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Acid-Induced Free-Radical Decomposition of Hydroperoxides: Polymerization of Methyl Methacrylate with Tert-Butyl Hydroperoxide and Sulfuric Acid

E. Rizzardo[a]; D. H. Solomon[a]
[a] Division of Applied Organic Chemistry, C. S. I. R. O. Melbourne, Victoria, Australia

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Acid-Induced Free-Radical Decomposition of Hydroperoxides: Polymerization of Methyl Methacrylate with Tert-Butyl Hydroperoxide and Sulfuric Acid

E. RIZZARDO and D. H. SOLOMON

Division of Applied Organic Chemistry
C. S. I. R. O.
Melbourne, Victoria, Australia

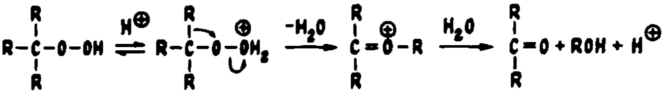
ABSTRACT

The interaction of strong acids with hydroperoxides at room temperature has been shown to result in the formation of radical species capable of initiating vinyl polymerization. For the reaction of tert-butyl hydroperoxide (tBHP) with sulfuric acid in methyl methacrylate (MMA), the rate of initiation of polymer varies in a complex manner with the concentration of the components but is first-order in [tBHP] and approximately second-order in [H_2SO_4] at low concentrations of tBHP and in the presence of excess acid. At high concentrations of tBHP, chain transfer to unprotonated hydroperoxide retards the rate of polymerization. The rate of polymer initiation parallels the ionization ratio [BH^+]/[B] of a weak base (B = 4-chloro-2-nitroaniline) in MMA-H_2SO_4 and the high order in [H_2SO_4] can be explained in terms of the requirement of more than one molecule of H_2SO_4 for the monoprotonation of the hydroperoxide (homoconjugation). Endgroup analysis of the polymers has shown that the initiating species are the tert-butoxy and hydroxy radicals. These data are consistent with the homolytic scission of the O–O bond of the hydroperoxide being facilitated by protonation of one of the oxygen atoms. Comparison

of the rate of polymer initiation with the overall rate of decomposition of tBHP has indicated that as much as 30% of the hydroperoxide decomposes by a radical path.

INTRODUCTION

The acid-catalyzed decomposition of organic hydroperoxides has received considerable attention and it has been widely accepted that the reaction proceeds by either or both of the heterolytic pathways (1) and (2) [1-4], (2) being of importance only in special circumstances [1-3].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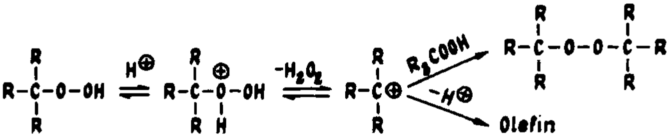
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Large numbers of hydroperoxides have been subjected to a variety of acidic conditions, and the products, often reported in high yield, have been rationalized exclusively in terms of the above heterolytic mechanisms.

In contrast to these findings, it had been noted in this laboratory [5] and elsewhere [6] that acidic substances (mineral acids, strong organic acids, Lewis acids, acidic minerals) accelerated the autoxidation of certain organic compounds, particularly in the presence of added hydroperoxides. This could be explained satisfactorily only if the assumption was made that an acid-induced free-radical decomposition of the hydroperoxides was taking place. In addition, we have established in a recent investigation [7] that the interaction of hydroperoxides with strong acids can result in the formation of free radicals capable of initiating vinyl polymerization.

The generality of free-radical formation in the interaction of a hydroperoxide with a strong acid in the presence of monomer was established by the observation that high molecular weight polymer resulted, at room temperature, from admixture of a reagent from each of the following groups: (a) tert-butyl hydroperoxide (tBHP), n-pentyl hydroperoxide, 2-pentyl hydroperoxide, 3-cyclohexenyl hydroperoxide, anhydrous hydrogen peroxide, and autoxidized methyl methacrylate; (b) sulfuric acid, 70% perchloric acid, trifluoromethanesulfonic acid, trifluoroacetic acid, boron trifluoride and acidic minerals, e. g., Hydrite 10; (c) methyl methacrylate (MMA), methyl acrylate, acrylic acid, and acrylonitrile.

The radical nature of the reaction was evidenced in the greatly reduced rate of polymerization in the presence of oxygen, hydroquinone or quinone and confirmed by copolymerization experiments with MMA-styrene [7].

The objective of the present work has been to elucidate the mechanism of the free-radical reaction and to determine the extent to which this process participates in the overall acid catalyzed decomposition of the hydroperoxides.

It seemed to us that one of the most appropriate methods of gaining this information would be to carry out a detailed study of the polymerization induced by the acid-hydroperoxide system. Thus (a) rates of vinyl polymerization and polymer molecular weight would provide a measure of the effective rates of radical formation; (b) the dependence of the rate of polymer initiation on the concentration of the components of the initiating system would yield the order of the radical reaction; (c) endgroup analysis of the polymer would identify the radical species involved in the initiation; and (d) overall rates of decomposition of the hydroperoxides would allow an estimation to be made of the proportion decomposing by a free-radical path.

For this, we chose to investigate the system t-butyl hydroperoxide-sulfuric acid-methyl methacrylate, because concentrated H_2SO_4 and MMA are miscible in all proportions, tBHP is readily available and relatively easy to purify, and because a large body of information is available about the free-radical polymerization of MMA.

RESULTS AND DISCUSSION

The Order of the Free-Radical Reaction

Before undertaking a detailed kinetic analysis of the polymerization process it is necessary to establish a number of conditions. First, neither the tBHP nor the sulfuric acid alone is capable of initiating MMA polymerization at the temperature (25°C) of our experiments. This is not surprising, since it is well known that MMA polymerizations are not initiated by acids and that tBHP acts as a free radical initiator only at temperatures well in excess of those employed in this investigation. Secondly, it was established by thin-layer chromatographic analysis [8] that under our experimental conditions transesterification of MMA with tBHP and dissociation of tBHP to hydrogen peroxide took place to only a very limited extent and that the tBHP remained largely unreacted during our kinetic runs. Also, it was shown that neither tert-butyl peroxymethacrylate nor hydrogen peroxide was responsible for any appreciable initiation of polymer. Thirdly, it was established in a number of selected experiments that the rates of polymerization were linear with respect to time so that rates determined gravimetrically at approximately 5% conversion were in fact a measure of the initial rate.

Our main interest for the moment is to ascertain the dependence of the rate of chain initiation (the effective rate of radical production) on the concentration of tBHP and H_2SO_4.

The rate of initiation R_i is related to the rate of polymerization R_p by the general kinetic expression (3):

$$R_i = 2k_tR_p^2/k_p^2[M]^2 \tag{3}$$

Plots of $R_p^2/[M]^2$ versus [tBHP] and $[H_2SO_4]$ are shown in Fig. 1 and Fig. 2, respectively, without regard for the time being, for the actual value of $2k_t/k_p^2$. Inspection of these plots indicates that when $[H_2SO_4] \gg [\text{tBHP}]$, the initiation reaction is first-order in [tBHP] and of an order slightly greater than 2 in $[H_2SO_4]$. At lower ratios of $[H_2SO_4]/[\text{tBHP}]$ the apparent order in [tBHP] approaches zero. Possible explanations for this effect will be considered later.

In the calculations of rates of initiations from Eq. (3) it is assumed that the initiating components have no significant influence on the rate of polymerization other than their role as chain initiators. This is a very important point, and any effect by the tBHP or H_2SO_4 must be delineated before rates of initiation can be relied upon. An indication of any modification to the polymerization process can be gained by examining the relationship between the rate of polymerization R_p and the number-average degree of polymerization $\overline{P}_n$. These two quantities are related by Eq. (4):

$$1/\overline{P}_n = (2k_{td} + k_{tc})R_p/k_p^2[M]^2 + C_M + C_I[I]/[M] + \ldots. \tag{4}$$

where k_{td} is the constant of termination by disproportionation; k_{tc} is the constant of termination by combination; k_p is the propagation constant; C_M is the transfer constant to monomer (M), and C_I is the transfer constant to initiator (I).

Clearly, then, a linear relationship between $1/\overline{P}_n$ and $R_p/[M]^2$, at varying initiator concentrations would be a necessary and sufficient

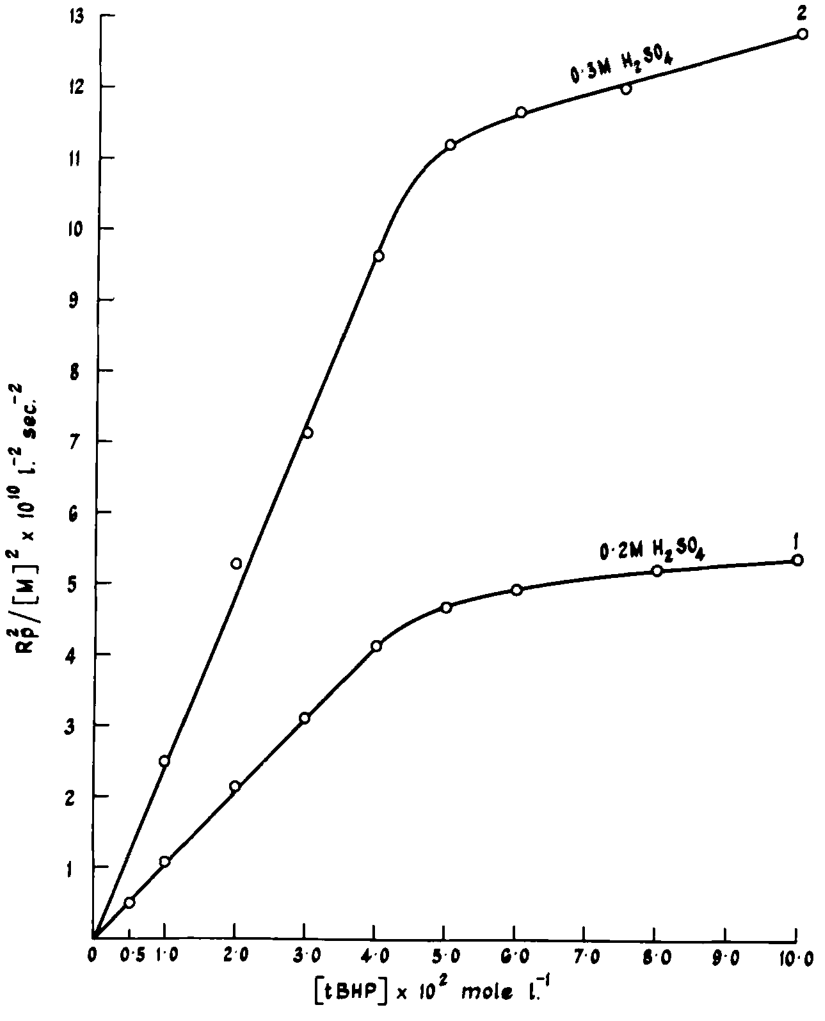


FIG. 1. Dependence of the initial $R_p^2/[M]^2$ (a measure of R_i) on the concentration of tBHP for the bulk polymerization of MMA at 25.0°C at 0.20 $\underline{M}$ and 0.30 $\underline{M}$ H_2SO_4.

condition for the absence of chain transfer to initiator and also for the absence of any modification to the rate constants for propagation and termination.

Such a linear plot is displayed by $1/\bar{P}_n$ versus $R_p/[M]^2$ for constant $[H_2SO_4]$ (0.2 $\underline{M}$) with changing hydroperoxide concentration up

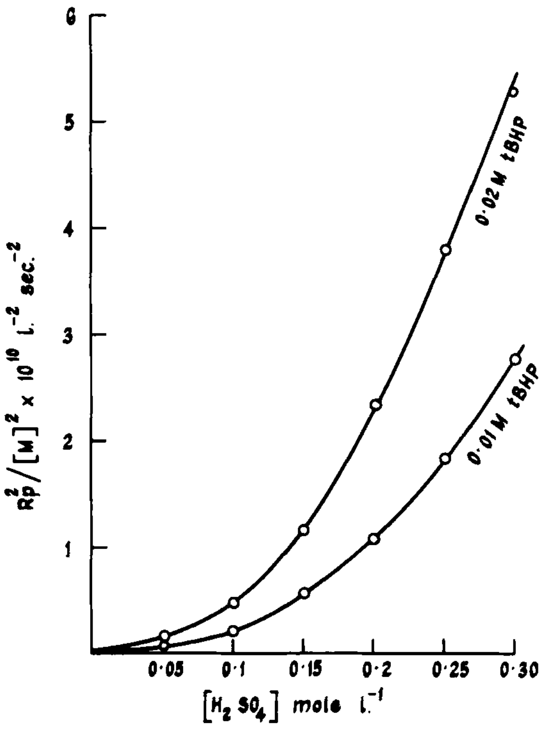


FIG. 2. Dependence of the initial $R_p^2/[M]^2$ (a measure of R_i) on the concentration of H_2SO_4 for the bulk polymerization of MMA at 25.0°C at 0.010 M and 0.020 M tBHP.

to approximately 0.04 M (Fig. 3, line 1). At higher [tBHP] the plot deviates markedly upwards in a manner consistent with the presence of an effective transfer agent; the situation that prevails when tert-butyl hydroperoxide is employed as the chain initiator in MMA polymerization [9].

In our experiments with 0.2 M H_2SO_4, chain transfer to hydroperoxide at [tBHP] > 0.04 M (Fig. 3, line 1) corresponds with a marked drop in the rate of change of the rate of polymerization (Fig. 1, line 1) and the obvious conclusion is that these two events are connected. To test this, we compared the rates of polymerization for azobisisobutyronitrile (AIBN)-initiated MMA in the presence and absence of tert-butyl hydroperoxide. At 60°C, 0.050 M AIBN in MMA produced a rate of polymerization of 22×10^{-5} mole/liter-sec, and this dropped to 10×10^{-5} mole/liter-sec in the presence of 0.052 M tBHP. This

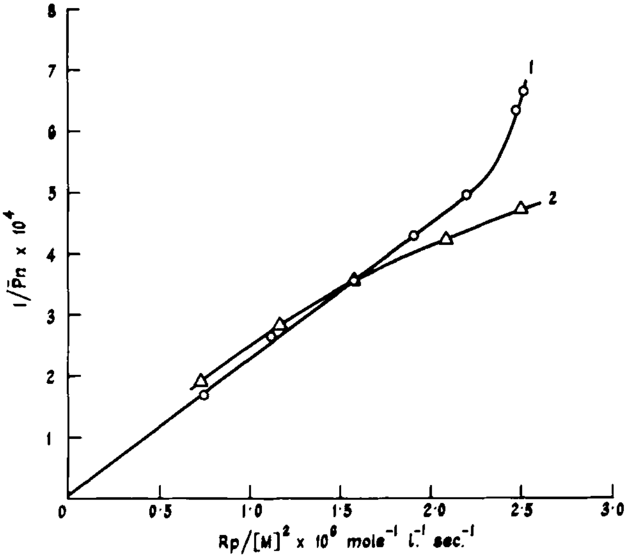


FIG. 3. $1/\bar{P}_n$ versus $R_p/[M]^2$ for the bulk polymerization of MMA at 25.0° initiated by tBHP-H_2SO_4: (1) [H_2SO_4] = 0.20 M, [tBHP] = 0.005, 0.010, 0.020, 0.030, 0.040, 0.080, 0.10 M; (2) [tBHP] = 0.020 M, [H_2SO_4] = 0.10, 0.15, 0.20, 0.25, 0.30 M.

effect is no doubt due to the hydroperoxy radical, formed by chain transfer to the hydroperoxide, being incapable of initiating MMA polymerization as efficiently as either the cyanopropyl or the poly-(methyl methacrylate)yl radicals. Although these experiments were carried out at 60°C, it is clear that chain transfer to hydroperoxide can result in a considerable reduction in the rate of polymerization in MMA-tBHP systems.

The shape of the plots in Fig. 1 and Fig. 3 (line 1) can be explained if we assert that the unprotonated form of the hydroperoxide acts as a chain transfer agent in MMA polymerizations whereas the protonated form does not. At low concentrations of tBHP and in the presence of a large excess of H_2SO_4 (over tBHP) in a medium of low basicity (MMA), the effective concentration of unprotonated hydroperoxide is expected to be very low and therefore chain transfer and retardation is not observed.

Having established that at low ratios of [tBHP]/[H_2SO_4] the hydroperoxide does not modify the polymerization process of MMA, we have shown that the experimentally determined rates of polymerization are indeed true measures of the rates of initiation and thus we have validated the first-order kinetics shown in Fig. 1.

The plot of $1/\overline{P}_n$ versus $R_p/[M]^2$ at constant hydroperoxide concentration (0.02 M) and varying sulfuric acid concentrations (Fig. 3, line 2) is not linear and displays clear evidence for chain lengthening by the sulfuric acid. Again, this effect was confirmed by examining the rates of polymerization of AIBN initiated MMA with and without added sulfuric acid. At 60° C, 0.2 M H_2SO_4 increased the rate of polymerization from 24×10^{-5} mole/liter-sec for pure AIBN (0.0058 M) to 27×10^{-5} mole/liter-sec, and this was accompanied by an increase in the degree of polymerization of the polymer. The higher rate with attendant increase in the degree of polymerization is indicative of a decrease in the rate constant for termination or an increase in the rate constant for propagation (or both) induced by the sulfuric acid.

Similar observations have been reported for the polymerization of MMA in the presence of silica [10], Lewis acids [11], and, more recently, orthophosphoric acid [12]. Here, the increase in molecular weight of the polymers has been attributed mainly to a retardation of the diffusion-controlled termination reaction brought about by the association of the growing chains as a result of complexing with orthophosphoric acid [12].

Regardless of the explanation, the decrease in k_t/k_p^2 with increasing acid concentration would result in an apparent higher order in H_2SO_4 for the initiation reaction as calculated by Eq. (3) and therefore our value of 2.2 estimated from Fig. 2 is expected to be slightly higher than the true order.

The chain-lengthening effect of the sulfuric acid can be nullified if rates of initiation are calculated from their relationship to the rates of polymerization and kinetic chain lengths ν [Eq. (5)]:

$$R_i = R_p/\nu = (1 + x)R_p/\overline{P}_n \qquad (5)$$

where x is the ratio of termination by combination to overall termination as defined by $x = k_{tc}/(k_{tc} + k_{td})$.

If we make the assumption that the proportion of termination by combination and disproportionation remains constant over a range of catalyst concentrations then a plot of $[H_2SO_4]$ versus $R_p/\overline{P}_n$ would supply the order of the initiation reaction with respect to sulfuric acid. As can be seen from Fig. 4, the rate of initiation varies with the concentration of H_2SO_4 to the approximate power of 2. Therefore, the overall rate of initiation for the polymerization of MMA by tBHP and sulfuric acid can be expressed as:

$$R_i \propto [\text{tBHP}][H_2SO_4]^2 \qquad (6)$$

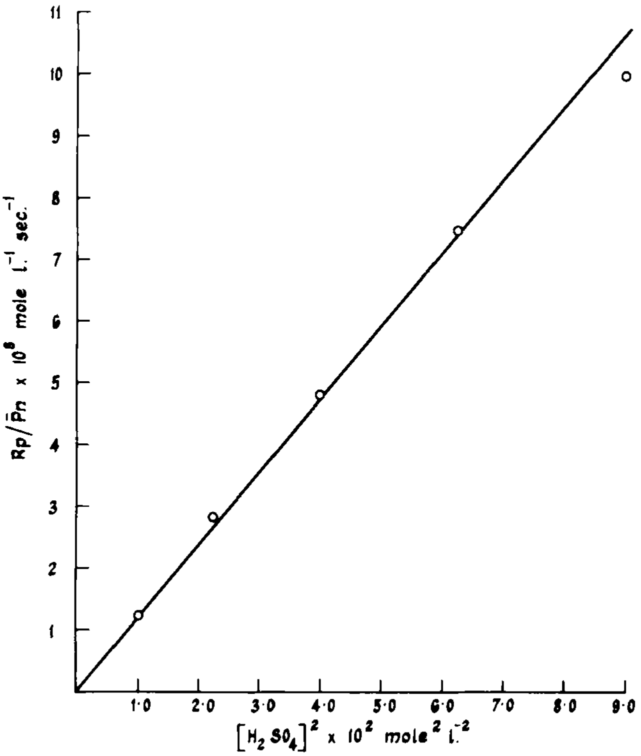


FIG. 4. Relationship between $R_p/\overline{P}_n$ (a measure of R_i) and $[H_2SO_4]^2$ for the bulk polymerization of MMA at 25.0°C initiated by tBHP-H_2SO_4; [tBHP] = 0.020 M.

provided that $[H_2SO_4] \gg [tBHP]$. Outside of this limitation, the added complications of chain transfer to, and retardation by, the tBHP would place any attempt to determine the order of the initiation reaction on a rather tenuous basis.

Endgroup Analysis of Polymers

The identity of the free-radical species that induce the polymerization would be of paramount importance in delineating possible mechanisms for the initiating process.

The most direct and reliable route to this information would be to identify the endgroups in the polymers obtained under conditions where chain transfer to catalyst is absent. Although endgroup analyses in high polymers is an extremely challenging task even under favorable circumstances, it was felt that an attempt should be made to search for the most logical species which might be produced in our tBHP-H_2SO_4 system. These we considered to be: tert-butoxy, hydroxy, sulfate, and sulfonates. The last two can be easily detected and estimated by the dye-partition technique [13]. Application of this test showed conclusively that our polymers were completely devoid of both sulfate and sulfonate endgroups.

The dye-partition technique has been utilized in the estimation of hydroxy endgroups following conversion of these to dye active sulfate groups by treatment with chlorosulfonic acid and pyridine [14]. We have modified and improved this method by making use of o-sulfobenzoic anhydride in place of the chlorosulfonic acid, a rather drastic reagent capable of producing undesirable side reactions [15].

In this way we found that the poly(methyl methacrylate) derived from the reaction of 0.02 M tBHP and 0.2 M H_2SO_4 in MMA contained an average of approximately 0.2 OH endgroups per polymer chain. This appeared to be a rather nondescript value until we established that the OH content of hydroxy-radical initiated (Fe^{2+}/H_2O_2) PMMA decreases steadily when exposed to H_2SO_4 in MMA. Here, the OH containing polymer most likely undergoes acid-catalyzed transesterification or 1,4-addition with MMA. This experiment suggests, therefore, that more than 20% of the polymer is being initiated by OH radicals in the tBHP-H_2SO_4 system, although the actual proportion remains indeterminable.

For the tert-butoxy endgroups, we discarded possible methods of determination based on ^{14}C labeling of the initiator [16] as being too laborious and not specific for the detection of the group as a whole. We have now devised a procedure for the estimation of this function based on cleavage of the ether linkage with boron trichloride and analysis for tert-butyl chloride by gas-liquid chromatography [17].

This procedure would not distinguish between tert-butoxy and tert-butylperoxy groups as both are expected to give tert-butyl chloride upon reaction with boron trichloride. In the polymerizations with tBHP-H_2SO_4, tert-butylperoxy groups might have arisen from tert-butylperoxy radical initiation or they might be present in the polymers as a tert-butylperoxy ester. The latter could arise either by direct transesterification of MMA with tBHP, to give tert-butylperoxy methacrylate, followed by copolymerization with MMA.

Attempts to detect and estimate the peroxide content (tert-butylperoxy ester [18] or dialkyl peroxide [19]) of the polymers by iodometric methods were inconclusive. The tests appeared to be negative but are not entirely reliable for trace amounts of peroxides since comparatively large blanks are involved in these determinations.

It should be possible, however, to distinguish between the tert-butoxy and tert-butylperoxy functions by taking advantage of the lower thermal stability of the latter. Accordingly, we analyzed for tert-butyl chloride by the procedure mentioned above; both before and after subjecting the polymer to a temperature of 120°C for 24 hr. The heat treatment had an insignificant effect on the values of the analysis, and we concluded that the polymer produced in the reaction of 0.02 M tBHP and 0.2 M H_2SO_4 in MMA contained approximately 0.4 tert-butoxy endgroups per chain. This figure should be compared with the value of 0.65 tert-butoxy endgroups per polymer chain that we obtained when MMA polymerization was initiated by di-tert-butyl peroxalate, where it was shown that the tert-butoxy radical initiates MMA polymerization partly by direct addition and partly via hydrogen abstraction [17].

Mechanism

Thus far, we have shown that tBHP in MMA decomposes to hydroxy and tert-butoxy radicals under the influence of sulfuric acid and that the rate of formation of the radical products is first-order in [tBHP] and second-order in $[H_2SO_4]$. Further, we have shown (qualitatively) that the rate of the radical forming reaction (as evidenced by the rate of polymerization) decreases with decreasing acidity of the medium. Addition of even small quantities of weak bases such as diethyl ether, methanol or water resulted in considerable retardation; undoubtedly these bases compete with the hydroperoxide for the proton of the acid. It is clear, therefore, that protonation of the hydroperoxide is an essential step in the radical producing process, in which case it is important to determine the protonating behavior of the H_2SO_4 in MMA (a weakly basic, nonhydroxylic solvent of low dielectric constant), before any consideration of possible mechanisms can be undertaken.

The most direct route to this information is to carry out acid-base indicator studies [20]. For this, we chose the Hammett indicator 4-chloro-2-nitroaniline, and its ionization ratios $[BH^+]/[B]$ were determined in MMA-H_2SO_4 by using an established spectrophotometric method [21]. The results are shown in Table 1, from which it can be deduced that the extent of conversion of 4-chloro-2-nitroaniline to its conjugate acid varies as the H_2SO_4 concentration to the power of approximately 2.1 within the range of 0.1-0.3 M H_2SO_4, with a deviation towards direct proportionality between $[BH^+]/[B]$ and $[H_2SO_4]$ at lower concentrations of H_2SO_4. This means that, over the range of acid concentration (0.1-0.3 M) of immediate interest to us, an average of approximately two molecules of H_2SO_4 are involved in the

TABLE 1. Rates of Polymerization R_p and Degree of Polymerization P_n for Bulk Polymerizations of MMA Containing 0.02 M tBHP and Various Concentrations of H_2SO_4 at 25°C[a]

$[H_2SO_4]$ (mole/liter)	$R_p \times 10^5$ (mole/liter)	$\bar{P}_n \times 10^{-3}$	$[BH^+]/[B]$
0.05	3.8	6.61	0.16
0.10	6.5	5.24	0.35
0.15	10.1	3.56	0.76
0.20	13.6	2.82	1.40
0.25	17.9	2.39	2.49
0.30	21.2	2.12	3.60

[a] $[BH^+]/[B]$ is the degree of ionization of 4-chloro-2-nitroaniline (5×10^{-4} M) in MMA containing the shown concentrations of H_2SO_4.

monoprotonation of a weak base (B) when MMA is the reaction medium, This can be depicted as shown in Eq. (7):

$$B + 2H_2SO_4 \rightleftharpoons BH^+\ HSO_4^- \cdots H_2SO_4 \qquad (7)$$

where the second molecule of H_2SO_4 acts to stabilize the anion through hydrogen bonding; a not uncommon phenomenon of acid-base reactions in solvents that are poor ion solvators [22]. A more complete picture of the protonating behavior of H_2SO_4 in MMA is likely to be very similar to that reported for H_2SO_4 in nitromethane in which the acid and base react in a ratio that varies from 1:1 at low H_2SO_4 concentrations (< 0.1 M) to 3:1 at higher H_2SO_4 concentrations [23].

The important point here, however, is that we have a reasonably close parallel between the ionization ratio of a weak base in MMA-H_2SO_4 and the rate of the acid-catalyzed free-radical breakdown of tBHP in MMA-H_2SO_4, i. e., the rate of polymer initiation in the tBHP-MMA-H_2SO_4 system. This relationship is shown in Fig. 5 as a log-log plot of $R_p/\bar{P}_n$ versus $[BH^+]/[B]$.

Since the behavior of a specific acid towards a base (present in low concentration) depends largely on the nature of the reaction

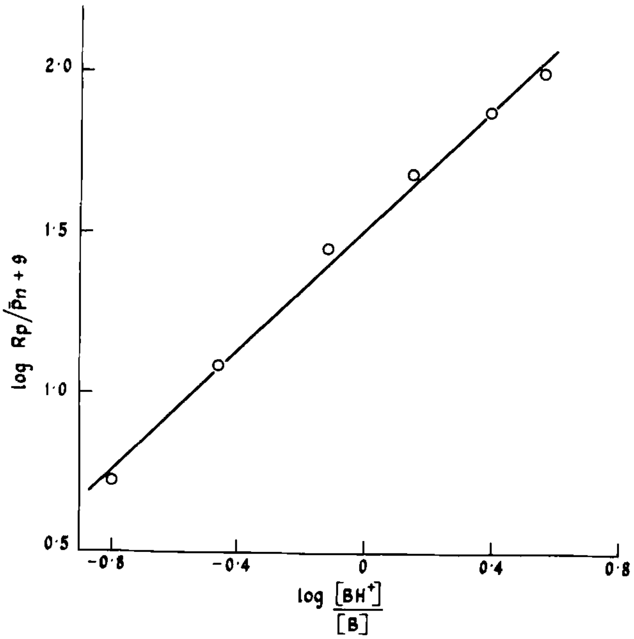


FIG. 5. Log-log plot of $R_p/\bar{P}_n$ (a measure of R_i) for the bulk polymerization of MMA at [tBHP] = 0.020 M and [H_2SO_4] = 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 M versus the ionization ratio of 4-chloro-2-nitroaniline, [BH^+]/[$\bar{B}$], determined at the same H_2SO_4 concentrations in MMA.

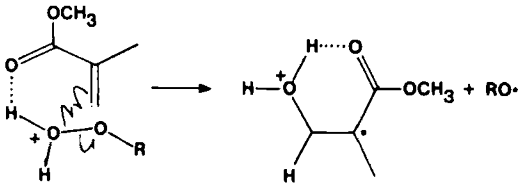
medium it seems reasonable to assume that the tBHP in MMA will be protonated by the H_2SO_4 by a similar process to that found for 4-chloro-2-nitroaniline [Eq. (7)]. This, then, explains our second-order dependence of the rate of initiation of polymer on the H_2SO_4 concentration and it allows us to exclude possible mechanisms for the free radical decomposition of tBHP based on diprotonation of the tBHP.

The most elementary mechanism that would fit our data would involve monoprotonation of the tBHP (at either oxygen atom) by two molecules of H_2SO_4 followed by O–O bond homolysis to give the tert-butoxy and hydroxy radicals, either "free" or complexed with the acid [Eq. (8) R = tert-butyl, X = $HSO_4H_2SO_4$]

$$\mathrm{ROOH} + 2\mathrm{H_2SO_4} \rightleftharpoons \mathrm{RO\overset{+}{O}H_2^{\cdot}\cdot\cdot X^-} \longrightarrow \mathrm{RO^{\cdot}} + \mathrm{{\cdot}OH{\cdot}\cdot\cdot H^+X^-} \qquad (8)$$

This would imply that protonation and complexation of the hydroperoxide with the acid has the effect of lowering the activation energy for O–O bond homolysis.

Our data do not exclude the possibility of the monomer taking part in the radical forming process, for example, by assisting in the homolytic scission of the O–O bond as shown in Eq. (9).



(9)

As a general rule, however, the acrylic moiety is not essential for the formation of free radicals from hydroperoxide and acid, since we have shown that H_2SO_4 (and other acids) will increase the rate of autoxidation of cumene and oleic acid in solvents such as dioxane, acetic acid, ethyl acetate, and acetonitrile, in the presence of tBHP [5].

Percentage of tBHP Decomposing by Free-Radical Path

In principle at least, the minimum proportion of hydroperoxide decomposing via a free-radical path can be secured by comparing the rate of initiation of polymer with the overall rate of peroxide disappearance. In practice, however, some difficulties arise.

The first is the unavailability of reliable data for the relative rates of combination and disproportionation in the termination of the poly(methyl methacrylate)yl radicals. This information is essential if accurate rates of initiation of polymer are to be calculated from rates of polymerization. Published values for k_{td}/k_{tc} at 25°C, obtained from kinetic data, vary from 0.34 [24] to 2.44 [25], and, although results from endgroup assays [26, 27], inhibitor consumption [27] and coupling experiments [28] agree more closely with the latter, the actual values remain in dispute.

The second, and equally serious problem, is the difficulty in determining the rates of hydroperoxide disappearance in a polymerization system. Here, measurements must be made at a low conversion of MMA to polymer and consequently represent small differences between large titration values (iodometric method). Rates of tBHP decomposition in similar but nonpolymerizing systems would be meaningless and obviously cannot serve as substitutes.

This limitation and the fact that we are dealing with competing reactions (ionic and free radical) for the overall decomposition of tBHP has made it impossible to fit the data to an empirical kinetic equation.

We can, however make broad estimates of the proportion of hydroperoxide decomposing by a free radical path at selected concentrations of tBHP and H_2SO_4. For example, the rate of initiation of polymer at 0.02 M tBHP and 0.2 M H_2SO_4 as calculated from equation (5) is in the range $6.2\text{-}8.4 \times 10^{-8}$ mole/liter-sec ($k_{td}/k_{tc} = 2.44$ or 0.34) and the rate of disappearance (R_d) of tBHP in the same system was estimated at 1.3×10^{-7} mole/liter-sec.

Then, assuming two radicals from each molecule of tBHP, the percentage of this reagent undergoing homolytic decomposition to species capable of initiating polymerization will be given by $100R_i/2R_d = 24\text{-}32\%$.

This value did not vary greatly over the concentrations where chain transfer was absent and obviously indicates that the free-radical path for hydroperoxide breakdown is one of considerable importance.

EXPERIMENTAL

Materials

Commercial tert-butyl hydroperoxide (Fluka) was purified via its sodium salt [29] and then fractionated at 20 mm pressure. Methyl methacrylate (Rohm and Haas) was purified by passage through an alumina column followed by careful fractionation at 80 mm pressure. For the kinetic runs, it was used immediately after purification. Sulfuric acid was BDH analytical reagent (98%). n-Pentyl and 2-pentyl hydroperoxide were prepared by the reaction of the corresponding alkyl methane sulfonates with 30% hydrogen peroxide [30]. 3-Cyclohexenyl hydroperoxide was obtained by the autoxidation of cyclohexene to low conversion [31]. The tert-butyl peroxymethacrylate was prepared as follows. Methacryloyl chloride was added to a stirred aqueous solution of the potassium salt of tert-butyl hydroperoxide at 0°C. Stirring was continued for 1 hr, the mixture was extracted with ether, and the ether solution was dried over anhydrous magnesium sulfate. The ether solution was then passed through a short column of silica gel and the ether evaporated at reduced pressure to give the perester as a colorless oil, shown to be of high purity by NMR and IR spectroscopy.

Procedure

Solutions of tBHP in methyl methacrylate were pipetted into specially cleaned and dry tubes, and the contents frozen in liquid nitrogen in a dry atmosphere. To these were added solutions of H_2SO_4 in MMA and MMA to make up the solutions to the desired concentrations. The tubes were then attached to a vacuum line via a high-vacuum stopcock and the contents were deoxygenated by repeated freezing and melting. To avoid premature reaction and polymerization during the melting cycle, the temperature was kept below -40°C. The tubes were then filled with high purity nitrogen, sealed, and transferred to a thermostatted bath at 25 ± 0.1°C. After a suitable reaction time, the polymer was precipitated by pouring the solution (transferred quantitatively with the aid of small volumes of ethyl acetate) into stirred methanol. The polymer was collected by filtration in preweighed sintered-glass crucibles, washed with methanol, and dried to constant weight of 50°C in a vacuum oven. Reaction times were chosen so as to give a conversion of monomer to polymer of the order of 4-6%.

The polymers were reprecipitated into methanol from benzene solutions before the determination of the degree of polymerization ($\overline{P}_n$). This was calculated from intrinsic viscosities $[\eta]$ by using the relation [9]: $\log \overline{P}_n = 3.420 + 1.13\,[\eta]$. Viscosity measurements were made on benzene solutions of the polymers at 20 ± 0.01°C by using a Ubbelohde viscometer.

Hydroperoxide concentrations before and after the polymerization reactions were determined by iodometric titrations [1], as follows. Glacial acetic acid (40 ml) containing potassium acetate, in slight excess over the amount required to neutralize the H_2SO_4 in the reaction mixture, was deoxygenated by the addition of a few small pieces of solid CO_2. To this was added the reaction mixture, containing the tBHP, H_2SO_4, MMA, and polymer, followed by solid sodium iodide (3 g). (For the reaction mixtures containing polymer, quantitative transfer was aided by a few milliliters of deoxygenated glacial acetic acid). The flask was then attached to a reflux condenser and the mixture was heated at gentle reflux for 10 min under a nitrogen atmosphere. The hot solution was then diluted with distilled water (50 ml) and titrated immediately with a standard solution of sodium thiosulfate. In this way, reproducible results were obtained with no detectable interference from MMA, H_2SO_4-KOAc, or small amounts of PMMA. Neutralization of the H_2SO_4 with KOAc was necessary in order to prevent the oxidation of I^- to I_2 by this agent [19].

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