which produce the very high solvent viscosity and boiling point. The weakly solvating alkali metal cations would then be expected to be relatively mobile, the mobility increasing with increasing crystallographic radius of the cation. Moreover the lability of the cation-to-solvent bonds involving the larger alkali metals may allow these solvated cations to move not as distinct solvated units, but with continual exchange of solvent molecules so that the cation moves with respect to even its innermost solvation sheath. Such a process is favored by the strong intermolecular forces between the ethanolamine molecules, since these forces resist the motion of solvent molecules relative to each other.

The $1/K_D$ values lend support to the above statements. The similar values for $AgNO_2$ and $Bu_4NI$ suggest that in the case of $Ag^+$ the solvated cation is considerably larger than its crystallographic radius of $Ag^+$, and that the strongly coordinated solvent molecules hinder the close approach of anions to form stable ion pairs. All sodium salts have higher dissociation constants than the potassium analogs and in the case of the alkali chlorides the order of $1/K$ values is $Li < Na < K$, suggesting again that the over-all solvated cation radius and the energy of solvation increases from K to Li. With increasing strength of alkali cation–solvent bond, close approach of the anion is increasingly hindered.

The order of anion conductances for the alkali salts is quite unique, being $NO_2^- > NO_3^- > CNS^- > Cl^- > Br^- > I^-$. This order for the halides is exactly the reverse of that obtained with the solvents dimethylformamide and N-methylacetamide studied by French and Glover.[11] This may be partly due to the different tendency toward solvation existing in the two types of solvent systems. The order of $1/K$ values, however, is $Cl > I > Br$ for both sodium and potassium salts, though the differences between iodide and bromide are small and may not be significant.

The over-all order of anion mobility is difficult to explain in detail due to the differences in the structure of the anions. Factors such as size, charge, dipole moment and symmetry would all be expected to affect the anion–solvent attraction and, therefore, the ionic conductances and ion pair formation. If the anions are slightly solvated, then their relative sizes may be the chief factor affecting the mobilities, and the greater conductance of nitrite than nitrate and the decreasing order of conductance for chloride, bromide and iodide can be understood.

[11] C. M. French and K. H. Glover, *Trans. Faraday Soc.*, **51**, 1427 (1955).

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

# The Mechanism of Oxidative Scission in Natural Rubber[1]

BY A. V. TOBOLSKY AND A. MERCURIO[2]

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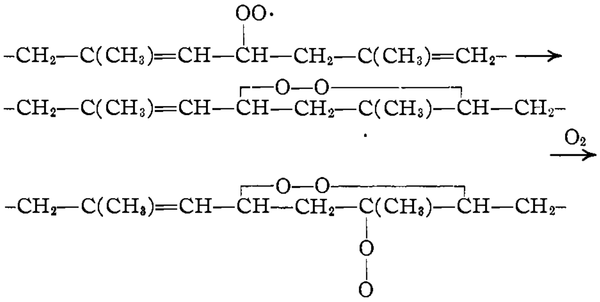
The free radical producers 2-azobisisobutyronitrile, di-*t*-butyl peroxide and benzoyl peroxide have been used to initiate the oxidation of natural rubber in dilute benzene solutions at 60–80°. Quantitative comparisons are made between the measured rate of scission of natural rubber and the known rate of initiation of oxidation chains (in the kinetic sense) by these agents under these conditions. We find that one scission occurs for each initiating radical produced. This is interpreted to mean that scission occurs in the termination step of the radical chain reaction. A possible chemical mechanism for the oxidative scission of natural rubber is discussed.

Natural rubber oxidation by molecular oxygen involves a radical chain reaction[3] very similar to the mechanism proposed to explain the oxidation of ethyl linoleate.[4] In the case where an external initiator (a free radical source) is used, the following mechanism applies at intermediate or high oxygen pressure

$$\begin{array}{lll}
\text{(a)} & \text{Initiator} \longrightarrow 2R'\cdot & \\
\text{(a')} & R'\cdot + RH \longrightarrow R\cdot + R'H & \left.\right\} \text{Initiation} \\
\text{(b)} & R\cdot + O_2 \longrightarrow RO_2\cdot & \\
\text{(c)} & RO_2\cdot + RH \longrightarrow ROOH + R\cdot & \left.\right\} \text{Propagation} \\
\text{(d)} & RO_2\cdot + RO_2\cdot \longrightarrow & \\
 & \qquad \text{Termination products} & \text{Termination}
\end{array}$$

In the above equations RH represents natural rubber $(-CH_2-CH=C(CH_3)CH_2-)_n$. Radicals originating from the external initiator interact with the rubber in step (a′) to form R· either by the abstraction of an α-methylenic hydrogen atom or by attack at the double bond. A side reaction occurring in propagation is the intramolecular reaction of $RO_2\cdot$ as[5]



A very noticeable consequence of the oxidation is scission of polyisoprene chains. In this paper, we have associated the scission reaction with a

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[1] This article is based upon a dissertation submitted by A. Mercurio in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

[2] Thiokol Chemical Corporation Fellow 1957–1958.

[3] Reviewed in N. Grassie, "The Chemistry of High Polymer Degradation Processes," Interscience Publishers, Inc., New York, N. Y., 1956, Chapter 4.

[4] J. Bolland and G. Gee, *Trans. Faraday Soc.*, **42**, 236 (1946).

[5] J. Bolland and H. Hughes, *J. Chem. Soc.*, 492 (1949).

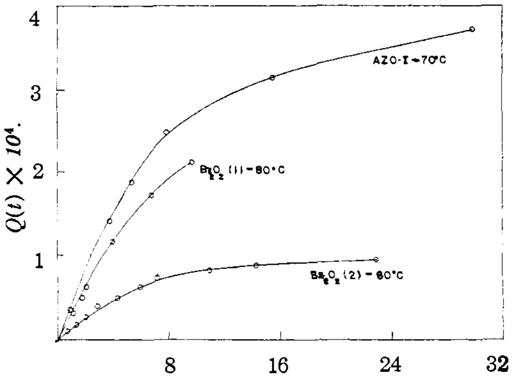

Fig. 1.

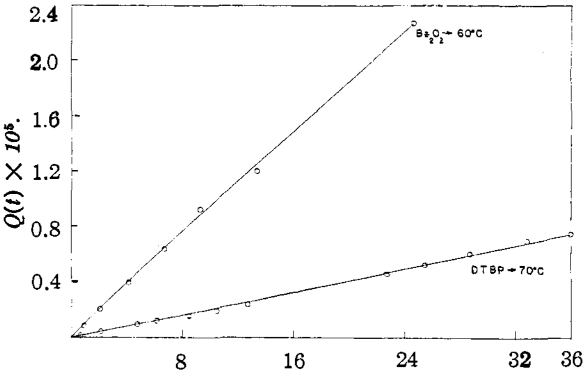

Fig. 2.

definite step in the kinetic sequence outlined above.

This was accomplished by a kinetic study of scission of unvulcanized natural rubber in the form of dilute solutions of rubber in benzene which were exposed to a continuous supply of molecular oxygen at one atmosphere pressure. The studies were made in the temperature range 60–80°, and the oxidation chains were initiated by the well studied catalysts benzoyl peroxide ($Bz_2O_2$), di-*t*-butyl peroxide (DTBP) and 2-azobisisobutyronitrile (AZO-I). The rates at which these catalysts produce radicals are very accurately known from other studies. The oxidation of natural rubber (and the accompanying scission) which occurs in the absence of external initiators is largely initiated by the hydroperoxides formed along the rubber chain. This is clearly an autocatalytic reaction and for this reason the oxidation in the absence of external initiators is called autoxidation. Under the conditions of the kinetic studies reported here, autoxidation and autoxidative scission were negligible compared with the oxidation and accompanying scission produced by the external initiators.

Scission was measured by following the number average molecular weight of the rubber as a function of time. The total number of cuts per cc. of rubber which have occurred up to time $t$ is denoted by $Q(t)$ and can be obtained from

$$Q(t) = dN[1/\bar{M}_n(t) - 1/M_n(0)] \qquad (1)$$

where $M_n(t)$ is the number average molecular weight at time $t$, $M$n(0) is the initial number average molecular weight, $d$ is the density, and $N$ is Avogadro's number.

The rate $R_i$ (in moles per cc. per second) at which the initiators used produce radicals is given by

$$R_i = 2k_d[\text{Init.}] \qquad (2)$$

where $k_d$ is the rate constant for spontaneous first-order homolytic cleavage of the individual initiators, Integration of (2) gives

$$\{R\cdot\}_t = 2[\text{Init.}]_0[1 - \exp(-k\,t)] \qquad (3)$$

where $\{R.\}_t$ is the total number of radicals per cc. which have been produced to time $t$. The values of $k_d$ are well known for these initiators at the temperatures used, hence $\{R\cdot\}_t$ can be computed. Table I shows the experimental conditions of initiator concentration, temperature and rubber concentration in benzene at which the scission studies were made. The experimental data is plotted as $Q(t)$ *vs.* time in Figs. 1 and 2.

TABLE I

EXPERIMENTAL CONDITIONS FOR THE SCISSION STUDY

| Initator | $[\text{Init.}]_0 \times 10^4$ (moles/cc. of rubber) | RH concn. (cc./l.) | Temp., °C. | $k_d$, sec.$^{-1}$ | Ref. |
|---|---|---|---|---|---|
| Azo-I | 1.76 | 1.16 | 70 | $3.80 \times 10^{-5}$ | 6 |
| DTBP | 19.5 | 1.39 | 70 | $1.44 \times 10^{-8}$ | 7 |
| $Bz_2O_2$ | 1.01 | 1.02 | 60 | $3.34 \times 10^{-6}$ | 8 |
| $Bz_2O_2$ | 0.89 | 0.944 | 80 | $4.3 \times 10^{-5}$ | 8 |
| $Bz_2O_2$ | 3.02 | 1.00 | 80 | $4.3 \times 10^{-5}$ | 8 |
| $Bz_2O_2$ | 1.78 | 1.06 | 80 | $4.3 \times 10^{-5}$ | 8 |

In Table II are listed the data obtained for $\{R\cdot\}_t$ from equation 3 and $Q(t)/N$ from equation 1 under the experimental conditions used. It is seen that for all three initiators $Q(t)/\{R.\}_tN$ was of the order of magnitude of unity. These values will reflect our neglect of the efficiency factor $f$ with which generated free radicals initiate oxidation chains. However, it has been shown from both oxidation studies[9] and polymerization studies[10] that $f$ lies in the range 0.5 to unity for these initiators. Clearly one scission must occur for every oxidation chain.

Since widely different initiation rates were used, scission could occur in the propagation step of the chain reaction only if under all our initiating conditions the kinetic chain length was unity. But this would mean one scission per oxygen molecule absorbed. However, it has been shown that at these temperatures under purely thermal initiation approximately 30 molecules of oxygen are absorbed per cut.[11] These facts rule out the possibility of scission in the propagation steps.

We next consider the possibility that scission occurs in the initiation step. The radicals R·′ from the initiator can either react with rubber

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(6) J. P. Van Hook and A. V. Tobolsky, THIS JOURNAL, **80**, 779 (1958).

(7) J. A. Offenbach and A. V. Tobolsky, *ibid.*, **79**, 278 (1957).

(8) C. G. Swain, W. Stockmayer and T. Clarke, Jr., *ibid.*, **72**, 5426 (1950).

(9) L. Bateman and A. L. Morris, *Trans. Faraday Soc.*, **48**, 1149 (1952).

(10) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954.

(11) E. M. Bevilacqua, *Rubber Age*, **80**, 271 (1956).

TABLE II

RADICALS PRODUCED *versus* CHAIN CLEAVAGES MEASURED DURING OXIDATION OF NATURAL RUBBER

| Azo-I 70° Time (hr.) | $Q(t) \times 10^4/N$ | $\{R\cdot\}_t \times 10^4$ | $Q(t)/\{R\cdot\}_tN$ |
|---|---|---|---|
| 2.08 | 0.601 | 0.99 | 0.61 |
| 3.93 | 1.38 | 1.47 | 0.94 |
| 5.35 | 1.86 | 1.82 | 1.02 |
| 7.73 | 2.48 | 2.22 | 1.12 |
| 15.60 | 3.14 | 3.10 | 1.01 |
| 29.93 | 3.72 | 3.45 | 1.08 |
| DTBP 70° Time (hr.) | $Q(t) \times 10^6/N$ | $\{R\cdot\}_t \times 10^6$ | $Q(t)/\{R\cdot\}_tN$ |
| 2.05 | 0.38 | 0.41 | 1.08 |
| 3.37 | .75 | .68 | 1.10 |
| 4.68 | .93 | .95 | 0.98 |
| 6.17 | 1.20 | 1.25 | .96 |
| 8.42 | 1.59 | 1.70 | .94 |
| 10.45 | 1.90 | 2.12 | .90 |
| 12.63 | 2.35 | 2.56 | .90 |
| 22.75 | 4.50 | 4.60 | .98 |
| 25.45 | 5.20 | 4.90 | 1.06 |
| 28.70 | 6.05 | 5.80 | 1.04 |
| 32.78 | 6.99 | 6.61 | 1.06 |
| 36.00 | 7.56 | 7.29 | 1.04 |
| $Bz_2O_2$ 60° Time (hr.) | $Q(t) \times 10^5/N$ | $\{R\cdot\}_t \times 10^5$ | $Q(t)/\{R\cdot\}_tN$ |
| 2.18 | 0.184 | 0.54 | 0.34 |
| 4.13 | .382 | 1.00 | .38 |
| 6.70 | .631 | 1.57 | .40 |
| 9.25 | .920 | 2.12 | .43 |
| 13.30 | 1.20 | 2.97 | .40 |
| 24.60 | 2.28 | 5.15 | .44 |
| $Bz_2O_2$(1) 80° Time (hr.) | $Q(t) \times 10^5/N$ | $\{R\cdot\}_t \times 10^5$ | $Q(t)/\{R\cdot\}_tN$ |
| 1.95 | 2.40 | 4.65 | 0.52 |
| 2.87 | 3.37 | 6.36 | .53 |
| 4.27 | 4.50 | 8.63 | .52 |
| 5.87 | 5.55 | 10.52 | .53 |
| 7.17 | 6.39 | 11.99 | .53 |
| 10.97 | 7.35 | 14.50 | .51 |
| 14.52 | 7.95 | 15.94 | .50 |
| 22.92 | 8.66 | 17.31 | .50 |
| $Bz_2O_2$(2) 80° Time (hr.) | $Q(t) \times 10^4/N$ | $\{R\cdot\}_t \times 10^4$ | $Q(t)/\{R\cdot\}_tN$ |
| 1.80 | 0.481 | 1.48 | 0.33 |
| 3.87 | 1.15 | 2.72 | .42 |
| 6.76 | 1.71 | 3.93 | .44 |
| 9.65 | 2.12 | 4.70 | .45 |

hydrocarbon RH to start an oxidation chain or they may add oxygen to form $R'O_2\cdot$. The direct attack of $R\cdot'$ on RH cannot cause scission. Proof of this is given in Fig. 3 where in the absence of oxygen, but in the presence of $Bz_2O_2$, $Q(t)$ is greatly diminished ($Q(t) = 0.45\{R\cdot\}_t$ for $Bz_2O_2$ in oxygen).[12] It is likewise very difficult to envisage that $R'O_2\cdot$ reacting with RH to start an oxidation chain will produce cleavage of RH. If this were so, there would be also cleavage in the propagation step $RO_2\cdot + RH \rightarrow ROOH + R\cdot$ since it is difficult to conceive that $R'O_2\cdot$ from *all* the initiators used should be uniquely different from $RO_2\cdot$.

It was therefore concluded that scission occurs in the termination step of the reaction where the collision of two peroxy radicals results in two cleavages.

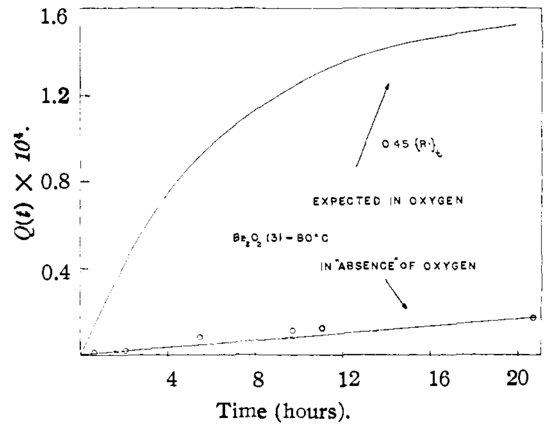
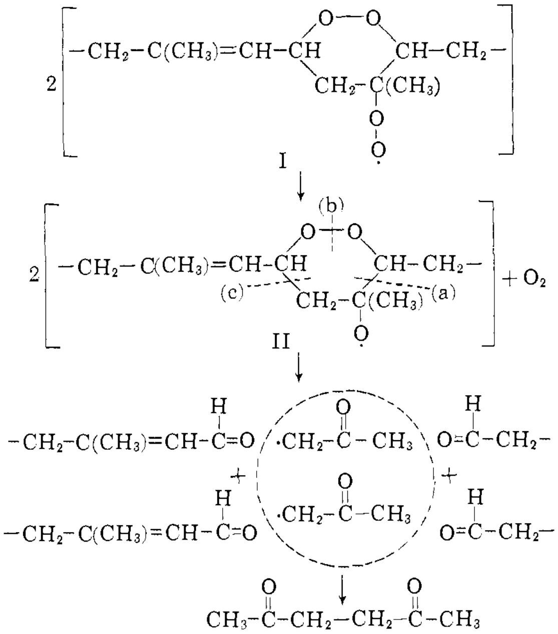


Fig. 3.

A speculation on the chemical mechanism by which oxidative scission occurs is



III, acetonyl acetone

At all but the lowest oxygen pressures the most important termination reaction is between oxygenated radical chain carriers. As shown in the introduction of this paper, these oxygenated radicals have the cyclic diperoxide structure I. Normally, the termination reaction for olefins is written as $RO_2\cdot + RO_2\cdot \rightarrow RO_2R + O_2$ where $RO_2R$ represents an intermolecular peroxide cross-link. In the case of natural rubber, cross-linking obviously does not occur. Rather, the bimolecular termination of $RO_2\cdot$ must result in cleavage of carbon to carbon bonds in the main chain. The mode of dismutation of the oxy radicals II which is shown (by the breaking of bonds a, b, and c in that order) is in agreement with the general pattern of alkoxy radical decomposition as noted by George and Walsh[13] and by Rust, Seubold and Vaughan.[14]

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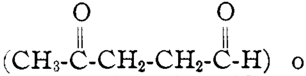
(12) In the absence of oxygen these initiators eventually cause cross linking by the reaction of R· with the double bonds of neighboring chains.

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

(14) F. F. Rust, F. H. Seubold and W. E. Vaughan, THIS JOURNAL, **72**, 338 (1950).

The result is that four aldehyde chain ends are formed (corresponding to two chain cleavages) and two acetonyl radicals are split out. The termination condition is satisfied by the combination of the two acetonyl radicals to give acetonylacetone (III).

An excellent series of papers by Bevilacqua[11,15] deal in a quantitative way with evolved products of natural rubber autoxidation. The following observations made in that work would tend to support the proposed formation of acetonylacetone as the primary scission product.

(1) A methyl ketone is evolved in proportion to and of the same order of magnitude as the number of chain scissions which have occurred.[15c] This product gives a positive pyrrole test, a general reaction of $\gamma$-dicarbonyl compounds. Although the compound was assumed to be levulinaldehyde  ($CH_3\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}H$) only the methyl ketone group could be identified.

(2) Under the experimental conditions used[15] (natural rubber latex, 1 atmosphere $O_2$ pressure, 70–140°) the primary scission product is trapped in the aqueous phase and rapidly oxidized to the identified $CO_2$, acetic acid and formic acid which are formed in the stoichiometric ratio of 3:1:1. The amount of scission was measured concurrently by determining the intrinsic viscosity of the oxidized rubber. The Carter, Scott and Magat[16] equation was used to relate intrinsic viscosity to molecular weight. In the experimental section which follows, we point out that this equation (applicable to sharp molecular weight fractions of natural rubber) should be modified when applied to oxidized rubber characterized by a random molecular weight distribution. Applying such a correction to the data of reference 11 one obtains

$$\frac{\text{moles of } CO_2 \text{ evolved}}{\text{moles of cuts}} = 1.44$$

$$\frac{\text{total moles of acid evolved}}{\text{moles of cuts}} = 1.0$$

This corresponds to the evolution of $3CO_2$, 1 acetic acid and 1 formic acid per two cuts, which is in excellent stoichiometric agreement with the oxidation of acetonylacetone.

## Experimental

**Materials.**—**Natural rubber** was in the form of sheets cast from deammoniated latex. Natural inhibitor was removed by extracting samples in acetone for several days at room temperature. **Benzene**, Allied Chemical Corporation, thiophene free, was used without further purification. **Initiators** were purified according to procedures outlined in the references given: Azo-I,[6] DTBP,[7] $Bz_2O_2$.[17]

**Procedure.**—Homogeneous benzene solutions of natural rubber were obtained by dissolving cast latex in benzene at room temperature and filtering off gel particles which were present. The initial $\bar{M}_n$ of the rubber so obtained was in the range 5.9–6.4 × $10^5$.

A concentrated solution of rubber and of initiator (in benzene) was added to a reservoir of benzene at reaction temperature to give a final concentration of about 1 cc. rubber per liter. The reaction flask was thermostated in a water-bath (±0.1°) and had provision for a condenser, stirrer, and introduction of a constant flow of molecular oxygen at atmospheric pressure. Samples were removed periodically and immediately frozen in liquid nitrogen. They were thawed only previous to measurement of the intrinsic viscosity in an Ubbelohde dilution viscometer at 25°. Molecular weights were calculated from the relationship

$$[\eta] = 7.56 \times 10^{-4} \bar{M}_n^{0.667}$$

This expression is derivable[18] from the equation of Carter, Scott and Magat[16] (applicable to sharp fractions) on the assumption that the oxidized rubber is characterized by a random distribution of molecular weights.

The experiment in the "absence" of oxygen was performed by placing 12-ml. samples of $Bz_2O_2$ and rubber solution in Pyrex ampoules, degassing the solution three times and finally sealing the ampoules at $10^{-2}$ mm. The ampoules were then placed in a water-bath at 80 ± 0.1°.

PRINCETON, N. J.

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(15) (a) E. M. Bevilacqua, THIS JOURNAL, **77**, 5394 (1955); (b) **77**, 5396 (1955); (c) **79**, 2915 (1957); (d) *J. Org. Chem.*, **21**, 369 (1956).

(16) W. C. Carter, R. L. Scott and M. Magat, THIS JOURNAL, **68**, 1480 (1946).

(17) T. H. Meltzer and A. V. Tobolsky, *ibid.*, **76**, 5178 (1954).

(18) C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.* (*London*), **A192**, 311, 329 (1948).