JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 74 AUGUST 21, 1952 NUMBER 16

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY AND FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Some Inhibitors and Retarders in the Polymerization of Liquid Vinyl Acetate. II. 1,3,5-Trinitrobenzene and Sulfur[1]

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RECEIVED JANUARY 26, 1952

1,3,5-Trinitrobenzene and sulfur are both strong inhibitors of the polymerization of liquid vinyl acetate, but the kinetics of the inhibited polymerization, followed dilatometrically under the simplified conditions of Part I of this series, does not fit the equations which apply to the moderate and strong inhibitors there described. This is found to be due to the fact that trinitrobenzene, in the act of stopping two polymerization chains, is converted into another inhibitory substance whose rate constant for reaction with growing chains is only 7% of that of trinitrobenzene itself, but which is still comparable with duroquinone or *o*-dinitrobenzene in its effect upon polymerization. In this second stage of chain-terminating activity two more chains are stopped, and the nitro compound is converted into a weak retarder. A kinetic equation derived on the basis of this picture, and ignoring the final weak retarder, fits the experimental facts and permits the determination of the relative terminator efficiencies shown in Table II. Elemental sulfur behaves similarly, but the spread between the inhibitory efficiencies of its successive stages is less than with trinitrobenzene, and there is no clearly defined end to the period of inhibition even after the stopping of four chains per S_8 molecule. It has been possible to apply the same equation to sulfur as to trinitrobenzene by treating the third-stage terminator as a weak retarder with $k_4/k_2 = 40$ and correcting for its concentration at each point where a rate of polymerization has been determined. A stepwise mechanism for the chain-terminating action of sulfur is proposed.

In Part I of this series a method was described for following with a dilatometer the accelerating polymerization of liquid vinyl acetate in the presence of minute controlled concentrations of various inhibitors and retarders. By using concentrations of these substances which were very small compared to those of the free-radical producing initiator, it was possible to translate the instantaneous polymerization rates into concentrations of the disappearing inhibitory substance and, by means of kinetic equations, to test the validity of a simple mechanism of chain termination and to derive certain numerical data, including relative rate constants for the chain terminating and propagating steps, from the experimental results. The terminators examined fell into four classes: weak retarders such as nitrobenzene, whose concentration changed almost inappreciably during the period of measurement; moderate inhibitors such as the dinitrobenzenes or duroquinone, which reacted with growing chains at a rate proportional to the concentration of the inhibitor; iodine, which reacted with growing chains at a rate proportional to the 3/2 power of its concentration; and the powerful inhibitor 2,2-diphenyl-1-picrylhydrazyl, whose relative terminator efficiency was too great to measure even at concentrations of the order of 10^{-5} M.

1,3,5-Trinitrobenzene and elemental sulfur stand in efficiency as inhibitors below diphenyl picrylhydrazyl, but above any of the other inhibitors which we have measured. Their behavior in vinyl acetate, however, is not fitted by the equations which are applicable to the other terminators; and it is qualitatively apparent upon comparison of the curves for these cases (Figs. 1 and 2) with those for the other inhibitors that the inhibitory power of trinitrobenzene and of sulfur lingers on and does not disappear as rapidly as in the case of the inhibitors which fit the common pattern. In common with the dinitrobenzenes, the end of the inhibitory period is marked by an approach of the slope $(-\mathrm{d} \ln (M)/\mathrm{d}t)$ to constancy, but not to the value which it would have in the absence of any inhibitor. (For the definitions of this and other symbols, see below.)

The Chain-Stopping Equivalence of Trinitrobenzene and Sulfur.—The number of chains stopped by a molecule of inhibitor can be estimated as accurately as the end of the period of inhibition can be determined. In the case of trinitrobenzene,

(1) Part I: THIS JOURNAL, **72**, 1051 (1950). The experimental work of Parts I and II is from the Ph.D. thesis of Harold Kwart, Harvard University, January, 1948. The interpretation presented in this paper was worked out during the summer of 1950 while the senior author was a visiting professor at U.C.L.A.

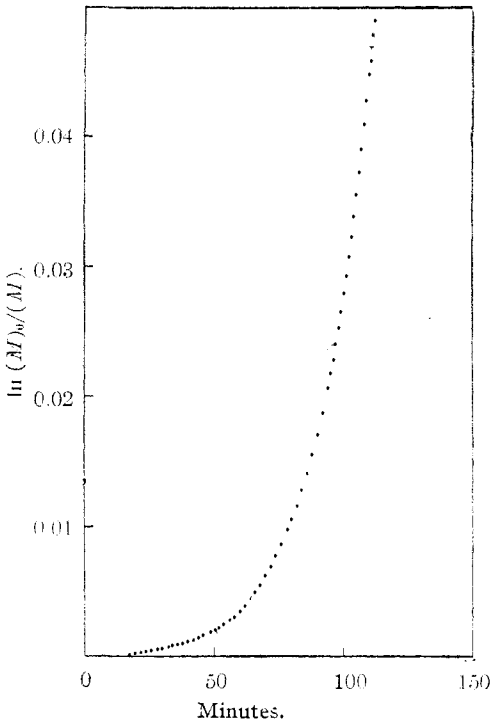

Fig. 1.—Run 4 on inhibition of vinyl acetate polymerization by 1,3,5-trinitrobenzene: Z_0 =3.35 × 10^{-5} mole/kg.; P_0 = 3.89 × 10^{-2} mole/kg.

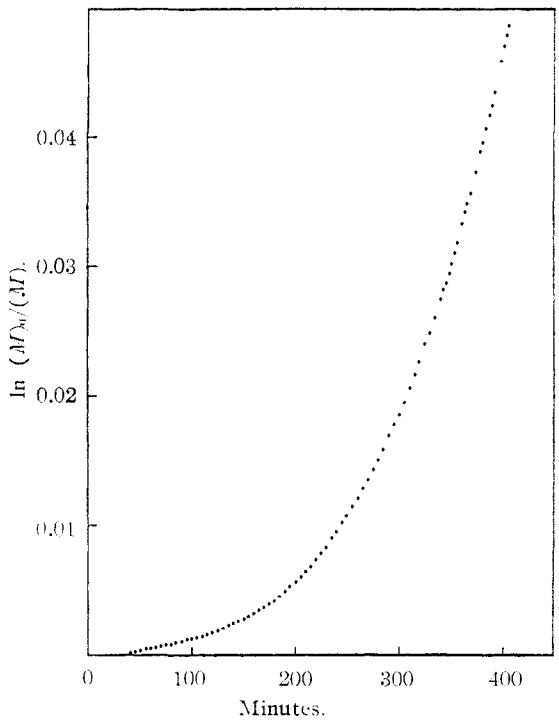

Fig. 2.—Run 1 on inhibition of vinyl acetate polymerization by sulfur: Z_0 = 5.65 × 10^{-5} mole/kg.; P_0 = 3.02 × 10^{-2} mole/kg.

a graph of ln $(M)_0/(M)$ against time shows a well marked approach to a constant slope, corresponding to the presence of a residue from the action of the inhibitor having only low retarding power. The values of the limiting slope in Runs 1, 2 and 4 are 0.0315, 0.088 and 0.00161, respectively, and correspond by Equation 22 of reference 1 to the presence of a weak retarder having values of yk_4/k_2 of 11.4, 14.1 and 7.5 in the three cases, or an average of 11.0. By noting the point where the slope of the curve of log $(M)_0/(M)$ against time becomes indistinguishable from its final slope, the lengths of the inhibition periods shown in the second column of Table I have been determined. The number of chains started, and hence stopped, during this interval is equal to $2k_iP_0t$, where k_i is the rate constant of chain initiation by benzoyl peroxide at 45° in vinyl acetate, and has been determined as 1.34 × 10^{-5} min.$^{-1}$; P_0 is the initial concentration of initiator and is approximately constant during the experiment; and t is the length of the inhibition period. The number of chains started, divided by Z_0, the initial concentration in moles per liter of the inhibitor, is the functionality or chain-stopping equivalence of the inhibitor, *i.e.*, the number of kinetic chains terminated by a molecule of inhibitor by the end of the inhibition period.

Through a miscalculation, Run TNB 3 was not carried far enough to establish the arrival at constant slope, although the data from this run are useful in the application of the following kinetic treatment.

It appears from Table I that at the end of the period of marked inhibition trinitrobenzene has stopped an average of 3.9 kinetic chains per molecule.

Similar determinations for sulfur yield less clear results, since the slopes of the sulfur curves change more and more slowly but never reach a constant value; their increase is so gradual that no sharp end to the inhibition can ever be determined. In two sulfur runs the last group of points seems to fall on a straight line, but its slope is far from that for an uninhibited reaction. In Run S 1 after 382 minutes, ten apparently collinear points yield a value of $(-\mathrm{d}\ \ln\ (M)/\mathrm{d}t)$ equal to 3.64 × 10^{-4}, which, by Equation 22 of reference 1, corresponds to the presence of a retarder with yk_4/k_2 = 38. Run S 2 similarly indicates a final slope of 4.9 × 10^{-4} and a yk_4/k_2 of 37, after 284 minutes. At these points the inhibitor has already stopped 5.5 and 5.3 kinetic chains, respectively, per molecule of S_8. It is obvious that sulfur is considerably more than a quadrifunctional inhibitor, and that the retarding power of its residue is too great to justify fully the use of the equation for weak retarders which assumes that the retarders are present over a period of time at undiminished concentration.

TABLE I

FUNCTIONALITY, OR CHAIN-STOPPING EQUIVALENCE, OF 1,3,5-TRINITROBENZENE AT 45°

Run No.	Length of inhibition period (min.)	P_0	$2k_iP_0t$ × 10^5	Z_0 × 10^5	Functionality
TNB 1	830	0.0144	32.0	8.96	3.6
TNB 2	216	.0368	21.3	5.21	4.1
TNB 4	130	.0389	13.5	3.35	4.0

Kinetics of the Inhibited Polymerization.—When a molecule reacts with a free radical to terminate a reaction chain, the product of this en-

counter must be a more or less stabilized free radical, and the likelihood of its reacting rapidly with a second chain carrier is rather great. The product of this follow-up reaction, however, again contains only paired electrons and it follows that any inhibitor which stops more than two chains must do so as the result of a second rate-determining encounter, this time between a chain carrying radical and the inhibitor as altered by its previous reaction. The rate constant for this new reaction will in general be lower than for the first inhibition, and we must therefore take account of the stopping of chains in successive stages. In the case of trinitrobenzene the inhibition is so powerful and the final retardation so slight that a simple theory might be applicable which would neglect the final retardation altogether and treat the inhibitor as stopping chains by a stepwise process involving two different rate constants.

Kinetic Treatment of Stepwise Inhibition.—It is supposed that an inhibitor Z_a reacts with a growing radical chain with a rate constant k_a, with or without an immediate follow-up reaction, so that each such reaction stops a number y_a of growing chains (two in the actual cases here considered). In this process Z_a is converted into another inhibitor Z_b, which in turn reacts with a rate constant k_b, stopping y_b chains. The total rate at which chains are stopped is constant, for it is equal to the rate of chain initiation ($2k_1(P)$) by the initiator present at constant concentration. However, the fraction of chains $y_ak_a(Z_a)/(y_ak_a(Z_a) + y_bk_b(Z_b))$ which are stopped by the more active inhibitor, Z_a, will change continuously during the inhibition period, as will the total inhibitory level of the solution, $(y_ak_a(Z_a) + y_bk_b(Z_b)) = E$. That latter quantity, during the inhibition period, will determine the free radical concentration and rate of polymerization, and will replace $k_4(Z)^m$ in Equations (7) and (10) of reference 1.

The rates of disappearance of the two successive inhibitors will be governed by the equations

$$\frac{d(Z_a)}{dt} = -\frac{2k_1}{y_a}(P)\frac{y_ak_a(Z_a)}{E} = -2k_1(P)\frac{k_a(Z_a)}{E} \quad (1)$$

$$\frac{d(Z_b)}{dt} = -\frac{d(Z_a)}{dt} - \frac{2k_1}{y_b}(P)\frac{y_bk_b(Z_b)}{E} = 2k_1(P)\frac{k_a(Z_a) - k_b(Z_b)}{E} \quad (2)$$

The concentration of the second inhibitor can be obtained as a function of the first by combining (1) and (2) to yield

$$\frac{d(Z_b)}{d(Z_a)} = \frac{k_b(Z_b) - k_a(Z_a)}{k_a(Z_a)} \quad (3)$$

and integrating to

$$\frac{k_b}{k_b - k_a}\ln\left\{\pm\frac{k_b - k_a}{k_b}\frac{k_b(Z_b)}{k_a(Z_a)} \mp 1\right\} = \frac{k_b}{k_a}\ln\frac{(Z_a)}{Z_0} \quad (4)$$

where Z_0 is the value of (Z_a) at zero time.

By defining a quantity $r = (k_a - k_b)/k_a$, and substituting, we reduce equation (4) to

$$\frac{(Z_b)}{(Z_a)} = \frac{1}{r}\left\{\left[\frac{(Z_a)}{Z_0}\right]^{-r} - 1\right\} \quad (5)$$

Substitution for (Z_b) in the expression for E yields

$$E = (Z_a)\left(y_ak_a + \frac{y_bk_b}{r}\left\{\left[\frac{(Z_a)}{Z_0}\right]^{-r} - 1\right\}\right) \quad (6)$$

an equation which expresses the total inhibitory level as a function of the fractional consumption of Z_a and of the relative efficiencies of the first and second inhibitors. To relate $(Z_a)/Z_0$ to time, we combine equations (1) and (6)

$$\frac{-d(Z_a)}{dt} = \frac{2k_1k_a(P)}{y_ak_a + \frac{y_bk_b}{r}\left\{\left[\frac{(Z_a)}{Z_0}\right]^{-r} - 1\right\}} \quad (7)$$

If, as is found to be the case with the present inhibitors, $y_a = y_b = y$, the treatment can be simplified by making this substitution. Then, on integration and replacement of k_a and k_b by their equivalent functions of r, the following equation results for the relation between $(Z_a)/Z_0$ and time

$$\frac{2k_1}{y}(P)t = 2Z_0 + (Z_a)\left\{\frac{1 - 2r}{r} - \frac{1}{r}\left[\frac{(Z_a)}{Z_0}\right]^{-r}\right\} \quad (8)$$

A similar elimination of k_a and k_b can be accomplished in the expression for the inhibitory effectiveness by defining this in relative terms

$$\Omega = \frac{E}{y_ak_aZ_0} = \frac{(Z_a)}{Z_0}\left\{\frac{2r - 1}{r} + \frac{1 - r}{r}\left[\frac{(Z_a)}{Z_0}\right]^{-r}\right\} \quad (9)$$

Ω thus expressed the inhibitory level at any time as a fraction of what it was at the beginning of the reaction, the equality of y_a and y_b being again assumed.

Equations (8) and (9) permit the calculation of a theoretical curve of Ω as a function of time for any assumed value of r. With these equations, however, it is necessary to choose a set of values of $(Z_a)/Z_0$ and from each value to calculate separately values of time and of inhibitory level. A more convenient procedure is possible using a measure of the relative time remaining in the inhibition period, defined as

$$\theta = 2 - \frac{2k_1(P)}{yZ_0}t = \frac{(Z_a)}{Z_0}\left\{\frac{2r - 1}{r} + \frac{1}{r}\left[\frac{(Z_a)}{Z_0}\right]^{-r}\right\} \quad (10)$$

It then becomes apparent from equations (9) and (10) that

$$\theta - \Omega = \left[\frac{(Z_a)}{Z_0}\right]^{1-r} \quad (11)$$

and equations can be written containing only θ, Ω and r

$$\theta = \frac{2r - 1}{r}(\theta - \Omega)^{1/(1-r)} + \frac{1}{r}(\theta - \Omega) \quad (12)$$

$$\Omega = \frac{2r - 1}{r}(\theta - \Omega)^{1/(1-r)} + \frac{1 - r}{r}(\theta - \Omega) \quad (13)$$

Application of the Equations to the Data on Trinitrobenzene.—Equations (12) and (13) must hold regardless of variations in the initial concentrations of initiator and inhibitor, yielding the same plot of Ω *vs.* θ for all experiments calculated with the same value of r. From the above definitions Ω is related to our rate data by the equation

$$\Omega = \frac{2k_1k_2(P)}{y_ak_aZ_0\frac{(-d\ln M)}{dt}} \quad (14)$$

and is therefore proportional to the fraction $(P)/Z_0(-d\ln M/dt)$. By equation (10), θ is a linear

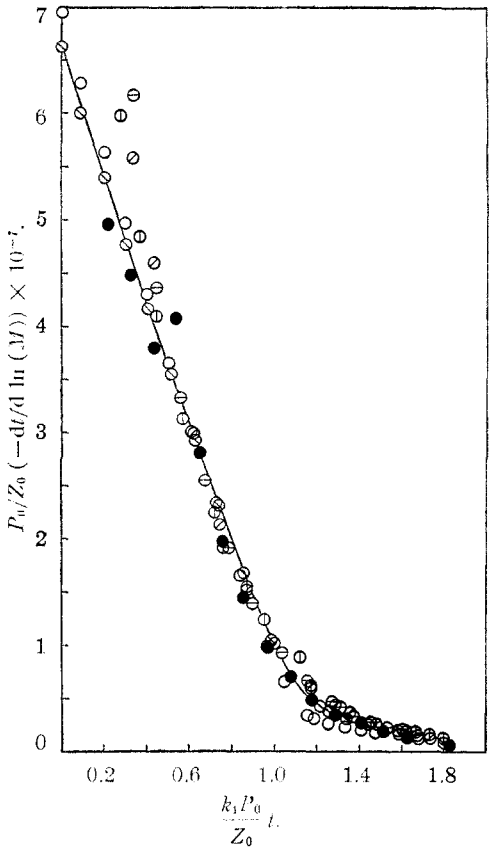

Fig. 3.—Inhibition of vinyl acetate polymerization by 1,3,5-trinitrobenzene: ●, run 1, $P_0 = 1.44 \times 10^{-2}$; $Z_0 = 8.96 \times 10^{-5}$; ○, run 2, $P_0 = 3.68 \times 10^{-2}$; $Z_0 = 5.21 \times 10^{-5}$; ⊖, run 3, $P_0 = 3.07 \times 10^{-2}$; $Z_0 = 4.40 \times 10^{-5}$; ⊘, run 4, $P_0 = 3.89 \times 10^{-2}$; $Z_0 = 3.35 \times 10^{-5}$; ◔, calculated for $r = 0.93$; ◑, calculated for $r = 0.95$.

function of $(P)t/Z_0$. This theory therefore demands that all our kinetic runs should fall on a common curve when $(P)/Z_0(-\mathrm{d}\ln M/\mathrm{d}t)$ is plotted against $k_1(P)t/Z_0$. Figure 3 shows such a plot for four runs with trinitrobenzene in which the ratio $(P)/Z_0$ was varied from 161 to 1150. The value of k_1 was taken as 1.34×10^{-5} sec.$^{-1}$, as previously determined.[1] The solid curve is that calculated with an assumed value of 0.93 for r. This value was arrived at by successive trials. A curve calculated for $r = 0.95$ deviated seriously below the experimental points from 1.05 to 1.5 on the time scale. This is within the most indicative part of the inhibition period, where the slopes representing the values of $-\mathrm{d}\ln M/\mathrm{d}t$ can be determined with the greatest accuracy. Near the beginning or end of the period of inhibition (see Fig. 1) where the slope is near its initial or final limit, the accuracy is much less. This may well account for the poor superposability of the experimental curves near the beginning of the reaction, where deviations of as much as 25% between runs appear, whereas for values of θ less than 1.5 the concordance of the runs with one another is very good.

The value of $r = 0.93$ means that $k_b = 0.07\,k_a$. The relative values of k_a and k_b follow from the form of the relation between polymerization rate and time. We can now express the inhibitory efficiencies of the two steps, as has been done previously,[1] as the fractions k_a/k_2 and k_b/k_2, from a measurement of the initial value of the polymerization rate, as

$$(-\mathrm{d}\ln M/\mathrm{d}t)_{t=0} = k_2(R)_0 = 2k_1k_2(P)/yk_aZ_0 \quad (15)$$

where $(R)_0$ is the concentration of growing free radicals immediately following the establishment of the steady state (compare equations (7) and (9), ref. 1).[2]

Application of the Equations to the Data on Sulfur.—It is a reasonable hypothesis that sulfur, S_8, should terminate radical chains in at least four successive stages with a value of $y = 2$ for each stage. If this is so, the equations relating Ω to θ for a two-stage inhibitor might be applied to sulfur up to the point where four chains per molecule have been stopped, if it were possible to make a simple correction for the third stage of inhibition. We have attempted this by treating the third-stage inhibitor as a retarder with $y_ck_c/k_2 = 40$ whose concentration at any time is equal to the accumulation of all the Z_b which has reacted. For sulfur we then re-define E by adding a term

$$E_{\mathrm{sulfur}} = y_ak_a(Z_a) + y_bk_b(Z_b) + y_ck_c(Z_c)$$
$$= 2k_a(Z_a) + 2k_b(Z_b) + 40[Z_0 - (Z_a) - (Z_b)]$$

Again the data from the three runs with sulfur as an inhibitor and with varying concentrations of initiator and of inhibitor fall close to a common curve when $\frac{P_0}{Z_0}\frac{\mathrm{d}t}{\mathrm{d}\ln(M)}$ is plotted against k_1P_0t/Z_0, and the curve calculated with an assumed value of $r = 0.76$ fits the data without a trend (Fig. 4). The grouping of the points from the different experiments about the common curve is not as close as in the case of trinitrobenzene, which is not surprising in view of the approximation which had to be made in applying the equation. The fit yields the values for sulfur, $k_a/k_2 = 470$, $k_b/k_2 = 113$.

Comparison of the Different Inhibitors.—Table II summarizes the relative inhibitory powers, expressed as k_a/k_2 and k_b/k_2, for the five inhibitors for which we have measurements at successive stages of inhibition and y_ck_c/k_2 for trinitrobenzene and sulfur. Assuming that $y = 2$ throughout, the ratio of the first and second inhibitory rate constants for trinitrobenzene (14) lies close to the lowest observed for a nitro compound, 16 for *m*-dinitrobenzene. The ratio of the second and third constants for trinitrobenzene, 12, is similar in value.

TABLE II

STEPWISE INHIBITORS OF VINYL ACETATE POLYMERIZATION AT 45°

Inhibitor	k_a/k_2	k_b/k_2	y_ck_c/k_2	k_a/k_b	k_b/k_c
o-Dinitrobenzene	96	3[a]	..	64[b]	...
m-Dinitrobenzene	105	13[a]	..	16[b]	...
p-Dinitrobenzene	267	8[a]	..	66[b]	...
Trinitrobenzene	890	62	11	14	12[b]
Sulfur	470	113	40	4	6[b]

[a] These are values of y_bk_b/k_2. y cannot be determined for weak retarders. [b] Assuming that $y = 2$ throughout.

(2) In equations (6), (7), (8) and (10) of reference 1, k_4 should be replaced by yk_4.

The constants measured cover an approximately 600-fold range, from 890 for trinitrobenzene to 1.5 (if $y_b = 2$) for the residual retarder from *o*-dinitrobenzene. If we assume that k_2 at 45° has the value 2.24×10^3,[3] then the measured values of k_4 cover the range from 2×10^6 to 3.4×10^3. The results are consistent with the view that the attack of a free radical upon an aromatic nitro compound occurs at a nitro group rather than upon the nucleus.[4]

Mechanism of Inhibition by Sulfur.—The difference in rate constant between successive stages of inhibition by sulfur is less than in any nitro compound investigated. Only a decrease of 4-6-fold is noted in the rate constant for chain termination in passing from sulfur to its first transformation product and from the first transformation product to the second. This makes it appear that the ability of this sulfur family of inhibitors to stop radical chains is not dependent upon a very specific coupling between groups which is damped during the inhibitory process, as in the di- and trinitro compounds. These facts are consistent with what is probably the simplest kind of mechanism by which octatomic sulfur could act as a chain breaker

$$R\cdot + S_8 \xrightarrow{k_a} RS_8\cdot$$

$$RS_8\cdot + R\cdot \xrightarrow{\text{fast}} RS_8R$$

$$RS_8R + R\cdot \xrightarrow{k_b} RS_2R + RS_6\cdot$$

$$RS_6\cdot + R\cdot \xrightarrow{\text{fast}} RS_6R$$

$$RS_6R + R\cdot \xrightarrow{k_c} RS_2R + RS_4\cdot$$

etc.

Each step in which sulfur or a polysulfide reacts with a free radical is thus regarded as a displacement of sulfur on sulfur by carbon, a reaction which becomes slower as the S–S bond acquires the heightened strength characteristic of the shorter polysulfides, and as the point of attack of the radical on the sulfur comes closer to the polyvinyl acetate end chains. There is no reason to suppose that the reaction depicted for k_b occurs specifically at the second sulfur atom from the carbon, forming a *di*sulfide; it is more likely to be a random attack, forming any compound RS_xR and any radical $RS_{(8-x)}\cdot$, and the superposition of these several species may contribute to the poorly defined separation of stages of the inhibition. It is also unlikely that RS_2R represents a uniform end product of the series; for this cannot be the case following the formation of any polysulfide RS_xR in which x is odd.

A possible alternative fate for a radical RS_8 would be to undergo cleavage to $RS_2\cdot$ and hexatomic sulfur, which is known to be formed in the acidification of sodium thiosulfate[5,6] and which has been characterized spectroscopically[6] and crystallographically.[7] Such an occurrence in the present case is improbable in view of the observation[6] that hexatomic sulfur is attacked by bromine about twice as fast as is octatomic sulfur. The cleavage of RS_8 to yield S_6 and a free radical would therefore probably have the effect of causing *four* chains to be terminated rapidly following the first encounter of a sulfur molecule with a free radical.

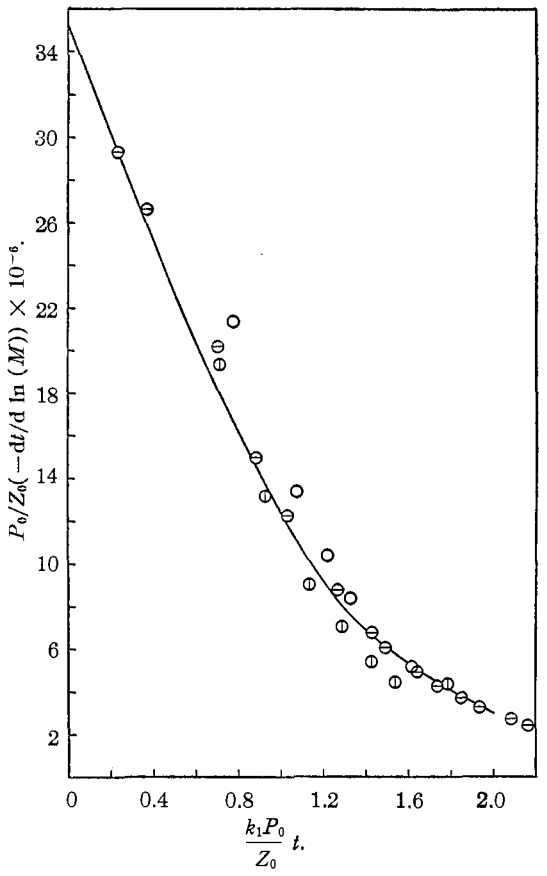

Fig. 4.—Inhibition of vinyl acetate polymerization by sulfur: ○, run 1, $P_0 = 3.02 \times 10^{-2}$; $Z_0 = 5.65 \times 10^{-5}$; ⊖, run 2, $P_0 = 7.02 \times 10^{-2}$; $Z_0 = 10.1 \times 10^{-5}$; ⊙, run 3, $P_0 = 3.89 \times 10^{-2}$; $Z_0 = 3.35 \times 10^{-5}$. Curve calculated for $r = 0.76$.

Experimental

1,3,5-Trinitrobenzene from the Eastman Kodak Co. was recrystallized from 80% ethanol. It melted at 121–121.5°.

Reagent grade sulfur was employed. The crystals were ground to a fine powder in an agate mortar before weighing out the small amounts required for each run. This fine state of subdivision was necessary to assure rapid solution of the sulfur, whose solubility in vinyl acetate is quite small.

The technique and procedure were identical with that described in Part I, ref. 1.

CAMBRIDGE, MASSACHUSETTS

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