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# Dilatometric Studies of the Behavior of Some Inhibitors and Retarders in the Polymerization of Liquid Vinyl Acetate. I

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The polymerization of liquid vinyl acetate is characterized by long kinetic chains and great sensitivity to impurities present in low concentrations.[1-8] This fact, coupled with the large volume change accompanying the polymerization,[9] renders dilatometry a peculiarly delicate tool for the investigation of the inhibition and retardation by low concentrations of added substances. In the present paper we describe some of the results that have been obtained and some of the conclusions that can be drawn solely from accurate measurements of the manner in which polymerization is begun and accelerated in the presence of concentrations as low as $10^{-5}$ $M$ of added substances dissolved in highly purified liquid vinyl acetate. The terms "inhibitor" and "retarder" are used in their generally accepted senses,[10] but since the difference between these types of substance is one of degree only,[11] it will be convenient to use the general term "terminator" to embrace both the reactive inhibitors and the less reactive retarders.

The "inhibitors" investigated by Foord were characterized by apparently total arrest of polymerization for a definite length of time, followed by polymerization at the rate observed in the absence of any inhibitory substance. Our procedure yields a magnified view of the "elbow" in the curve of polymerization against time; it is not surprising to find that this elbow is in nearly every case curved and not angular in form. By means of a dilatometer in a well-controlled thermostat it is possible to obtain from fifty to one hundred or more experimental points indicating the progress of polymerization with time before more than a few per cent. of the vinyl acetate has polymerized. Suitable low concentrations of initiator (benzoyl peroxide) and a strong inhibitor can be so chosen that the change in concentration of initiator during this time is negligible, but that the concentration of the terminator falls from a value which produces sharp retardation of polymerization to a value so low that polymerization has reached practically its normal rate. Under these conditions, where the concentrations of monomer and of initiator may be assumed to be constant, the shape of the curve of accelerating polymerization with time is subject to detailed interpretation. In the following analysis it will be shown that such experiments tell the concentration of the terminator as a function of time, in certain cases the rate of decomposition of the initiator, in others the number of chains stopped by one terminator molecule, the kinetic order of the reaction between free radicals and terminator molecules, and the relative reactivity of growing radicals toward monomer and terminator. Incomplete as this method still leaves our knowledge of inhibition and retardation, the method gives the above information more accurately than direct measurement has been able to do, and it affords a few mechanistic conclusions of interest. The terminators studied in the present work fall into four classes: (1) weak retard-

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(1) J. W. Breitenbach and R. Raff, *Ber.*, **69**, 1107 (1936).

(2) J. W. Breitenbach, *Z. Elektrochem.*, **43**, 323 (1937).

(3) A. C. Cuthbertson, G. Gee and E. K. Rideal, *Nature*, **140**, 889 (1937).

(4) L. Meunier and G. Vaissière, *Compt. rend.*, **206**, 677 (1938).

(5) Kia-Khwe Jeu and H. N. Alyea, THIS JOURNAL, **55**, 575 (1933).

(6) H. N. Alyea, J. J. Gartland, Jr., and H. R. Graham, Jr., *Ind. Eng. Chem.*, **34**, 458 (1942).

(7) Ch. Bagdassarian, *Acta Physicochim. U. R. S. S.*, **19**, 266 (1944).

(8) K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 2377 (1946).

(9) H. W. Starkweather and G. B. Taylor, *ibid.*, **52**, 4708 (1930).

(10) S. G. Foord, *J. Chem. Soc.*, 48 (1940).

(11) P. D. Bartlett, G. S. Hammond and H. Kwart, "Disc. Faraday Soc.," No. 2, 342 (1947).

ers, with such a low value of $k_4/k_2$ (see equations 2 and 4) that they are not rapidly consumed during the induction period, (2) strong retarders and inhibitors which are consumed only in the course of a second-order reaction with growing chains, (3) one immeasurably strong inhibitor, 2,2-diphenyl-1-picrylhydrazyl and (4) iodine, which falls in class (2) except for the order of the reaction in which the chains are stopped.

## Experimental

**Dilatometer.**—Figure 1 is a schematic representation of the type of dilatometer most used in these studies. Its use was as follows: A weighed amount of vinyl acetate, purified as described below, was introduced through H into the storage reservoir A of capacity approximately 100 cc. A weighed amount of benzoyl peroxide was added to the same reservoir. When the inhibitor to be used was non-volatile and without reaction at room temperature with peroxide and monomer, a weighed amount of the inhibitor was also added to reservoir A. In other cases the inhibitor was introduced separately into tube E where it could be separately frozen and degassed. Tubes G and H were sealed off at their constrictions and the high vacuum pump attached at F was started and the frozen contents of A and E were degassed by successive evacuations and thawings until the characteristic oxygen discharge was no longer evident on bringing up a spark coil to the tube. The dilatometer was then sealed off at F and its contents allowed to warm to about 15° in the dark.

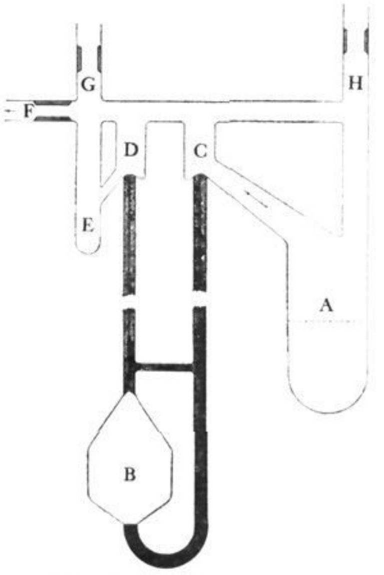

Fig. 1.—Dilatometer.

The reactants, when not already mixed, were now mixed by inverting the dilatometer and vigorously agitating it in the thermostat. After thermal equilibrium had been attained the dilatometer was restored to its upright position and the two capillaries and the reservoir B were filled by tilting in the direction of the arrow so that the contents of A flowed into C, down the capillary into the bottom of the bulb B and thence up, finally overflowing into D and E. By appropriate tilting the height of the liquid in the capillaries could be adjusted. In the case of powerful inhibitors a check on the existence of thermal equilibrium was obtained by noting the stationary position of the meniscus at this stage of the experiment. Readings of the liquid level in the capillaries were taken with a cathetometer through the plane glass sides of the thermostat in which the dilatometer assembly was totally immersed. The temperature in the immediate vicinity of the dilatometer was observed with a Beckmann thermometer which varied less than ±0.001° from 45°.

Between runs the dilatometer was rinsed nine or ten times with acetone and cleaned after every third run with hot concentrated nitric acid. After such cleaning a flame was played up the dilatometer during evacuation to remove any volatile residue.

**Calibration of the Dilatometer.**—The dilatometer capillaries were made of Trubore tubing which showed negligible variation in the length of a mercury thread with position in the capillary. Calibration was accomplished with a weighed amount of distilled mercury whose volume was varied by making changes in the temperature of the thermostat at 2–3° intervals. The volume of the dilatometer was 33.013 ml. to the upper mark. The contraction in volume per centimeter of height in the two capillaries was found to be 0.0154 ml., or 0.0467%. By extrapolation of the data of Starkweather and Taylor[12] to 45° 100% polymerization of vinyl acetate appears to correspond to 23.6% contraction in volume. This means a polymerization of 0.198% per centimeter fall of the meniscus in our capillaries.

**Materials.**—Vinyl acetate was obtained from the Niacet Chemical Company and was distilled through a special 100-plate Lecky-Ewell column according to the method of Nozaki and Bartlett.[8] Middle fractions of the distillate, each fraction of the correct size for one dilatometric experiment, were collected under nitrogen and sealed in ampoules of red, low actinic glass. Such samples could be stored without change for as long as six months but in practice they were used within a few weeks of the time of distillation. This material, tested with the procedure of Nozaki and Bartlett, polymerized without an induction period and checked their rate constants. Benzoyl peroxide from the Eastman Kodak Company was recrystallized twice from chloroform and petroleum ether. Iodometric analysis gave an assay of 100% for the dried peroxide. The material was handled only with glass or porcelain spatulas. Duroquinone was prepared according to the method of "Organic Syntheses."[13] The resublimed material melted at 109.0–109.5°. *m*-Dinitrobenzene from the Eastman Kodak Company, after two recrystallizations from 95% ethanol, melted at 90–90.5°. *p*-Dinitrobenzene was furnished by Dr. George S. Hammond and twice recrystallized from 95% ethanol. The product was colorless, melting at 173–173.5°. *o*-Dinitrobenzene was furnished by Dr. George S. Hammond and melted at 116.5–117°. Dinitrodurene, a student preparation made by the method of "Organic Syntheses"[13] was recrystallized from 95% ethanol and melted at 209–209.5°. Iodine, Mallinckrodt analytical reagent, was sublimed before use. According to the reported analysis this material contained no more than 0.003% total bromine and chlorine. 2,2-Diphenyl-1-picrylhydrazyl was prepared and recrystallized in the form of small plates according to the method of Goldschmidt and Renn.[14] Nitrobenzene from the Eastman Kodak Company was purified at different times by distillation through a 68-plate concentric-tube column at 100-mm. pressure, repeated recrystallization from absolute alcohol, and an azeotropic distillation with thiophene-free benzene to ensure the removal of the solvent. The material was dried with phosphorus pentoxide before the 68-plate distillation. *p*-Nitrotoluene from the Eastman Kodak Company was twice recrystallized from 50% ethanol and melted at 51.5–52°.

The results are reported separately below for the several terminators.

## Kinetic Treatment of Retardation and Inhibition

Let

P = initiating peroxide, its concentration changing only negligibly during an experiment
M = monomer, its concentration changing only negligibly during an experiment
R = any free radical chain carrier
Z = terminator
X = stable product

The following mechanism for initiation, propagation and termination of polymerization is assumed to be fundamentally correct.[11]

$$\mathrm{P} \xrightarrow{k_1} 2\mathrm{R} \qquad (1)$$

$$\mathrm{R} + \mathrm{M} \xrightarrow{k_2} \mathrm{R} \qquad (2)$$

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(12) H. W. Starkweather and G. B. Taylor, THIS JOURNAL, **52**, 4711 (1930).

(13) L. I. Smith, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 254.

(14) S. Goldschmidt and K. Renn, *Ber.*, **55**, 628 (1922).

$$R + R \xrightarrow{k_3} X \qquad (3)$$

$$nR + mZ \xrightarrow{k_4} X \qquad (4)$$

The coefficients $n$ and $m$ in equation 4 refer to the number of free radicals and of terminator molecules participating in the first stage of the retardation process. (In all our cases except that of iodine the experimental results are consistent with the assumption $n = m = 1$.) However, it may often be that a terminator molecule reacts in stages to stop two growing chains. When this happens it is likely that the product of the first stage, being a free radical, will react with a further R with a rate constant much greater than $k_4$, and that the kinetics implied in the present scheme will be disturbed only by the appearance of a coefficient of 2 before $k_4$. The coefficients $n$ and $m$ can be evaluated by comparing the data with the requirements of equations derived by assigning trial values to these constants.

According to this kinetic scheme, at the steady state

$$d(R)/dt = 2k_1(P) - k_3(R)^2 - yk_4(R)^n(Z)^m \cong 0 \quad (5)$$

where $y$ is the number of growing chains (probably either one or two) stopped by one terminator molecule as a result of a single rate-determining encounter. The constants $k_3$ and $k_4$ are defined by eq. 5 as the rate constants for the disappearance of single radicals by these respective processes. (A different definition of $k_3$ is used in current work with the rotating sector.) In the presence of an efficient terminator, (R) will rise during polymerization from a low value equal to $(2k_1(P)/k_4(Z)_0^m)^{\frac{1}{n}}$ to an upper limit, $\sqrt{2k_1(P)/k_3} = (R)_{max.}$ The fraction of chain termination occurring by way of interaction between chain-carrying free radicals at any time is equal to $k_3(R)^2/2k_1(P) = k_3(R)^2/k_3(R)^2_{max.}$ and it follows that when (R) is equal to 20% of its upper limiting value for uninhibited polymerization, only 4% of the chains are being terminated by interaction of radicals with one another. At all stages of the reaction earlier than this we may neglect the term $k_3(R)^2$ in comparison to $k_4(R)^n(Z)^m$ and solve the simplified steady-state equation

$$d(R)/dt = 2k_1(P) - k_4(R)^n(Z)^m \cong 0 \quad (6)$$

$$(R) = (2k_1(P)/k_4(Z)^m)^{\frac{1}{n}} \quad (7)$$

The form of this equation explicit in (Z) is

$$(Z) = (2k_1(P)/k_4(R)^n)^{\frac{1}{m}} \quad (8)$$

From equation 2 it is clear that

$$-d(M)/dt = k_2(R)(M), \text{ or } -d\ln(M)/dt = k_2(R) \quad (9)$$

The dilatometric measurements are made with sufficient frequency and accuracy to permit the evaluation of $(-d \ln(M)/dt)$ at each time from a plot of $\ln(M)_0/(M)$ against time, the ordinates being calculated from the dilatometer readings, the dimensions of the apparatus, and the densities of vinyl acetate and polyvinyl acetate (see Experimental Section). The slopes afford a measure of *relative* free radical concentrations from the beginning of the reaction over the period of measurement. The slopes up to 20% of the maximum limiting slope should obey equation 9 to a satisfactory approximation. By combining equations 8 and 9 we find that

$$(Z) = \left[\frac{2k_1k_2^n(P)}{k_4\left(\frac{-d\ln(M)}{dt}\right)^n}\right]^{\frac{1}{m}} \quad (10)$$

The reciprocals of $(-d \ln (M)/dt)$, or some power thereof, accordingly provide a measure of *relative* terminator concentration over the range of validity of equation 9. Since we know the initial concentration of terminator, these relative values can be translated directly into absolute values of terminator concentration whenever the initial value of $(-d \ln (M)/dt)$ is distinguishable from zero, permitting an evaluation of the quantity $k_1(k_2/k_4)(P)$.

**The Mode of Disappearance of Terminator.**—According to the current theory of the inhibitory process the inhibitor is so altered in the act of removing its quota of chain-carrying radicals as to lose its inhibitory power. An inhibitor which is capable of stopping $y$ growing chains should therefore disappear from the solution at a rate equal to $1/y$ times the rate of chain initiation. If this is the only mode of disappearance of the terminator, then in the present experiments the terminator concentration should be a linear function of time, since the initiator is present at an essentially constant concentration and the rate of starting of chains is therefore constant. In such a case the terminator concentration will obey the equation

$$(Z) = (Z)_0 - (2k_1(P)t/y) \quad (11)$$

where $(Z)_0$ is the initial concentration of terminator and $2k_1$ is the rate constant for the *initiation of chains* by the initiator; $k_1$ may or may not be identical with the rate constant for decomposition of the initiator, depending upon whether or not chain decomposition or other wastage of the initiator is occurring.[15]

By combination of Equations 10 and 11 a predicted relation is established between the slopes of the $\ln[(M)_0/(M)] - t$ curves and time

$$\left[\frac{2k_1k_2^n(P)}{k_4(-d\ln(M)/dt)^n}\right]^{\frac{1}{m}} = (Z)_0 - \frac{2k_1(P)t}{y} \quad (12)$$

To obtain the greatest amount of information from the use of these equations it is necessary to evaluate $n$, $m$, $k_1$, $k_2/k_4$ and $y$. The values of $n$ and $m$ are most directly arrived at by considering the relation between the rates of disappearance of monomer and of terminator

$$-d(M)/dt = k_2(M)(R) \quad (13)$$

$$-\frac{d(Z)}{dt} = \frac{k_4}{y}(R)^n(Z)^m \quad (14)$$

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[15] K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946).

Hence

$$\frac{d(Z)}{d(M)} = \frac{k_4}{yk_2}\frac{(Z)^m}{(M)}(R)^{n-1} \qquad (15)$$

Substituting for (R) from equation 7

$$\frac{d(Z)}{d(M)} = \frac{k_4}{yk_2}\frac{(Z)^m}{(M)}\left(\frac{2k_1(P)}{k_4(Z)^m}\right)^{(n-1)/n} = \frac{k_4{}^{1/n}}{yk_2}\frac{(Z)^{m/n}}{(M)}(2k_1(P))^{(n-1)/n}$$

Integration yields

$$\frac{1}{\frac{m}{n}-1}\left[(Z)^{1-(m/n)} - (Z)_0{}^{1-(m/n)}\right] = \frac{k_4{}^{1/n}}{yk_2}(2k_1(P))^{(n-1)/n}\ln\frac{(M)_0}{(M)}\ (m \neq n) \qquad (16a)$$

or

$$\ln\frac{(Z_0)}{(Z)} = \frac{k_4{}^{1/n}}{yk_2}(2k_1(P))^{(n-1)/n}\ln\frac{(M)_0}{(M)}\ (m = n) \qquad (16b)$$

Substitution of the value of (Z) from equation 10 yields

$$\left(\frac{-d\ln(M)}{dt}\right)^{(m-n)/m} = \left(\frac{m}{n}-1\right)(2)^{(m-1)/m}\frac{k_4{}^{1/m}}{yk_2{}^{n/m}}(k_1(P))^{(m-1)/m}\ln\frac{(M)_0}{(M)} + \text{const.}\ (m \neq n) \qquad (17a)$$

or

$$\ln\left(\frac{-d\ln(M)}{dt}\right) = \frac{k_4{}^{1/n}}{yk_2}(2k_1(P))^{(n-1)/n}\ln\frac{(M)_0}{(M)} + \text{const.}\ (m = n) \qquad (17b)$$

Or, from Equation 11

$$\left[(Z)_0 - \frac{2k_1(P)t}{y}\right]^{1-(m/n)} = \left(\frac{m}{n}-1\right)\frac{k_4{}^{1/n}}{yk_2}(2k_1(P))^{(n-1)/n}\ln\frac{(M)_0}{(M)} + \text{const.}\ (m \neq n) \qquad (18a)$$

or

$$-\ln\left[(Z)_0 - \frac{2k_1(P)t}{y}\right] = \frac{k_4{}^{1/n}}{yk_2}(2k_1(P))^{(n-1)/n}\ln\frac{(M)_0}{(M)} + \text{const.}\ (m = n) \qquad (18b)$$

When the correct values of $m$ and $n$ are introduced into equations 12, 17 and 18, good linear plots of the data are obtained; for all values of $m$ and $n$ bearing an incorrect ratio to each other, the plots are curved. Values of $m$ and $n$ in the correct ratio, but individually incorrect, will yield straight lines but the slopes of the lines from different equations will not yield concordant values of the rate constant ratios.

**The Determination of $k_1$ by Means of 2,2-Diphenylpicrylhydrazyl and Duroquinone.**—The distinction between the rate of decomposition of benzoyl peroxide and the rate of initiation of chains has been the subject of previous studies.[15,16] Nozaki and Bartlett[15] attempted to assign a rate constant of "spontaneous" decomposition to benzoyl peroxide by distinguishing the first-order from the 3/2-order decomposition of benzoyl peroxide in solvents, but later[17] found that induced decomposition of peroxide may appear as a first-order reaction or as one of higher order, depending upon the prevailing mode of chain termination. Several investigators[18,19,20] have previously used inhibitors to determine the rate of chain initiation in polymerization.

2,2-Diphenyl-1-picrylhydrazyl, being a stable free radical, might be expected to be a more reactive interceptor of radical chains than most molecules. Furthermore it would seem probable that such very high reactivity would be restricted to the reaction of a picrylhydrazyl molecule with a single free radical, minimizing the uncertainty as to the value of $y$ which is present with the molecular inhibitors. A solution of picrylhydrazyl in vinyl acetate at a concentration of about $3 \times 10^{-5}$ $M$ shows a characteristic permanganate-like color. In the presence of benzoyl peroxide, in the dilatometer, no change in volume of such solutions can be detected for periods dependent upon the exact concentration of inhibitor taken. After such an induction period the reaction begins, the graph showing a slope which, even by this method of observation, makes a sharp angle with the axis. This point coincides with the disappearance of the color of the picrylhydrazyl radical. This therefore provides a method of observing the end of the induction period. Typical curves are shown in Fig. 2. The number of equivalents per liter of free radicals generated in time, $t$, from an initiator (P) at constant concentration should be equal to $2k_1t$(P). This must also be equal to the number of equivalents per liter of a highly efficient inhibitor which have disappeared by time, $t$, namely, $y(Z)_0$ at the end of the induction period. We may then estimate $k_1$ simply as the quotient $(Z_0)/2(P)t$, assuming that for an inhibitor which is a free radical $y = 1$. Three experiments such as those shown in Fig. 2 yield values of 1.38, 1.37 and $1.46 \times 10^{-5}$ min.$^{-1}$ for $k_1$. Because of the short induction periods these are not considered the most accurate of the measurements obtained by various methods. The results with picrylhydrazyl could not be improved by working with higher concentrations because the first stage of powerful inhibition is followed by a second stage of strong retardation characteristic of an aromatic polynitro-compound, and the yellow color of this material becomes conspicuous at higher concentrations.

Duroquinone does not produce total inhibition and shows no visible color change at the end of the induction period. Nevertheless the approach to the final uninhibited rate of polymerization is sharp, and the change of the curve of ln (M)$_0$ (M) $vs.$ $t^{11}$ to its limiting slope from one-fifth of this limiting slope occurs in such a short space of time

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[16] J. T. Clarke, Thesis, Massachusetts Institute of Technology, 1948.

[17] P. D. Bartlett and K. Nozaki, THIS JOURNAL, **69**, 2299 (1947).

[18] G. M. Burnett and H. W. Melville, *Proc. Roy. Soc.* (*London*), **A189**, 456 (1947).

[19] G. Dixon-Lewis, *Disc. Faraday Soc.*, **2**, 320 (1947).

[20] M. S. Matheson, E. B. Bevilacqua, E. E. Auer, E. J. Hart, ref. 23, p. 2610.

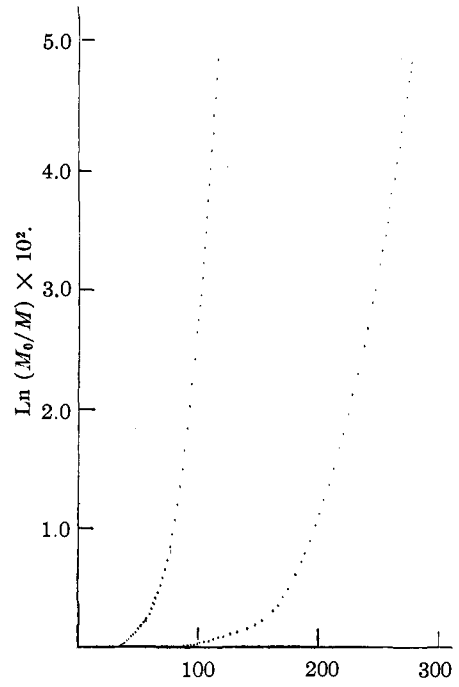


Fig. 2.—Some typical polymerizations of vinyl acetate in the presence of 2,2-diphenyl-1-picrylhydrazyl, where each dot represents an experimental determination.

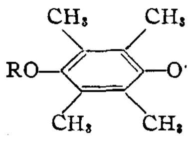
that a reasonable point may be assigned from the graph as the end of the inhibition period. The times involved with this terminator, at concentrations from 1.4 to 9.2 × $10^{-4}$, run from 170 to 525 minutes, and the accuracy of their determination justifies the use of the equations for the end of the inhibition period

$$y(Z)_0 = 2((P)_0 - (P)_e) = 2(P)_0\,(1 - e^{-k_1t}) \qquad (19)$$

and

$$\ln\left(1 - \frac{y(Z)_0}{2(P)_0}\right) = -k_1t \qquad (20)$$

which take into account the small change in (P) during the inhibition period.[21] As Fig. 3 shows, even equation 11 yields a good straight line; and its slope is equal to that of the similar line for picrylhydrazyl when $y$ is taken to be *the same for duroquinone as for picrylhydrazyl.* This rather surprising result may be interpreted by assuming that both terminators stop one growing radical per molecule, or that both stop two growing radicals per molecule. To us the reasons seem best for assigning unit equivalence in the strong inhibition step to the free radical, picrylhydrazyl. In this case duroquinone must terminate chains by the formation of a relatively stable alkoxyphenoxyl radical



which dimerizes in preference to reacting with a second growing chain.[21a] We have not succeeded in establishing the nature of the process experimentally.

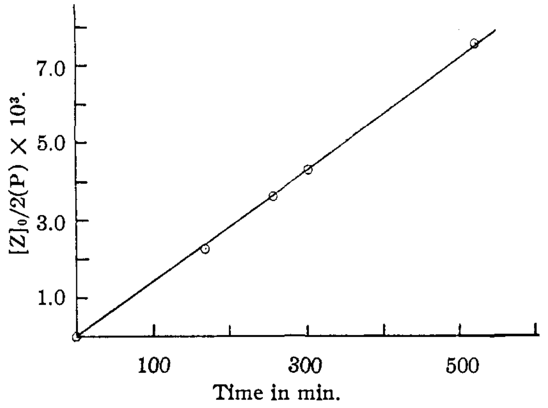


Fig. 3.—The interval of inhibited polymerization of vinyl acetate in the presence of duroquinone as a function of initial inhibitor and peroxide concentration.

Figure 4 shows the application of equation 18 to the data for several polymerizations in the presence of duroquinone, the values of $y$ and of $m$ both being taken as 1. Figure 5 is a plot of equation 12

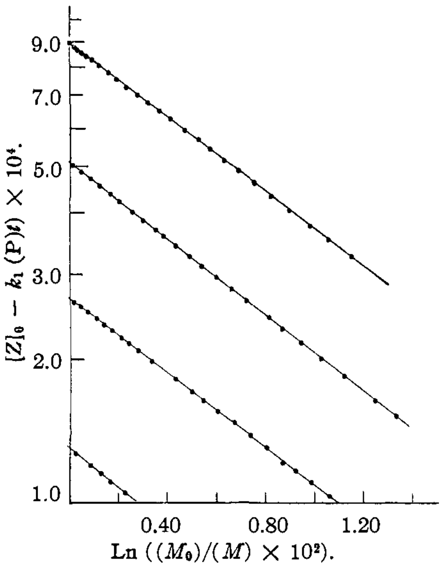


Fig. 4.—Data from several runs of vinyl acetate polymerization inhibited by duroquinone plotted according to equation 18, $m = n = 1$.

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[21] This correction for changing (P) is still only an approximate one, since it rests upon an assumed identity between $k_1(P)$ and $-d(P)/dt$. Clarke[16] has found that vinyl acetate does not eliminate induced decomposition of benzoyl peroxide in dioxane as do styrene and methyl methacrylate.

[21a] Matheson and co-workers[23] have also concluded that benzoquinone stops one chain per molecule. A similar opinion was expressed by F. R. Mayo and R. A. Gregg, THIS JOURNAL, **70**, 1284 (1948).

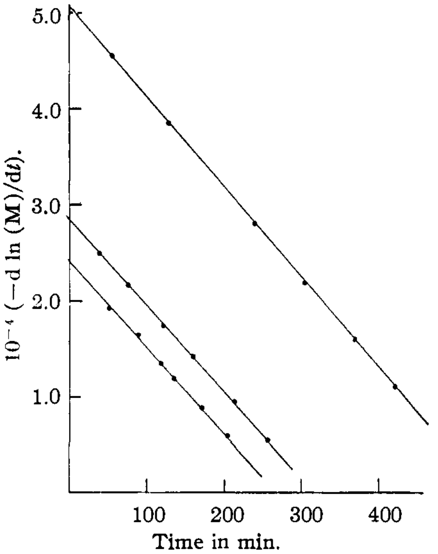

Fig. 5.—Data from several runs of vinyl acetate polymerization inhibited by duroquinone plotted according to equation 12, $m = n = 1$.

for three of the same runs. These plots serve to confirm the general theory and to indicate the values of $y$, $m$ and $n$, and their slopes agree on a value of 95 ± 10% for $k_4/k_2$. This quantity cannot be evaluated for the immeasurably efficient inhibitor, picrylhydrazyl. By rewriting equation 12 with $y = m = n = 1$

$$1/(-\ \mathrm{d}\ \ln\ (\mathrm{M})/\mathrm{d}t) = \frac{k_4}{k_2}\frac{(\mathrm{Z}_0)}{2k_1(\mathrm{P})} - \frac{k_4}{k_2}t \quad (12a)$$

it can be seen that in the plot of $1/[-\mathrm{d}\ \ln\ (\mathrm{M})/\mathrm{d}t]$ *vs.* $t$, the slope measures $k_4/k_2$ while the intercept affords a determination of $k_1$. This method has given the most reliable measurements of $k_1$ for benzoyl peroxide in vinyl acetate at 45°, the value taken being $1.34 \times 10^{-5}$ min.$^{-1}$, using the value of $k_4/k_2 = 90$ indicated by the plots for all three runs.

**Iodine.**—Iodine has a remarkable dual effect upon polymerizable olefins. A solution of iodine in vinyl acetate at moderate concentration undergoes spontaneous heating and blows out of its vessel, leaving iodine fumes and a polymeric residue. In concentrations as low as $10^{-4}$ *M*, however, iodine behaves as an efficient inhibitor of the peroxide-induced polymerization of vinyl acetate. It is clear from this fact that the polymerization brought about by stronger solutions of iodine has a polar mechanism and not an atomic one, and is of an order higher than first in iodine. This has been proved in the related case of styrene.[22]

A consequence of the high reactivity of iodine with vinyl acetate at higher concentrations is that it is difficult to prepare solutions of iodine in vinyl acetate which still contain in available form all the iodine which was introduced. This is apparently due to reaction in the regions of high local concentration surrounding the dissolving iodine crystals during the making up of the solution. The initial concentration of iodine in the solution, if it is assumed to be equal to $2k_1(\mathrm{P})t/y$ at the end of the induction period, with $y = 2$, is lower by 4–21% in four runs than the calculated value from the quantity of iodine introduced. If the values of $(\mathrm{Z})_0$ determined in this way are considered to be correct, the kinetics throughout the period of inhibition is clean and the conclusions from application of the equations are quite definite.

From the two representative curves of the dilatometer results shown in Fig. 6 it is evident that iodine behaves as a rather strong inhibitor, polymerization being apparently totally arrested in run 2 for two hundred minutes, and all inhibition being ended by two hundred and seventy minutes.

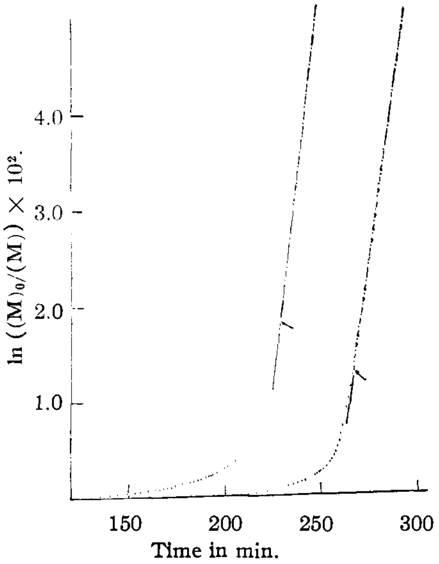

Fig. 6.—Some typical polymerizations of vinyl acetate at 45° in the presence of iodine; each dot represents an experimental determination: left-hand curve: $[\mathrm{I}_2]_0 = 8.44 \times 10^{-5}$, $[\mathrm{P}]_0 = 2.67 \times 10^{-2}$; right-hand curve: $[\mathrm{I}_2]_0 = 9.11 \times 10^{-5}$, $[\mathrm{P}]_0 = 2.53 \times 10^{-2}$.

The determination of $m$ is shown in Fig. 7, where the data have been plotted according to equation 18 for $m = 1$, $m = 1/2$ and $m = 3/2$. Only the value $m = 3/2$ yields a linear plot, the results leaving no room for uncertainty on this point. It follows that the step in which iodine is consumed is of the 3/2 order in iodine, and first order in radicals.

The most direct interpretation of this peculiarity is that the equilibrium

$$3\mathrm{I}_2 \leftrightarrows 2\mathrm{I}_3. \quad (21)$$

is rapidly established in comparison to the time of these experiments, and that growing chains are terminated by collision with the $\mathrm{I}_3$. radical. This radical is less well known than the $\mathrm{I}_3^-$ ion, but the same stabilizing forces might well be present in the two cases. That free iodine atoms do not

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[22] D. S. Trifan, Thesis, Harvard University, 1948.

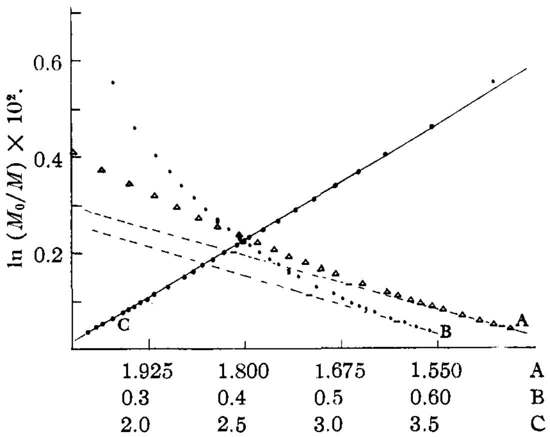

Fig. 7.—Data from polymerization of vinyl acetate inhibited by iodine plotted according to equation 18: Δ, $m = 1$; ■, $m = {}^1/_2$; ●, $m = {}^3/_2$; $A = -\ln(1 - (k_1Pt)/(Z)_0$; $B = (1 - (k_1Pt)/(Z)_0^{1/2}$; $C = (1 - (k_1Pt)/(Z)_0^{-1/2}$.

figure in the terminating process (corresponding to $m = 1/2$) would have to be due to a very favorable equilibrium in the conversion of iodine atoms and iodine molecules into triiodide radicals. Of the value of $K$, the forward equilibrium constant for equation 21, we know only that it must be small enough so that at $10^{-5}$ $M$ the concentration of $I_3\cdot$ is small compared to that of iodine. This type of "dissociation" equilibrium is shifted toward free radicals by an increase in concentration.

According to this interpretation the chain-terminating step has a rate equal to $k_4(R)(I_3\cdot) = k_4K^{1/2}(R)(I_2)^{3/2}$. The slope of the line C in Fig. 7 has the value $(4k_2/k_4K^{1/2})(Z)^{-1/2}$ and the intercept affords a check on the assumed value of $(Z)_0$ as determined from measurement of the total period of inhibition. The two runs performed at 45° yield values of $k_2/k_4K^{1/2}$ of $3.19 \times 10^{-6}$ and $5.37 \times 10^{-6}$. Four runs at 47° yield a mean value of $3.54 \times 10^{-6}$ for this quantity, with a mean deviation of $0.31 \times 10^{-6}$ or 9%. The reciprocal of this slope, or $2.8 \times 10^5$, is a measure of the over-all efficiency of iodine in stopping polymerization chains indicating that iodine at $6 \times 10^{-5}$ $M$ is about 23 times as effective an inhibitor as duroquinone. The radical $I_3\cdot$ itself must of course be much more effective still. If we were to assume the rate constant for reaction between R and $I_3\cdot$ to be the same as that between two R's, $k_3 = 5.9 \times 10^7$ at 25°,[23] and ignore the small temperature coefficient, then $k_4/k_2$ would be of the order of $5.9 \times 10^7/977 = 6.0 \times 10^4$, corresponding to $K = 25$, with about 1.6% of the iodine in the form of $I_3\cdot$ at $10^{-5}$ $M$, but with about 70% of the iodine in this form at 1 $M$ concentration. While this may present a difficulty in the interpretation, the reaction of two very unlike radicals should be a great deal faster than that of two like radicals, thus permitting $K$ to be much smaller than the above hypothetical value. The principal difficulties with the hypothesis of triatomic iodine radicals are: (a) that it requires rapid equilibration in the breaking and reforming of the I–I bond and (b) that it requires an unknown but very high degree of reactivity of $I_3\cdot$ toward chain-carrying radicals. It may be noted that any transition state for the terminating process which involves two radicals and three iodine molecules would account for the linear plots but not for the concordant values of $k_4/k_2$ obtained from equations 12, 17 and 18 applied to one and the same experiment. Examination of these equations will reveal that the relation between the slope of the curve and $k_4/k_2$ varies from one of these equations to another in a manner which depends upon the values taken for $n$ and $m$ as well as for their ratio.

**Three Weak Retarders: Dinitrodurene, *p*-Nitrotoluene and Nitrobenzene.**—Figure 8 shows typical dilatometric records of polymerizations in the presence of dinitrodurene, *p*-nitrotoluene and nitrobenzene. The first is such a weak retarder that its concentration is not appreciably diminished during the run and $\ln[(M)_0/(M)]$ remains a linear function of time throughout the experiment. *p*-Nitrotoluene and nitrobenzene are also weak retarders, but their concentrations drop sufficiently during the run to cause the polymerization curve to depart from the linear after a time.

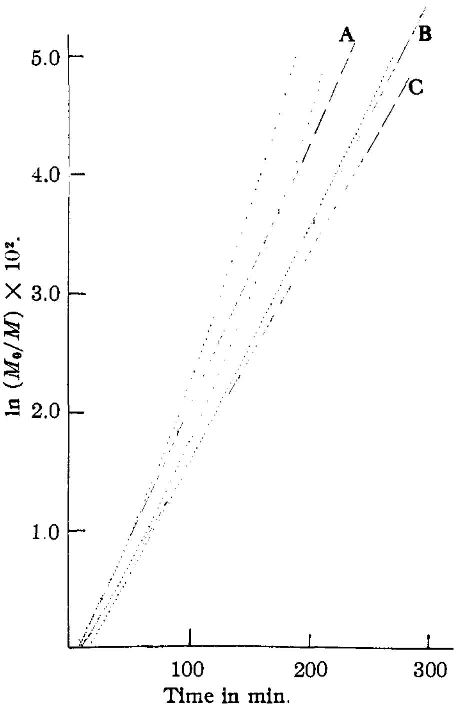

Fig. 8.—Polymerization of vinyl acetate in the presence of dinitrodurene, *p*-nitrotoluene and nitrobenzene: A, *p*-nitrotoluene; B, dinitrodurene; C, nitrobenzene; each dot represents an experimental determination.

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[23] M. S. Matheson, E. B. Bevilacqua, E. E. Auer and E. J. Hart, THIS JOURNAL, **71**, 2610 (1949); H. Kwart and P. D. Bartlett, Abs. 115th Meeting, Am. Chem. Soc., San Francisco, March 27–April 1, 1949; *cf.* C. G. Swain and P. D. Bartlett, *ibid.*, **68**, 2381 (1946).

In each case it is easy to assign an initial slope to the curve of ln $(M)_0/(M)$ *vs.* time and to compare this slope with that for a polymerization without retarder. The value of $k_4/yk_2$ can be obtained by combining equations 5 and 9 to yield

$$\frac{yk_4}{k_2} = -\frac{1}{(Z)}\left\{\frac{k_3}{k_2^2}\left[\frac{-\,\mathrm{d}\ln(M)}{\mathrm{d}t}\right] - \frac{2k_1(P)}{[-\mathrm{d}\ln(M)/\mathrm{d}t]}\right\} \tag{22}$$

where $n = m = 1$ and the terminator is considered to be present at constant concentration. The value of $k_1$ for use in equation 22 is known from the experiments with picrylhydrazyl and duroquinone, while for $k_3/k_2^2$ the value 0.246 was taken as an average from the data of Nozaki and Bartlett[8] combined with two runs without terminator and the ends of several iodine runs. Table I lists the data on the runs with the three weak retarders.

TABLE I

EFFECTIVENESS OF WEAK RETARDERS IN POLYMERIZATION OF VINYL ACETATE

| Retarder | Run | $(-\mathrm{d}\ln(M)/\mathrm{d}t) \times 10^4$ | $(Z)_0 \times 10^4$ | $(P)_0 \times 10^2$ | $k_4/yk_2$ |
|---|---|---|---|---|---|
| Dinitrodurene | 1 | 3.35 | 11.3 | 2.63 | 1.5 |
| | 2 | 1.44 | 22.6 | 1.37 | 1.0 |
| Nitrobenzene | 1 | 1.73 | 45.5 | 5.90 | 20 |
| | 2 | 2.12 | 21.5 | 3.06 | 18 |
| *p*-Nitrotoluene | 1 | 2.15 | 19.6 | 3.00 | 19 |
| | 2 | 1.79 | 28.6 | 4.05 | 21 |

These results shed little light on the mode or point of attack of the radical upon the nitro compounds of the retardation of polymerization. Both the view[24] that the radical attacks the nucleus and the view[25] that the radical attacks the oxygen of the nitro group predict that dinitrodurene will be a less efficient terminator than nitrobenzene, the reason by the latter hypothesis being that the resultant radical is not well stabilized by resonance on account of forced non-coplanarity of the ring and the system involving the nitro group. The comparison between nitrobenzene and nitrotoluene shows that the activation of hydrogen in the methyl group of the latter probably does not introduce any important mechanism for chain termination beyond that present in nitrobenzene.

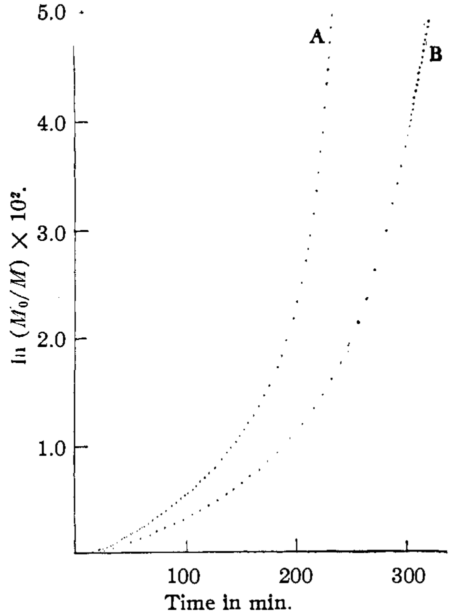

Fig. 9.—The polymerization of vinyl acetate in the presence of the dinitrobenzene inhibitors: A, *o*-dinitrobenzene; B, *m*-dinitrobenzene; each dot represents an experimental determination.

**The Dinitrobenzenes.**—Typical rate curves for the polymerization of vinyl acetate in the presence of the dinitrobenzenes are shown in Fig. 9. They are similar to the curves with duroquinone with an important exception: the final constant slope after the end of inhibition is not the slope of an unretarded polymerization, but corresponds to the presence of a retarder so weak that its concentration is essentially constant. Unlike duroquinone, therefore, the dinitro compounds in the course of stopping chains yield a product which has a retarding power somewhat less than that of nitrobenzene and greater than that of dinitrodurene. The original inhibition is so much stronger than this that the transition between the two stages of action of the terminator is as sharp as the end of the induction period with duroquinone. This makes it possible to estimate the chain-stopping equivalence of the dinitro compounds, as was done for duroquinone, by comparison with picrylhydrazyl and iodine, which appear to be reasonable calibration points with $y = 1$ and 2, respectively. In contrast to duroquinone, which appears to stop just one growing chain per molecule, each of the three dinitrobenzenes has an equivalence of two chains per molecule during the period of strong inhibition, and an unknown number thereafter. The methods used to study the period of strong inhibition are the same as those employed with duroquinone: Fig. 10

TABLE II

DINITROBENZENES AS TERMINATORS IN VINYL ACETATE POLYMERIZATION AT 45°

| Isomer | $(Z)_0 \times 10^4$ | $(P)_0 \times 10^2$ | Calcd. $k_1$ min.$^{-1}$ $\times 10^5$ | $k_4/k_2$, relative efficiency as terminator Early stage | Late stage |
|---|---|---|---|---|---|
| Ortho | 0.87 | 3.22 | 1.43 | 95 | 3.1 |
| | 0.91 | 2.80 | 1.47 | 94 | |
| | 5.09 | 6.51 | 1.60 | 98 | |
| Meta | 0.61 | 4.08 | 1.11 | 106 | 13.0 |
| | 0.83 | 3.83 | 1.20 | 106 | |
| | 1.31 | 3.74 | 1.25 | 104 | |
| Para | 1.08 | 4.20 | 1.42 | 278 | 8.2 |
| | 0.64 | 3.63 | 1.33 | 259 | |
| | 0.82 | 4.05 | 1.31 | 263 | |

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[24] C. C. Price, "Advancing Fronts in Chemistry," Vol. I Reinhold Publishing Corp., New York, N. Y., 1945, p. 44.

[25] G. S. Hammond, Thesis, Harvard, 1948.

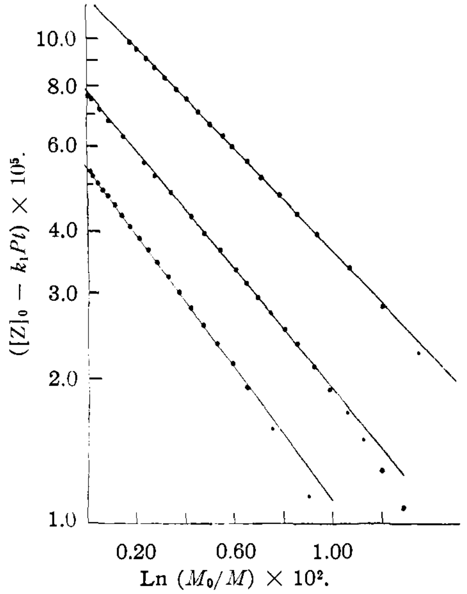

Fig. 10.—Data from several runs of vinyl acetate polymerization inhibited by *m*-dinitrobenzene, plotted according to equation 18, $m = n = 1$.

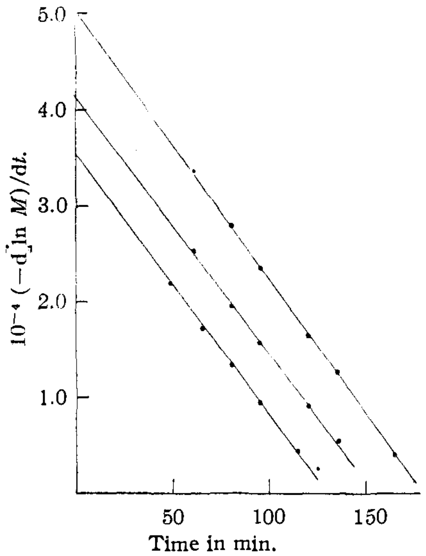

Fig. 11.—Data from several runs of vinyl acetate polymerization inhibited by *p*-dinitrobenzene plotted according to equation 12, $m = n = 1$.

shows a plot of equation 18, $m = n = 1$, for *m*-dinitrobenzene, and Fig. 11 shows a plot of equation 12, $m = n = 1$, for *p*-dinitrobenzene. In each case there is entire agreement with the demands of the theory, one radical and one terminator molecule being involved in the terminating step.

The late stage of weak retardation can be handled by the same methods as in the case of dinitrodurene and the mononitro compounds. Table II summarizes the initiator concentrations, terminator concentrations and terminating efficiencies deduced from the data.

The mechanism for termination of polymerization by dinitro compounds which involves attack by a radical on the benzene ring yields a product which has most of the chemical features of the original terminator. The only limitation upon a monoalkyldinitrobenzene functioning again as an inhibitor by this same mechanism would be steric hindrance, either direct or by way of damped resonance between the ring and a nitro group in the ortho position to the new chain substituent. The rather sharp drop, by factors of from 8 to 30, in the efficiency of the terminator after it has stopped two chains, presumably undergoing a single substitution, seems to accord better with the view that the attack of free radicals is on the oxygen of a nitro group, definitely depriving one of the nitro groups of its nitro character in the course of inhibition.

## Summary

The behavior of 2,2-diphenyl-1-picrylhydrazyl, duroquinone, dinitrodurene, nitrobenzene, *p*-nitrotoluene, iodine and *o*-, *m*- and *p*-dinitrobenzenes as inhibitors or retarders of the peroxide-induced polymerization of vinyl acetate at 45° has been studied kinetically by the dilatometric method. The inhibitors and retarders have been studied at concentrations of the order of $10^{-5}$ $M$; at such concentrations kinetic analysis of the shape of the curve representing accelerating polymerization with exhaustion of the inhibitor yields information about the rate of initiation, the order and relative speed of the chain-terminating step, and the number of chains stopped by a molecule of terminator. Duroquinone and 2,2-diphenyl-1-picrylhydrazyl stop one chain per molecule of inhibitor; iodine and the dinitrobenzenes in their early stage of strong inhibition stop two chains per molecule. Iodine is unique among the inhibitors reported here in that the reaction by which it stops growing chains is of the three-halves order with respect to iodine. It is suggested that diatomic iodine is in equilibrium with a triatomic iodine radical which does the actual combining with growing radicals.

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