulcanizate maintained at constant length as a function of time. Let us suppose that at a time t at which q cuts per gram have resulted from oxi-

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[17] A. V. Tobolsky, I. B. Prettyman and J. H. Dillon, *J. App. Phys.*, **15**, 380 (1944).

[18] R. D. Andrews, R. B. Mesrobian and A. V. Tobolsky, *Trans. ASME*, **67**, 569 (1945).

[19] A. V. Tobolsky and R. D. Andrews, *J. Chem. Phys.*, **13**, 3 (1945).

[20] R. D. Andrews, A. V. Tobolsky and E. E. Hanson, *J. App. Phys.*, **17**, 352 (1946).

[21] We are employing the term "effective" number of chains to include the effects of chain ends, entanglements, etc. (ref. 22, 23).

[22] L. R. G. Treloar, *Trans. Faraday Soc.*, **39**, 241 (1943).

[23] F. T. Wall, *J. Chem. Phys.*, **11**, 527 (1943).

[24] E. Guth, H. M. James and H. Mark, "Advances in Colloid Science," Volume II, Interscience Pub., New York, N. Y., 1946.

[25] P. J. Flory, *Chem. Rev.*, **35**, 51 (1944).

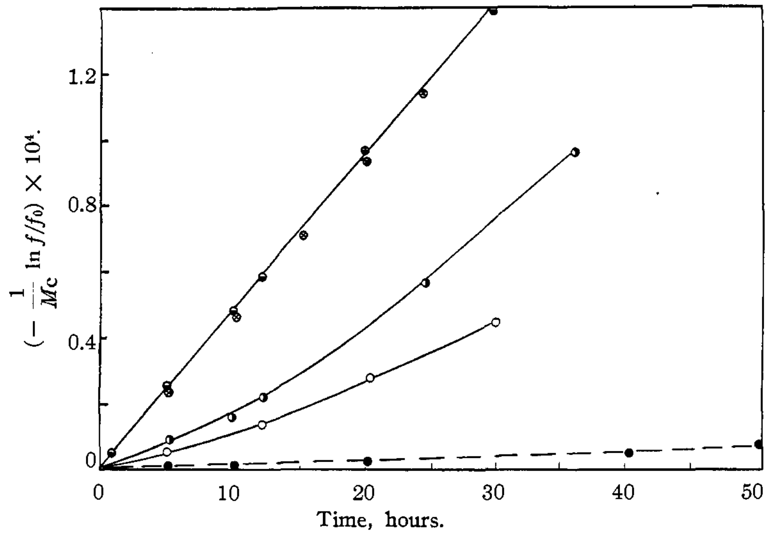

Fig. 8.—Chain scission *vs.* time for translucent natural rubber gum vulcanizate at 50°: relative light intensities × 6.6 × 10^{13} quanta/sec./sq. cm.: O, 1.5; ◑, 2.5; ⊗, 4.5; ⊖, 10.0; ●, thermal.

dative cleavage, the number of network "chains" per gram still supporting the stress at fixed relative length α is $N(q)$. The stress at this time will be

$$f = \rho N(q)RT\left[\alpha - \left(\frac{1}{\alpha}\right)^2\right] \quad (23)$$

In a previous paper[19] it was shown that f/f_0 as a function of time is independent of the relative length, α, up to at least a value of 2.5, provided α is maintained constant during the experiment. It is clear from equations (22) and (23) that

$$f/f_0 = N(q)/N_0 \quad (24)$$

It is now necessary to derive a relationship between $N(q)$ and q so that q may be obtained from the experimentally determined values of f/f_0. We shall assume that oxidative chain cleavage occurs randomly throughout the rubber network, so that a network chain once cut can be cut again with equal likelihood. This assumption presumes that the number of available sites for cleavage along a network chain is large. The number of chains, $N(q)$ per gram, supporting the stress in a rubber vulcanizate maintained at constant length will correspond only to the number of chains per gram that have never been cut. Those cuts which occur in previously cut chains will not decrease $N(q)$ and will therefore not cause a decay of stress. The relationship between $N(q)$ and q is

$$-\frac{dN(q)}{dq} = \frac{N(q)}{N_0} \quad (25)$$

upon integration

$$\frac{q}{N_0} = -\ln\frac{N(q)}{N_0} \quad (26)^{26}$$

From equations (21) and (24)

$$q = -1/M_c \ln f/f_0 \quad (27)$$

Inasmuch as M_c can be determined by measuring stress and relative length according to equation (22), and f/f_0 can be determined from stress relaxation studies, equation (27) provides a means of measuring q, the total number of cuts per gram rubber as a function of time. The value of q may now be compared to the experimentally determined number of moles of oxygen absorbed per gram as a function of time.

Experimental Details

Materials.—For the studies of chain scission the following natural and synthetic rubber gum vulcanizates were used. Only the first rubber listed could be used for photoactivated studies.

(1) *Translucent* natural rubber.—This is the same 2 mil thick rubber specimen used for the studies described in Part II. The molecular weight between cross links (M_c) calculated from equation (22) for this rubber is 6,500.

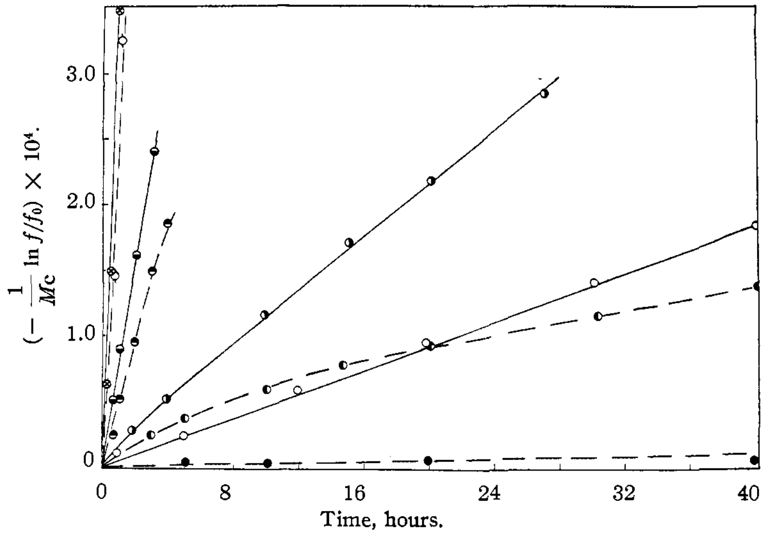

Fig. 9.—Effect of temperature on chains cission of translucent natural rubber gum vulcanizate, light intensity = 6.6 × 10^{13} quanta/sec./sq. cm.: 10 thermal, 50°; O, photo, 50°; ◐, thermal, 75°; ◑, photo, 75°; ◓, thermal, 100°; ⊖, photo, 100°; ϕ, thermal, 120°; ⊗, photo, 120°.

(2) Specially prepared natural, butyl and GR-S (butadiene-styrene 75/25) rubbers obtained from the Firestone Tire and Rubber Co. The compounding formulations for these rubbers, listed under the code numbers 198, B-3, and

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[26] An exact statistical treatment of the relationship between q and $N(q)$ when neither q, N_0 nor $N(q)$ are large, has been derived for us by Professor J. W. Tukey of Princeton University. The result is: $N(q) = N_0[1 - 1/N_0]^q$. This expression reduces to equation (26) when N_0 is large.

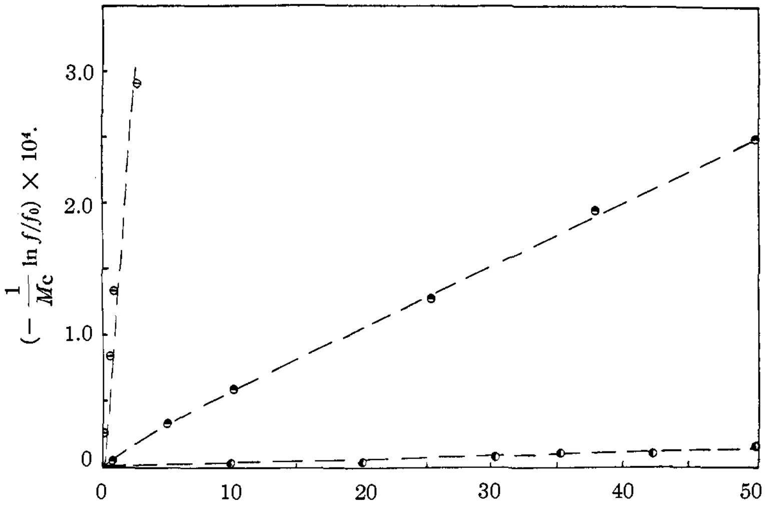

Fig. 10.—Effect of temperature on chain scission of natural rubber gum vulcanizate (198): ◐, thermal, 75°; ◓, thermal, 100°; ⊖, thermal, 130°.

202, respectively, have been previously reported.[17] Values of M_c have been determined by swelling measurements and from stress-strain relationships (equation (22)) and are reported to be in agreement by ±10%.[27] The values of M_c from stress–strain data are

Natural rubber	7600
GR-S	6000
Butyl	9000

(3) Vulcanizates of butadiene–dichlorostyrene copolymer (75/25, M_c = 7,600); butadiene–vinylpyridine (75/25, M_c = 8,500); butadiene–styrene–vinylpyridine (75/20/5, M_c = 6,600) and isoprene–styrene 75/25, M_c = 6,900) obtained from the U. S. Rubber Company. Calculations for M_c were made from stress–strain data only. The cure time for these rubbers was sixty minutes.[28]

Apparatus.—The light source used in studies of photoactivated chain scission is described in Part II.

For measurements of chain scission a beam balance stress relaxometer similar to those previously reported was used.[17] A slight modification in sensitivity was necessary, however, to enable small stresses to be measured. In photoactivated runs the door of the constant temperature box was fitted with a Corex glass window to permit the penetration of light to the rubber sample.

Experimental Results

The first set of studies to be described here on thermal and photoactivated chain scissions of the *translucent* natural rubber gum vulcanizate were designed to supplement the oxygen absorption studies presented in Part II. In Fig. 8 data on chain scission at 50° are given for both thermal and photoactivated runs. As previously noted for oxygen absorption studies (Part II), the rate of scission increases with light intensity until a limiting rate of chain scission is reached whereupon any further increase in light intensity does not change the scission rate. The ordinate in Fig. 8 labeled $-1/M_c \ln f/f_0$ represents the number of chain cuts (moles/gram rubber) in accordance with equation (27). In Fig. 9 the effect of temperature on the thermal and photoactivated rates of chain scission at 50, 75, 100 and 120° is shown. It should be noted that at 120° the presence of light results in a negligible increase over the thermal rate of scission as contrasted to the large effect light has upon the rate of scission at 50°.

Thermal studies of chain scission at 75, 100 and 130° for the natural rubber gum vulcanizate (Code No. 198) obtained from the Firestone Tire and Rubber Co. are shown in Fig. 10.

Oxygen absorption and chain scission data at 130° for the butyl, GR-S and four copolymer rubbers are summarized in Table I. Calculated ratios of oxygen absorbed to chain cuts are also listed in Table I. The experimental data from which this table is compiled have been previously reported.[16,17]

Discussion

The direct manner in which rates of oxygen absorption and chain scission can be experimentally measured for three-dimensional macromolecular hydrocarbons affords a convenient method to evaluate the ratio between oxygen absorbed and chain scission.

In Fig. 11 a plot of moles of oxygen absorbed per gram of rubber against moles of chain cuts per gram of rubber, at equivalent times of measurement, is given for the *translucent* natural rubber gum vulcanizate. In order to retain graphical clarity only the results obtained at 50

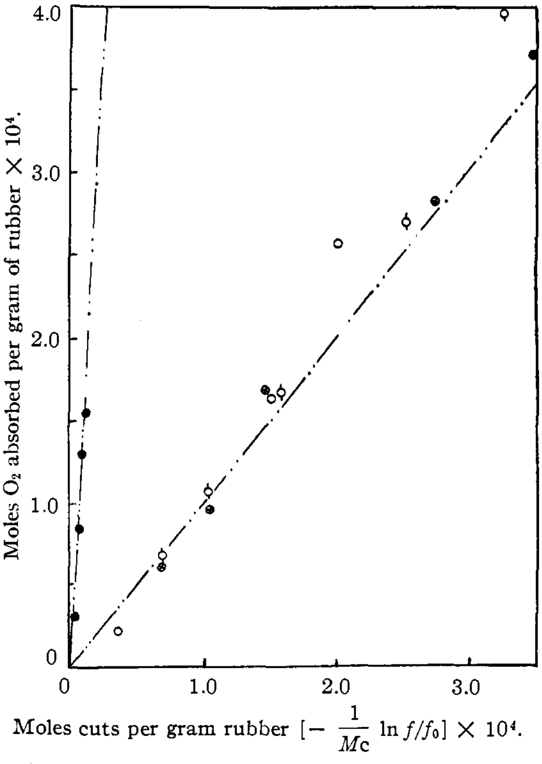

Fig. 11.—Relationship between moles of oxygen absorbed and moles of cuts for translucent natural rubber gum vulcanizate: ●, thermal, 50°; ○, photo, 50°; ϕ, thermal, 120°; ⊗, photo, 120°.

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[27] These data may be found in a dissertation presented to the Department of Chemistry, Princeton University, June, 1946, by Dr. R. L. Scott.

[28] Compounding formulas will be made available on request.

TABLE I

SUMMARIZED DATA ON OXYGEN ABSORPTION AND CHAIN SCISSION AT 130° FOR VARIOUS SYNTHETIC RUBBER GUM VULCANIZATES

Time, hours	f/f_0	Moles cuts/ gram rubber $[-1/M_c \ln f/f_0] \cdot 10^4$	Moles oxygen absorbed/ gram rubber $\cdot 10^4$	$\frac{\text{Moles oxygen absorbed}}{\text{moles cuts}}$
		GR-S		
0	1.0	0	0	..
1.0	0.65	0.72	0.23	0.3
3.0	.50	0.82	.45	.6
6.0	.39	1.57	.76	.5
10.0	.30	2.0	1.33	.7
25.0	.15	3.16	3.12	1.0
		Butyl		
0	1.0	0	0	..
0.4	0.80	0.25	0.05	0.2
1.0	.68	.43	.13	.3
4.0	.50	.77	.53	.7
10.0	.30	1.45	1.3	1.0
20.0	.20	1.78	2.68	1.5
30.0	.10	2.56	3.9	1.5
		Isoprene–Styrene		
0	1.0	0	0	..
1.0	0.80	0.32	0.22	0.7
3.0	.63	0.67	0.46	.7
8.0	.42	1.26	1.07	.9
15.0	.26	1.95	2.81	1.4
20.0	.20	2.33	4.06	1.7
30.0	.13	2.96	7.28	2.5
		Butadiene–Dichlorostyrene		
0	1.0	0	0	..
1.0	0.74	0.40	0.13	0.5
4.0	.60	.67	.26	.4
12.0	.50	.91	.58	.6
33.0	.40	1.21	2.20	1.8
		Butadiene–Vinylpyridine		
0	1.0	0	0	..
1.0	0.66	0.49	0.18	0.34
2.0	.55	.70	.36	.51
4.0	.46	.91	.85	.93
6.0	.39	1.11	1.34	1.21
10.0	.30	1.42	2.14	1.51
25.0	.20	1.92	4.82	2.51
		Butadiene–Styrene–Vinylpyridine		
0	1.0	0	0	..
1.0	0.75	0.44	0.22	0.50
3.0	.60	0.77	.36	.47
9.0	.41	1.35	.80	.59
20.0	.31	1.77	2.01	1.13
36.0	.24	2.16	4.42	2.04

and 120° are shown on the graph. At 50° the thermal studies indicate that approximately fifteen molecules of oxygen are absorbed for each chain cut. However, under maximum rate conditions of photoactivated oxidation and chain scission at 50° the ratio is close to unity. At 120° the ratio of oxygen absorbed to chain cuts is nearly unity for both the thermal and the photoactivated runs. Similar comparisons of data for runs made at the intermediate temperatures 75 and 100° show the expected results: namely, under maximum rate conditions of oxidation and chain scission the ratio is close to unity whereas the thermal ratios at 75 and 100° are about five and two, respectively.

The last column in Table I lists the ratio of moles of oxygen absorbed to moles of chain cuts for the synthetic GR-S, butyl and four copolymer rubbers. In almost every instance the ratios at 130° are two or less. The values obtained during the early times of measurement may be less precise than those for later times of measurement. During the initial stages of oxidation volatile products are often evolved, and if these are present in sufficient quantity the measured amount of oxygen absorbed will be less than the actual amount.

In Fig. 12 the relationship between oxygen absorbed and chain cuts for the natural rubber gum vulcanizate (198) is given at 75, 100 and 130°. For this rubber the ratio of oxygen absorbed to chain cuts is thirty at 75° and approaches unity at 130°.

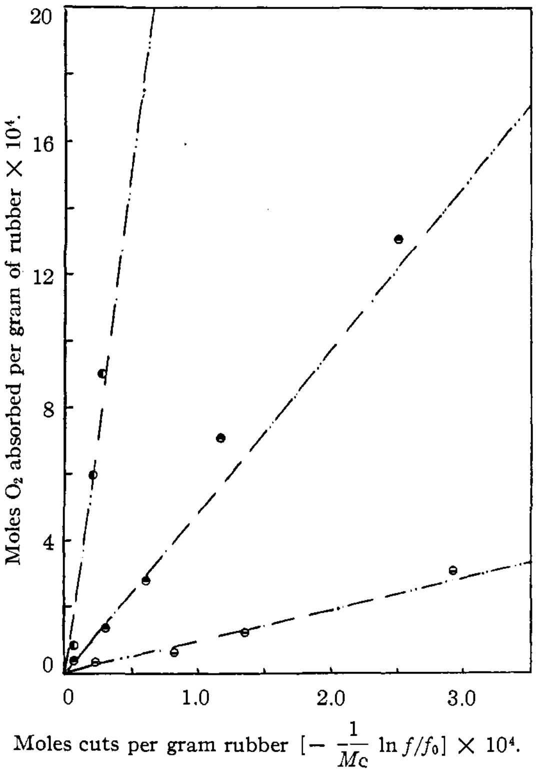

Fig. 12.—Relationship between moles of oxygen absorbed and moles of cuts for natural rubber gum vulcanizate (198): ◐, thermal, 75°; ◓, thermal, 100°; ⊖, thermal, 130°.

It should be pointed out that the data given in Table I and Figs. 11 and 12 represent an average of the total number of oxygen molecules absorbed until time t and an average of the total number of cuts that have occurred until time t. A scission ratio would be more exactly defined by the ratio of the *rate* of oxygen absorption at a given time to the *rate* of scission at the same time. The present calculations, which are sufficiently accurate for the data at hand, represent an average value of this scission ratio.

In other studies on pure unvulcanized natural rubber, Farmer and Sundralingham[29] have observed scission ratios as high as 75 during photoautoxidation at 35°. The number of cuts in this case was measured by the decrease in molecular weight of the polymer during oxidation in benzene solution.

It would be of great importance to ascertain whether the scission reaction can be directly associated with any of the steps in the autoxidation chain reaction, *e. g.*, initiation, propagation, or termination, or whether it is to be regarded as a side reaction. Our results are not sufficient to completely elucidate the nature of the scission reaction, which will be achieved only if more kinetic studies and more chemical evidence as regards the nature of the oxidation products become available. On the other hand, the observed fact that the scission ratio is close to unity under conditions of maximum rate, but larger than unity in the thermal reaction at relatively low temperatures should be of aid in delimiting the possible scission reactions.

For example, if chain scission were to occur in every initiation step (*i. e.*, as a result of hydroperoxide decomposition) then the scission ratio would be an exact measure of the oxidation chain length. If this were true, then during a typical autocatalytic oxidation the scission ratio should be high at first and approach unity as the maximum rate is approached. We have not observed this to occur under the specified conditions of the present studies.

Summary

Experimental data on the relationship between moles of oxygen absorbed and moles of chain cleavage during oxidation of three dimensional macromolecular hydrocarbons in the range 50–130° are presented. For the six different natural and synthetic rubbers studied, it is found that the ratio of oxygen absorbed to chain cleavages is close to unity when a steady rate of oxidation is observed. Under conditions of autoxidation, however, up to 30 moles of oxygen per mole of chain cleavage are found. An expression is derived to obtain the total number of chain cleavages from stress relaxation measurements.

BROOKLYN 2, N. Y. RECEIVED JUNE 28, 1949

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[29] E. H. Farmer and A. Sundralingham, *J. Chem. Soc.*, 125 (1943).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Argentometric Amperometric Titration of Cysteine and Cystine

BY I. M. KOLTHOFF AND W. STRICKS

Introduction

In the present studies it has been shown potentiometrically, polarographically and by solubility experiments that cysteine forms one or more compounds with silver ions in which the silver is bound very strongly. The chemistry of these compounds is unknown. From preliminary work which will be presented in a subsequent paper it appears to be very complex.

In this paper it is shown polarographically that at a *p*H in the neighborhood of 9, a slightly soluble silver cysteine compound is formed upon addition of silver nitrate to a buffered cysteine solution. This compound which is designated in this paper as RSAg gives a reduction wave at the dropping mercury electrode at a very negative potential indicating that the silver ion activity of the solution of the complex is extremely small. This behavior can be made the basis of an amperometric titration using the dropping mercury electrode as indicator electrode. Titrations with the dropping electrode do not give accurate and precise results at concentrations of 10^{-4} M or greater. Especially for the analysis of cysteine in biological materials it is desirable to have a rapid method for the determination of this substance. From the polarographic results it was concluded that under suitable conditions it should be possible to titrate traces of cysteine (further designated as RSH) with silver nitrate using the rotating platinum wire electrode in a way similar to that given by Kolthoff and Harris[1] for mercaptans.

When the present work was finished a paper appeared by Benesch and Benesch[2] who applied without essential change the procedure given by Kolthoff and Harris to the determination of sulfhydryl groups in amino acids and proteins. They mostly used solutions of high alcohol content as is required in the mercaptan determination.

In the present paper it is shown that accurate results can be obtained in aqueous medium if the titration is carried out under proper conditions.

The proposed method can also be applied for

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[1] I. M. Kolthoff and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **18**, 161 (1946).

[2] R. Benesch and R. E. Benesch, *Arch. Biochem.*, **19**, 35-45 (1948).