[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

On the Catalyzed Oxidative Degradation of Natural Rubber Networks[1]

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Natural rubber networks prepared by electron irradiation of unvulcanized rubber have been subjected to air oxidation at elevated temperatures in the presence of the initiators benzoyl peroxide and tetramethylthiuram disulfide (TMTD). In the case of benzoyl peroxide the rate of oxidation chain scission deduced from stress relaxation experiments is essentially the same as the rate of production of radicals from the benzoyl peroxide. This result has also been found in studies of oxidative scission in dilute solutions of natural rubber in benzene. This result is consistent with the occurrence of chain scission in the termination step of the free radical oxidation. Data on the rate of chain scission observed with TMTD are compared with reported polymerization data using the same initiator. Initiation by this system is best described as a bimolecular reaction between TMTD and substrate (either monomer or isoprene segments in rubber).

In the previous paper, it was demonstrated that natural rubber in dilute benzene solution is degraded by molecular oxygen in a simple fashion when external free radical initiators are present.[3] Formation of initiating free radicals (from added initiator) and chain scission in the rubber (as determined by molecular weight measurements) proceed at essentially the same rate. This behavior has been attributed to the occurrence of chain scission in the termination step of the free radical oxidation mechanism.[3]

The present investigation was made (1) to determine whether the kinetics of chain scission found in dilute benzene solution also apply to the air oxidation of natural rubber networks containing added initiator and (2) to use the measurement of rate of chain scission in natural rubber as a way of obtaining rate of initiation data on the initiator tetramethylthiuran disulfide (TMTD).

The method of stress relaxation has been used to measure chain scission in natural rubber crosslinked by irradiation. Vulcanization by irradiation has been selected since in this way no unwanted impurities are introduced into the network.

Experimental

Natural rubber was in the form of sheets cast from deammoniated latex and was freed of natural inhibitor by acetone extraction. Samples of 0.04 inch thickness were sealed in 0.001 inch aluminum foil by Apiezon sealing compound and then subjected to 1 Mev. electrons from a Van de Graaf source for ten minutes. The intensity of the beam was controlled at one microamp. The irradiation was performed at room temperature.

The initiators benzoyl peroxide (Bz_2O_2) and TMTD were added in the manner to be described; vulcanizates were swelled in benzene and then dried to constant weight *in vacuo* at room temperature. Samples were reswelled in benzene containing initiator and again dried to constant weight *in vacuo*. The amount of initiator incorporated was determined both by weight difference and by the known amount of benzene solution absorbed.

The instrument and technique which have been used to follow stress relaxation are described elsewhere.[4] The samples and instrument were placed in a thermostatted air oven with a temperature control of ±0.2°.

During an experiment, a sample is held at constant extension (*ca.* 20%) and the relative stress decay $f(t)/f_0$ is recorded, where $f(t)$ is the stress at time t and f_0 is the initial stress. The amount of chain scission is calculated from the equation[5]

$$q(t) = -N_0 \ln (f(t)/f_0) \qquad (1)$$

where $q(t)$ is the total number of moles of cleavages that have occurred up to time t in each cc. of rubber and N_0 is the initial number of moles of network chains per cc. of rubber. The quantity N_0 is obtained from the initial stress by the relation

$$f_0 = N_0RT\left[\frac{l}{l_0} - \left(\frac{l_0}{l}\right)^2\right] \qquad (2)$$

where R is the gas constant, T the absolute temperature, and l_0 and l are the initial and stretched lengths, respectively. The samples in this study had $N_0 = 7.3 \times 10^{-5}$ mole/cc. as obtained from equation (2).

Results and Discussion

The measured oxidative degradation at 80° of a natural rubber network containing $(Bz_2O_2) = 9.58 \times 10^{-5}$ mole/cc. is shown by the points in the $q(t)$ plot of Fig. 1. For comparison, Fig. 1 includes the calculated $0.7\{R\cdot\}_t$ which is obtained from the integrated form of the rate of initiation expression

$$\{R\cdot\}_t = 2(Bz_2O_2)_0(1 - e^{-k_dt}) \qquad (3)$$

for Bz_2O_2 where $\{R\cdot\}_t$ is the total moles of radicals per cc. produced up to time t and k_d ($= 4.3 \times 10^{-5}$ at 80°)[6] is the specific rate constant for the first order cleavage of Bz_2O_2. The value of $0.7\{R\cdot\}_t$, which gives the best fit with experiment, is quite reasonable in view of the fact that radicals from Bz_2O_2 are found to initiate radical reactions with an efficiency somewhat less than unity. We conclude that the catalyzed air oxidation of natural rubber networks produces chain scission in the same manner as described for unvulcanized rubber in dilute benzene solution, *i.e.*, random chain scission occurring in the termination step of the oxidation mechanism.

The data of Fig. 2 are an attempt to clarify the initiator characteristics of TMTD by measurement of chain scission. The stress relaxation experiments on natural rubber were performed at 70, 80 and 100° in the presence of $(TMTD) = 2.87 \times 10^{-5}$ mole/cc. By graphically determining a number of tangents to each curve and extrapolating back to zero time, we obtain the initial rate of scission at each temperature. These values are presented in Table I.

In view of the previous results, these values also represent the initial rate of initiation by TMTD at each temperature. For reasons discussed below,

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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.

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(3) A. V. Tobolsky and A. Mercurio, THIS JOURNAL, **81**, 5535 (1959).

(4) A. V. Tobolsky, I. B. Prettyman and J. H. Dillon, *J. Appl. Phys.*, **15**, 380 (1944); J. A. Offenbach, Ph.D. Thesis, Princeton University, 1955.

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

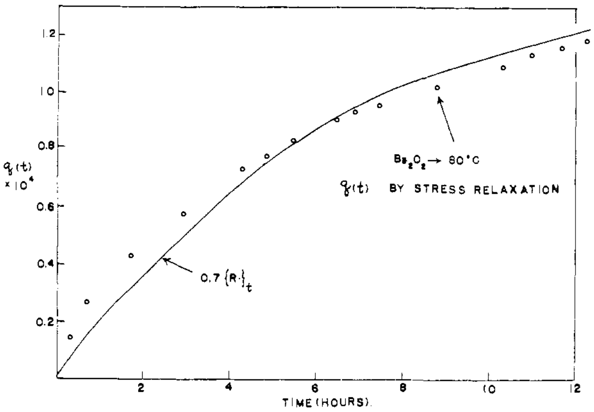

Fig. 1.

it appears that TMTD forms initiating free radicals by a bimolecular reaction, *i.e.*

$$\text{TMTD} + \text{X} \xrightarrow{k_2} \text{initiating radicals}$$

$$R_i = 2k_2(\text{TMTD})(\text{X})$$

where k_2 is a second order rate constant, and (X) will represent monomer concentration in polymerization experiments and will stand for the concentration of isoprene units in these oxidation experiments. Proceeding on this basis, an Arrhenius plot of the data in Table I gives

Table I

Temp., °C.	$\left[\frac{dq(t)}{dt}\right]_{t=0}$ $\frac{\text{moles}}{\text{cc.-sec.}}$
70	1.50×10^{-10}
80	4.91×10^{-10}
100	5.51×10^{-9}

$$\frac{\left[\frac{dq(t)}{dt}\right]_{t=0}}{(\text{TMTD})(\text{isoprene units})} = 0.9 \times 10^{12}e^{-28.5\ \text{kcal}/RT}\ \frac{\text{liters}}{\text{mole-sec.}}$$

where (isoprene units) = 12.4 moles/liter.

Data of Otsu and Nayatani[7] on the polymerization of styrene by TMTD yield by standard procedures[8b]

$$\frac{R_i'}{(\text{TMTD})(\text{styrene})} = 1.32 \times 10^{12}e^{-29.2\ \text{kcal}/RT}\ \frac{\text{liters}}{\text{mole-sec.}}$$

where R_i' is the rate of initiation deduced from polymerization data.

Finally, recalculation of data on the TMTD initiated polymerization of methyl methacrylate (MMA)[8a] gives

$$\frac{R_i'}{(\text{TMTD})(\text{MMA})} = 3.7 \times 10^{13}e^{-30.9\ \text{kcal}/RT}\ \frac{\text{liters}}{\text{mole-sec.}}$$

These three expressions for the second order rate constant are indeed quite similar, although in all cases the pre-exponential factor seems somewhat high for a bimolecular reaction. Bimolecular initiation by TMTD has been proposed because (A) it was found that TMTD essentially does not initiate oxidation and oxidative scission when one attempts to degrade natural rubber in dilute benzene solution at a rubber concentration $^1/_{1000}$ as large as that in the present instance. This is in contrast to the results obtained with known unimolecularly decomposing initiators.[3] (B) In the experiments of Otsu and Nayatani,[7] it was shown that when styrene at several concentrations is polymerized by TMTD, the rate of polymerization is proportional to the three-halves power of monomer concentration. Such a dependence on monomer concentration would be expected if monomer takes part in the initiation step.[8b] The rate of polymerization exhibits a first power monomer dependence when unimolecularly decomposing initiators are used.

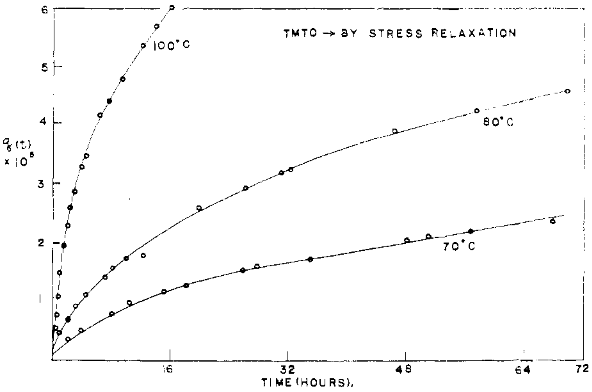

Fig. 2.

The shapes of the curves for *q(t) versus t* shown in Fig. 2 follow closely the expression for $\{R\cdot\}_t$

$$\{R\cdot\}_t = 2(\text{TMTD})_0(1 - \exp[-k_2\,(\text{isoprene})_0 t])$$

This expression follows from the bimolecular rate law for R_i because the concentration of isoprene segments is in great excess and may be assumed constant.

The results of this paper and the previous paper[3] provide strong evidence that scission during the oxidation of natural rubber (RH) occurs in the termination step of the chain reaction. This can be written schematically as

$$RO_2\cdot + RO_2\cdot \longrightarrow RO\cdot + RO\cdot + O_2 \longrightarrow \text{chain scission}$$

The dismutation tendencies of alkoxy radicals are well known.

It will be interesting to determine how general this mechanism is for hydrocarbon and polymer oxidation.

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Princeton, N. J.

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